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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 focuses primarily on the scientific air quality criteria for O_3 and, to a lesser extent, on those for other photochemical oxidants such as hydrogen peroxide and the peroxyacyl nitrates.

The EPA promulgates the NAAQS on the basis of scientific information contained in air quality criteria issued under Section 108 of the Clean Air Act. The previous 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 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 1995.

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

Air Quality Criteria for Ozone and Related Photochemical Oxidants

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Chapter 3. Tropospheric Ozone and Its Precursors

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Executive Summary

1.1 Introduction

Air Quality Criteria for Ozone and Related Photochemical Oxidants evaluates the latest scientific information useful in deriving criteria that form the scientific basis for U.S. Environmental Protection Agency (EPA) decisions regarding the National Ambient Air Quality Standards (NAAQS) for ozone (O_3). This Executive Summary concisely summarizes key conclusions from the document, which comprises nine chapters. Following this Executive Summary is a brief Introduction (Chapter 2) containing information on the legislative and regulatory background for review of the O_3 NAAQS, as well as a brief discussion of the issues presented and the format for their discussion in the document. Chapter 3 provides information on the chemistry, sources, emissions, measurement, and transport of O_3 and related photochemical oxidants and their precursors, whereas Chapter 4 covers environmental concentrations, patterns, and exposure estimates of O_3 and oxidants. Chapter 5 deals with environmental effects, and Chapters 6, 7, and 8 discuss animal toxicological studies, human health effects, and extrapolation of animal toxicological data to humans, respectively. The last chapter, Chapter 9, provides an integrative, interpretative characterization of health effects associated with exposure to O_3. The following sections conform to the chapter organization of the criteria document.

1.2 Legislative and Regulatory Background

The photochemical oxidants found in ambient air in the highest concentrations are O_3 and nitrogen dioxide (NO_2). Other oxidants, such as hydrogen peroxide (H_2O_2) and peroxyacyl nitrates, also have been observed, but in lower and less certain concentrations. In 1971, EPA promulgated NAAQS to protect the public health and welfare from adverse effects of photochemical oxidants, at that time, defined on the basis of commercially available measurement methodology. After 1971, however, O_3-specific commercial analytical methods became available, as did information on the concentrations and effects of the related non-O_3 photochemical oxidants. As a result, the chemical designation of the standards was changed in 1979 from photochemical oxidants to O_3.

The EPA is required under Sections 108 and 109 of the Clean Air Act to evaluate periodically the air quality criteria that reflect the latest scientific information relevant to review of the O_3 NAAQS. These air quality criteria are useful for indicating the kind and extent of all identifiable effects on public health or welfare that may be expected from the presence of O_3 and related photochemical oxidants in ambient air. The last O_3 criteria

document was released in 1986, and a supplement was released in 1992. These documents were 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 consideration more recent scientific information that has been published since the last literature review in early 1989. The purpose of this revised criteria document, therefore, is to summarize the pertinent information contained in the previous O_3 criteria document and to critically evaluate and assess the more recent scientific data associated with exposure to O_3 and, to a lesser extent, to H_2O_2 and the peroxyacyl nitrates, particularly peroxyacetyl nitrate (PAN). This document will be used by EPA's Office of Air Quality Planning and Standards to provide a staff paper assessing the most significant scientific information and presenting staff recommendations on whether revisions to the O_3 NAAQS are appropriate.

1.3 Tropospheric Ozone and Its Precursors

Introduction

Ozone is found in the stratosphere, the "free" troposphere, and the planetary boundary layer (PBL) of the earth's atmosphere. In the PBL, background O_3 occurs as the result of (1) the intrusions of stratospheric O_3 into the "free" troposphere and downward transport into the PBL, and (2) photochemical reactions of methane (CH_4), carbon monoxide (CO), and nitrogen oxides (NO_x). These processes contribute to the background O_3 near the surface. The major source of O_3 in the PBL is the photochemical process involving anthropogenic and biogenic emissions of NO_x with the many classes of volatile organic compounds (VOCs).

The topics considered in this section of the document include: tropospheric O_3 chemistry; meteorological influences on O_3 formation and transport; precursor VOC and NO_x emissions, ambient concentrations of VOCs and NO_x, and source apportionment and reconciliation of measured VOC ambient concentrations with emission inventories; O_3 air quality models; and analytical methods for oxidants and precursors.

Tropospheric Ozone Chemistry

Ozone occurs in the stratosphere as the result of chemical reactions initiated by short-wavelength radiation from the sun. In the "free" troposphere, O_3 occurs as the result of incursions from the stratosphere; upward venting from the PBL (the layer next to the surface of the earth) through certain cloud processes; and photochemical formation from precursors, notably CH_4, CO, and NO_x.

The photochemical production of O_3 and other oxidants found at the surface of the earth (in the PBL, troposphere, or ambient air [used interchangeably in this summary]) is the result of atmospheric physical processes and complex, nonlinear chemical processes involving two classes of precursor pollutants: (1) reactive anthropogenic and biogenic VOCs and (2) NO_x. The only significant initiator of the photochemical production of O_3 in the polluted troposphere is the photolysis of NO_2, yielding nitric oxide (NO) and a ground-state oxygen atom that reacts with molecular oxygen to form O_3. The O_3 thus formed reacts with NO, yielding oxygen and NO_2. These cyclic reactions attain equilibrium in the absence of VOCs. However, in the presence of VOCs, which are abundant in polluted ambient air, the equilibrium is upset, resulting in a net increase in O_3. Methane is the chief VOC found in the free troposphere and in most "clean" areas of the PBL. The VOCs found in polluted ambient

air are much more complex and more reactive than CH_4, but, as with CH_4, their atmospheric oxidative degradation is initiated through attack on the VOCs by hydroxyl (OH) radicals. As in the CH_4 oxidation cycle, the conversion of NO to NO_2 during the oxidation of VOCs is accompanied by the production of O_3 and the efficient regeneration of the OH radical. The O_3, PAN, and higher homologues formed in polluted atmospheres increase with the NO_2/NO concentration ratio.

At night, in the absence of photolysis of reactants, the simultaneous presence of O_3 and NO_2 results in the formation of the nitrate (NO_3) radical. Reactions with NO_3 radicals appear to constitute major sinks for alkenes, cresols, and several other compounds, although the chemistry is not well characterized.

Most inorganic gas-phase processes (i.e., the nitrogen cycle and its interrelationships with O_3 production) are well understood. The chemistry of the VOCs in ambient air is not as well understood. It is well known, however, that the chemical loss processes of gas-phase VOCs include reaction with OH and NO_3 radicals and O_3, and photolysis. Reaction with the OH radical is the only important atmospheric reaction (loss process) for alkanes, aromatic hydrocarbons, and the higher aldehydes and ketones that lack >C=C< bonds; and the only atmospheric reaction of alcohols and ethers. Photolysis is the major loss process for formaldehyde and acetone. Reactions with OH and NO_3 radicals and with O_3 are all important loss processes for alkenes and for carbonyls containing >C=C< bonds.

Uncertainties in the atmospheric chemistry of the VOCs can affect quantification of the NO-to-NO_2 conversion and of O_3 yields, and can present difficulties in representation of chemical mechanisms, products, and product yields in O_3 air quality models. Major uncertainties in understanding the atmospheric chemistry of the VOCs with NO_x in both urban and rural atmospheres include chemistry of alkyl nitrate formation, mechanisms and products of >C4 *n*-alkanes and branched alkanes, mechanisms and products of alkene-O_3 reactions, and mechanisms and products of aromatic hydrocarbons.

It should be noted that the atmospheric chemical processes involved in the photooxidation of certain higher molecular weight VOCs and in the formation of O_3 also can lead to the formation of particulate-phase organic compounds. The OH radicals produced not only can oxidize VOCs to particulate-phase organic compounds but also can react with NO_2 and sulfur dioxide (SO_2) to form nitric acid (HNO_3) and sulfuric acid (H_2SO_4), respectively, portions of which become incorporated into aerosols as particulate nitrate and sulfate.

Meteorological Influences on Ozone Formation and Transport

The surface energy (radiation) budget of the earth strongly influences the dynamics of the PBL. The redistribution of energy through the PBL creates thermodynamic conditions that influence vertical mixing. Growing evidence indicates that the strict use of mixing heights in modeling is an oversimplification of the complex processes by which pollutants are redistributed within urban areas, and that it is necessary to treat the turbulent structure of the atmosphere directly and acknowledge the vertical variations in mixing. Energy balances therefore require study so that more realistic simulations can be made of the structure of the PBL.

Day-to-day variability in O_3 concentrations depends heavily on day-to-day variations in meteorological conditions, including temperature, solar radiation, and the degree of mixing that occurs between release of a pollutant or its precursors and their arrival at a

receptor; the occurrence of inversion layers (layers in which temperature increases with height above ground level); and the transport of O_3 left overnight in layers aloft and subsequent downward mixing of that O_3 to the surface.

The transport of O_3 and its precursors beyond the urban scale (≤50 km) to neighboring rural and urban areas has been well documented. Episodes of high O_3 concentrations in urban areas are often associated with high concentrations of O_3 in the surroundings. Areas of O_3 accumulation usually are characterized by synoptic-scale subsidence of air in the free troposphere, resulting in development of an elevated inversion layer; relatively low wind speeds associated with the weak horizontal pressure gradient around a surface high pressure system; a lack of cloudiness; and high temperatures.

Ultraviolet (UV) radiation from the sun plays a key role in initiating the photochemical processes leading to O_3 formation and affects individual photolytic reaction steps. Still, there is little empirical evidence in the literature linking day-to-day variations in observed UV radiation levels to variations in O_3 levels. An association, however, between tropospheric O_3 concentrations and temperature has been demonstrated. Empirical data from four urban areas, for example, show an apparent upper bound on O_3 concentrations that increases with temperature. A similar qualitative relationship exists at a number of rural locations.

The relationship between wind speed and O_3 buildup varies from one part of the country to another.

Statistical techniques (e.g., regression techniques) can be used to help identify real trends in O_3 concentrations, both intra- and interannual, by normalizing meteorological variability.

Precursors

Volatile Organic Compound Emissions

Hundreds of VOCs, usually containing from 2 to 12 carbon atoms, are emitted by evaporative and combustion processes from a large number of source types. Total U.S. anthropogenic VOC emissions in 1991 were estimated at 21.0 Tg; the two largest source categories were (1) industrial processes (10.0 Tg) and (2) 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 for both stationary and mobile sources.

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.

Although the biogenic VOC emission estimates exceed the anthropogenic estimates, the biogenic emissions are more diffusely distributed than the anthropogenic emissions, which tend to be concentrated in population centers. However, the large uncertainties in both biogenic and anthropogenic VOC emission inventories prevent establishing the relative contributions of these two categories.

Nitrogen Oxides Emissions

Anthropogenic NO_x is associated with combustion processes. The primary pollutant emitted is NO, formed at high combustion temperatures from nitrogen and oxygen in the 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 generating plants and highway vehicles. Because a large proportion of anthropogenic NO_x emissions come from distinct point sources, published annual estimates are thought to be much more reliable than VOC estimates.

Natural NO_x sources include stratospheric intrusion, oceans, lightning, soil, and wildfires. Lightning and soil emissions are the only two significant natural sources of NO_x in the United States. It is estimated that combined natural sources contribute about 2.2 Tg of NO_x to the troposphere over the continental United States; however, uncertainties in natural NO_x emission inventories are much greater than those for anthropogenic NO_x emissions.

Concentrations of Volatile Organic Compounds in Ambient Air

The VOCs most frequently analyzed in ambient air are the nonmethane hydrocarbons (NMHCs). Morning (6:00 to 9:00 a.m.) concentrations most often have been measured because of the use of morning data in the Empirical Kinetic Modeling Approach (EKMA) and in air quality simulation models.

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 carbon (C) and terpenes from 0.001 to 0.030 ppm C.

Concentrations of Nitrogen Oxides in Ambient Air

Measurements of NO_x made in 22 and 19 U.S. cities in 1984 and 1985, respectively, showed median 6:00-to-9:00 a.m. NO_x concentrations ranging from 0.02 to 0.08 ppm in most of these cities. Nonurban NO_x concentrations, reported as average seasonal or annual NO_x, range from <0.005 to 0.015 ppm.

Ratios of Concentrations of Nonmethane Organic Compounds to Nitrogen Oxides

Ratios of 6:00-to-9:00 a.m. nonmethane organic compounds (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 multicity studies conducted in 1984 and 1985. Rural NMOC/NO_x ratios tend to be higher than urban ratios. The NMOC/NO_x ratios trended downward to well below 10 in the South Coast Air Basin and in cities in the eastern United States during the 1980s. Based on these low ratios, hydrocarbon control should be more effective than NO_x control within a number of cities. Morning (6:00-to-9:00 a.m.) NMOC/NO_x ratios are used in the EKMA type of trajectory model. The correlation of NMOC/NO_x ratios with maximum 1-h O_3 concentrations, however, was weak in a recent analysis.

Source Apportionment and Reconciliation

Source apportionment (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.

Recent findings have shown that vehicle exhaust was the dominant contributor to ambient VOCs in seven of eight U.S. cities studied. Whole gasoline contributions were estimated to be equal to vehicle exhaust in one study and to 20% of vehicle exhaust in a second study.

Estimates of biogenic VOCs at a downtown site in Atlanta, GA, in 1990 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, CA; Columbus, OH; and Atlanta; and for refinery emissions in Chicago, IL.

Ozone Air Quality Models

Models and Their Components

Photochemical air quality models are used to predict how O_3 concentrations change in response to prescribed changes in source emissions of NO_x and VOCs. These models operate on sets of input data that characterize the emissions, topography, and meteorology of a region and produce outputs that describe air quality in that region.

Two kinds of photochemical models are recommended in guidelines issued by EPA: (1) the use of EKMA is accepted under certain circumstances, and (2) the grid-based Urban Airshed Model (UAM) is recommended for modeling O_3 over urban areas. The 1990 Clean Air Act Amendments mandate the use of three-dimensional (grid-based) air quality models such as UAM in developing state implementation plans for areas designated as "extreme", "severe", "serious", or "multistate moderate". General descriptions of EKMA and grid-based models were given in the 1986 EPA criteria document for O_3.

The EKMA-based method for determining O_3 control strategies has limitations, the most serious of which is that predicted emissions reductions are critically dependent on 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 time and space in an urban area.

Spatial and temporal characteristics of VOC and NO_x emissions are major inputs to a grid-based 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.

A chemical kinetic mechanism, representing the important chemical 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.

Dry deposition is an important removal process for O_3 on both urban and regional scales and is included in all urban- and regional-scale models. Wet deposition is generally not included in urban-scale photochemical models, because O_3 episodes do not occur during periods of significant clouds or rain.

Concentration fields of all species computed by the model must be specified at the beginning of the simulation ("initial conditions"). These initial conditions are determined mainly with ambient measurements, either from routinely collected data or from special studies; but interpolation can be used to distribute the surface ambient measurements.

Use of Ozone Air Quality Models

Photochemical air quality models are used for control strategy evaluation by first demonstrating that a past episode or episodes can be simulated adequately. The hydrocarbon or NO_x emissions or both are reduced in the model inputs, and the effects of these reductions on O_3 in the region are assessed. The adequacy of control strategies based on grid-based models depends, in part, on the nature of input data for simulations and model validation, on input emissions inventory data, and on the mismatch between the spacial output of the model and the current form of the NAAQS for O_3. Uncertainties in models obviously can affect their outputs. Uncertainties exist in all components of grid-based O_3 air quality models: emissions, meteorological modules, chemical mechanisms, deposition rates, and determination of initial conditions.

Grid-based models that have been widely used to evaluate control strategies for O_3 or acid deposition, or both, are the UAM, the California Institute of Technology/Carnegie Institute of Technology model, the Regional Oxidant Model, the Acid Deposition and Oxidant Model, and the Regional Acid Deposition Model. The UAM (Version IV) is the grid model approved nationwide for control strategy development at this time.

Despite the many uncertainties in photochemical air quality modeling, including emission inventories, these models are essential for regulatory analysis and solving the O_3 problem. Grid-based O_3 air quality modeling is superior to the available alternatives for O_3 control planning, but the chances of its incorrect use must be minimized.

Analytical Methods for Oxidants and Their Precursors

Oxidants

Current methods used to measure O_3 are chemiluminescence (CL); UV absorption spectrometry; and newly developed spectroscopic and chemical approaches, including chemical approaches applied to passive sampling devices (PSDs) for O_3.

The CL method has been designated as the reference method by EPA. Detection limits of 0.005 ppm and a response time of <30 s are typical of currently available commercial instruments. A positive interference from atmospheric water vapor was reported in the 1970s and recently has been confirmed. Proper calibration can minimize this source of error.

Commercial UV photometers for measuring O_3 have detection limits of about 0.005 ppm and a response time of <1 min. Because 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, the wavelength at which O_3 is measured, will cause 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 aerometric data for the potentially interfering species. There also can be some interference from water, possibly from the condensation of moisture in sampling lines.

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 calibration method approved by EPA. Ozone is unstable and must be generated in situ at time of use to produce calibration mixtures.

Peroxyacetyl nitrate and the higher peroxyacyl nitrates normally are measured by gas chromatography (GC) using an electron capture detector. Detection limits have been extended to 1 to 5 ppt. The preparation of reliable calibration standards is difficult because PAN is unstable, but several methods are available.

Volatile Organic Compounds

The method recommended by EPA for total NMOC measurement involves the cryogenic preconcentration of NMOCs and the measurement of the revolatilized NMOCs using flame ionization detection (FID). The primary technique for speciated NMOC/NMHC measurements is cryogenic preconcentration followed by GC-FID. Systems for sampling and analysis of VOCs have been developed that require no liquid cryogen for operation.

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 most common method currently in use for measuring gas-phase carbonyl compounds in ambient air, the high-performance liquid chromatography method, which employs 2,4-dinitrophenylhydrazine derivatization in a silica gel cartridge. Use of an O_3 scrubber has been recommended to prevent interference by O_3 in this method in ambient air.

Oxides of Nitrogen

Nitric oxide and NO_2 comprise the NO_x compounds involved as precursors to O_3 and other photochemical oxidants.

The most common method of NO measurement is the gas-phase CL reaction with O_3, which is essentially specific for NO. Commercial NO monitors have detection limits of a few parts per billion by volume (ppbv) in ambient air but may not have sensitivity sufficient for surface measurements in rural or remote areas or for airborne measurements. Direct spectroscopic methods for NO exist that have very high sensitivity and selectivity for NO, but their complexity, size, and cost restrict these methods to research applications. No PSDs exist for measurement of NO.

Chemiluminescence analyzers are the tools of choice for NO_2 measurement, even though they do not measure NO_2 directly. Minimum detection levels for NO_2 have been reported to be 5 to 13 ppb, but more recent evaluations have indicated detection limits of 0.5 to 1 ppbv. Reduction of NO_2 to NO is required for measurement. These analyzers actually measure NO_y (NO_x + PAN + HNO_3 + other reactive nitrogen species); however, for most urban atmospheres, NO_x is the predominant species measured diurnally.

Several spectroscopic approaches to NO_2 detection have been developed but share the drawbacks of spectroscopic NO methods. Passive samplers for NO_2 exist but are still in the developmental stage for ambient air monitoring.

Calibration of methods for NO measurement is done using standard cylinders of NO in nitrogen. Calibration of methods for NO_2 measurement include use of cylinders of NO_2 in nitrogen or air, use of permeation tubes, and GPT.

1.4 Environmental Concentrations, Patterns, and Exposure Estimates

Ozone is measured at concentrations above the minimum detectable level at all monitoring locations in the world. In this section, hourly average concentration and exposure information is summarized for urban, rural forested, and rural agricultural areas in the United States.

Because O_3 from urban area emissions is transported to rural downwind locations, elevated O_3 concentrations can occur at considerable distances from urban centers. Urban O_3 concentration values are often depressed because of titration by NO. Because of the absence of chemical scavenging, O_3 tends to persist longer in nonurban areas than in urban areas, and nonurban exposures may be higher than those in urban locations.

Trends

Ozone hourly average concentrations have been recorded for many years by the state and local air pollution agencies who report their data to EPA. The 10-year (1983 to 1992) composite average trend for the second highest daily maximum hourly average concentration during the O_3 season shows that the 1992 composite average for the trend sites was 21% lower than the 1983 average. The 1992 value was the lowest composite average of the 10-year period and was significantly less than each of the previous nine years, 1983 to 1991. The relatively high O_3 concentrations in 1983 and 1988 likely were attributable, in part, to hot, dry, stagnant conditions in some areas of the country, which were especially conducive to O_3 formation.

From 1991 to 1992, the composite mean of the second highest daily maximum 1-h O_3 concentrations decreased 7%, and the composite average of the number of estimated exceedances of the O_3 standard decreased by 23%. Nationwide VOC emissions decreased 3% from 1991 to 1992. The composite average of the second daily maximum concentrations decreased in 8 of the 10 EPA regions from 1991 to 1992, and remained unchanged in Region VII. Except for Region VII, the 1992 regional composite means were lower than the corresponding 1990 levels. Although meteorological conditions in the east during 1993 were more conducive to O_3 than those in 1992, the composite mean level for 1993 was the second lowest composite average of the decade, 1984 to 1993.

Surface Concentrations

Published data provide evidence showing the occurrence at some sites of multihour periods within a day of O_3 at levels of potential health effects. Although most of these analyses were made using monitoring data collected from sites in or near nonattainment areas, in one analysis of five sites (two in New York state, two in rural California, and one in rural Oklahoma), none of which was in or near a nonattainment area, O_3 concentrations showed only moderate peaks but showed multihour levels above 0.1 ppm.

A small amount of the O_3 concentration measured at a monitoring site is produced by sources distant to the photochemical reactions occurring on an urban or regional scale. Typical sources include stratospheric intrusions into the troposphere, photochemical production by the $CH_4/CO/NO_x$ cycle in the troposphere, and transport of very distant anthropogenic or biogenic VOCs and NO_x. The specific concentrations of this "background" O_3 vary with averaging times ranging from the daily 1-h maximum to daily, monthly, seasonal, or annual values. The background concentrations also vary with geographical region and with elevation of the monitoring site.

On the basis of O_3 data from isolated monitoring sites, EPA has indicated that a reasonable estimate of O_3 background concentration near sea level in the United States is from 0.020 to 0.035 ppm for an annual average, 0.025 to 0.045 ppm for an 8-h daily summer seasonal average, and from 0.03 to 0.05 ppm for the average summertime 1-h daily maximum. This estimate includes a 0.005 to 0.015 ppm O_3 contribution from stratospheric intrusions into the troposphere.

Diurnal Variations

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 of O_3 typically show a rise in concentration from low levels, or levels near minimum detectable amounts, to an early afternoon peak. The diurnal pattern of concentrations can be ascribed 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 NO at ground level, and (3) in situ photochemical production of O_3.

Seasonal Patterns

Seasonal variations in O_3 concentrations in urban areas usually show the pattern of high O_3 in the late spring or in the summer and low levels in the winter; however, 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.

Average O_3 concentrations tend to be higher in the second versus the third quarter of the year for many isolated rural sites. 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. However, for several clean rural sites, the highest exposures have occurred in the third quarter rather than in the second. For rural O_3 sites in the southeastern United States, the daily maximum 1-h average concentration was found to peak during the summer months.

Spatial Variations

Concentrations of O_3 vary with altitude and with latitude. There appears to be no consistent conclusion concerning the relationship between O_3 exposure and elevation.

Indoor Ozone

Until the early 1970s, very little was known about the O_3 concentrations experienced inside buildings; to date, the database on this subject is not large, and a wide range of indoor/outdoor O_3 concentration relationships can be found in the literature (reported indoor/outdoor values for O_3 are highly variable). Indoor/outdoor O_3 concentration ratios

generally fall in the range from 0.1 to 0.7 and indoor concentrations of O_3 almost invariably will be less than outdoors.

Estimating Exposure

Both fixed-site monitoring information and human exposure models are used to estimate risks associated with O_3 exposure. Because, for most cases, it is not possible to estimate population exposure solely from fixed-station data, several human exposure models have been developed. These models also contain submodels depicting the sources and concentrations likely to be found in each microenvironment, including indoor, outdoor, and in-transit settings. Two distinct types of O_3 exposure models exist: (1) those that focus narrowly on predicting indoor O_3 levels and (2) those that focus on predicting O_3 exposures on a community-wide basis. These latter models and their distinguishing features are:

1. pNEM/O_3 based on the National Air Quality Standards Exposure Model (NEM) series of models
   - Uses mass-balance approach and seasonal considerations for I/O ratio estimation.
   - Variables affecting indoor exposure obtained by Monte Carlo sampling from empirical distributions of measured data.
2. Systems Applications International (SAI)/NEM
   - More districts and microenvironments and more detailed mass-balance model than pNEM/O_3.
   - Human activity data outdated and inflexible.
3. Regional Human Exposure Model (REHEX)
   - More detailed geographic resolution than NEM.
   - Uses California-specific activity data and emphasizes in-transit and outdoor microenvironments.
4. Event probability exposure model (EPEM)
   - Estimates probability that a randomly selected person will experience a particular exposure regime.
   - Lacks multiday continuity.

Few data are available for individuals using personal exposure monitors. Results from a pilot study demonstrated that fixed-site ambient measurements may not adequately represent individual exposures. Models based on time-weighted indoor and outdoor concentrations explained only 40% of the variability in personal exposures.

Peroxyacyl Nitrates

Peroxyacetyl nitrate and peroxypropionyl nitrate (PPN) are the most abundant of the non-O_3 oxidants in ambient air in the United States, other than the inorganic nitrogenous oxidants such as NO_2, and possibly HNO_3. Most of the available data on concentrations of PAN and PPN in ambient air are from urban areas. The levels to be found in nonurban areas will be highly dependent on the transport of PAN and PPN or their precursors from urban areas, because the concentrations of the NO_x precursors to these compounds are considerably lower in nonurban areas than in urban areas.

Co-occurrence

Studies of the joint occurrence of gaseous NO_2/O_3 and SO_2/O_3 at rural sites have concluded that the periods of co-occurrence represent a small portion of the potential plant-growing period. For human ambient exposure considerations, in most cases, the simultaneous co-occurrence of NO_2/O_3 and SO_2/O_3 was infrequent. Some researchers have reported the joint occurrence of O_3, nitrogen, and sulfur in forested areas, combining cumulative exposures of O_3 with data on dry deposition of sulfur and nitrogen. One study reported that several forest landscapes with the highest dry deposition loadings of sulfur and nitrogen tended to experience the highest average O_3 concentrations and largest cumulative exposure. Although the authors concluded that the joint concentrations of multiple pollutants in forest landscapes were important, nothing was mentioned about the hourly co-occurrences of O_3 and SO_2 or O_3 and NO_2. Acid sulfates, which are usually composed of H_2SO_4, ammonium bisulfate, and ammonium sulfate, have been measured at a number of locations in North America. The potential for O_3 and acidic sulfate aerosols to co-occur at some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is real and requires further characterization. For human ambient exposures, the simultaneous co-occurrence of NO_2 and O_3 was infrequent.

In one study, the relationship between O_3 and hydrogen ions in precipitation was explored using data from sites that monitored both O_3 and wet deposition simultaneously and within one minute latitude and longitude of each other. It was reported that individual sites experienced years in which both hydrogen ion deposition and total O_3 exposure were at least moderately high. With data compiled from all sites, it was found that relatively acidic precipitation occurred together with relatively high O_3 levels approximately 20% of the time, and highly acidic precipitation occurred together with a high O_3 level approximately 6% of the time. Sites most subject to relatively high levels of both hydrogen ions and O_3 were located in the eastern part of the United States, often in mountainous areas.

The co-occurrence of O_3 and acidic cloudwater in high-elevation forests has been characterized. The frequent O_3-only and pH-only single-pollutant episodes, as well as the simultaneous and sequential co-occurrences of O_3 and acidic cloudwater, have been reported. Both simultaneous and sequential co-occurrences were observed a few times each month above cloud base.

1.5 Environmental Effects of Ozone and Related Photochemical Oxidants

Ozone is the gaseous pollutant most injurious to agricultural crops, trees, and native vegetation. Exposure of vegetation to O_3 can inhibit photosynthesis, alter carbon (carbohydrate) allocation, and interfere with mycorrhizal formation in tree roots. Disruption of the important physiological processes of photosynthesis and carbon allocation can suppress the growth of crops, trees, shrubs, and herbaceous vegetation by decreasing their capacity to form the carbon (energy) compounds needed for growth and maintenance and their ability to absorb the water and mineral nutrients that they require from the soil. In addition, loss of vigor impairs the ability of trees and crops to reproduce and increases their susceptibility to insects and pathogens. The following section summarizes key environmental effects associated with O_3 exposure.

Effects on Agroecosystems

Methodologies Used in Vegetation Research

Most of the knowledge concerning the effects of O_3 on vegetation comes from the exposure-response studies of important agricultural crop plants and some selected forest and urban tree species, mostly as seedlings. A variety of methodologies have been used, ranging from field exposures without chambers to open-top chambers and to exposures conducted in chambers under highly controlled conditions. In general, the more controlled conditions are most appropriate for investigating specific responses and for providing the scientific basis for interpreting and extrapolating results. The greatest body of knowledge is from OTC studies.

Mode of Action

Leaves are important regulators of plant stress and function. Stress resulting from exposure to O_3 produces a leaf-mediated response. Effects expressed within cells in the leaf (i.e., inhibition of photosynthesis) affect a plant's carbon (energy) budget. Plant processes are impaired only by the O_3 that enters the plant through the stomata (opening in the leaves). An effect will occur only if sufficient O_3 reaches sensitive sites within the leaf cells. The uptake and movement of O_3 to sensitive cellular sites within a leaf are subject to various biochemical and physiological controls. Leaf injury will not be detected if the rate of uptake is small enough for the plant to detoxify or metabolize O_3 and its derivatives, or the plant is able to repair or compensate for the impact at a rate equal to or greater than the rate of uptake. Impairment of leaf cellular processes is the basis for all other plant effects. The diurnal pattern of stomatal opening plays a critical role in O_3 uptake, particularly at the canopy level.

Visible injury is usually the first observable indication of cellular response; injury can occur, however, with no visible effects. Early senescence of leaves or needles is also a result of cellular response. Impairment of cellular processes inhibits the rate of photosynthesis, reduces carbon (sugars, carbohydrate) production, and alters carbon allocation, causing a shift in growth pattern that favors shoots over roots. The reduced allocation of carbon to leaf repair and new leaf formation limits the availability of carbon for reproduction; stem and root growth; and, particularly, the formation of the mycorrhizae on roots necessary for nutrient and water uptake. Reduction of plant vigor by O_3 can result in mortality, particularly when plant susceptibility to insects and pathogens is increased.

Factors That Modify Plant Response

Plant response to O_3 exposure is influenced by a variety of biological, chemical, and physical factors. When determining the impact of O_3 exposure on plants, both the influence of environmental factors on plant response and the effects of O_3 on that response must be considered. Biological factors within plants that affect their response to stresses include, genetic composition, stage of development, and the diurnal pattern of stomatal opening. Genotype significantly influences plant sensitivity to O_3. Individuals, varieties, and cultivars of a species are known to differ greatly in their responses to a given O_3 exposure. Genotype also influences the ability of plants to compete with one another for space, nutrients, light, and water.

The magnitude of response of a particular species, variety, or cultivar depends on a number of environmental factors. The plant's present and past environmental milieu, which includes the temporal exposure pattern and stage of development, dictates the plant response. The corollary is also true: exposure to O_3 can modify plant response to other environmental

variables. Available light, temperature, atmospheric turbulence and moisture, in both the atmosphere and soil; soil nutrition; and exposure to and interaction with other pollutants such as agricultural chemical sprays also influence the magnitude of plant response.

Drought can reduce visible injury and the adverse effects of O_3 on growth and yield of crops. However, in the case of crops, drought, per se, much more adversely affects yield than the effects of O_3. Ozone, on the other hand, tends to reduce the water-use efficiency of well-watered crops. In some plants, O_3 exposure reduces cold/winter hardiness. Although exposure to O_3 tends to reduce attacks by obligate pathogens, susceptibility of plants to facultative pests and pathogens increases.

Effects-Based Air Quality Exposure Indices

Environmental scientists for many years have attempted to characterize and mathematically represent plant exposures to O_3. A variety of averaging times have been used. Although most studies have characterized exposure by using mean concentrations, such as seasonal, monthly, weekly, daily, or peak hourly means, other studies have used cumulative measures (e.g., the number of hours above selected concentrations). None of these statistics completely characterizes the relationships among O_3 concentration, exposure duration, interval between exposures, and plant response.

The use of a mean concentration with long averaging times implies that all concentrations of O_3 are equally effective in causing plant responses and minimizes the contributions of the peak concentrations to the response. Ozone effects are cumulative; therefore, exposure duration should be included in any index if it is to be biologically relevant. Present evidence suggests that cumulative effects of episodic exposures to either peak or mid-range concentrations, or both, can play an important role in producing growth responses. The key to plant response is timing because peak and mid-range concentrations do not occur at the same time. Potentially, the greatest effect of O_3 on plants will occur when stomatal conductance is greatest. When peaks occur at the time of greatest stomatal conductance, the effect of mid-range concentrations will not be observable. Atmospheric conductivity also strongly influences plant response because O_3 must be in contact with the leaf surface if it is to be taken up by a plant. Effects on vegetation appear when the amount of pollutant entering exceeds the ability of the plant to repair or compensate for the impact. Increasing uptake of O_3 will inhibit photosynthesis and result in increased reductions in biomass production.

An index of ambient exposures that relates well to plant response should incorporate, directly or indirectly, environmental influences (e.g., temperature, humidity, soil-moisture status) and exposure dynamics. Peak indices (e.g., second highest daily maximum) imply that a single high-concentration exposure (1- or 8-h concentration) during the course of a 70- to 120-day growing season is related to eventual yield or growth reductions. On the other hand, mean indices (e.g., 7-h seasonal mean) imply that duration of the exposure is not important, and that all concentrations have equal effect on plants. Neither of these indices relates ambient O_3 concentrations to biological effects on plants because these indices do not consider the duration of exposure. An index that cumulates all hourly concentration during the season and gives greater weight to higher concentrations appears to be a more appropriate index for relating ambient exposures to growth or yield effects.

No experimental studies have been designed specifically to evaluate the adequacy of the various peak-weighted indices that have been proposed. In retrospective analyses in which O_3 is the primary source of variation in response, year-to-year variations in plant

response are minimized by peak-weighted, cumulative exposure indices. However, a number of different forms of peak-weighted, cumulative indices have been examined for their ability to properly order yield responses from the large number of studies of the National Crop Loss Assessment Network (NCLAN) program. These exposure indices (i.e., SUM00, SUM06, SIGMOID, W126) all performed equally well, and it is not possible to distinguish among them on the basis of statistical fits of the data. The biological basis for these indices has not been determined.

Exposure Response of Plant Species

The emphasis of experimental studies usually has been on the more economically important crop plants and tree species, as seedlings. Crop species usually are monocultures that are fertilized and, in many cases, watered. Therefore, because crop plants are usually grown under optimal conditions, their sensitivity to O_3 exposures can vary from that of native trees, shrubs, and herbaceous vegetation.

The concept of limiting values was used in both the 1978 and 1986 criteria documents to summarize visible foliar injury. Limiting values are defined as concentrations and durations of exposure below which visible injury does not occur. The limit for visible injury indicating reduced plant performance was an O_3 exposure of 0.05 ppm for several hours per day for more than 16 days. When the exposure period was decreased to 10 days, the O_3 concentration required to cause injury was increased to 0.10 ppm. A short, 6-day exposure further increased the concentration to 0.30 ppm. These exposure and concentration periods apply for those crops where appearance or aesthetic value (e.g, spinach, cabbage, lettuce) is considered important. Limiting values for foliar injury to trees and shrubs range from 0.06 to 0.10 ppm for 4 h.

The following assertions can be made based on information from the 1986 criteria document, its 1992 supplement, and literature published since 1986. Ambient O_3 concentrations in several regions of the country are high enough to impair growth and yield of sensitive plant species. This clearly is indicated by comparison of data obtained from crop yield in charcoal-filtered and unfiltered (ambient) exposures. These elevated levels are further supported by data from studies using chemical protectants. These response data make possible the extrapolation to plants not studied experimentally. Both approaches mentioned above indicate that effects occur with only a few exposures above 0.08 ppm. Data from regression studies conducted to develop an exposure-response function for estimating yield loss indicated that at least 50% of the species and cultivars tested could be predicted to exhibit a 10% yield loss at 7-h seasonal mean O_3 concentrations of 0.05 ppm or less.

Effects on Natural Ecosystems

The responses of the San Bernardino mixed forest of Southern California to 50 or more years of chronic ozone exposures based on many studies, present a classic example of ecosystem response to severe stress. Data from an inventory conducted from 1968 through 1972 indicated that for 5 mo of each year, trees were exposed to O_3 concentrations greater than 0.08 ppm for more than 1,300 h. Concentrations rarely decreased below 0.05 ppm at night near the crest of the mountain slope, approximately 5,500 ft. In addition, during the years 1973 to 1978, average 24-h O_3 concentrations ranged from a background of 0.03 to 0.04 ppm in the eastern part of the San Bernardino Mountains to a maximum of 0.10 to 0.12 ppm in the western part during May through September.

Plants accumulate, store, and use the energy in carbon compounds (sugars) produced during photosynthesis to build their structures and to maintain the physiological processes necessary for life. The patterns of carbon allocation to roots, stems, and leaves directly influence growth. The strategy for carbon allocation changes during the life of a plant, as well as with environmental conditions. Mature trees have a higher ratio of respiration to photosynthetic tissue. Impairment of photosynthesis shifts carbon allocation from growth and maintenance to repair; increased respiration can result in resource imbalances. The significant changes observed in the San Bernardino forest ecosystem were a possible outcome of the combined influences of O_3 on carbon, water, and nutrient allocation.

The biochemical changes within the leaves of ponderosa and Jeffrey pine in the San Bernardino forest, expressed as visible foliar injury, premature needle senescence, reduced photosynthesis, and reduced carbohydrate production and allocation, resulted in reduced tree vigor, growth, and reproduction. Reduced vigor increases susceptibility of trees to insect pests and fungal pathogens. Premature needle senescence alters microorganismal succession on confer needles and changes the detritus-forming process and associated nutrient cycling.

Altered carbon allocation is important in the formation of mycorrhizae (fungus roots), which are an extremely important but unheralded component of all ecosystems; the majority of all plants depend on them because they are integral in the uptake of mineral nutrients and water from the soil. Carbon-containing exudates from the roots are necessary for the formation of mycorrhizae. Reduced carbon allocation to plant roots affects mycorrhizal formation and impacts plant growth. Exposure to ozone, therefore, affects plant growth both above and below ground.

Small changes in photosynthesis or carbon allocation can alter profoundly the structure of a forest. Ecosystem responses to stress begin with the response of the most sensitive individuals of a population. Stresses, whose primary effects occur at the molecular level (within the leaves), must be propagated progressively through more integrated levels of organ physiology (e.g., leaf, branch, root) to whole plant physiology, then to populations within the stand (community), and finally to the landscape level to produce ecosystem effects. Only a small fraction of stresses at the molecular level become disturbances at the tree, stand, or landscape level. The time required for a stress to be propagated from one level to the next (it can take years) determines how soon the effects of the stress can be observed or measured.

The primary effect of O_3 on ponderosa and Jeffrey pine, two of the more susceptible members of the San Bernardino forest community, was that the trees were no longer able to compete effectively for essential nutrients, water, light, and space. Decline in the sensitive trees, a consequence of altered competitive conditions, permitted the enhanced growth of more tolerant species. Removal of the ecosystem dominants at the population level changed its structure and altered the processes of energy flow and nutrient cycling, returning the ecosystem to a less complex stage.

The San Bernardino Mountains continue to experience exposure to O_3; however, there has been a gradual decline in concentrations and length of exposure. Ozone concentrations of 0.06 ppm or higher of varying durations capable of causing injury to trees in forest ecosystems have been observed during the past 5 years in the Sierra Nevada Mountains and the Appalachian Mountains from Georgia to Maine. Visible injury to forest trees and other vegetation in these areas has been observed.

Injury to sensitive trees from exposure to ozone concentrations 0.06 ppm or greater in the Sierra Nevada Mountains and the Appalachian Mountains has never had the impact on these ecosystems that it did on the San Bernardino forest. Forest stands differ greatly in age, species composition, stability, and capacity to recover from disturbance. In addition, the position in the stand or community of the most sensitive species is extremely important. Ponderosa and Jeffrey pine were the dominant species in the San Bernardino forest. Removal of populations of these trees altered both ecosystem structure and function. Both the Sierra Nevada Mountains and the Appalachian Mountains are biologically more diverse. Removal of sensitive individuals of eastern white pine and black cherry has not visibly altered the forest ecosystems along the Appalachian Mountains, possibly because of the absence of population changes in these species. Decline and dieback of trees on Mt. Mitchell, NC, and Camel's Hump, VT, cannot be related solely to O_3 injury.

Effects on Agriculture, Forestry, and Ecosystems: Economics

A number of economic assessments of the effects of O_3 on agriculture have been performed over the last decade. All use NCLAN response data to predict crop yield changes. Although these studies employ somewhat different economic assessment methodologies, each shows national-level economic losses to major crops in excess of $1 billion (1990 dollars) from exposure to ambient concentrations of O_3. These studies also evaluate the sensitivity of the economic estimates to uncertainties in data, including the NCLAN response data. The economic assessment models used could be adapted to future O_3-crop yield response findings, if available.

The plant science literature shows that O_3 adversely influences physiological performance of both urban and native tree species; the limited economic literature also demonstrates that changes in growth have economic consequences. However, the natural science and economic literature on the topic are not yet mature enough to conclude unambiguously that ambient O_3 is imposing economic costs. The economic effects of O_3 on ecosystems have not yet been addressed in the published literature. There is, however, an emerging interest in applying economic concepts and methods to the management of ecosystems.

Effects on Materials

Over four decades of research show that O_3 damages certain materials such as elastomers, textile fibers, and dyes. The amount of damage to actual in-use materials and the economic consequences of that damage are poorly characterized.

Natural rubber and synthetic polymers of butadiene, isoprene, and styrene, used in products like automobile tires and protective outdoor electrical coverings, account for most of the elastomer production in the United States. The action of O_3 on these compounds is well known, and concentration-response relationships have been established and corroborated by several studies. These relationships, however, must be correlated with adequate exposure information based on product use. For these and other economically important materials, protective measures have been formulated to reduce the rate of oxidative damage. When antioxidants and other protective measures are incorporated in elastomer production, the O_3-induced damage is reduced considerably, although the extent of reduction differs widely according to the material and the type and amount of protective measures used.

Both the type of dye and the material in which it is incorporated are important factors in the resistance of a fabric to O_3. Some dyed fabrics, such as royal blue and red rayon-acetate and plum cotton are resistant to O_3. On the other hand, anthraquinone dyes on nylon fibers are sensitive to fading by O_3. Field studies and laboratory work show a positive association between O_3 levels and dye fading of nylon materials. At present, the available research is insufficient to quantify the amount of damaged materials attributable to O_3 alone.

The degradation of fibers from exposure to O_3 is poorly characterized. In general, most synthetic fibers, such as modacrylic and polyester, are relatively resistant, whereas cotton, nylon, and acrylic fibers have greater but varying sensitivities to O_3. Ozone reduces the breaking strength of these fibers, and the degree of strength reduction depends on the amount of moisture present. The limited research in this area indicates that O_3 in ambient air may have a minimal effect on textile fibers, but additional research is needed to verify this conclusion.

A number of artists' pigments and dyes are sensitive to O_3 and other oxidants; in particular, many organic pigments are subject to fading or other color changes when exposed to O_3. Although most, but not all, modern fine arts paints are more O_3 resistant, many older works of art are at risk of permanent damage due to O_3-induced fading.

A great deal of work remains to be done to develop quantitative estimates of the economic damage to materials from photochemical oxidants. Most of the available studies are outdated in terms of O_3 concentrations, technologies, and supply-demand relationships. Additionally, little is known about the physical damage functions, so cost estimates have been simplified to the point of not properly recognizing many of the scientific complexities of the impact of O_3.

1.6 Toxicological Effects of Ozone and Related Photochemical Oxidants

Respiratory Tract Effects of Ozone

Biochemical Effects

Knowledge of molecular targets provides a basis for understanding mechanisms of effects and strengthening animal-to-human extrapolations. Ozone reacts with polyunsaturated fatty acids and sulfhydryl, amino, and some electron-rich compounds. These elements are shared across species. Several types of reactions are involved, and free radicals may be created. Based on this knowledge, it has been hypothesized that the O_3 molecule is unlikely to penetrate the liquid linings of the respiratory tract (RT) to reach the tissue, raising the possibility that reaction products exert effects.

In acute and short-term exposure studies, a variety of lung lipid changes occur, including an increase in arachidonic acid, the further metabolism of which produces a variety of biologically active mediators that can affect host defenses, lung function, the immune system, and other functions.

The level of lung antioxidant metabolism increases after O_3 exposure, probably as a result of the increase in the number of Type 2 cells, which are rich in antioxidant enzymes.

Collagen (the structural protein involved in fibrosis) increases in O_3-exposed lungs in a manner that has been correlated to structural changes (e.g., increased thickness of the tissue between the air and blood after prolonged exposure). Some studies found that the increased collagen persists after exposure ceases.

Generally, O_3 enhances lung xenobiotic metabolism after both short- and long-term exposure, possibly as a result of morphological changes (increased numbers of nonciliated bronchiolar epithelial cells). The impact of this change is dependent on the xenobiotics involved; for example, the metabolism of benzo[*a*]pyrene to active metabolites was enhanced by O_3.

Lung Inflammation and Permeability Changes

Elevated concentrations of O_3 disrupt the barrier function of the lung, resulting in the entry of compounds from the airspaces into the blood and the entry of serum components (e.g., protein) and white blood cells (especially polymorphonuclear leukocytes [PMNs]) into the airspaces and lung tissue. This latter impact reflects the initial stage of inflammation. These cells can release biologically active mediators that are capable of a number of actions, including damage to other cells in the lung. In lung tissue, this inflammation also can increase the thickness of the air-blood barrier.

Increases in permeability and inflammation have been observed at levels as low as 0.1 ppm O_3 (2 h/day, 6 days; rabbits). After acute exposures, the influence of the time of exposure (from two to several hours) increases as the concentration of O_3 increases. Long-term exposure effects are discussed under lung morphology.

The impacts of these changes are not fully understood. At higher O_3 concentrations (e.g., 0.7 ppm, 28 days), the diffusion of oxygen into the blood decreases, possibly because the air-blood barrier is thicker; cellular death may result from the enzymes released by the inflammatory cells; and host defense functions may be altered by mediators.

Effects on Host Defense Mechanisms

Exposure to elevated concentrations of ozone results in alterations of all defense mechanisms of the RT, including mucociliary and alveolobronchiolar clearance, functional and biochemical activity of the alveolar macrophage (AM), and immunologic competence. These effects can cause susceptibility to bacterial respiratory infections.

Mucociliary clearance, which removes particles and cellular debris from the conducting airways, is slowed by acute, but not repeated exposures to O_3. Ciliated epithelial cells that move the mucous blanket are altered or destroyed by acute and chronic exposures. Neonatal sheep exposed to O_3 do not have normal development of the mucociliary system. Such effects could prolong the retention of unwanted substances (e.g., inhaled particles) in the lungs, allowing them to exert their toxicity for a longer period of time.

Alveolar clearance mechanisms, which center on the functioning of AMs, are altered by O_3. Short-term exposure to levels as low as 0.1 ppm O_3 (2 h/day, 1 to 4 days; rabbits) accelerates clearance, but longer exposures do not. Even so, after a 6-week exposure of rats to an urban pattern of O_3, the retention of asbestos fibers in a region protected by alveolar clearance is prolonged.

Alveolar macrophages engulf and kill microbes, as well as clear the deeper regions of the lungs of nonviable particles; AMs also participate in immunological responses, but little is known about the effects of O_3 on this function. Acute exposures of rabbits to levels as low as 0.1 ppm O_3 decrease the ability of AMs to ingest particles. This effect is displayed in decreases in the ability of the lung to kill bacteria after acute exposure of mice to levels as low as 0.4 ppm O_3.

Both the pulmonary and systemic immune system are affected by O_3, but in a poorly understood way. It appears that the part of the immune system dependent on T-cell function is more affected than is the part dependent on B-cell function.

Dysfunction of host defense systems results in enhanced susceptibility to bacterial lung infections. For example, acute exposure to O_3 concentrations as low as 0.08 ppm for 3 h can overcome the ability of mice to resist infection with streptococcal bacteria, resulting in mortality. However, more prolonged exposures (weeks, months) do not cause greater effects on infectivity.

Effects on antiviral defenses are more complex and less well understood. Only high concentrations (1.0 ppm O_3, 3 h/day, 5 days; mice) increase viral-induced mortality. Apparently, O_3 does not impact antiviral clearance mechanisms. Although O_3 does not affect acute lung injury from influenza virus infection, it does enhance later phases of the course of an infection (i.e., postinfluenzal alveolitis).

Morphological Effects

Elevated concentrations of O_3 cause similar types of alterations in lung structure in all laboratory animal species studied, from rats to monkeys. In the lungs, the most affected cells are the ciliated epithelial cells of the airways and Type 1 epithelial cells of the gas-exchange region. In the nasal cavity, ciliated cells are also affected.

The centriacinar region (CAR; the junction of the conducting airways and gas-exchange regions) is the primary target, possibly because this area receives the greatest dose of O_3. The ciliated cells can be killed and replaced by nonciliated cells (i.e., cells not capable of clearance functions that also have increased ability to metabolize some foreign compounds). Mucous-secreting cells are affected, but to a lesser degree. Type 1 cells, across which gas exchange occurs, can be killed; they are replaced by Type 2 cells, which are thicker and produce more lipids. An inflammatory response also occurs in the tissue. The tissue is thickened further in later stages when collagen (a structural protein increased in fibrosis) and other elements accumulate. Although fibrotic changes have been observed in the CAR, they have not been distributed throughout the whole lung.

The distal airway is remodeled; more specifically, bronchiolar epithelium replaces the cells present in alveolar ducts. Concurrent inflammation may play a role. This effect has been observed at 0.25 ppm O_3 (8 h/day, 18 mo) in monkeys; at a higher concentration, this remodeling persists after exposure stops.

The progression of effects during and after a chronic exposure is complex. Over the first few days of exposure, inflammation peaks and then drops considerably, plateauing for the remainder of exposure, after which it largely disappears. Epithelial hyperplasia increases rapidly over the first few days and rises slowly or plateaus thereafter; when exposure ends, it begins to return toward normal. In contrast, fibrotic changes in the tissue between the air and blood increase very slowly over months of exposure, and, after exposure ceases, the changes sometimes persist or increase.

The pattern of exposure can make a major difference in effects. Monkeys exposed to 0.25 ppm O_3 (8 h/day) every other month of an 18-mo period had equivalent changes in lung structure, more fibrotic changes, and more of certain types of pulmonary function changes than did monkeys exposed every day over the 18 mo. From this work and rat studies, it appears that natural seasonal patterns may be of more concern than more continuous exposures. Thus, long-term animal studies with uninterrupted exposures may underestimate some of the effects of O_3.

The morphologic lesions described in early publications on laboratory animals exposed to O_3 do not meet the current criteria for emphysema of the type seen in human lungs.

Effects on Pulmonary Function

Pulmonary function changes in animals resemble those observed in humans after acute exposure.

During acute exposure, the most commonly observed alterations are increased frequency of breathing and decreased tidal volume (i.e., rapid, shallow breathing). This has been reported at exposures as low as 0.2 ppm O_3 for 3 h (rats). Typically, higher concentrations (around 1 ppm) are required to affect breathing mechanics (compliance and resistance). Extended characterizations of pulmonary function show types of changes generally seen in humans. For example, there are decreased lung volumes at levels ≥0.5 ppm O_3 (a few hours; rats).

When rats are exposed to O_3 for 2 h/day for 5 days, the pattern of attenuation of pulmonary function responses is similar to that observed in humans. Other biochemical indicators of lung injury did not return to control values by Day 5, and morphological changes increased in severity over the period of exposure. Thus, attenuation did not result in protection against all the effects of O_3.

Long-term exposures have provided mixed results on pulmonary function, including no or minimal effects, restrictive effects, and obstructive effects. When changes occurred and postexposure examinations were performed, pulmonary function recovered.

Genotoxicity and Carcinogenicity of Ozone

The chemical reactivities of O_3 give it the potential to be a genotoxic agent.

In vitro studies are difficult to interpret because the culture systems used allowed the potential formation of artifacts, and high or very high concentrations of O_3 often were used. Generally, in these studies, O_3 causes DNA strand breaks, sometimes is weakly mutagenic, and causes cellular transformation and chromosomal breakage. The latter finding has been investigated in vivo, with mixed results in animals.

The few earlier long-term carcinogenic studies in laboratory animals, with or without coexposure to known carcinogens, are either negative or ambiguous.

The National Toxicology Program (NTP) completed chronic rat and mouse cancer bioassays using commonly accepted experimental approaches and designs. Both male and female rats and mice were studied. Animals were exposed for 2 years (6 h/day, 5 days/week) to 0.12, 0.5, and 1.0 ppm O_3 or for a lifetime to the same levels (except 0.12 ppm). Following their standard procedures for determination of weight-of-evidence for carcinogenicity, the NTP reported "no evidence" in rats, "equivocal evidence" in male mice, and "some evidence" in female mice. The increases in adenomas and carcinomas were observed only in the lungs. There was no concentration response. One of the reasons for the designation of "some evidence" in female mice was that when the 2-year and lifetime exposure studies were combined, there was a statistically significant increase in total tumors at 1.0 ppm. Lung tumors from control and O_3-exposed mice also were examined for the presence of mutated Ha-ras oncogenes. Although the types of mutations found were similar in both groups, a higher incidence of mutations was found in lung tumors from the O_3-exposed mice. At the present time, however, there is inadequate information to provide

mechanistic support for the finding in mice. Thus, the potential for animal carcinogenicity is uncertain.

In a companion NTP study, male rats were treated with a tobacco carcinogen and exposed for 2 years to 0.5 ppm O_3. Ozone did not affect the response and therefore had no tumor promoting activity.

Systemic Effects of Ozone

Ozone causes a variety of effects on tissues and organs distant from the lung. Because O_3 itself is not thought to penetrate the lung, these systemic effects are either secondary to lung alterations or result from reaction products of O_3. Effects have been observed on clinical chemistry, white blood cells, red blood cells, the circulatory system, the liver, endocrine organs, and the central nervous system. Most of these effects cannot be interpreted adequately at this time and have not been investigated in humans, but it is of interest to note that O_3 exposures causing effects on the RT of animals cause a wide array of effects on other organs also.

Several behavior changes occur in response to O_3. For example, 0.12 ppm O_3 (6 h, rats) decreases wheel-running activity, and 0.5 ppm (1 min) causes mice to avoid exposure. These effects are not fully understood, but they may be related to lung irritation or decreased ability to exercise.

Although cardiovascular effects, such as slowed heart rate and decreased blood pressure, occur in O_3-exposed rats, some observed interactions with thermoregulation prevent qualitative extrapolation of these effects to humans at this time.

Developmental toxicity studies in pregnant rats summarized in the 1986 O_3 criteria document showed that levels up to about 2.0 ppm O_3 did not cause birth defects. Rat pups from females exposed to 1.0 ppm O_3 during certain periods of gestation weighed less or had delays in development of behaviors (e.g., righting, eye opening). No "classical" reproductive assays with O_3 were found.

Other studies have indicated that O_3 can affect some endocrine organs (i.e., pituitary-thyroid-adrenal axis, parathyroid gland). It appears that the liver has less ability to detoxify drugs after O_3 exposure, but assays of liver enzymes involved in xenobiotic metabolism are inconsistent.

Interactions of Ozone with Other Co-occurring Pollutants

Animal studies of the effects of O_3 in combination with other air pollutants show that antagonism, additivity, and synergism can result, depending on the animal species, exposure regimen, and health endpoint. Thus, these studies clearly demonstrate the major complexities and potential importance of interactions but do not provide a scientific basis for predicting the results of interactions under untested ambient exposure scenarios.

1.7 Human Health Effects of Ozone and Related Photochemical Oxidants

This section summarizes key effects associated with exposure to O_3, the major component of photochemical oxidant air pollution that is clearly of most concern to the health of the human population. Another, often co-occurring photochemical oxidant component of

"smog" is PAN, but this compound has been demonstrated to be primarily responsible for induction of smog-related eye irritation (stinging of eyes). Limited pulmonary function studies have shown no effects of PAN at concentrations below 0.13 to 0.30 ppm, which are much higher than the generally encountered ambient air levels in most cities.

Controlled Human Studies of Acute Ozone Effects

Effects on Lung Function

Controlled studies in healthy adult subjects have demonstrated O_3-induced decrements in pulmonary function, characterized by alterations in lung volumes and flow and airway resistance and responsiveness. Respiratory symptoms, such as cough and pain on deep inspiration, are associated with these changes in lung function.

Ozone-induced decreases in lung volume, specifically forced vital capacity (FVC) and forced expiratory volume in 1 s (FEV_1), largely can be attributed to decreases in inspiratory capacity (the ability to take a deep breath), although at higher exposure concentrations, there is clearly an additional component that is not volume dependent. Lung volumes recover to a large extent within 2 to 6 h; normal baseline function typically is reestablished within 24 h, but not fully with more severe exposures.

Ozone causes increased airway resistance and may cause reductions in expiratory flow and the FEV_1/FVC ratio.

Ozone causes an increase in airway responsiveness to nonallergenic stimuli (e.g., histamine, methacholine) in healthy and asthmatic subjects. There is no clear evidence of a relationship between O_3-induced lung volume changes and changes in airway responsiveness.

Inflammation and Host Defense Effects

Controlled studies in healthy adult subjects also indicate that O_3 causes an inflammatory response in the lungs characterized by elevated levels of PMNs, increased epithelial permeability, and elevated levels of biologically active substances (e.g., prostaglandins, proinflammatory mediators, cytokines).

Inflammatory responses to O_3 can be detected within 1 h after a single 1-h exposure with exercise to concentrations ≥0.3 ppm; the increased levels of some inflammatory cells and mediators persist for at least 18 h. The temporal response profile is not defined adequately, although it is clear that the time course of response varies for different mediators and cells.

Lung function and respiratory symptom responses to O_3 do not seem to be correlated with airway inflammation.

Ozone also causes inflammatory responses in the nose, marked by increased numbers of PMNs and protein levels suggestive of increased permeability.

Alveolar macrophages removed from the lungs of human subjects after 6.6 h of exposure to 0.08 and 0.10 ppm O_3 have a decreased ability to ingest microorganisms, indicating some impairment of host defense capability.

Ozone Exposure-Response Relationships

Functional, symptomatic, and inflammatory responses to O_3 increase with increasing exposure dose of O_3. The major determinants of the exposure dose are O_3 concentration (C), exposure duration (T), and the amount of ventilation ($\dot{V}_E$).

Exercise increases response to O_3 by increasing $\dot{V}_E$ (greater mass delivered), tidal volume, inspiratory flow (greater percentage delivery), and the intrapulmonary O_3 concentration.

Repeated daily exposures to relatively high levels of O_3 doses ($C \times T \times \dot{V}_E$) causing substantial reductions in FEV_1 (≥20% decrement) typically cause exacerbation of the lung function and respiratory symptom responses on the second exposure day. However, attenuation of these responses occurs with continued exposures for a few days. Most inflammatory responses also attenuate; for example, the PMN influx is absent after five consecutive exposures.

Multihour exposures (e.g., for up to 7 h) to O_3 concentrations as low as 0.08 ppm cause small but statistically significant decrements in lung function, increases in respiratory symptoms, and increases in PMNs and protein levels. Ozone C is a more important factor than exercise $\dot{V}_E$ or T in predicting responses to multihour low-level O_3 exposure. There is clear evidence of a response plateau in terms of lung volume response to prolonged O_3 exposure. This evidence suggests that for a given combination of exercise and O_3 concentration (i.e., dose rate), there is a response plateau; continued exposure (i.e, increased T) at that dose rate will not increase response. Therefore, quantitative extrapolation of responses to longer exposure durations is not valid.

Mechanisms of Acute Pulmonary Responses

The mechanisms leading to the observed pulmonary responses induced by O_3 are beginning to be better understood. The available descriptive data suggest a number of mechanisms leading to the alterations in lung function and respiratory symptoms, including O_3 delivery to the tissue (i.e., the inhaled concentration, breathing pattern, airway geometry; O_3 reactions with the airway lining fluid and epithelial cell membranes; local tissue responses, including injury and inflammation; and stimulation of neural afferents (bronchial C-fibers) and the resulting reflex responses and symptoms. The cyclooxygenase inhibitors block production of prostaglandin E_2 and interleukin-6 as well as reduce lung volume responses; however, these drugs do not reduce inflammation and levels of cell damage markers such as lactate dehydrogenase.

Effects on Exercise Performance

Maximal oxygen uptake, a measure of peak exercise performance capacity, is reduced in healthy young adults if preceded by O_3 exposures sufficient to cause marked changes in lung function (i.e., decreases of at least 20%) and increased subjective symptoms of respiratory discomfort. Limitations in exercise performance may be related to increased symptoms, especially those related to breathing discomfort.

Factors Modifying Responsiveness to Ozone

Many variables have the potential for influencing responsiveness to O_3; however, most are addressed inadequately in the available clinical data to make definitive conclusions.

Active smokers are less responsive to O_3 exposure, which may reverse following smoking cessation, but these results should be interpreted with caution.

The possibility of age-related differences in response to O_3 has been explored, although young adults historically have provided the subject population for controlled human studies. Children and adolescents have lung volume responses to O_3 similar to those of young adults, but lack respiratory symptoms. Pulmonary function responsiveness in adults

appears to decrease with age, whereas symptom rates remain similar to young adults. Group mean lung function responses of adults over 50 years of age are less than those of children, adolescents, and young adults.

The available data have not demonstrated conclusively that men and women respond differently to O_3. Likewise, pulmonary function responses of women have been compared during different phases of the menstrual cycle, but the results are conflicting. If gender differences exist for lung function responsiveness to O_3, they are not based on hormonal changes, differences in lung volume, or the ratio of FVC to $\dot{V}_E$.

There is no compelling evidence, to date, suggesting that any ethnic or racial groups have a different distribution of responsiveness to O_3.

Seasonal and ambient factors may vary responsiveness to O_3, but further research is needed to determine how they affect individual subjects. Individual sensitivity to O_3 may vary throughout the year, related to seasonal variations in ambient O_3 concentrations.

The specific inhalation route appears to be of minor importance in exercising adults. Exposure to O_3 by oral breathing (i.e., mouthpiece) yields results similar to exposure by oronasal breathing (i.e., chamber exposures).

Population Groups at Risk from Ozone Exposure

Population groups that have demonstrated increased responsiveness to ambient concentrations of O_3 consist of exercising healthy and asthmatic individuals, including children, adolescents, and adults.

Available evidence from controlled human studies on subjects with preexisting disease suggests that mild asthmatics have similar lung volume responses, but greater airway resistance responses to O_3 than nonasthmatics; and that moderate asthmatics may have, in addition, greater lung volume responses than nonasthmatics.

Of all the other population groups studied, those with preexisting limitations in pulmonary function and exercise capacity (e.g., chronic obstructive pulmonary disease, chronic bronchitis, ischemic heart disease) would be of primary concern in evaluating the health effects of O_3. Unfortunately, limitations of subject selection, standardized methods of subject characterization, and range of exposure hamper the ability to make definitive conclusions regarding the relative responsiveness of most chronic disease subjects.

Effects of Ozone Mixed with Other Pollutants

No significant enhancement of respiratory effects has been demonstrated consistently for simultaneous exposures of O_3 mixed with SO_2, NO_2, H_2SO_4, HNO_3, particulate aerosols, or combinations of these pollutants. It is fairly well established that simultaneous exposure of healthy adults and asthmatics to mixtures of O_3 and other pollutants for short periods of time (<2 h) induces pulmonary function responses not significantly different from those following O_3 alone when studies are conducted at the same O_3 concentration. Exposure to PAN has been reported to induce greater pulmonary function responses than exposure to O_3 alone, but at PAN concentrations (>0.27 ppm) much higher than ambient levels. Unfortunately, only a limited number of pollutant combinations and exposure protocols have been investigated, and subject groups are small and are representative of only small portions of the general population. Thus, much is unknown about the relationships between O_3 and the complex mix of pollutants found in the ambient air.

Prior exposure to O_3 in asthmatics may cause an increase in response to other pollutant gases, especially SO_2. Likewise, prior exposure to other pollutants can enhance responses to O_3 exposure.

Controlled Human Studies of Ambient Air Exposures

Mobile laboratory studies of lung function and respiratory symptoms in a local subject population exposed to ambient photochemical oxidant pollution provide quantitative information on exposure-response relationships for O_3. A series of these studies from Los Angeles has demonstrated pulmonary function decrements at mean ambient O_3 concentrations of 0.14 ppm in exercising healthy adolescents and increased respiratory symptoms and pulmonary function decrements at 0.15 ppm in heavily exercising athletes and at 0.17 ppm in lightly exercising healthy and asthmatic subjects. Comparison of the observed effects in exercising athletes with controlled chamber studies at comparable O_3 concentrations showed no significant differences in lung function and symptoms, suggesting that coexisting ambient pollutants have a minimal contribution to the measured responses under typical summer ambient conditions in Southern California.

Field and Epidemiology Studies of Ambient Air Exposures

Individual-level field studies and aggregate-level time-series studies have addressed the acute effects of O_3 on lung function decrements and increased morbidity and mortality in human populations exposed to real-world conditions of O_3 exposure.

Camp and exercise studies of lung function provide quantitative information on exposure-response relationships linking lung function declines with O_3 exposure occurring in ambient air. Combined statistical analysis of six recent camp studies in children yields an average relationship between decrements in FEV_1 and previous-hour O_3 concentration of −0.50 mL/ppb. Two key studies of lung function measurements before and after well-defined outdoor exercise events in adults have yielded exposure-response slopes of −0.40 and −1.35 mL/ppb. The magnitude of pulmonary function declines with O_3 exposure is consistent with the results of controlled human studies.

Daily life studies support a consistent relationship between O_3 exposure and acute respiratory morbidity in the population. Respiratory symptoms (or exacerbation of asthma) and decrements in peak expiratory flow rate are associated with increasing ambient O_3, particularly in asthmatic children; however, concurrent temperature, particles, acidity (hydrogen ions), aeroallergens, and asthma severity or medication status also may contribute as independent or modifying factors. Aggregate results show greater responses in asthmatic individuals than in nonasthmatics, indicating that asthmatics constitute a sensitive group in epidemiologic studies of oxidant air pollution.

Summertime daily hospital admissions for respiratory causes in various locations of eastern North America have consistently shown a relationship with ambient levels of O_3, accounting for approximately one to three excess respiratory hospital admissions per hundred parts per billion O_3 per million persons. This association has been shown to remain even after statistically controlling for the possible confounding effects of temperature and copollutants (e.g., hydrogen ions, sulfate, and particles less than 10 µm), as well as when considering only concentrations below 0.12 ppm O_3.

Many of the time-series epidemiology studies looking for associations between O_3 exposure and daily human mortality have been difficult to interpret because of

methodological or statistical weaknesses, including the a failure to account for other pollutant and environmental effects. One of the two most useful new studies on O_3-mortality found a small but statistically significant association in Los Angeles when peak 1-h maximum O_3 concentrations reached concentrations greater than 0.2 ppm during the study period. A second study in regions with lower (≤0.15 ppm) maximum 1-h O_3 concentrations (St. Louis, MO, and Kingston-Harriman, TN) did not detect a significant O_3 association with mortality.

Only suggestive epidemiologic evidence exists for health effects of chronic ambient O_3 exposure in the population. All of the available studies of chronic respiratory system effects in exposed children and adults are limited by a simplistic assignment of exposure or by their inability to isolate potential effects related to O_3 from those of other pollutants, especially particles.

1.8 Extrapolation of Animal Toxicological Data to Humans

There have been significant advances in O_3 dosimetry since 1986 that better enable quantitative extrapolation with marked reductions in uncertainty. Experiments and models describing the uptake efficiency and delivered dose of O_3 in the RT of animals and humans are beginning to present a clearer picture than has existed previously.

The total RT uptake efficiency of rats at rest is approximately 50%. Within the RT of the rat, 50% of the O_3 taken up by the RT is removed in the head, 7% in the larynx/trachea, and 43% in the lungs.

In humans at rest, the total RT uptake efficiency is between 80 and 95%. Total RT uptake efficiency falls as flow increases. As tidal volume increases, uptake efficiency increases and flow dependence lessens. Pulmonary function response data and O_3 uptake efficiency data in humans generally indicate that the mode of breathing (oral versus nasal versus oronasal) has little effect on upper RT or on total RT uptake efficiency, although one study suggests that the nose has a higher uptake efficiency than the mouth.

When all of the animal and human in vivo O_3 uptake efficiency data are compared, there is a good degree of consistency across data sets. This agreement raises the level of confidence with which these data sets can be used to support dosimetric model formulations.

Several mathematical dosimetry models have been developed since 1986. Generally, the models predict that net O_3 dose to lung lining fluid plus tissue gradually decreases distally from the trachea toward the end of the tracheobronchial region and then rapidly decreases in the pulmonary region.

When the dose of O_3 to lung tissue is computed theoretically, it is found to be very low in the trachea; to increase to a maximum in the terminal bronchioles of the first generation pulmonary region; and then to decrease rapidly, moving further into the pulmonary region. The increased tidal volume and flow, associated with exercise in humans, shifts O_3 dose further into the periphery of the lung and causes a disproportionate increase in distal lung dose.

Predictions of delivered dose have been used to investigate both acute and chronic O_3 responses in the context of intra- and interspecies comparisons. In the case of intraspecies comparisons, for example, the distribution of predicted O_3 tissue dose to a ventilatory unit in a rat as a function of distance from the bronchoalveolar duct junction is very consistent with

the distribution of alveolar wall thickening. In the case of interspecies comparisons (using the delivered O_3 dose to the proximal alveolar regions), although the functional responses (e.g., rapid, shallow breathing) differ markedly between rats and humans, there is similarity of acute dose-response patterns in inflammation (influx of cells and protein) among species, with humans and guinea pigs more responsive than rats and rabbits, and similarity of chronic dose-response patterns for increased alveolar interstitial thickness in the CAR of the lung, with monkeys being more responsive than humans and rats less responsive. In other words, the quantitative relationship between animal and human responses is dependent on the animal species and the endpoint.

In summary, there is an emerging consistency among a variety of O_3 dosimetry data sets and between the experimental data and theoretical predictions of O_3 dose. The convergence of experimental data with theoretical predictions lends a degree of confidence to the use of theoretical models to predict total and regional O_3 dose. The use of O_3 dosimetry data and models is beginning to provide a useful extrapolation of effects between animals and humans. The data and models have thus far helped demonstrate that humans may be more responsive to O_3 than rats, but less responsive than monkeys with respect to acute and chronic inflammatory responses. However, the monkey, with its similarity to the human in distal airway structure, provides chronic effects data that may best reflect the degree to which a comparably exposed human would respond. These findings, therefore, suggest that long-term exposure to O_3 could impart a chronic effect in humans.

1.9 Integrative Summary of Ozone Health Effects

This section summarizes the primary conclusions derived from an integration of the known effects of O_3 provided by animal toxicological, human clinical, and epidemiological studies.

1. What are the effects of short-term (<8-h) exposures to ozone?

Recent epidemiology studies addressing the effects of short-term ambient exposure to O_3 in the population have yielded significant associations with a wide range of health outcomes, including lung function decrements, aggravation of preexisting respiratory disease, increases in daily hospital admissions and emergency department visits for respiratory causes, and increased mortality. Results from lung function epidemiology studies generally are consistent with the experimental studies in laboratory animals and humans.

Short-term O_3 exposure of laboratory animals and humans causes changes in pulmonary function, including tachypnea (rapid, shallow breathing), decreased lung volumes and flows, and increased airway responsiveness to nonspecific stimuli. Increased airway resistance occurs in both humans and laboratory animals, but typically at higher exposure levels than other functional endpoints. In addition, adult human subjects experience O_3-induced symptoms of airway irritation such as cough or pain on deep inspiration. The changes in pulmonary function and respiratory symptoms occur as a function of exposure concentration, duration, and level of exercise. Adult human subjects with mild asthma have responses in lung volume and airway responsiveness to bronchoconstrictor drugs that are qualitatively similar to those of nonasthmatics. Respiratory symptoms are also similar, but wheezing is a prevalent symptom in O_3-exposed asthmatics in addition to the other demonstrated symptoms of airway irritation. Airway resistance, however, increases relatively

more in asthmatics from an already higher baseline. Recovery from the effects of O_3 on pulmonary function and symptoms is usually complete within 24 h of the end of exposure, although other responses may persist somewhat longer.

- An association between daily mortality and O_3 concentration for areas with high O_3 levels (e.g., Los Angeles) has been suggested, although the magnitude of such an effect is unclear.
- Increased O_3 levels are associated with increased hospital admissions and emergency department visits for respiratory causes. Analyses from data in the northeastern United States suggest that O_3 air pollution is associated with a substantial portion (on the order of 10 to 20%) of all summertime respiratory hospital visits and admissions.
- Pulmonary function in children at summer camps in southern Ontario, Canada, in the northeastern United States, and in Southern California is associated with O_3 concentration. Meta-analysis indicates that a 0.5-mL decrease in FEV_1 is associated with a 1-ppb increase in O_3 concentration. For preadolescent children exposed to 120 ppb (0.12 ppm) ambient O_3, this amounts to an average decrement of 2.4 to 3.0% in FEV_1. Similar responses are reported for children and adolescents exposed to O_3 in ambient air or O_3 in purified air for 1 to 2 h while exercising.
- Pulmonary function decrements generally are observed in healthy subjects (8 to 45 years of age) after 1 to 3 h of exposure as a function of the level of exercise performed and the O_3 concentration inhaled during the exposure. Group mean data from numerous controlled human exposure and field studies indicate that, in general, statistically significant pulmonary function decrements beyond the range of normal measurement variability (e.g., 3 to 5% for FEV_1) occur
  (1) at >0.50 ppm O_3 when at rest,
  (2) at >0.37 ppm O_3 with light exercise (slow walking),
  (3) at >0.30 ppm O_3 with moderate exercise (brisk walking),
  (4) at >0.18 ppm O_3 with heavy exercise (easy jogging), and
  (5) at >0.16 ppm O_3 with very heavy exercise (running).
  Smaller group mean changes (e.g., <5%) in FEV_1 have been observed at lower O_3 concentrations than those listed above. For example, FEV_1 decrements have been shown to occur with very heavy exercise in healthy adults at 0.15 to 0.16 ppm O_3, and such effects may occur in healthy young adults at levels as low as 0.12 ppm. Also, pulmonary function decrements have been observed in children and adolescents at concentrations of 0.12 and 0.14 ppm O_3 with heavy exercise. Some individuals within a study may experience FEV_1 decrements in excess of 15% under these exposure conditions, even when the group mean decrement is less than 5%.
- For exposures of healthy subjects performing moderate exercise during longer duration exposures (6 to 8 h), 5% group mean decrements in FEV_1 were observed at
  (1) 0.08 ppm O_3 after 5.6 h,
  (2) 0.10 ppm O_3 after 4.6 h, and
  (3) 0.12 ppm O_3 after 3 h.

For these same subjects, 10% group mean FEV_1 decrements were observed at 0.12 ppm O_3 after 5.6 and 6.6 h. As in the shorter duration studies, some individuals experience changes larger than those represented by the group mean changes.

- An increase in the incidence of cough has been reported at O_3 concentrations as low as 0.12 ppm in healthy adults during 1 to 3 h of exposure with very heavy exercise. Other respiratory symptoms, such as pain on deep inspiration, shortness of breath, and lower respiratory scores (a combination of several symptoms), have been observed at 0.16 to 0.18 ppm O_3 with heavy and very heavy exercise. Respiratory symptoms also have been observed following exposure to 0.08, 0.10, and 0.12 ppm O_3 for 6.6 h with moderate levels of exercise.
- Increases in nonspecific airway responsiveness in healthy adults have been observed after 1 to 3 h of exposure to 0.40 but not 0.20 ppm O_3 at rest and have been observed at concentrations as low as 0.18 but not to 0.12 ppm O_3 during exposure with very heavy exercise. Increases in nonspecific airway responsiveness during 6.6-h exposures with moderate levels of exercise have been observed at 0.08, 0.10, and 0.12 ppm O_3.

Short-term O_3 exposure of laboratory animals and humans disrupts the barrier function of the lung epithelium, permitting materials in the airspaces to enter lung tissue, allowing cells and serum proteins to enter the airspaces (inflammation), and setting off a cascade of responses.

- Increased levels of PMNs and protein in lung lavage fluid have been observed following exposure of healthy adults to 0.20, 0.30, and 0.40 ppm with very heavy exercise and have not been studied at lower concentrations for 1- to 3-h exposures. Increases in lung lavage protein and PMNs also have been observed at 0.08 and 0.10 ppm O_3 during 6.6-h exposures with moderate exercise; lower concentrations have not been tested.

Short-term O_3 exposure of laboratory animals and humans impairs AM clearance of viable and nonviable particles from the lungs and decreases the effectiveness of host defenses against bacterial lung infections in animals and perhaps in humans. The ability of AMs to engulf microorganisms is decreased in humans exposed to 0.08 and 0.10 ppm O_3 for 6.6 h with moderate exercise.

2. What are the effects of repeated, short-term exposures to ozone?

During repeated short-term exposures, some of the O_3-induced responses are partially or completely attenuated. Over a 5-day exposure, pulmonary function changes are typically greatest on the second day, but return to control levels by the fifth day of exposure. Most of the inflammatory markers (e.g., PMN influx) also attenuate by the fifth day of exposure, but markers of cell damage (e.g., lactate dehydrogenase enzyme activity) do not attenuate but continue to increase. Attenuation of lung function decrements is reversed following 7 to 10 days without O_3. Some inflammatory markers also are reversed during this time period, but others still show attenuation even after 20 days without O_3. The mechanisms and impacts involved in attenuation are not known, although animal studies show that the underlying cell damage continues throughout the attenuation process. In addition, attenuation may alter the normal distribution of O_3 within the lung, allowing more O_3 to reach sensitive

regions, possibly affecting normal lung defenses (e.g., PMN influx in response to inhaled microorganisms).

3. What are the effects of long-term exposures to ozone?

Available data indicate that exposure to O_3 for months and years causes structural changes in several regions of the RT, but effects may be of the greatest importance in the CAR (where the alveoli and conducting airways meet); this region typically is affected in most chronic airway diseases of the human lung. This information on O_3 effects in the distal lung is extrapolated from animal toxicological studies because, to date, comparable data are not available from humans. The apparent lack of reversal of effects during periods of clean air exposure raises concern that seasonal exposures may have a cumulative impact over many years. The role of adaptive processes in this response is unknown but may be critically dependent on the temporal frequency or profile of exposure. Furthermore, the interspecies diversity in apparent sensitivity to the chronic effects of O_3 is notable, with the rat representing the lower limit of response, and the monkey the upper limit. Epidemiological studies attempting to associate chronic health effects in humans with long-term O_3 exposure provide only suggestive evidence that such a linkage exists.

Long-term exposure of one strain of female mice to high O_3 levels (1 ppm) caused a small, but statistically significant increase in lung tumors. There was no concentration-response relationship, and rats were not affected. Genotoxicity data are either negative or weak. Given the nature of the database, the effects in one strain of mice cannot yet be extrapolated qualitatively to humans. Ozone (0.5 ppm) did not show tumor-promoting activity in a chronic rat study.

4. What are the effects of binary pollutant mixtures containing ozone?

Combined data from laboratory animal and controlled human exposure studies of O_3 support the hypothesis that coexposure to pollutants, each at low-effect levels, may result in effects of significance. The data from human studies of O_3 in combination with NO_2, SO_2, H_2SO_4, HNO_3, or CO show no more than an additive response on lung spirometry or respiratory symptoms. The larger number of laboratory animal studies with O_3 in mixture with NO_2 and H_2SO_4 show that effects can be additive, synergistic, or even antagonistic, depending on the exposure regimen and the endpoint studied. This issue of exposure to copollutants remains poorly understood, especially with regard to potential chronic effects.

5. What population groups are at risk as a result of exposure to ozone?

Identification of population groups that may show increased sensitivity to O_3 is based on their biological responses to O_3, preexisting lung disease (e.g., asthma), activity patterns, personal exposure history, and personal factors (e.g., age, nutritional status).

The predominant information on the health effects of O_3 noted above comes from clinical and field studies on healthy, nonsmoking, exercising subjects, 8 to 45 years of age. These studies demonstrate that, among this group, there is a large variation in sensitivity and responsiveness to O_3, with at least a 10-fold difference between the most and least responsive individuals. Individual sensitivity to O_3 also may vary throughout the year, related to seasonal variations in ambient O_3 exposure. The specific factors that contribute to this large intersubject variability, however, remain undefined. Although differences in response may be due to the dosimetry of O_3 in the RT, available data show little difference on O_3 deposition in the lungs for inhalation through the nose or mouth.

Daily life studies reporting an exacerbation of asthma and decrease in peak expiratory flow rates, particularly in asthmatic children, appear to support the controlled studies; however, those studies may be confounded by temperature, particle or aeroallergen exposure, and asthma severity of the subjects or their medication use. In addition, field studies of summertime daily hospital admissions for respiratory causes show a consistent relationship between asthma and ambient levels of O_3 in various locations in the northeastern United States, even after controlling for independent contributing factors. Controlled studies on mild asthmatics suggest that they have similar lung volume responses but greater airway resistance changes to O_3 than nonasthmatics. Furthermore, limited data from studies of moderate asthmatics suggest that this group may have greater lung volume responses than nonasthmatics.

Other population groups with preexisting limitations in pulmonary function and exercise capacity (e.g., chronic obstructive pulmonary disease, chronic bronchitis, ischemic heart disease) would be of primary concern in evaluating the health effects of O_3. Unfortunately, not enough is known about the responses of these individuals to make definitive conclusions regarding their relative responsiveness to O_3. Indeed, functional effects in these individuals with reduced lung function may have greater clinical significance than comparable changes in healthy individuals.

Currently available data follow on personal factors or personal exposure history known or suspected of influencing responses to O_3.

- Human studies have identified a decrease in pulmonary function responsiveness to O_3 with increasing age, although symptom rates remain similar. Toxicological studies are not easily interpreted but suggest that young animals are not more responsive than adults.
- Available toxicological and human data have not demonstrated conclusively that males and females respond differently to O_3. If gender differences exist for lung function responsiveness to O_3, they are not based on differences in baseline pulmonary function.
- Data are not adequate to determine whether any ethnic or racial group has a different distribution of responsiveness to O_3. In particular, the responses of nonwhite asthmatics have not been investigated.
- Information derived from O_3 exposure of smokers is limited. The general trend is that smokers are less responsive than nonsmokers. This reduced responsiveness may wane after smoking cessation.
- Although nutritional status (e.g., vitamin E deficiency) makes laboratory rats more susceptible to O_3-induced effects, it is not clear if vitamin E supplementation has an effect in human populations. Such supplementation has no or minimal effect in animals. The role of such antioxidant vitamins in O_3 responsiveness, especially their deficiency, has not been well studied.

Based on information presented in this document, the population groups that have demonstrated increased responsiveness to ambient concentrations of O_3 consist of exercising, healthy and asthmatic individuals, including children, adolescents, and adults.

2

Introduction

The photochemical oxidants found in ambient air in the highest concentrations are ozone (O_3) and nitrogen dioxide (NO_2). Other oxidants, such as hydrogen peroxide (H_2O_2) and the peroxyacyl nitrates, also have 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. The 1971 photochemical oxidant standards were promulgated on the basis of (1) commercially available measurement methodology,[1] (2) uncertainties over the concentrations of O_3 and non-O_3 photochemical oxidants in the atmosphere resulting from the nonspecificity of the measurement methodology, and (3) uncertainties regarding the health and welfare effects of the non-O_3 photochemical oxidants found in ambient air. After 1971, however, O_3-specific commercial analytical methods became available, as did additional information on concentrations and effects of the non-O_3 photochemical oxidants. As a result, the chemical designation of the standards was changed in 1979 from photochemical oxidants to O_3. This document focuses primarily on the scientific air quality criteria for O_3 and, to a lesser extent, on those for H_2O_2 and the peroxyacyl nitrates, particularly peroxyacetyl nitrate. The scientific air quality criteria for NO_2 are discussed in a separate document (U.S. Environmental Protection Agency, 1993).

The previous O_3 air quality criteria document (AQCD), *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 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 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 document is to summarize the air quality criteria for O_3 available in the published literature through early 1995. This review was performed in accordance with provisions of the Clean Air Act (CAA) to provide the scientific basis for periodic reevaluation of the O_3 NAAQS.

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[1]The term "photochemical oxidants" historically has been defined as those atmospheric pollutants capable of oxidizing neutral iodide ions (U.S. Environmental Protection Agency, 1978). A number of oxidants other than O_3 are measured, qualitatively if not quantitatively, by potassium iodide methods.

This chapter provides a general introduction to the legislative and regulatory background for decisions on the O_3 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 certain 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, are 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, are 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. Thus, the Administrator may find that EPA's review and revision of criteria make appropriate the proposal of new or revised standards. 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[2]

On April 30, 1971, EPA promulgated primary and secondary NAAQS for photochemical oxidants under Section 109 of the CAA (Federal Register, 1971). These standards were set at an hourly average of 0.08 ppm total photochemical oxidants not to be exceeded more than 1 h/year. On April 20, 1977, EPA announced (Federal Register, 1977) the first review and updating of the 1970 *Air Quality Criteria for Photochemical Oxidants* in accordance with Section 109(d) of the CAA. In preparing a revised AQCD, 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 O_3 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, EPA announced (Federal Register, 1979) a final decision to revise the NAAQS for photochemical

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

oxidants on February 8, 1979. The final ruling revised the level of the primary standard from 0.08 to 0.12 ppm, set the secondary standard identical to the primary standard, changed the chemical designation of the standards from photochemical oxidants to O_3, 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[a]

Date of Promulgation	Primary and Secondary NAAQS	Averaging Time
February 8, 1979	0.12 ppm[b] (235 $\mu g/m^3$)	1 h[c]

[a]See Appendix A for abbreviations and acronyms.
[b]1 ppm = 1,962 $\mu g/m^3$, 1 $\mu g/m^3$ = 5.097×10^{-4} ppm at 25 °C, 760 mm Hg.
[c]The standard is attained when the expected number of days per calendar year with a maximum hourly average concentration above 0.12 ppm (235 $\mu g/m^3$) is equal to or less than one.

On March 17, 1982, in response to requirements of Section 109(d) of the CAA, EPA announced (Federal Register, 1982) that it was undertaking plans to revise the existing 1978 AQCD for O_3 and other photochemical oxidants, and, on August 22, 1983, it announced (Federal Register, 1983) that review of the primary and secondary NAAQS for O_3 had been initiated. Public peer-review workshops on draft chapters of a revised AQCD were held December 15 through 17, 1982, and November 16 through 18, 1983. The EPA considered comments made at both workshops in preparing the first external review draft that was made available (Federal Register, 1984) on July 24, 1984, for public review.

On February 13, 1985 (Federal Register, 1985), and on April 2, 1986 (Federal Register, 1986), EPA announced two public meetings of the Clean Air Scientific Advisory Committee (CASAC) of EPA's SAB to be held March 4 through 6, 1985, and April 21 and 22, 1986, respectively. At these meetings, CASAC reviewed external review drafts of the revised AQCD for O_3 and other photochemical oxidants. After completion of this review, CASAC sent the EPA Administrator a closure letter, dated October 22, 1986, indicating that the document "represents a scientifically balanced and defensible summary of the extensive scientific literature." The EPA released the final draft document in August 1986.

The first draft of the Staff Paper "Review of the National Ambient Air Quality Standards for Ozone: Assessment of Scientific and Technical Information" was reviewed by CASAC at a public meeting on April 21 and 22, 1986. At that meeting, CASAC recommended that new information on prolonged exposure effects of O_3 be considered in a second draft of the Staff Paper prior to closure. The CASAC reviewed this second draft and also a presentation of new and emerging information on the health and welfare effects of O_3 at a public review meeting held on December 14 and 15, 1987. The CASAC concluded that sufficient new information existed to recommend incorporation of relevant new data into a supplement to the 1986 AQCD (O_3 supplement) and in a third draft of the Staff Paper.

A draft O_3 supplement, *Summary of Selected New Information on Effects of Ozone on Health and Vegetation: Draft Supplement to Air Quality Criteria for Ozone and Other Photochemical Oxidants*, and the revised Staff Paper were made available to CASAC and to the public for review in November 1988. The O_3 supplement reviewed and evaluated selected literature concerning exposure- and concentration-response relationships observed for health effects in humans and experimental animals and for vegetation effects. This literature appeared as peer-reviewed journal publications or as proceedings papers from 1986 through late 1988.

On December 14 and 15, 1988, CASAC held a public meeting to review these documents. The CASAC sent the EPA Administrator a closure letter dated May 1, 1989, indicating that the draft O_3 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 O_3 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 O_3 NAAQS. A final version of the O_3 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 EPA to complete its review of the criteria and standards for O_3. On May 4, 1992, the U.S. District Court for the Eastern District of New York issued an order requiring the Administrator of EPA to sign a proposed decision on whether to revise the standards for O_3 by August 1, 1992, and to sign EPA's final decision by March 1, 1993.

On August 1, 1992, the Administrator signed a proposed decision not to revise the existing NAAQS for O_3 (Federal Register, 1992a), then, on March 1, 1993, signed EPA's final decision, concluding that revision of the NAAQS was inappropriate at that time (Federal Register, 1993a). For reasons indicated in the proposed and final decisions, the March 1993 decision did not take into consideration a number of recent studies on the health and welfare effects of O_3 that had been published since the last literature review in early 1989. The EPA estimated that approximately 3 years would 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 O_3 NAAQS in the *Federal Register*.

The EPA intends to complete the current review of the criteria and standards for O_3 as rapidly as possible. Accordingly, the National Center for Environmental Assessment (formerly the Environmental Criteria and Assessment Office [ECAO]) of EPA's Office of Research and Development, located in Research Triangle Park, NC, has given very high priority to review and revision of the air quality criteria for O_3. The ECAO began by announcing the commencement of the review and identification of new information (Federal Register, 1992b). After assessing and evaluating pertinent new studies, ECAO prepared a preliminary draft of a revised AQCD that was reviewed in a series of expert peer reviewed workshops (Federal Register, 1993b,c). Comments received at the workshops were used to revise the preliminary draft for external review (Federal Register, 1994a). Public peer review meetings were held by CASAC to provide advice on the scientific and technical adequacy of the external review draft (Federal Register, 1994b) and the subsequent revised draft (Federal Register, 1995). The final document was prepared on the basis of comments received from the public and CASAC reviews and provides a scientific basis for review of the existing O_3 standards. The EPA's Office of Air Quality Planning and Standards

(OAQPS) is completing its preparation of a draft staff paper assessing the most significant information contained in this AQCD and presenting staff recommendations on whether revisions to the NAAQS for O_3 are appropriate. After reviews of the draft staff paper by the public and CASAC, the Administrator will decide whether to propose revisions to the O_3 NAAQS.

2.3 Summary of Major Scientific Topics Presented

A number of separate topics and issues are addressed in this O_3 criteria document. Some of the key questions addressed are highlighted below by document section.

2.3.1 Air Chemistry

- What concerns still exist regarding precision and accuracy of measurements of O_3 and its precursors?
- What is the order of magnitude of current estimates of natural emissions of O_3 precursors and emissions from anthropogenic sources and their relevance to tropospheric O_3 photochemistry?
- What new scientific information exists on the roles of meteorologic and climatologic factors in O_3 formation and transport?
- Are the reaction pathways of all major precursors to O_3 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 O_3 concentrations across the United States?
- What are diurnal and seasonal patterns of 1-h average O_3 concentrations for urban and nonurban sites and for attainment versus nonattainment areas?
- What is known about patterns of co-occurrence of O_3 with other pollutants in the atmosphere?
- What O_3 exposure assessment data are available for agricultural crops and forests?
- To what level and to what extent are humans typically exposed to O_3 in the course of normal, everyday activities?

2.3.3 Environmental Effects

- What are the effects of ambient O_3 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 O_3 exposures on natural ecosystems?
- Is there important new information on the effects of O_3 on nonbiological materials?

2.3.4 Health Effects

- What O_3 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 O_3-induced lung injury?
- Can dosimetry models predict human population responses to O_3 on the basis of laboratory animal data?
- Does long-term exposure to O_3 lead to the development of chronic lung disease or to an increased frequency or exacerbation of other chronic respiratory outcomes?
- What segments of the population are most susceptible to effects from exposure to O_3?

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 O_3 and related photochemical oxidants present in ambient air. Although the document is not intended to be an exhaustive literature review, it is intended to selectively cover the pertinent literature through 1995. 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 O_3, 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 O_3 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 O_3 criteria document (U.S. Environmental Protection Agency, 1986). Some of these newer studies were reviewed briefly in the supplement to that document (U.S. Environmental Protection Agency, 1992), but more intense evaluation of these studies has been included. 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. Emphasis is placed on studies conducted at or near O_3 concentrations found in ambient air. For animal toxicology studies, typically only those studies conducted at less than 1 ppm O_3 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 discussed briefly in the text. Other, older studies also are 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 O_3. The reader should, however, consult the more extensive discussion of these "key" studies in the previous document. Generally, only published information that has undergone scientific peer review is included in the criteria document.

Certain issues of direct relevance to standard setting are not explicitly addressed in this document, but instead are analyzed in documentation prepared by OAQPS as part of its regulatory review process. Such issues include (1) determining what constitutes an "adverse

effect" and delineation of particular adverse effects that the primary and secondary NAAQS are intended to protect against, (2) exposure assessment, (3) assessment of consequent risks based on health and exposure analyses, and (4) factors to be considered in determining an adequate margin of safety. Key points and conclusions from such analyses are summarized in the Staff Paper prepared by OAQPS and reviewed by CASAC and the public. Although scientific data contribute significantly to decisions regarding the above issues, their resolution cannot be achieved solely on the basis of experimentally acquired information. Final decisions on items 1 and 4 are made by the EPA Administrator, as mandated by the CAA.

A fourth issue directly pertinent to standard setting is identification of populations at risk, which is basically a determination by EPA of the subpopulations to be protected by the promulgation of a given standard. This issue is addressed only partially in the criteria document. For example, information is presented on factors, such as preexisting disease, that biologically may predispose individuals and subpopulations to more severe effects from exposures to O_3. The identification of a population at risk, however, requires information above and beyond data on biological predisposition, such as information on levels of exposure, activity patterns, and personal habits. Such information is included in the Staff Paper developed by OAQPS.

Finally, the O_3 air quality document considers only the scientific and technical issues that are important for standard setting, not those issues relative to implementation of the O_3 NAAQS. For example, certain issues related to the control strategies for attainment of the standard and to possible atmospheric consequences of control strategy design are not discussed in this document. This limitation also includes discussion of impacts consequent to possible changes in the O_3 NAAQS. These issues would be better addressed in regulatory impact analyses or cost-benefit analyses that may be prepared as part of the O_3 NAAQS decision package.

This document is structured as follows: Chapter 1 (executive summary and conclusions) provides a concise presentation of key information and conclusions from all subsequent chapters. This is followed by this brief introduction (Chapter 2) containing information on the legislative and regulatory background for review of the O_3 NAAQS, as well as an overview of the organization of this document. Chapter 3 provides information on the chemistry, sources, emissions, measurement, and transport of O_3 and related photochemical oxidants and their precursors, and Chapter 4 covers environmental concentrations, patterns, and exposure estimates of O_3 and oxidant air quality. This is followed by Chapter 5, which deals with environmental effects of O_3 and related photochemical oxidants. Chapters 6, 7, and 8 discuss animal toxicological studies, human health effects, and extrapolation of animal toxicological data to humans, respectively. Finally, Chapter 9, provides an integrative and interpretive evaluation of health effects associated with exposure to O_3.

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3

Tropospheric Ozone and Its Precursors

3.1 Introduction

Ozone (O_3) and other oxidants found in ambient air, such as peroxyacyl nitrates (PANs) and hydrogen peroxide (H_2O_2), 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 O_3 and other oxidants from these precursors is a complex, nonlinear function of many factors, including temperature, the intensity and spectral distribution of sunlight, atmospheric mixing and related meteorological conditions, the concentrations of the precursors in ambient air and the ratio between VOC and 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 O_3 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 National Ambient Air Quality Standards (NAAQS) for O_3. In addition, the identification and quantification of O_3 precursors in ambient air are essential, along with emission inventories or emission models, for the development, verification, and refinement of photochemical air quality models and for comparisons of ambient concentrations with emission inventories (source reconciliation), as a check on the accuracy of measurements and of inventories.

Product identification and quantification of yields, in both chambers and 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 O_3 and related oxidants of multiple air pollutants.

The ability to measure O_3 and its precursors, its reaction products, and the products of the atmospheric reactions of its respective precursors is essential for understanding the atmospheric chemistry of O_3 formation, verifying chemical mechanisms and models, quantifying emission rates, and adequately characterizing exposure-response factors for both biological and nonbiological receptors.

For these reasons, this chapter presents information on a broad range of topics. The chapter describes the chemical processes by which O_3 and other photochemical oxidants are formed in ambient air (Section 3.2). The chapter also characterizes the nature of the precursors in terms of their sources and emissions into the atmosphere and their

concentrations in ambient air (Section 3.4), as well as the methods by which their concentrations in ambient air are measured (Section 3.5).

In addition to information on the chemistry of oxidants and their precursors, this chapter includes a discussion of meteorological processes (Section 3.3) that contribute to the formation of O_3 and other oxidants and govern their transport and dispersion. Finally, an overview is given (Section 3.6) of models of the relationships between precursor emissions and O_3 formation in the atmosphere.

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

3.2 Tropospheric Ozone Chemistry

3.2.1 Background Information

Ozone is formed photochemically in the stratosphere and transported downward, resulting in the presence of O_3 in the natural or "clean" troposphere. The presence of O_3 in the clean troposphere, in the absence of perturbations caused by human activities, is highly important because O_3 is a precursor to the hydroxyl (OH) radical, the key intermediate species in the tropospheric degradation of VOCs emitted into the atmosphere. Although O_3 at relatively low concentrations is an integral part of the clean troposphere, its presence at higher concentrations is detrimental.

The chemical processes occurring in the atmosphere that lead to the formation of O_3 and other photochemical air pollutants are complex. Tropospheric O_3 is formed as a result of (1) the emissions of NO_x and VOCs into the atmosphere from anthropogenic and natural sources, (2) the transport of these emissions and their reaction products, and (3) chemical reactions occurring in the atmosphere concurrent with transport and dispersion of the emissions. These processes lead to the formation of O_3 and other photochemical oxidants, such as peroxyacetyl nitrate (PAN), nitric acid (HNO_3), and sulfuric acid (H_2SO_4), and to other compounds, such as particulate matter and formaldehyde (HCHO) and other carbonyl compounds. Additionally, deposition of gases and particles along the trajectory of an air parcel occurs, reducing the concentrations of precursors and products in the atmosphere, but possibly leading to adverse impacts on the earth's environment.

The basic process leading to the photochemical formation of O_3 in the troposphere involves the photolysis of nitrogen dioxide (NO_2) to yield nitric oxide (NO) and a ground-state oxygen atom, $O(^3P)$,

$$NO_2 + h\nu \rightarrow NO + O(^3P), \tag{3-1}$$

which then reacts with molecular oxygen to form O_3:

$$O(^3P) + O_2 + M \rightarrow O_3 + M, \text{ where } M = \text{air}. \tag{3-2}$$

The NO and O_3 react to reform NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{3-3}$$

The presence of reactive VOCs leads to the conversion of NO to NO_2 without the intermediary of O_3 (Reaction 3-3), and the photolysis of NO_2 then leads to the formation of elevated levels of O_3:

$$NO \xrightarrow{VOC} NO_2 . \tag{3-4}$$

The photochemical cycles leading to O_3 production are best understood through a knowledge of the chemistry of the atmospheric oxidation of methane (CH_4), which can be viewed as being the chemistry of the clean or unpolluted troposphere (although this is a simplification because vegetation releases large quantities of complex VOCs into the atmosphere). Although the chemistry of the VOCs emitted from anthropogenic and biogenic sources in polluted urban and rural areas is more complex, a knowledge of the CH_4 oxidation reactions aids in understanding the chemical processes occurring in the polluted atmosphere because the underlying chemical principles are the same.

This section first describes the structure of the atmosphere, followed by discussions of the formation of the OH radical and of tropospheric NO_x chemistry. The photochemical formation of tropospheric O_3 from the oxidation of CH_4 then is discussed in some detail because the CH_4 oxidation cycle serves as a model for the photochemical formation of O_3. In Section 3.2.4, the chemistry of the major classes of nonmethane VOCs and the formation of O_3 from these VOCs are discussed. Finally, in Section 3.2.5, a brief account of the photochemical formation of aerosols is given because the same processes that lead to the formation of elevated levels of O_3 result in the formation of both particulate matter (leading to visibility degradation) and atmospheric acidity.

3.2.2 Structure of the Atmosphere

Earth's atmosphere is composed of a number of layers (McIlveen, 1992). For the purposes of this chapter, those of concern are the troposphere and the stratosphere, and the boundary between them, the tropopause.

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

The stratosphere extends from the tropopause to an altitude of ≈50 km. In the stratosphere, the temperature increases with increasing altitude from ≈210 to 220 K at the tropopause to ≈270 K at the top of the stratosphere. The pressure in the stratosphere decreases with increasing altitude from ≈100 torr at the tropopause to ≈1 torr at the top of the stratosphere.

3.2.2.1 Vertical and Horizontal Mixing in the Atmosphere

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

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

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

3.2.2.2 Formation of Stratospheric Ozone

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

$$O_2 + h\nu \rightarrow 2\ O(^3P), \tag{3-5}$$

followed by the reaction of $O(^3P)$ atoms with O_2 in the presence of a third body, M, to form O_3:

$$O(^3P) + O_2 + M \rightarrow O_3 + M, \text{ where } M = \text{air}. \tag{3-2}$$

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

$$O_3 + h\nu \rightarrow O_2 + O, \tag{3-6}$$

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

$$O(^1D) + M \rightarrow O(^3P) + M, \text{ where } M = N_2, O_2, Ar, \text{ and } CO_2. \quad (3\text{-}7)$$

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

$$O(^3P) + O_3 \rightarrow 2\ O_2. \quad (3\text{-}8)$$

These reactions, called the Chapman reactions (Chapman, 1930), are responsible for the layer of O_3 found in the stratosphere. Because the stratospheric O_3 layer absorbs the sun's radiation below ≈290 nm, only radiation of wavelengths $\gtrsim$290 nm can penetrate into the troposphere and impact the earth's surface. Any depletion of the stratospheric O_3 layer allows shorter wavelength ultraviolet radiation (<320 nm) to be transmitted through the stratosphere and into the troposphere.

In addition to the biological effects expected from increased ultraviolet B (UV-B) radiation (290 to 320 nm), increased penetration of UV-B into the troposphere can lead to changes in tropospheric O_3. Model calculations indicate that O_3 in the troposphere could increase with increasing UV-B in urban and rural areas impacted by anthropogenic NO_x emissions (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 O_3 concentrations leading to corresponding changes in the intensity of UV-B radiation impacting the troposphere, short-term changes (including daily changes) in stratospheric O_3 levels lead to short-term changes in the rates of photolysis of several important species. These include the photolysis of formaldehyde to produce radicals and of O_3 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 O_3 concentrations is needed as input to urban and regional airshed computer models of photochemical air pollution formation.

In the clean atmosphere, stratospheric O_3 also is influenced by the emission of nitrous oxide (N_2O) from soils and oceans (World Meteorological Organization, 1992). Because N_2O is chemically inert in the troposphere and does not photolyze (Prinn et al., 1990), it therefore is 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 N_2O 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).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3\text{-}3)$$

The Chapman reactions and the NO_x catalytic cycle reactions control the O_3 concentrations in the lower clean stratosphere.

Additional reaction sequences leading to the removal of stratospheric O_3 arise from the ClO_x and BrO_x catalytic cycles, which result when chlorine (Cl)- and bromine

$$NO_2 + O(^3P) \rightarrow NO + O_2 \qquad (3\text{-}9)$$

Net: $$O(^3P) + O_3 \rightarrow 2\ O_2$$

(Br)-containing organic compounds are emitted into the atmosphere. These O_3-depleting compounds include the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), carbon tetrachloride (CCl_4), methyl chloroform, halons, and methyl bromide (Anderson et al., 1991; Rowland, 1990, 1991; World Meteorological Organization, 1992). Analogous to N_2O, the CFCs, CCl_4, and certain halons (CF_3Br and CF_2ClBr) are inert in the troposphere and are transported into the stratosphere, where they photolyze to generate Cl or Br atoms (World Meteorological Organization, 1992). Methyl bromide and the HCFCs react to a large extent in the troposphere, so that only a fraction of these Cl- and Br-containing species that are emitted into the troposphere are transported into the stratosphere (World Meteorological Organization, 1990b, 1992).

3.2.3 Background Ozone in the Troposphere

As noted in Section 3.2.1, O_3 is present in the troposphere even in the absence of human activities. Although this "natural" O_3 has received widely varying estimates in the literature, there has not been an attempt to standardize the definition because natural background O_3 is a multidimensional and complex concept. Concentrations of background O_3 can vary with temperature; wind speed and direction; vertical motion; geographical location, including latitude and altitude; and season of the year. Because of the decrease of total pressure with increasing altitude, the O_3 concentration in the clean troposphere may be taken to be reasonably independent of altitude at $\approx 7 \times 10^{11}$ molecules cm^{-3}.

For purposes of this document, the primary focus is on the background O_3 concentration near the surface over the United States during the O_3 season. However, the length of the O_3 season varies from state-to-state, depending predominantly on latitude (see Chapter 4). These variations in O_3 season affect the determination of which seasonal averaging period to apply when estimating O_3 concentrations. Based on available assessments of O_3 monitoring measurements, a daytime, 7-h (0900 to 1559 hours), seasonal (April to October) average O_3 concentration of 25 to 45 ppb can be assumed (Altshuller and Lefohn, 1996) as an estimated background concentration (see Chapter 4). Although one component of this background is of natural origin, the other can be attributed to anthropogenic contributions associated with long-range transport of O_3. This assumption is consistent with the relatively long lifetime of O_3 in the troposphere, which can be as long as 30 to 60 days.

The background of O_3 can be attributed to the following sources: downward transport of stratospheric O_3 through the free troposphere to near ground level, in situ O_3 production from methane emitted from swamps and wetlands reacting with natural NO_x emitted from soils and lighting strikes and from the downward transport of NO from the stratosphere into the troposphere, and in situ production of O_3 from the reactions of biogenic VOCs with natural NO_x (National Research Council, 1991). Another source to be considered is the long-range transport of O_3 from distant pollutant sources.

It is important to appreciate that NO_x has a limited lifetime, often estimated to be as short as 6 h in plumes (Altshuller, 1986) and possibly up to 1 to 2 days under less polluted conditions. Because of this relatively short lifetime, the NO_x emitted from cultivated areas in

the United States as a result of agricultural practices may not survive long enough to interact with substantial emissions of biogenic VOCs in distant forested areas. There also is no direct way to distinguish natural NO_x from anthropogenic NO_x in a rural or remote location.

3.2.3.1 Tropospheric Hydroxyl Radicals

It is now recognized that the key reactive species in the troposphere is the 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 O_3 and, hence, to O_3 concentrations above those encountered in the clean troposphere. The OH radical is produced from the ultraviolet (UV) photolysis of O_3. Ozone photolyzes in the UV radiation at wavelengths <320 nm to generate the electronically excited $O(^1D)$ atom (DeMore et al., 1992; Atkinson et al., 1992a),

$$O_3 + h\nu \rightarrow O_2 + O(^1D). \tag{3-6a}$$

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

$$O(^1D) + H_2O \rightarrow 2\ OH. \tag{3-10}$$

The $O(^3P)$ atoms formed directly in the photolysis of O_3 or formed from deactivation of $O(^1D)$ atoms (Reaction 3-7) reform O_3 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 O_3. Hydroxyl radical production from Reactions 3-6a and 3-10 is balanced by reaction of the OH radical with carbon monoxide (CO) and CH_4. Because the water vapor mixing ratio decreases with increasing altitude in the troposphere (Logan et al., 1981; World Meteorological Organization, 1992) and the O_3 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 for an understanding of tropospheric chemistry and to reliably calcuate the lifetimes of chemical compounds. Because OH and hydroperoxyl (HO_2) radicals are interrelated through a series of reactions (Section 3.2.3.3), concurrent measurements of OH and HO_2 radical concentrations improve the 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 molecules cm^{-3}. A global, annually, seasonally, and diurnally averaged tropospheric OH radical concentration also can 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 CH_3CCl_3 (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 molecules cm^{-3} (equivalent to a 12-h daytime average of 1.6×10^6 molecules cm^{-3} [≈0.1 ppt]). Ambient air measurements of the decay of nonmethane

hydrocarbons in urban plumes (Blake et al., 1993) give OH radical concentrations of similar magnitude to those derived from direct tropospheric measurements and globally averaged estimates.

3.2.3.2 Tropospheric Nitrogen Oxides Chemistry

The presence of NO_x is necessary for the formation of O_3 from the oxidation of CH_4 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) (see 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:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3-3}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{3-1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M. \tag{3-2}$$

Because Reaction 3-2 is fast (the lifetime of an $O(^3P)$ atom at 298 K and 760 torr of air is $\approx 10^{-5}$ s), the O_3 concentration at photoequilibrium is given by

$$[O_3] = J_1[NO_2]/k_3[NO], \tag{3-11}$$

where J_1 and k_3 are the photolysis rate of NO_2 (≈ 0.5 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,

$$NO_2 + O_3 \rightarrow NO_3 + O_2, \tag{3-12}$$

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

$$NO_3 + NO_2 \overset{M}{\rightleftharpoons} N_2O_5. \tag{3-13, -3-13}$$

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

$$NO_3 + h\nu \longrightarrow \begin{cases} NO + O_2 & (10\%) \quad (3\text{-}14a) \\ NO_2 + O(^3P) & (90\%), \quad (3\text{-}14b) \end{cases}$$

its concentration remains low during daylight hours, but can increase after sunset to nighttime concentrations of $<5 \times 10^7$ to 1×10^{10} molecules 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 molecules 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 HNO_3.

$$OH + NO_2 \xrightarrow{M} HNO_3 \qquad (3\text{-}15)$$

$$N_2O_5 \xrightarrow{H_2O} HNO_3 \qquad (3\text{-}16)$$

The gas-phase reaction of the OH radical with NO_2 is the major and ultimate removal process for NO_x in the troposphere. This reaction removes radicals (OH and NO_2) and competes with the reaction of the OH radical with VOCs. Gaseous HNO_3 formed from Reaction 3-15 undergoes wet and dry deposition, including combination with gaseous ammonia (NH_3) to form particulate phase ammonium nitrate ($N_2H_4O_3$). 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. It should be noted that OH radicals also can react with NO to produce nitrous acid (HNO_2):

$$OH + NO \xrightarrow{M} HNO_2. \qquad (3\text{-}17)$$

In urban areas, HNO_2 also can 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;

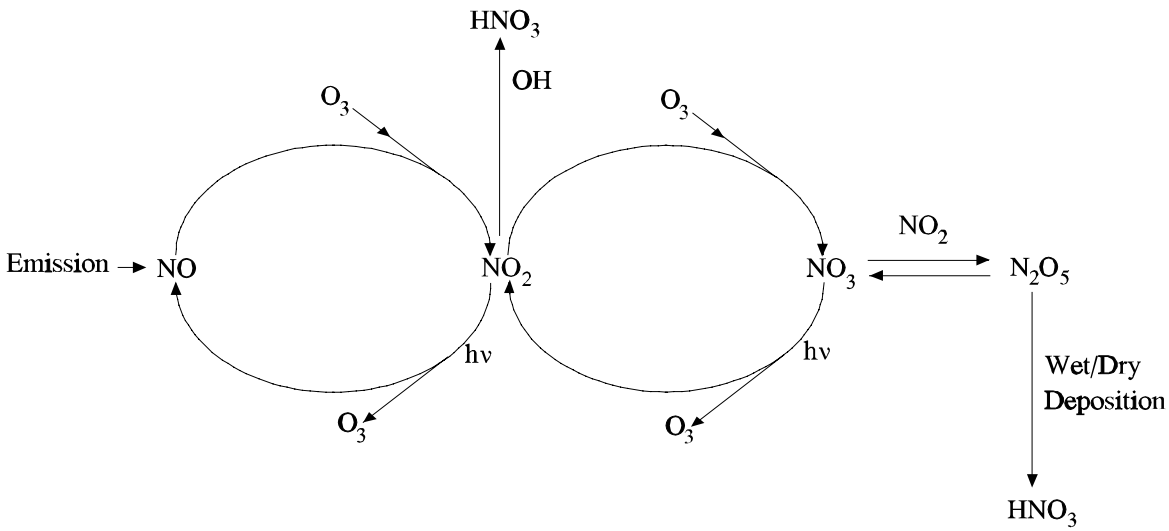


Figure 3-1. The cyclic reactions of tropospheric nitrogen oxides.

Jenkin et al., 1988; Lammel and Perner, 1988; Notholt et al., 1992a,b). The photolysis of HNO_2 during the early morning hours,

$$HNO_2 + h\nu \rightarrow OH + NO, \tag{3-18}$$

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

In the troposphere, the initially emitted NO is converted to NO_x ($NO + NO_2$), then to reservoir and termination species (PAN and its homologues, organic nitrates, HNO_3, and particulate nitrate). These reservoir and termination species are referred to as NO_z. The term "NO_y" refers to the total amount of nitrogen, with $NO_y = (NO_x + NO_z)$. Parrish et al. (1993) have investigated the partitioning between the individual nitrogen-containing species at several rural sites in the eastern United States, and Trainer et al. (1993) and Olszyna et al. (1994) have shown that, in rural areas in the eastern United States, there is a good correlation between the O_3 levels and NO_y. Trainer et al. (1993) further showed that O_3 levels correlate even better with NO_z than with NO_y, as may be expected because NO_z quantifies the amount of initially emitted NO that has been processed photochemically, forming O_3 in the process.

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 CH_4 is by reaction with the OH radical, with the CH_4 lifetime equal to

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

where k_{21} is the rate constant for Reaction 3-21, and [OH] is the (variable) atmospheric OH radical concentration. The calculated lifetime of CH_4 in the troposphere is ≈10 to 12 years. As for other saturated organic compounds, the OH radical reaction with CH_4 proceeds by hydrogen (H)-atom abstraction from the carbon (C)-H bonds to form the methyl (CH_3) radical:

$$OH + CH_4 \rightarrow H_2O + \dot{C}H_3. \tag{3-20}$$

In the troposphere, the methyl radical reacts solely with O_2 to yield the methyl peroxy ($CH_3O_2^{\cdot}$) radical (Atkinson et al., 1992a):

$$\dot{C}H_3 + O_2 \xrightarrow{M} CH_3O_2^{\cdot}. \tag{3-21}$$

In the troposphere, the methyl peroxy radical can react with NO, NO_2, HO_2 radicals, and other organic peroxy ($RO_2^{\cdot}$) radicals, with the reactions with NO and HO_2 radicals being the most important (see, for example, World Meteorological Organization, 1990b). The reaction with NO leads to the formation of the methoxy ($CH_3\dot{O}$) radical,

$$CH_3O_2^{\cdot} + NO \rightarrow CH_3\dot{O} + NO_2. \tag{3-22}$$

The reaction with the HO_2 radical leads to the formation of methyl hydroperoxide (CH_3OOH),

$$CH_3O_2^{\cdot} + HO_2 \rightarrow CH_3OOH + O_2, \tag{3-23}$$

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

$$CH_3OOH + h\nu \rightarrow CH_3\dot{O} + OH, \tag{3-24}$$

$$OH + CH_3OOH \rightarrow H_2O + CH_3O_2^{\cdot} \tag{3-25a}$$

$$OH + CH_3OOH \rightarrow H_2O + \dot{C}H_2OOH \xrightarrow{\text{fast}} HCHO + OH. \tag{3-25b}$$

Methyl hydroperoxide also undergoes wet and dry deposition or incorporation into cloud water. The lifetime of CH_3OOH 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 HCHO and the HO_2 radical,

$$CH_3\dot{O} + O_2 \rightarrow HCHO + HO_2. \tag{3-26}$$

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

$$HCHO + h\nu \rightarrow H_2 + CO \quad (55\%) \tag{3-27a}$$

$$HCHO + h\nu \rightarrow H + H\dot{C}O \quad (45\%), \tag{3-27b}$$

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

$$OH + HCHO \rightarrow H_2O + H\dot{C}O. \tag{3-28}$$

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

$$H + O_2 + M \rightarrow HO_2 + M \tag{3-29}$$

$$H\dot{C}O + O_2 \rightarrow HO_2 + CO. \tag{3-30}$$

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

The final step in the oxidation of CH_4 in the earth's atmosphere involves the oxidation of CO by reaction with the OH radical (the only tropospheric reaction of CO) to form CO_2:

$$OH + CO \rightarrow H + CO_2 \tag{3-31}$$

$$H + O_2 + M \rightarrow HO_2 + M. \tag{3-29}$$

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

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

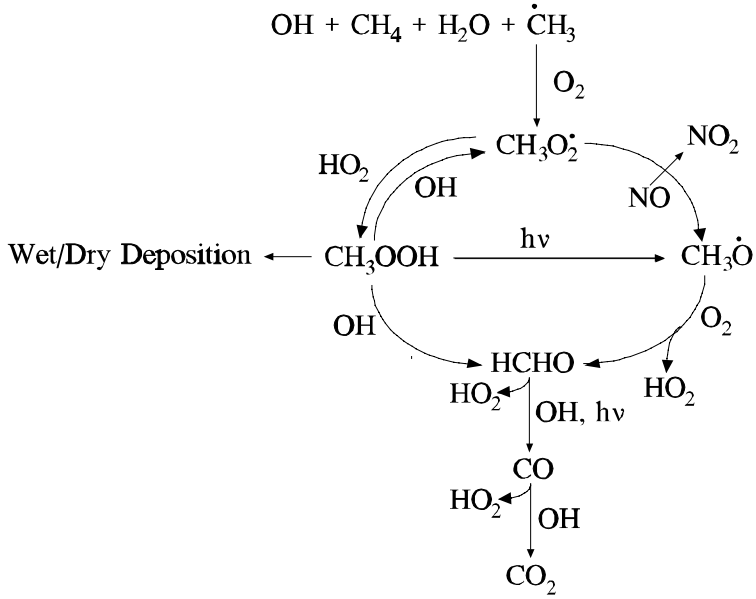


Figure 3-2. Atmospheric reactions in the complete oxidation of methane.

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

Hydroperoxy radicals formed from, for example, Reactions 3-26, 3-29, and 3-30 can react with NO, O_3, or themselves, depending mainly on the concentration of NO. The reaction with NO leads to regeneration of the OH radical,

$$HO_2 + NO \rightarrow OH + NO_2, \tag{3-32}$$

whereas the reactions with O_3 and HO_2 radicals lead to a net destruction of tropospheric O_3:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{3-33}$$

$$HO_2 + O_3 \rightarrow OH + 2\ O_2. \tag{3-34}$$

This net loss of tropospheric O_3 occurs because the photolytic production of the OH radical from O_3, via the intermediary of the $O(^1D)$ atom, represents a loss process for tropospheric O_3. Hence, the absence of any O_3 formation from the CH_4 oxidation cycle is equivalent to a net O_3 loss. Using the rate constants reported for Reactions 3-32 and 3-34 (Atkinson et al., 1992a) and the tropospheric O_3 mixing ratios given above, it is calculated that the HO_2 radical reaction with NO dominates over reaction with O_3 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 HO_2 radical reaction with NO dominates over the self-reaction of HO_2 radicals.

There are therefore two regimes, depending on the fate of HO_2 and CH_3O_2 radicals: (1) a high-NO regime in which HO_2 and CH_3O_2 radicals react with NO to convert NO to NO_2, regenerate the OH radical, and, through the photolysis of NO_2, produce O_3; and (2) a low-NO regime in which HO_2 and CH_3O_2 radicals combine (Reaction 3-23), and HO_2 radicals undergo self-reaction and react with O_3 (Reactions 3-33 and 3-34), leading to a net destruction of O_3 and inefficient OH radical regeneration (see also Ehhalt et al., 1991; Ayers et al., 1992).

Under high-NO conditions, the oxidation of CH_4 leading to the formation of HCHO can be written as the net reaction,

$$OH + CH_4 + 2\ NO + 2\ O_2 = H_2O + HCHO + 2\ NO_2 + OH, \qquad (3\text{-}35)$$

indicating the conversion of two molecules of NO to NO_2 and regeneration of the OH radical. Because NO_2 photolyzes to form O_3 in the presence of O_2,

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3\ , \qquad (3\text{-}1,\ 3\text{-}2)$$

the oxidation of CH_4 to HCHO under high-NO conditions can be written as

$$OH + CH_4 + 4\ O_2 = H_2O + HCHO + 2\ O_3 + OH, \qquad (3\text{-}36)$$

showing the formation of O_3 from CH_4 oxidation in the troposphere. The reaction cycles oxidizing CH_4 to HCHO, converting NO to NO_2, and forming O_3 are shown schematically in Figure 3-3.

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

$$0.2\ OH + HCHO + 0.92\ NO \xrightarrow{O_2} CO + 0.44\ H_2 + 0.2\ H_2O + 0.92\ NO_2 + 0.92\ OH. \qquad (3\text{-}37)$$

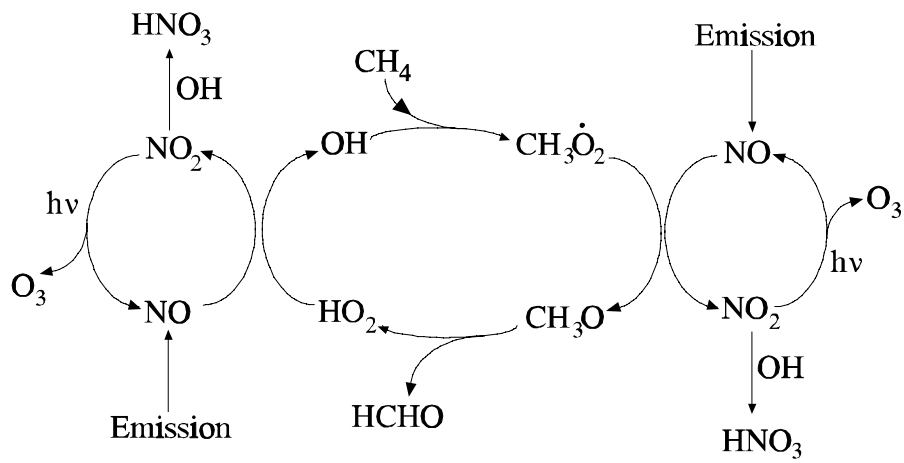


Figure 3-3. Cyclic reactions of methane oxidation to formaldehyde, conversion of nitric oxide to nitrogen dioxide, and concomitant formation of ozone in the atmosphere.

Formaldehyde photooxidation is thus a source of HO_2 radicals (and of OH radicals in high-NO conditions) (Ehhalt et al., 1991), especially in urban areas where the concentration of HCHO 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 CH_4 will lead to a net destruction of O_3 (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, NO mixing ratios are high enough (high NO-conditions) for CH_4 oxidation to lead to net O_3 formation (Carroll et al., 1990; World Meteorological Organization, 1992).

3.2.3.4 Cloud Processes in the Methane-Dominated Troposphere

In addition to the dry and wet deposition of certain products of the NO_x-CH_4-air photooxidation (e.g., wet and dry deposition of HNO_3 and CH_3OOH [Atkinson, 1988, and references therein; Hellpointner and Gäb, 1989]), cloud processes can have significant effects on the gas-phase chemistry of the clean troposphere (Lelieveld and Crutzen, 1990, 1991; Warneck, 1991, 1992). Lelieveld and Crutzen (1990, 1991) have postulated from modeling studies that the uptake of HCHO, HO_2 radicals, and N_2O_5 into clouds can decrease markedly the production of O_3. The incorporation of HCHO into cloudwater removes HCHO from the gas phase and, hence, reduces the gas-phase formation of HO_2. The uptake of HO_2 radicals into cloudwater has the same effect. Moreover, the aqueous-phase reactions of $CH_2(OH)_2$ (the hydrated form of HCHO) lead to the formation of O_2^-, which reacts with dissolved O_3 to act as a sink for O_3 during cloudy periods. During nighttime, N_2O_5 formed in the gas phase from Reactions 3-3, 3-12, and 3-13 can be readily incorporated into cloudwater with hydrolysis to HNO_3, precluding the reformation of NO_x during the following day from Reactions -3-13 and 3-14. Dentener and Crutzen (1993) have also concluded from a computer modeling study that

the heterogeneous reactions of NO_3 radicals and N_2O_5 on aerosols can have significant effects on global O_3 mixing ratios and on OH concentrations by reducing NO_x levels.

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

3.2.4 Photochemistry of the Polluted Atmosphere

Human activities lead to the emissions of NO_x ($NO + NO_2$) and both CH_4- and nonmethane organic compounds (NMOC) into the atmosphere (Table 3-1). Methane emissions are important on a global scale (World Meteorological Organization, 1992), whereas nonmethane VOC emissions are most important in urban and regional areas. In addition to the emissions of nonmethane VOCs from anthropogenic sources, large quantities of biogenic nonmethane VOCs (mainly of isoprene [2-methyl-1, 3-butadiene] and monoterpenes, [$C_{10}H_{16}$]) are emitted, both in polluted and nonpolluted areas, into the atmosphere from vegetation (see, for example, Isidorov et al., 1985; Lamb et al., 1987; Arey et al., 1991a,b).

Table 3-1. Estimated Emissions of Methane, Nonmethane Organic Compounds, Nitrous Oxide, and Nitrogen Oxides into the Earth's Atmosphere from Biogenic and Anthropogenic Sources[a]

	Emissions (Tg/year[b])	
Chemical	Biogenic Sources	Anthropogenic Sources
CH_4[c]	≈150	≈350
NMOC[d]	≈1,000	≈100
N_2O (as N)[e]	≈7	≈6
NO_x (as N)[f]	≈10	≈40

[a]See Appendix A for abbreviations and acronyms.
[b]Teragram = 10^{12} g, or ≈10^6 metric tons.
[c]Fung et al. (1991a); World Meteorological Organization (1992). Emissions from ruminants, rice paddies, and biomass burning are considered as anthropogenic emissions.
[d]Logan et al. (1981); World Meteorological Organization (1992), with biogenic emissions being assumed to be 50% isoprene and 50% monoterpenes.
[e]Prinn et al. (1990).
[f]National Research Council (1991); World Meteorological Organization (1992); biogenic sources ≈50% from soils and ≈50% from lightning.

Analogous to the photooxidation of CH_4, 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 areas (Trainer et al., 1987; Roselle et al., 1991; Chameides et al., 1992).

In essence, the chemistry of the polluted urban and regional atmosphere is an extension of that of the clean, CH_4-dominated troposphere, with a number of additional complexities due to 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, CA, 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 often is 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 often is 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 nonzero absorption cross-section, σ_λ, in this wavelength region). Having absorbed radiation, a chemical compound must then undergo chemical change (i.e., have a nonzero 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, $k_{photolysis}$, for the process,

$$C + h\nu \rightarrow \text{products} \tag{3-38}$$

is given by

$$k_{photolysis} = \int J_\lambda \, \sigma_\lambda \, \phi_\lambda \, d\lambda, \tag{3-39}$$

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

$$\tau_{photolysis} = k_{photolysis}^{-1}. \tag{3-40}$$

For the reaction of a VOC with a reactive species, X (for tropospheric purposes, X = OH, NO_3, and O_3), the lifetime for the reaction process, C + X → products, is given by

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

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, NO_3 radicals, and O_3 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 often are 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); NO_3 radicals, a 12-h nighttime average concentration of 5×10^8 molecule cm^{-3} (Atkinson, 1991); and O_3, 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 constants and the assumed ambient concentrations of OH radicals, NO_3 radicals, and O_3. Uncertainties in the ambient concentrations of the reactive species translate directly into corresponding uncertainties in the lifetimes.

The following brief discussions of the tropospheric chemistry of the important classes of VOCs are based on the recent review and evaluation article of Atkinson (1994), which should be consulted for further details of the tropospheric reactions of VOCs.

Alkanes

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

$$OH + RH \rightarrow H_2O + \dot{R}, \tag{3-42}$$

Table 3-2. Calculated Tropospheric Lifetimes of Selected Volatile Nonmethane Organic Compounds Due to Photolysis and Reaction with Hydroxyl and Nitrate Radicals and with Ozone[a]

Organic	Lifetime Due to Reaction with			
	OH	NO_3	O_3	h*v*
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 *t*-butyl ether	4.9 days	—	—	
Ethyl *t*-butyl ether	1.6 days	—	—	
Methylglyoxal	10 h	—	>4.5 years	2 h

[a]See Appendix A for abbreviations and acronyms.

Sources: Lifetimes resulting from reaction with OH, NO_3, and O_3 were calculated using rate constants given in Atkinson and Carter (1984) and Atkinson (1989, 1991, 1994); 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, NO_3 radical, and O_3 concentrations used (molecule cm^{-3} were: OH, 12-h average of 1.6×10^6; NO_3, 12-h average of 5×10^8; O_3, 24-h average of 7×10^{11}.

which rapidly adds O_2 to form an alkyl peroxy radical ($RO_2^{\cdot}$),

$$\dot{R} + O_2 \xrightarrow{M} RO_2^{\cdot}, \qquad (3\text{-}43)$$

with the simplest of the $RO_2^{\cdot}$ radicals being the methylperoxy radical, described in Section 3.2.3.3 dealing with methane oxidation. Alkyl peroxy radicals can react with NO, NO_2, and HO_2 radicals, and other organic peroxy radicals ($R'O_2^{\cdot}$):

$$RO_2^{\cdot} + NO \rightarrow R\dot{O} + NO_2 \tag{3-44a}$$

$$RO_2^{\cdot} + NO_2 \rightleftharpoons ROONO_2 \tag{3-45}$$

$$RO_2^{\cdot} + HO_2 \rightarrow ROOH + O_2 \tag{3-46}$$

$$RO_2^{\cdot} + R'O_2^{\cdot} \rightarrow R\dot{O} + R'\dot{O} + O_2 \tag{3-47a}$$

$$RO_2^{\cdot} + R'O_2^{\cdot} \rightarrow \alpha \text{ carbonyl} + (1 - \alpha)\ ROH + O_2 + \text{products of } R'O_2^{\cdot}\ . \tag{3-47b}$$

The reactions with organic peroxy radicals are expected to be of less importance in the troposphere than the other reactions listed. Because low NO conditions occur even in air masses in urban areas, the HO_2 radical reactions with RO_2 radicals and the subsequent chemistry must be considered. However, because of space constraints and a general lack of knowledge concerning the tropospheric chemistry of RO_2 radicals under low-NO conditions, only the reactions occurring under high-NO conditions are presented and discussed here. For the $\geq C_3$ alkyl peroxy radicals, in addition to the reaction pathway leading to NO-to-NO_2 conversion (Reaction 3-44a), a second reaction pathway leading to formation of an alkyl nitrate becomes important:

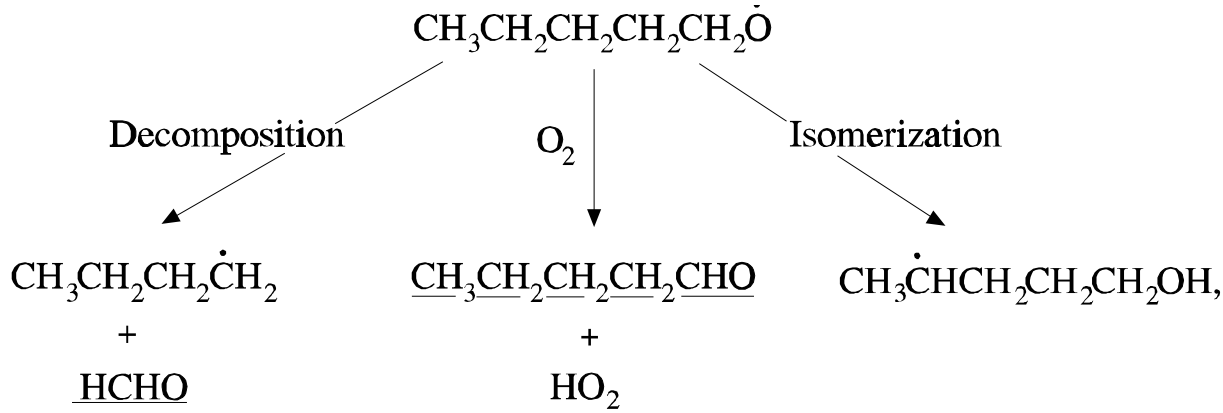
$$RO_2^{\cdot} + NO \xrightarrow{M} RONO_2. \tag{3-44b}$$

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 ($RO_2^{\cdot}$) formed from the higher alkanes that have an abstractable H atom can react with O_2 to form the HO_2 radical and a carbonyl; for example,

$$(CH_3)_2CH\dot{O} + O_2 \rightarrow CH_3C(O)CH_3 + HO_2. \tag{3-48}$$

In addition, unimolecular decomposition by C-C bond scission and unimolecular isomerization via a six-member transition state (Atkinson and Carter, 1991; Atkinson, 1994) can be important for the larger alkoxy radicals. For example, the following chemistry can occur for the 1-pentoxy radical:



with the alkyl radicals $C_4\dot{H}_9$ and $HOCH_2CH_2CH_2\dot{C}HCH_3$ undergoing further reaction.

The majority of the reaction rate constants and reaction pathways in the alkane degradation schemes are arrived at by analogy from the chemistry of C_1-C_3 alkyl, alkyl peroxy, and alkoxy radicals (Atkinson, 1990, 1994; 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 the relative importance of alkoxy radical reaction with O_2, decomposition and isomerization, and the reactions occurring subsequent to the isomerization reaction; the formation of alkyl nitrates from the reactions of the peroxy radicals with NO; and reactions of the alkyl peroxy radicals with HO_2 and other peroxy radicals, reactions that can be important in the nonurban troposphere.

Alkenes (Anthropogenic and Biogenic)

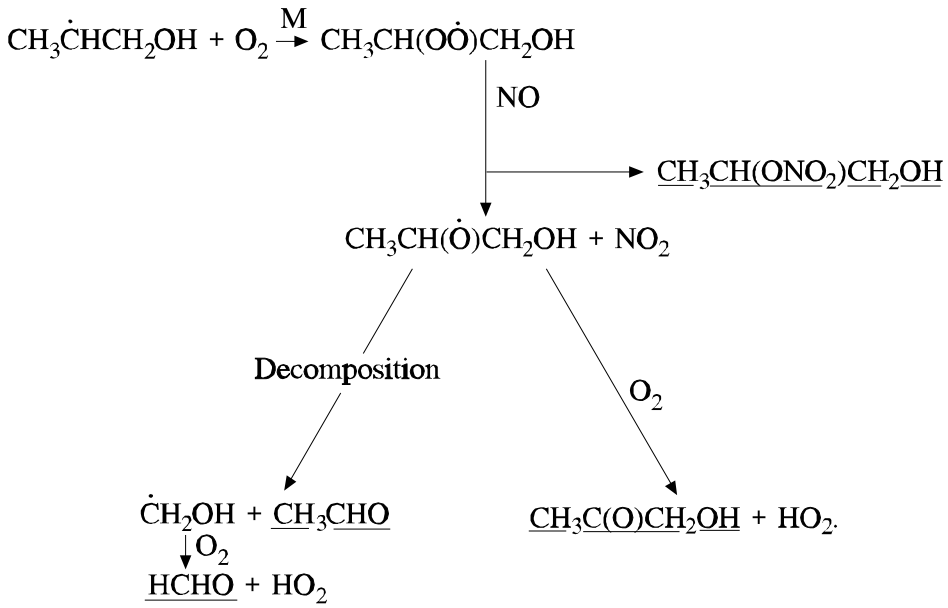
The alkenes emitted from anthropogenic sources are mainly ethene, propene, and the butenes, with lesser amounts of the $\geq C_5$ alkenes. The major biogenic alkenes emitted from vegetation are isoprene (2-methyl-1,3-butadiene) and $C_{10}H_{16}$ monoterpenes (Isidorov et al., 1985; Winer et al., 1992), 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., 1993, 1994).

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 >C=C< bonds. 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< bonds. For example, the OH radical reaction with propene leads to the formation of the two OH-containing radicals,

$$OH + CH_3CH{=}CH_2 \xrightarrow{M} CH_3CH(OH)\dot{C}H_2 + CH_3\dot{C}HCH_2OH. \qquad (3\text{-}49)$$

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.

However, this is not the case for the more complex alkenes of biogenic origin. The product studies of Tuazon and Atkinson (1990a) and Paulson et al. (1992a) for the OH radical reaction with isoprene in the presence of NO_x show that the products expected from reaction schemes analogous to that shown above for propene (i.e., HCHO + methyl vinyl ketone [$CH_3C(O)CH{=}CH_2$] and HCHO + methacrolein [$CH_2{=}C(CH_3)CHO$], arising from initial OH radical addition to the $CH_2{=}CH$- and $CH_2{=}C<$ bonds, respectively) do not account for the entire reaction pathways. The product yields obtained from the studies of Tuazon and Atkinson (1990a) and Paulson et al. (1992a) are methyl vinyl ketone, 34%; methacrolein, 24%; 3-methylfuran, 5%; organic nitrates, ≈12%; and unidentified carbonyl compounds, ≈25% (Tuazon and Atkinson, 1990a; Paulson et al., 1992a; Atkinson, 1994). The HCHO yield was consistent with being a co-product formed with methyl vinyl ketone and methacrolein (Tuazon and Atkinson, 1990a). Aerosol formation for isoprene photooxidation has been shown to be negligible under atmospheric conditions (Pandis et al., 1991; Zhang et al., 1992).

To date, few quantitative product studies have been carried out for the monoterpenes (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1993, 1994). Arey et al. (1990) and Hakola et al. (1993, 1994) have observed the C_7-C_{10} carbonyl compounds, as had been based on the analogous reaction scheme shown above for propene, but with total carbonyl formation yields of ≤50%. These data (Arey et al., 1990; Hakola et al., 1993, 1994) indicate the formation of other products in significant, and often dominant, yields. Hatakeyama et al. (1991) used Fourier transform infrared (FTIR) absorption spectroscopy and reported carbonyl compounds to be formed in high yield from α-pinene and β-pinene, in apparent disagreement with the data of Arey et al. (1990) and Hakola et al. (1994). Although Hatakeyama et al. (1991) ascribed these carbonyl products to those expected from oxidative

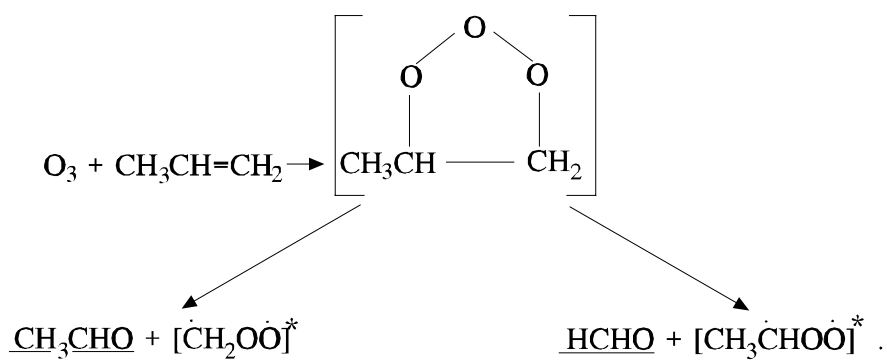
cleavage of the >C=C< bonds, it is possible that the yields reported for these carbonyls included contributions by other, as yet unidentified, carbonyl-containing products.

Nitrate Radical Reactions. The NO_3 radical reactions proceed by reaction schemes generally similar to the OH radical reactions, except that, when NO_3 radicals are present, NO concentrations are low (see above) and $RO_2^{\cdot}$ + $RO_2^{\cdot}$ and $RO_2^{\cdot}$ + HO_2 radical reactions are expected to dominate over $RO_2^{\cdot}$ + NO reactions. For propene, the initial reaction is

$$NO_3 + CH_3CH{=}CH_2 \rightarrow CH_3\dot{C}HCH_2ONO_2 \text{ and } CH_3CH(ONO_2)\dot{C}H_2\,, \qquad (3\text{-}50)$$

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, CH_3CHO, $CH_3CH(ONO_2)CHO$, and $CH_3C(O)CH_2ONO_2$ from propene). Few data are presently available concerning the products and detailed mechanisms of NO_3-alkene reactions (Atkinson, 1991, 1994, and references therein). In particular, the reaction products and mechanisms for the NO_3 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 O_3 reactions also proceed by addition of O_3 to the alkene, to form an energy-rich ozonide that rapidly decomposes to form carbonyls and energy-rich biradicals ([ ]*):



The energy-rich biradicals, $[\dot{C}H_2O\dot{O}]^*$ and $[CH_3\dot{C}HO\dot{O}]^*$, undergo collisional stabilization or decomposition:

$$[R_1R_2\dot{C}O\dot{O}]^* \xrightarrow{M} R_1R_2\dot{C}O\dot{O} \qquad (3\text{-}51a)$$

$$[R_1R_2\dot{C}O\dot{O}]^* \rightarrow \text{Decomposition.} \qquad (3\text{-}51b)$$

There are still significant uncertainties concerning the reactions of the energy-rich biradicals (Horie and Moortgat, 1991; Atkinson, 1990, 1994), with recent studies showing the production of OH radicals in high yields for several alkenes (Niki et al., 1987; Paulson et al., 1992a; Atkinson et al., 1992b; Paulson and Seinfeld, 1992b; Atkinson and Aschmann, 1993).

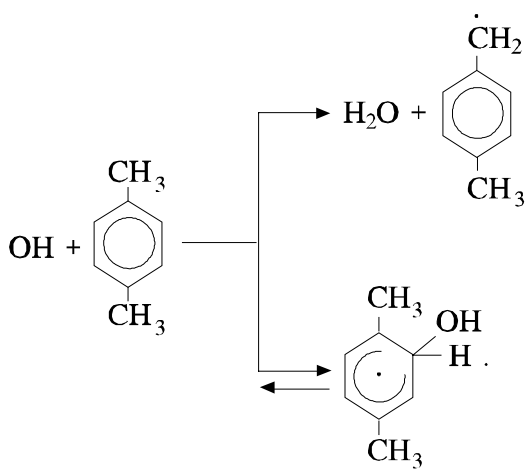
For isoprene, the major products are methacrolein and methyl vinyl ketone (Kamens et al., 1982; Niki et al., 1983; Paulson et al., 1992b). Paulson et al. (1992b) derived an OH radical and an $O(^3P)$ atom formation yield of 0.68 ± 0.15 and 0.45 ± 0.2, respectively, from the O_3 reaction with isoprene, indicating the dominance of secondary reactions. However, Atkinson et al. (1992b) derived a significantly lower OH radical formation yield of 0.27 (uncertain to a factor of ≈1.5). Clearly, further studies of this important reaction are needed.

The only quantitative studies of the gas-phase O_3 reactions with the monoterpenes are those of Hatakeyama et al. (1989) for α- and β-pinene and Hakola et al. (1993, 1994) for a series of monoterpenes. Additionally, Atkinson et al. (1992b) derived OH radical formation yields from these reactions under atmospheric conditions.

Several groups (Gäb et al., 1985; Becker et al., 1990, 1993; Simonaitis et al., 1991; Hewitt and Kok, 1991) have reported the formation of H_2O_2 and organic peroxides from O_3 reactions with alkenes. However, there are significant disagreements in the quantitative results reported by Becker et al. (1990, 1993) and Simonaitis et al. (1991).

Aromatic Hydrocarbons

The chemistry of aromatic hydrocarbons is one of the major sources of uncertainty in the atmospheric chemistry of VOCs (National Research Council, 1991; Atkinson, 1994). The most abundant aromatic hydrocarbons in urban atmospheres are benzene, toluene, the xylenes, and the trimethylbenzenes (Grosjean and Fung, 1984; California Air Resources Board, 1992). As shown in Table 3-2, the only tropospherically important loss process for benzene and the alkyl-substituted benzenes is by reaction with the OH radical. For the alkyl-substituted benzenes, the OH radical reactions proceed by two pathways: (1) H-atom abstraction from the C-H bonds of the alkyl substituent groups and (2) OH radical addition to the aromatic ring, as shown below, for *p*-xylene:

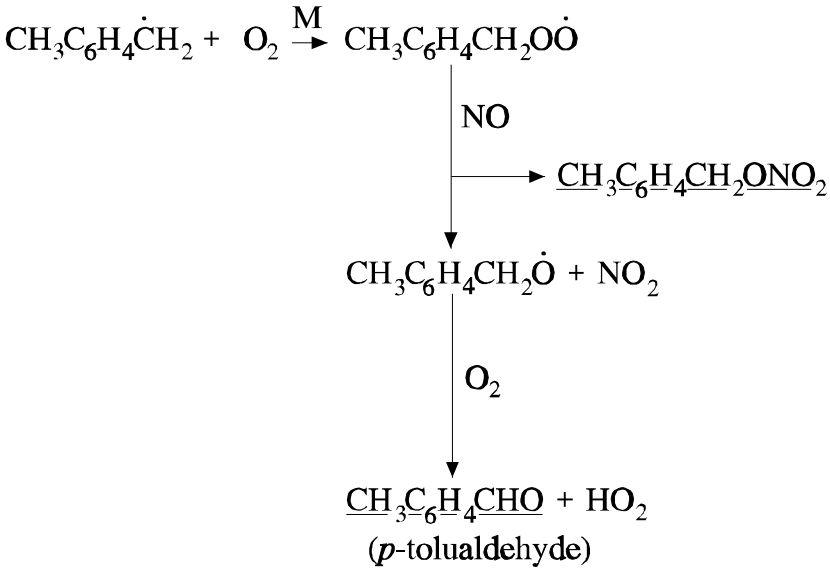


(3-52a)

(3-52b)

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, 1994), 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 NO_2 and O_2. Knispel et al. (1990) reported rate constants for the reactions of NO_2 and O_2 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 O_2. Laboratory studies of the formation of selected products from the gas-phase reactions of the OH radical with toluene, *o*-xylene, and 1,2,3-trimethylbenzene (Atkinson and Aschmann, 1994), and, in particular, of the formation of the ring-cleavage product 2,3-butanedione from *o*-xylene, are consistent with the kinetic data of Knispel et al. (1990). Thus, at least for the monocyclic aromatic hydrocarbons such as benzene, toluene, and the xylenes, the OH-aromatic adducts formed in Reaction 3-52b react with O_2 under atmospheric conditions. However, care must be taken in using product yields obtained in the laboratory at higher than ambient NO_2 concentrations because data may be influenced by the NO_2 reaction and, hence, may not be applicable to the O_2 reaction with the OH-aromatic adduct. Clearly, the products formed and their yields from the O_2 and NO_2 reactions with the OH-aromatic adducts need to be determined, and the detailed reaction mechanisms elucidated.

Despite these uncertainties, however, products from the OH radical addition pathway have been identified, and their formation yields determined (Atkinson, 1994, and references therein). The major products identified from the OH radical addition pathway are phenolic compounds (e.g., phenol from benzene and *o*-, *m*-, and *p*-cresol from toluene) and α-dicarbonyls (glyoxal, methylglyoxal, and 2,3-butanedione) resulting from the cleavage of the aromatic ring (see, for example, Atkinson, 1990, 1994, and references therein). Significant fractions (≥50% for benzene, toluene, and the xylenes) of the reaction products are, however, still not accounted for.

Carbonyl Compounds

As noted above, the OH radical reactions with the alkanes, alkenes, and aromatic hydrocarbons lead, often in large yield, to the formation of carbonyl compounds. Likewise, carbonyls are formed during the reactions of NO_3 radicals and O_3 with alkenes. As a first approximation, the carbonyl compounds of tropospheric interest are HCHO (see Section 3.2.3.3), acetaldehyde, and the higher aliphatic aldehydes; benzaldehyde; acetone, 2-butanone, and the higher ketones; and simple dicarbonyls such as glyoxal, methylglyoxal, and 2,3-butanedione.

The tropospheric photooxidation of isoprene leads to the formation of methyl vinyl ketone ($CH_3C(O)CH{=}CH_2$) and methacrolein ($CH_3C(CHO){=}CH_2$). The OH radical-initiated reactions of these two carbonyl compounds in the presence of NO_x have been studied by Tuazon and Atkinson (1989, 1990b).

The tropospherically important loss processes of the carbonyls not containing >C=C< bonds are photolysis and reaction with the OH radical. As shown in Tables 3-2, photolysis is a major tropospheric loss process for the simplest aldehyde (HCHO) and the simplest ketone ($CH_3C(O)CH_3$), 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 CH_3CHO, the reaction proceeds by H-atom abstraction from the -CHO group to form the acetyl ($CH_3\dot{C}O$) radical,

$$OH + CH_3CHO \rightarrow H_2O + CH_3\dot{C}O, \qquad (3\text{-}53)$$

which rapidly adds O_2 to form the acetyl peroxy radical:

$$CH_3\dot{C}O + O_2 \xrightarrow{M} CH_3C(O)O\dot{O}. \qquad (3\text{-}54)$$

This O_2 addition pathway is in contrast to the reaction of O_2 with the formyl ($H\dot{C}O$) 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,

$$CH_3C(O)O\dot{O} + NO \rightarrow CH_3C(O)\dot{O} + NO_2 \qquad (3\text{-}55)$$

$$CH_3C(O)\dot{O} \xrightarrow{\text{fast}} \dot{C}H_3 + CO_2$$

$$CH_3C(O)O\dot{O} + NO_2 \overset{M}{\rightleftharpoons} CH_3C(O)OONO_2, \qquad (3\text{-}56,\ \text{-}3\text{-}56)$$

with the NO_2 reaction forming the thermally unstable PAN. The higher aldehydes also lead to PANs (Roberts, 1990); for example, propionaldehyde reactions lead to the formation of

peroxypropionyl nitrate (PPN). Although 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, therefore will dominate as the loss processes of PANs in the upper troposphere (Atkinson et al., 1992a).

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

Because the $\dot{C}H_3$ radical formed from the NO reaction with $CH_3C(O)O\dot{O}$ leads to HCHO formation, the OH radical reaction with CH_3CHO subsequently leads to the formation of HCHO. The same process occurs for propionaldehyde, which reacts to form CH_3CHO and then HCHO. Benzaldehyde appears to behave as a phenyl-substituted aldehyde, with respect to its OH radical reaction, and the analog to PAN is then peroxybenzoyl nitrate, PBzN ($C_6H_5C(O)OONO_2$).

The formation of HCHO from CH_3CHO and of CH_3CHO and then HCHO from propionaldehyde are examples of "cascading", in which the photochemical degradation of emitted VOCs leads to the formation of further VOCs, typically containing fewer carbon atoms than the precursor VOC. This process continues until the degradation products are removed by wet and dry deposition or until CO or CO_2 are the degradation products. The reactions of each of these VOCs (i.e., the initially emitted VOC and its first-, second-, and successive-generation products), in the presence of high concentrations of NO, can lead to the formation of O_3.

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

Alcohols and Ethers

A number of alcohols and ethers are used in gasolines and in alternative fuels. The alcohols include methanol, ethanol, and *tert*-butyl alcohol, and the ethers include methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). Table 3-2 shows that in the troposphere these VOCs react only with the OH radical. The relatively long calculated lifetime of methanol in the troposphere (15 days), due to reaction with the OH radical (Table 3-2), suggests that methanol also will be removed from the troposphere by wet and dry deposition and that these physical loss processes may dominate the OH radical reactions proceded by H-atom abstraction from the C-H bonds (and to a minor extent from the O-H bonds in the alcohols), for example, for methanol,

$$OH + CH_3OH \rightarrow H_2O + CH_3O \qquad (15\%) \quad (3\text{-}57a)$$

$$OH + CH_3OH \rightarrow H_2O + CH_2OH. \qquad (85\%) \quad (3\text{-}57b)$$

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

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{3-58}$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \tag{3-59}$$

The overall reaction is then

$$OH + CH_3OH + O_2 \rightarrow H_2O + HCHO + HO_2. \tag{3-60}$$

The reaction sequence for ethanol is similar (Atkinson, 1994). Product studies of the OH radical-initiated reactions of MTBE and ETBE in the presence of NO_x have been carried out by Japer et al. (1990), Smith et al. (1991a, 1992), Tuazon et al. (1991), and Wallington and Japar (1991). The major products from MTBE are *tert*-butyl formate, HCHO, and methyl acetate [$CH_3C(O)OCH_3$] and, from ETBE, *tert*-butyl formate, *tert*-butyl acetate, HCHO, CH_3CHO, and ethyl acetate. The available product data and the reaction mechanisms have been reviewed by Atkinson (1994), 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., 1993a).

Primary Products and Areas of Uncertainty for the Tropospheric Degradation Reactions of Volatile Organic Compounds

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. A more lengthy and detailed discussion of the atmospheric chemistry of alkanes, alkenes, aromatic hydrocarbons, and oxygen- and nitrogen-containing organic compounds emitted into the atmosphere from anthropogenic and biogenic sources and of their atmospheric transformation products is given in the review and evaluation of Atkinson (1994), which also provides an assessment of the uncertainties in the product yields and the reaction rate constants. The first-generation products of the alkanes, alkenes, and aromatic hydrocarbons follow (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 ≈4% for propane to ≈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.

- Alkyl hydroperoxides are formed under low-NO conditions.
- Alkyl peroxynitrates ($ROONO_2$) 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 experimental conditions. These compounds are expected to be formed in low concentrations in the troposphere.

The major uncertainties in the atmospheric chemistry of the alkanes concern the formation of $RONO_2$ 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 that 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, NO_3 radical, and O_3 reactions.
- Organic acids are formed from the O_3 reactions, but probably in low yields.
- Hydroxynitrates and nitratocarbonyls are formed from the OH radical reactions and NO_3 radical reactions, respectively. The hydroxynitrates are formed in low yields from the OH radical reactions, whereas the nitratocarbonyls may be major products of the NO_3 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 O_3 reactions; these include CO, CO_2, esters, hydroperoxides, and, in the presence of NO_x, peroxyacyl nitrates ($RC(O)OONO_2$ and PANs).

The major areas of uncertainty concern the products and mechanisms of the O_3 reactions (in particular, the radical yields from these reactions that affect the O_3 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 shown to be major products of the atmospheric reactions of the aromatic hydrocarbons under laboratory conditions.
- Aromatic aldehydes, such as benzaldehyde, are formed in $\leq$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, therefore, are important products with respect to the photochemical activity of the aromatic hydrocarbons.
- Unsaturated carbonyl or hydroxycarbonyl compounds are formed, although there is little direct information concerning the formation of these products.

There is a lack of knowledge of the detailed reaction mechanisms and products for the aromatic hydrocarbons under tropospheric conditions (i.e., for the NO_x concentrations encountered in urban and rural areas). It is possible that the products observed in laboratory studies and their formation yields are not representative of the situation in the troposphere. This then leads to an inability to formulate detailed reaction mechanisms for the atmospheric

degradation reactions of the aromatic hydrocarbons, and the chemical mechanisms used in urban airshed models then must rely heavily on environmental (or "smog") chamber data.

Oxygenated Compounds.

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

The major area of uncertainty concerns the importance of photolysis of carbonyl compounds in the troposphere, and the products formed. In particular, there is a lack of information concerning the absorption cross-sections and photoodissociation quantum yields for most of the aldehydes and ketones other than HCHO, CH_3CHO, and CH_3COCH_3.

3.2.4.2 Chemical Formation of Ozone in Polluted Air

Major Steps in Ozone Formation

As discussed earlier, NO_x and VOCs interact under the influence of sunlight to form O_3 and other photochemical air pollutants. The major steps in this process are the conversion of NO to NO_2 by peroxy radicals, with the photolysis of NO_2 leading to O_3 production. In the absence of a VOC, Reactions 3-1 through 3-3,

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3\text{-}3)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3, \qquad (3\text{-}1,\ 3\text{-}2)$$

do not lead to any net formation of O_3. The reaction of a VOC with the OH radical, or its photolysis, leads to the formation of HO_2 and organic peroxy (RO_2) radicals, which react with NO under high-NO conditions:

$$VOC(+\ OH,\ h\nu) \xrightarrow{O_2} R\dot{O}_2 \qquad (3\text{-}61)$$

$$R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2 \qquad (3\text{-}44a)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \qquad (3\text{-}1,\ 3\text{-}2)$$

Net:

$$VOC(+\ OH,\ h\nu) \xrightarrow{O_2} R\dot{O}_2 + O_3. \qquad (3\text{-}62)$$

with the alkoxy (RO) radical producing further HO_2 or RO_2 radicals or both, and, hence, resulting in further production of O_3. This process is shown schematically in Figure 3-4.

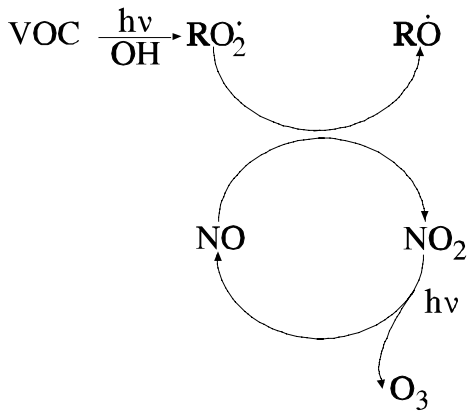


Figure 3-4. Major steps in production of ozone in ambient air (R = H, alkyl or substituted alkyl, or acyl).

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 reactions described below.

The conversion of NO to NO_2 occurs through the oxidation reactions:

$$\text{organic}(+\ OH,\ h\nu,\ O_3) \rightarrow R\dot{O}_2 \tag{3-63}$$

$$R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2 \tag{3-44a}$$

$$R\dot{O} \xrightarrow{O_2} \text{carbonyl} + HO_2 \tag{3-64}$$

$$HO_2 + NO \rightarrow OH + NO_2. \tag{3-32}$$

The maximum concentration of NO_2 is less than the initial NO + NO_2 concentration because NO_2 is removed through the reaction

$$OH + NO_2 \xrightarrow{M} HNO_3. \tag{3-15}$$

This reaction removes radicals (OH and NO_2) and NO_x from the system. In addition to the removal of NO_x through Reaction 3-15, NO_x also can be removed through the formation of temporary reservoir species such as organic nitrates (Reaction 3-44b) and PAN (Reaction 3-56).

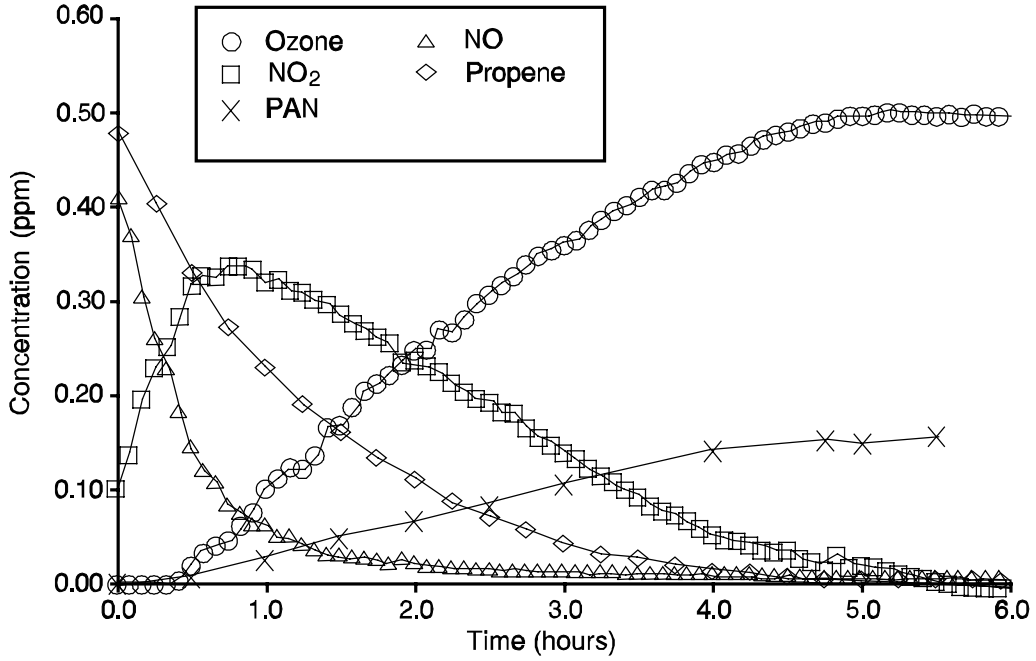


Figure 3-5. Time-concentration profiles for selected species during irradiations of a nitrogen oxide-propene-air mixture in an indoor chamber with constant light intensity.

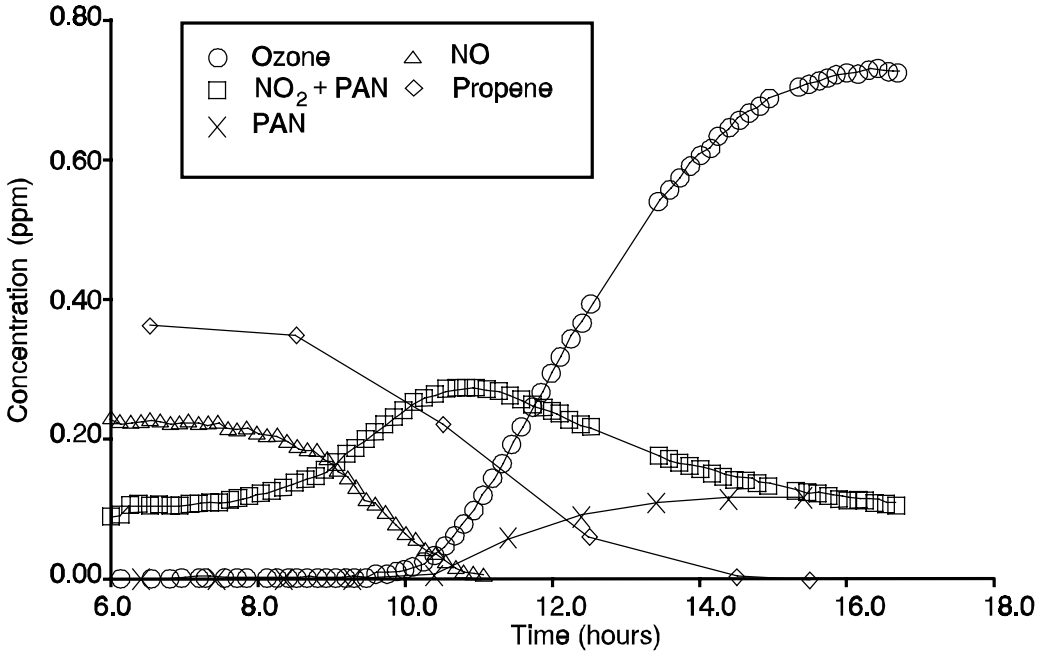


Figure 3-6. Time-concentration profiles for selected species during irradiations of a nitrogen oxide-propene-air mixture in an outdoor chamber with diurnally varying light intensity.

$$RO_2 + NO \rightarrow RONO_2 \quad (3\text{-}44b)$$

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2 \quad (3\text{-}56)$$

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.

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.

The removal processes for NO_x are by reaction of NO_2 with the OH radical to form HNO_3 (Reaction 3-16), the formation of organic nitrates from the $RO\dot{O}$ + NO Reaction 3-44b pathway, and the formation of PAN through Reaction 3-56. The initially present NO_x is converted to organic nitrates, HNO_3, and thermally unstable PANs. At ambient temperature, the PANs will gradually thermally decompose to yield NO_2 and the acylperoxy radicals; hence, the ultimate fate of NO_x will be to form HNO_3 and organic nitrates.

Effects of Varying Initial Nitrogen Oxide and Nonmethane Volatile Organic Compound Concentrations

As discussed in Section 3.2.4.2, 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). 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 major reactions in irradiated VOC-NO_x-air mixtures (see Section 3.2.4.2) include

$$OH + VOC \xrightarrow{O_2} RO_2, \quad (3\text{-}61)$$

which is in competition with Reaction 3-15,

$$OH + NO_2 \rightarrow HNO_3, \quad (3\text{-}15)$$

which removes both radicals and NO_x.

$$RO_2 + NO \rightarrow RO + NO_2 \quad (3\text{-}44a)$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \quad (3\text{-}1, 3\text{-}2)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3\text{-}3)$$

Based on these reactions, as the VOC/NO_x ratio decreases, Reaction 3-15 competes more successfully with Reaction 3-61 in removing radicals from the system for a constant source of OH radicals, and, thus, slows down the formation of O_3 (and vice-versa). The ultimate amount of O_3 formed depends on the NO_2 available for photochemical processing through

Reactions 3-44a, 3-1, 3-2, and 3-3. Because of the diurnal light intensity variation and the length of daylight available for reactions and photolysis to occur, O_3 formation from VOC-NO_x-air mixtures, especially as a function of the VOC/NO_x ratio, is complex and depends on the time or distance scale being considered (for example, transport of urban plumes to rural areas) (Wolff, 1993; Finlayson-Pitts and Pitts, 1993). In general, reducing the VOC/NO_x ratio by reducing VOC emissions slows down the formation rate of O_3, leading to lower O_3 levels in urban areas and in areas downwind of urban complexes. Reduction of NO_x emissions leads to a more rapid formation of O_3, although with less O_3 formed, and, hence, inner-urban areas may experience higher O_3 levels with NO_x control than with VOC control, whereas suburban and rural areas may have lower O_3 levels with NO_x control (Trainer et al., 1993; Olszyna et al., 1994).

Effects of Biogenic Nonmethane Volatile Organic Compound 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 (Chameides et al., 1988; 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 NAAQS, at least in certain areas (Chameides et al., 1988). Thus, for the anthropogenic and biogenic VOC emissions considered by Chameides et al. (1988) for Atlanta, GA, changes in either the anthropogenic VOC emissions or biogenic VOC emissions have little effect on O_3 levels. Therefore, as discussed for the Atlanta region (Chameides et al., 1988), NO_x control may be more favorable than VOC control in urban areas with substantial biogenic NMOC emissions.

Although it is known that isoprene is reactive with respect to the formation of O_3 (Section 3.2.4.3) and that the monoterpenes react rapidly with OH radicals, NO_3 radicals, and O_3, the O_3-forming potentials of the various monoterpenes emitted into the atmosphere are not known.

3.2.4.3 Hydrocarbon Reactivity with Respect to Ozone Formation

As discussed in Section 3.2.4, VOCs are removed and transformed in the troposphere by photolysis and by chemical reaction with OH radicals, NO_3 radicals, and O_3. In the presence of sunlight, the degradation reactions of the VOCs lead to the conversion of NO to NO_2 and the formation of O_3 and various organic products. However, different VOCs react at differing rates in the troposphere because of their differing tropospheric lifetimes (Table 3-2). The lifetimes of most VOCs with respect to reaction with OH radicals and O_3 are in the range ≈1 h to ≈10 years. In large part, because of these differing tropospheric lifetimes and rates of reaction, VOCs exhibit a range of reactivities with respect to the formation of O_3 (Altshuller and Bufalini, 1971, and references therein).

A number of "reactivity scales" have been developed over the years (see, for example, Altshuller and Bufalini, 1971, and references therein; Darnall et al., 1976), including the rate of VOC disappearance in NO_x-VOC-air irradiations, the rate of NO to NO_2 conversion in NO_x-VOC-air irradiations, O_3 formation in NO_x-single VOC-air irradiations, eye

irritation, and the rate constant for reaction of the VOC with the OH radical. It appears, however, that a useful definition of "reactivity" is that of "incremental reactivity" (*IR*), defined as the amount of O_3 formed per unit of VOC added or subtracted from the VOC mixture in a given air mass under high-NO conditions (Carter and Atkinson, 1987, 1989b):

$$IR = \Delta[O_3]/\Delta[\mathrm{VOC}], \tag{3-65}$$

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

$$\mathrm{OH} + \mathrm{RH} \rightarrow \mathrm{H_2O} + \dot{\mathrm{R}} \tag{3-42}$$

$$\dot{\mathrm{R}} + \mathrm{O_2} \rightarrow \mathrm{R\dot{O}_2} \tag{3-43}$$

$$\mathrm{R\dot{O}_2} + \mathrm{NO} \rightarrow \mathrm{R\dot{O}} + \mathrm{NO_2} \tag{3-44a}$$

$$\mathrm{R\dot{O}} \rightarrow \mathrm{carbonyl} + \mathrm{HO_2} \tag{3-65}$$

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO_2}. \tag{3-32}$$

The net reaction,

$$\mathrm{OH} + \mathrm{RH} + 2\ \mathrm{NO} \xrightarrow{\mathrm{O_2}} \mathrm{carbonyl} + 2\ \mathrm{NO_2} + \mathrm{OH}, \tag{3-66}$$

can be viewed as involving the two separate reaction sequences:

(1) the formation of organic peroxy ($\mathrm{R\dot{O}_2}$) radicals from the reactions,

$$\mathrm{OH} + \mathrm{RH} \rightarrow \mathrm{H_2O} + \dot{\mathrm{R}}$$

$$\dot{\mathrm{R}} + \mathrm{O_2} \rightarrow \mathrm{R\dot{O}_2}$$

Net: $$\mathrm{OH} + \mathrm{RH} \rightarrow \mathrm{R\dot{O}_2},$$

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

$$\dot{RO}_2 + NO \rightarrow \dot{RO} + NO_2$$

$$\dot{RO} \rightarrow \text{carbonyl} + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$\text{Net:} \quad \dot{RO}_2 + 2\ NO \rightarrow \text{carbonyl} + 2\ NO_2 + OH\ .$$

The photolysis of NO_2 then leads to O_3 formation (Reactions 3-1 and 3-2). The first reaction sequence determines how fast $\dot{RO}_2$ radicals are generated from the VOC, which is called "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 NO_2 conversion, regeneration of OH radicals, and the formation of product species, determines the efficiency of formation of O_3 from the $\dot{RO}_2$ radicals formed from the first reaction sequence and is termed "mechanistic reactivity" (Carter and Atkinson, 1989b). The second reaction sequence can be represented as

$$\dot{RO}_2 + \alpha NO \rightarrow \beta\, NO_2 + \gamma OH + \delta \text{ products.} \tag{3-67}$$

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 O_3-forming potential of the VOC. Thus, the existence of NO_x sinks in the reaction mechanism (low values of β or values of α-$\beta > 0$) leads to a decrease in the amount of O_3 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 $\gamma < 1$, 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 $\dot{RO}_2$ 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 O_3 formed; although the formation or loss of OH radicals is most important at low VOC/NO_x ratios, affecting the initial rate at which O_3 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 Volatile Organic Compounds as a Function of the Volatile Organic Compound/Nitrogen Oxide Ratio for an Eight-Component Volatile Organic Compound Mixture[a] and Low-Dilution Conditions[b]

	VOC/NO_x Ratio (ppmC/ppm)			
NMOC	4	8	16	40
CO	0.011	0.022	0.016	0.005
Ethane	0.024	0.041	0.018	0.007
n-Butane	0.10	0.16	0.069	0.019
n-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
trans-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
m-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	0.41	0.32	0.088	0.011

[a]Eight-component VOC mixture used to simulate NMOC emissions in an urban area.
[b]See Appendix A for abbreviations and acronyms.

Source: Carter and Atkinson (1989b).

The O_3-forming potentials of large numbers of VOCs, including emissions from automobiles using gasoline and various alternative fuels such as methanol and ethanol blends and compressed natural gas, have been investigated by airshed computer models (Chang and Rudy, 1990; Chang et al., 1991a; Derwent and Jenkin, 1991; Andersson-Sköld et al., 1992; McNair et al., 1992, 1994; Carter, 1994). Consistent with the modeling studies of Carter and Atkinson (1987, 1989b), these computer-modeling studies show that VOCs differ significantly in terms of their O_3-forming potential, for single-day as well as multiday conditions (Derwent and Jenkin, 1991; Andersson-Sköld et al., 1992; Carter, 1994; McNair et al., 1994). However, there are some differences between the O_3-forming potentials derived by Derwent and Jenkin (1991) for multiday transport conditions over Europe and by Carter (1994) for 1-day urban airshed "maximum incremental reactivity" conditions, especially for HCHO, an important direct emission and atmospheric transformation product of most VOCs.

Recent modeling studies have been carried out by Carter (1994) and McNair et al. (1994) to determine the O_3-forming potential of alternative fuels. Emissions from vehicles using 85% methanol and 15% gasoline (M-85) were shown to have ≈40% of the O_3-forming

potential of emissions from gasoline-fueled vehicles. Emissions from vehicles using liquefied petroleum gas (LPG) and compressed natural gas (CNG) were shown to have O_3-forming potentials that are ≈50% and ≈18%, respectively, of the O_3-forming potential of emissions from gasoline-fueled vehicles (McNair et al., 1994).

3.2.5 Photochemical Production of Aerosols

The chemical processes involved in the formation of O_3 and other photochemical pollutants from the interaction of NO_x and VOCs lead to the formation of OH radicals and oxidized VOC reaction products that often are of lower volatility than the precursor VOC. The OH radicals that oxidize the VOCs and lead to the generation of RO_2 radicals and conversion of NO to NO_2 (with subsequent photolysis of NO_2 form O_3) also react with NO_2 and sulfur dioxide (SO_2) to form HNO_3 and H_2SO_4, respectively, which can become incorporated into aerosols as particulate nitrate (NO_3^-) and sulfate (SO_4^{2-}). The low-volatility VOC reaction products can condense onto existing particles in the atmosphere to form secondary organic aerosol matter. Hence, O_3 formation, acid formation, and secondary aerosol formation in the atmosphere are so related that controls aimed at reducing O_3 levels can 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 (e.g., 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, PL (Bidleman, 1988; Pankow and Bidleman, 1992). The available experimental data and theoretical treatments show that, as a rough approximation, organic compounds with PL > 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,

$$A + TSP \rightleftharpoons F, \tag{3-68}$$

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:

$$K = F/(TSP)A. \tag{3-69}$$

Because 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 also must increase and the chemical becomes more particle-associated (Pankow and Bidleman, 1991, 1992).

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

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

Particles can form in the atmosphere by condensation or by coagulation, generally occurring by coagulation in urban and rural areas. The photooxidation reactions of VOCs typically lead to the formation of more oxidized and less volatile product species. When the vapor pressures exceed the saturated vapor pressure (i.e., vapor pressure $< 10^{-6}$ Torr), the products will become particle-associated (Pandis et al., 1991, 1992). Accumulation-size particles are in the size range 0.08 to 2.5 µm diameter (Whitby et al., 1972).

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

- direct emissions of elemental carbon from, for example, diesel-powered vehicles (Larson et al., 1989);
- direct emissions of primary organic carbon from, for example, meat cooking operations, paved road dust, and wood-burning fireplaces and other combustion sources (Hildemann et al., 1991a,b; Rogge et al., 1991, 1993);
- secondary organic material formed in the atmosphere from the atmospheric photooxidations of gas-phase NMOC (Turpin and Huntzicker, 1991; Pandis et al., 1992);
- the conversion of NO and NO_2 to HNO_3, followed by neutralization by NH_4 or through combination with other cations to form aerosol nitrates:

$$NH_3(gas) + HNO_3(gas) \rightleftharpoons NH_4NO_3(aerosol); \qquad (3\text{-}69a)$$

- the conversion of SO_2 (and other sulfur-containing species) to H_2SO_4, which has sufficiently low volatility to move to the aerosol phase; and
- emission into the atmosphere of "fine dust", for example, 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 (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 O_3 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 HNO_3 and H_2SO_4, arising from the atmospheric oxidation of NO_x and SO_2, respectively. Reduced sulfur compounds emitted from biogenic sources and certain anthropogenic sources also may lead to SO_2 or sulfonic acids (Tyndall and Ravishankara, 1991).

The major sulfur-containing compound emitted into the atmosphere from anthropogenic sources is SO_2. In the troposphere, the important loss processes of SO_2 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 SO_2 with the OH radical is such that the lifetime of SO_2 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)

$$OH + SO_2 \xrightarrow{M} HOSO_2 \tag{3-70}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{3-71}$$

$$SO_3 + H_2O \rightarrow H_2SO_4. \tag{3-72}$$

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, because SO_2 has a fairly long lifetime, due to gas-phase chemical processes, and also 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, 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):

$$SO_2(gas) \rightleftharpoons SO_2(aqu) \tag{3-73}$$

$$SO_2(aqu) + H_2O \rightleftharpoons HSO_3^- + H^+ \rightleftharpoons SO_3^{2-} + 2\ H^+ \tag{3-74}$$

$$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O \tag{3-75}$$

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2. \tag{3-76}$$

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).

$$SO_3^{2-} + 1/2\ O_2 \rightarrow SO_4^{2-} \qquad (3\text{-}77)$$

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 (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% h^{-1}, whereas the aqueous-phase (cloud) oxidation rate may be as high as 10 to 50% h^{-1} (Schwartz, 1989).

The oxidation of NO_x to HNO_3 and nitrates was discussed in Section 3.2.3. During daylight hours, oxidation occurs by the gas-phase reaction of NO_2 with the OH radical:

$$OH + NO_2 \overset{M}{\rightarrow} HNO_3, \qquad (3\text{-}15)$$

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:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (3\text{-}12)$$

$$NO_3 + NO_2 \overset{M}{\rightleftharpoons} N_2O_5, \qquad (3\text{-}13,\ \text{-}3\text{-}13)$$

with N_2O_5 undergoing wet or dry deposition, or both. The reader is referred to Schwartz (1989) for further discussion of the conversion of NO_x to NO_3 and HNO_3 and of acid deposition.

3.3 Meteorological Processes Influencing Ozone Formation and Transport

Day-to-day variability in O_3 concentrations is, to a first approximation, the result of day-to-day variations in meteorological conditions. This section presents a succinct overview of those atmospheric processes that affect the concentrations of O_3 and other oxidants in urban and rural areas. Included in this list of processes are the vertical structure and

dynamics of the PBL; transport processes, including thermally-driven mesoscale circulations such as lake and sea breeze circulations; complex terrain effects on transport and dispersion; vertical exchange processes; deposition and scavenging; and meteorological controls on biogenic emissions and dry deposition.

3.3.1 Meteorological Processes

3.3.1.1 Surface Energy Budgets

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

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

$$Q_{sfc} = K\downarrow - K\uparrow + L\downarrow - L\uparrow + Q_H + Q_E . \qquad (3\text{-}78)$$

where $K\downarrow$ is the incoming short-wave radiation, $K\uparrow$ is the outgoing short-wave radiation, $L\downarrow$ is the incoming long-wave radiation from the atmosphere, $L\uparrow$ is the outgoing long-wave radiation, and Q_H and Q_E are the heat flux and latent heat flux to the soil, respectively. On a global annual average, Q_{sfc} is assumed to be near zero (i.e., the planet is not heating or cooling systematically, an assumption clearly being questioned with the growing debate on climatic change). On a day-to-day basis, however, Q_{sfc} will certainly vary from zero and will cause changes in surface temperature. Cloud cover, for example, will reduce the amount of short-wave radiation reaching the surface and will modify all the subsequent components of the radiation budget. Moreover, the redistribution of energy through the PBL creates thermodynamic conditions that influence vertical mixing. The treatment of energy budgets has been attempted on the scale of individual urban areas. These studies are summarized by Oke (1978).

For many of the modeling studies of the photochemical production of O_3, the vertical mixing has been parameterized by a single, well-mixed layer. However, because this is a great simplification of a complex structure, and because the selection of rate and extent of vertical mixing may influence local control options, future modeling and observational studies need to address the energy balances so that more realistic simulations can be made of the structure of the PBL.

4

Environmental Concentrations, Patterns, and Exposure Estimates

4.1 Introduction

The effects of ozone (O_3) on humans, animals, and vegetation have received extensive examination and are discussed elsewhere in this document. As indicated in the previous O_3 criteria document (U.S. Environmental Protection Agency, 1986), most of the human and welfare effects research has focused on evaluating those impacts on health or vegetation of exposure to O_3 that simulate ambient O_3 exposures (e.g., matching the occurrence of hourly average concentrations or more prolonged times of exposure). This information on concentrations obtained from extensive monitoring in the United States can be useful both for linking anthropogenic emissions of O_3 precursors with the protection of health and welfare (i.e., determining compliance with air standards) and for augmenting exposure assessment and epidemiology studies. The major emphasis in this chapter, however, 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 the environment. This chapter is not an exposure assessment for ambient O_3; rather, this chapter elucidates the features of O_3 concentration patterns and exposure possibilities.

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. Environmental Protection Agency (1994) for 1983 to 1993. 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, also are described. Specific focus is provided on O_3 monitoring sites that experience low maximum hourly average concentrations because these locations form the "basis for comparison" for O_3 concentrations and exposures. In Section 4.5, the seasonal patterns of hourly average concentrations 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 with those in high-elevation locations. For

comparing indoor to outdoor O_3 exposures or concentrations, information is provided in Section 4.7 on the latest data on indoor/outdoor (I/O) ratios. Section 4.8 describes efforts to estimate both human and vegetation exposure to O_3. Examples are provided on how both fixed-site monitoring information and human exposure models are used to estimate risks associated with O_3 exposure. A short discussion is provided on the importance of hourly average concentrations, which are used in human health and vegetation experiments that simulate "real world" exposures.

As indicated in the previous O_3 criteria document (U.S. Environmental Protection Agency, 1986), O_3 is the only photochemical oxidant other than nitrogen dioxide (NO_2) that is routinely monitored and for which a comprehensive aerometric database exists. Data for peroxyacetyl nitrate (PAN) and hydrogen peroxide (H_2O_2) have been obtained only as part of special research investigations. Consequently, no data on nationwide patterns of occurrence are available for these non-O_3 oxidants; nor are extensive data available on the correlations of levels and patterns of these oxidants with those of O_3. Sections 4.9 and 4.10 summarize the available data for these other oxidants. Section 4.11 describes the co-occurrence patterns of O_3 with NO_2; sulfur dioxide (SO_2); and acidic aerosols, precipitation, and cloudwater.

4.1.1 Characterizing Ambient Ozone Concentrations

It is important to distinguish among concentration, exposure, and dose when using air quality data to assess human health and vegetation effects. For this document, the following definitions apply:

1. The "concentration" of a specific air pollutant is the amount of that material per unit volume of air. Air pollution monitors measure pollutant concentrations, which may or may not provide accurate exposure estimates.
2. The term "exposure" is defined as the concentration of a pollutant encountered by the subject (animal, human, or plant) for a duration of time. Exposure implies that such an encounter leads to intake (i.e., through the respiratory tract or stomata).
3. The term "dose" is defined as that mass of pollutant delivered to an inner target. This term has numerous quantitative descriptions (e.g., micrograms of O_3 per square centimeter of lung epithelium per minute), so the context of the use of this term within the document must be considered. Human dosimetry is discussed in Chapter 8.

The dose incurred by an organism (e.g., plant, animal, or human) is a more complicated measure involving the concentration, the exposure duration, and the concurrent state of the organism’s susceptibility. These distinctions become important because the concentration of an airborne contaminant that is measured in an empty room or at a stationary outdoor monitor is not in fact an exposure. A measured concentration functions as an alternative to an exposure only to the degree to which it represents concentrations actually experienced by individuals.

Concentrations of airborne contaminants for vegetation are considered to represent an exposure when a plant is subjected to them over a specified time period. As indicated in Chapter 5 (see Section 5.5), dose has been defined historically by air pollution vegetation researchers as ambient air quality concentration multiplied by time (O’Gara, 1922). However, a more rigorous definition was required. Runeckles (1974) introduced the concept of "effective dose" as the amount or concentration of pollutant that is adsorbed by vegetation, in

contrast to that which is present in the ambient air. Fowler and Cape (1982) developed this concept further and proposed that the "pollutant adsorbed dose" be defined in units of grams per square meter (of ground or leaf area) and could be obtained as the product of concentration, time, and stomatal (or canopy) conductance for the gas in question. Taylor et al. (1982) suggested internal flux (milligrams per square meter per hour) as a measure of the dose to which plants respond. In this chapter, dose will be taken to signify, for the purposes of vegetation, that amount of pollutant absorbed by the plant.

In order to characterize the specific doses responsible for affecting human health and vegetation, there has to be a linkage between exposure and actual dose. Unfortunately, it is difficult to predict this relationship, even with the available models. For example, the sensitivity of vegetation to O_3 as a function of time of day, period of growth, or edaphic conditions can determine the severity of response. For example, high O_3 concentrations may cause minimum injury or damage to plants, whereas more moderate O_3 concentrations may cause a greater degree of injury or damage (Showman, 1991). Because not enough is known to quantify the links between exposure and dosage, and routine monitoring for O_3 is summarized as hourly average concentrations (i.e., potential exposure), most of the information provided in this chapter is characterized in terms of concentration and exposure.

As indicated in Chapter 5, for many years, air pollution specialists have explored alternative mathematical approaches for summarizing ambient air quality information in biologically meaningful forms that can serve as alternatives for characterizing dose.

For vegetation, as indicated in Chapter 5 (Section 5.5), extensive research has focused on identifying indicators of concentration and duration (exposure) that are firmly founded on biological principles. Many of these indicators have been based on research results indicating that the magnitude of vegetation responses to air pollution is determined more as a function of the magnitude of the concentration than of the length of the exposure (U.S. Environmental Protection Agency, 1992b). Short-term (1- to 8-h), high O_3 concentrations (>0.1 ppm) have been identified by many researchers as being more important than long-term, low O_3 concentrations for induction of visible injury to vegetation (see Chapter 5 for further discussion).

Long-term, average concentrations were used initially as an exposure indicator to describe O_3 concentrations over time when assessing vegetation effects (Heck et al., 1982). Based on the view presented in the previous criteria document (U.S. Environmental Protection Agency, 1986) that higher concentrations of O_3 should be given more weight than lower concentrations (see Section 5.5 for further details), the following specific concerns about the use of a long-term average to summarize exposures of O_3 began appearing in the literature: the use of a long-term average failed to consider the impact of peak concentrations and of duration; a large number of hourly data sets within the commonly used 7-h window (0900 to 1559 hours), although diversely distributed and implying potentially diverse exposure potentials, were characterized by the same 7-h seasonal mean; and high hourly average concentrations (e.g., values greater than 0.1 ppm) occurred outside of a fixed 7-h window.

In summarizing the hourly average concentrations in this chapter, specific attention is given to the relevance of the exposure indicators used. For example, for human health considerations, concentration (or exposure) indicators such as the daily maximum 1-h average concentrations, as well as the number of daily maximum 4-h or 8-h average concentrations, are used to characterize information in the population-oriented locations. For vegetation, several different types of exposure indicators are used. For example, much of the National Crop Loss Assessment Network (NCLAN) exposure information is summarized in terms of

the 7-h average concentrations. However, because peak-weighted, cumulative indicators (i.e., exposure parameters that sum the products of hourly average concentrations multiplied by time over an exposure period) have shown considerable promise in relating exposure and vegetation response (see Section 5.5), several exposure indicators that use either a threshold or a sigmoidal weighting scheme are discussed in this chapter to provide insight concerning the O_3 exposures that are experienced at a select number of rural monitoring sites in the United States. The peak-weighted, cumulative exposure indicators used in this chapter are SUM06 and SUM08 (the sums of all hourly average concentrations equal to or greater than 0.06 and 0.08 ppm, respectively) and W126 (the sum of the hourly average concentrations that have been weighted according to a sigmoid function [see Lefohn and Runeckles, 1987] that theoretically is based on a hypothetical vegetation response).

The exposure indicators used for human health considerations are in concentration units (i.e., parts per million), whereas the indicators used for vegetation are in both parts per million (e.g., 7-h seasonal average concentrations) and parts per million per hour (e.g., SUM06, SUM08, W126). The magnitude of the peak-weighted, cumulative indicators at specific sites can be compared with those values experienced at areas that experience low hourly average maximum concentrations. In some cases, to provide more detailed information about the distribution patterns for a specific O_3 exposure regime, the percentile distribution of the hourly average concentrations (in parts per million) 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 compliance with the National Ambient Air Quality Standards (NAAQS) for O_3. Most of the data presented in this chapter were obtained from data stored in the U.S. Environmental Protection Agency's (EPA's) computerized Aerometric Information Retrieval System (AIRS) and were collected after 1978. As pointed out in the previous criteria document for O_3 and other photochemical oxidants (U.S. Environmental Protection Agency, 1986), there was some difficulty in interpreting the O_3 data obtained at most sites across the United States prior to 1979 because of calibration problems.

In the United States, O_3 hourly average concentrations are monitored routinely 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 O_3 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 O_3, NAMS sites are located only in urban areas with populations exceeding 200,000. The other two types of sites are State and Local Air Monitoring Stations and Special Purpose Monitors, which meet the same rigid criteria for the NAMS sites but may be located in areas that do not necessarily experience high concentrations in populated areas.

For O_3, the reporting interval is 1 h, with the instruments operating continuously and producing an integrated hourly average measurement. In many cases, EPA summarizes

air quality data by an O_3 "season". Table 4-1 summarizes the O_3 season for the District of Columbia and each of the states in the United States.

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

[a]Air Quality Control Region (AQCR) Numbers 4, 5, 7, 10, and 11.
[b]AQCR Numbers 1, 2, 3, 6, 8, 9, and 12.

Source: Code of Federal Regulations (1991).

In this chapter, data are analyzed for the purpose of providing focus on specific issues of exposure-response relationships that are considered in the later effects chapters. The analyses proceed from a national picture of peak annual averages in Metropolitan Statistical Areas (MSAs), through national 10- and 3-year trends, to characteristic seasonal and diurnal patterns at selected stations, and then a brief examination of the incidence of episodic 1-h levels. Although there are O_3 data collected from monitoring stations not listed in AIRS, the major source of information was derived from ambient air concentrations from monitoring sites operated by the State and local air pollution agencies who report their data to AIRS. Because meteorology affects the identification of trends, methodologies that adjust for meteorology are described below.

To obtain a better understanding of the potential effect of ambient O_3 concentrations on human health and vegetation, hourly average concentration information was summarized for urban versus rural (forested and agricultural) areas in the United States. A land use characterization of "rural" does not imply that any specific location is isolated from anthropogenic influences. For example, Logan (1989) has noted that hourly average O_3 concentrations above 0.08 ppm are common in rural areas of the eastern United States in spring and summer, but are unusual in remote western sites. Consequently, for the purposes of comparing exposure regimes that may be characteristic of clean locations in the United States with those that are urban influenced (i.e., located in either urban or rural locations), this chapter characterizes data collected from those stations whose locations appear to be isolated from large-scale anthropogenic influences.

Long-term (multiyear) 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 separately.

4.2 Trends in Ambient Ozone Concentrations

Ozone concentrations and, thus, exposure change from year to year. High O_3 levels occurred in 1983 and 1988 in some areas of the United States. These levels more than likely were attributable, in part, to hot, dry, stagnant conditions. However, O_3 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 meteorological conditions that were less favorable for O_3 formation and to 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. Environmental Protection Agency (1993) has reported a 21% improvement in O_3 levels between 1983 and 1992, which, in part, may be attributed to relatively high O_3 levels in 1983, compared to the low O_3 exposure years from the period 1989 through 1992. However, new statistical techniques accounting for meteorological influences have been used by EPA and they appear to suggest an improvement (independent of meteorological considerations) of 10% for the 10-year period, 1983 to 1992 (U.S. Environmental Protection Agency, 1993).

The EPA summarizes trends for the 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 8 of the last 10 years. A companion analysis of the most recent 3 years requires valid data in all 3 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, and 672 sites are included in the 1990 to 1992 database. The NAMS sites comprise 196 of the long-term trends sites and 222 of the sites in the 3-year database.

Figure 4-1 displays the 10-year composite average trend for the second highest daily maximum hourly average concentration during the O_3 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 10 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. Environmental Protection Agency (1992a), the relatively high O_3 concentrations in 1983 and 1988 likely were attributable in part to hot, dry stagnant conditions in some areas of the country that were especially conducive to O_3 formation.

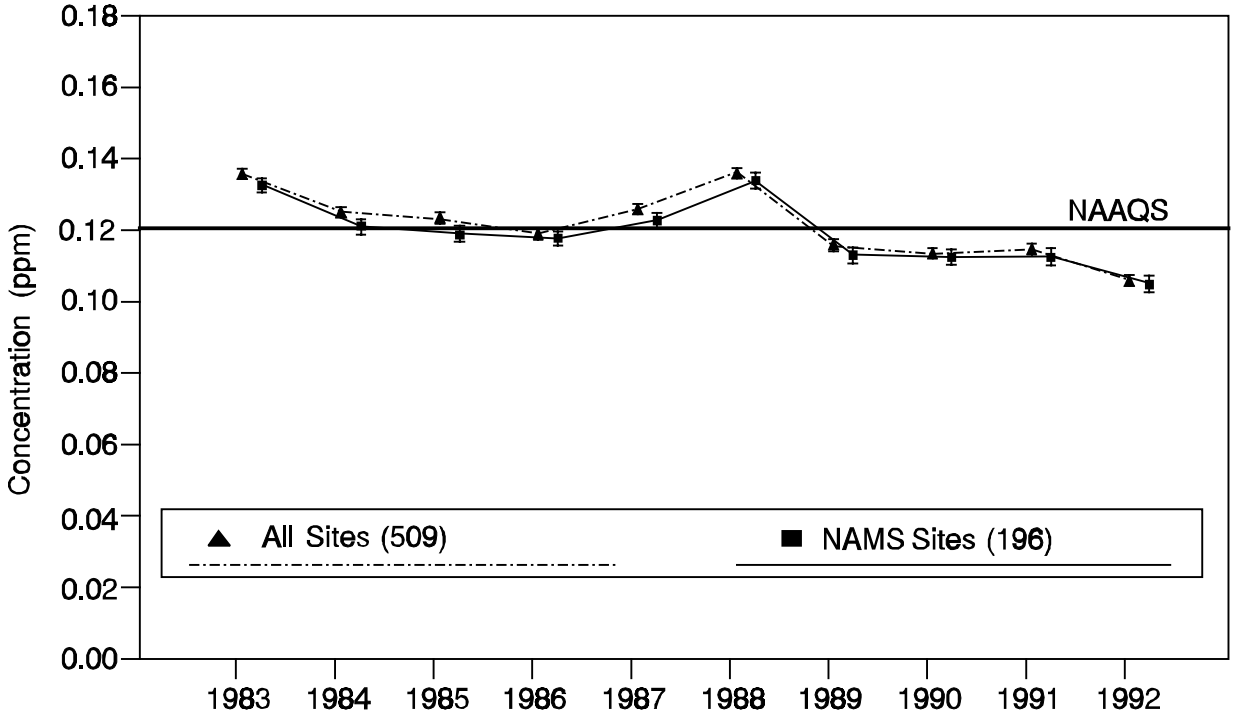


Figure 4-1. National trend in the composite average of the second highest maximum 1-h ozone concentration at both National Air Monitoring Stations (NAMS) and all sites with 95% confidence intervals, 1983 to 1992.

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

From 1991 to 1992, the composite mean of the second highest daily maximum 1-h O_3 concentrations decreased 7% at the 672 sites and 6% at the subset of 222 NAMS sites.

Also, from 1991 to 1992, the composite average of the number of estimated instances of O_3 exceeding the standard decreased by 23% at the 672 sites, and by 19% at the 222 NAMS sites. Nationwide volatile organic compound (VOC) emissions decreased 3% from 1991 to 1992 (U.S. Environmental Protection Agency, 1993).

The composite average of the second daily maximum concentrations decreased in 8 of the 10 EPA regions from 1991 to 1992, and remained unchanged in Region VII. Except for Region VII, the 1992 regional composite means are lower than the corresponding 1990 levels. Although meteorological conditions in the east during 1993 were more conducive to O_3 formation than those in 1992, the composite mean level for 1993 was the second lowest composite average for the decade (1984 to 1993) (U.S. Environmental Protection Agency, 1994).

Investigators have explored methods for investigating techniques for adjusting O_3 trends for meteorological influences (Stoeckenius and Hudischewskyj, 1990; Wakim, 1990; Shively, 1991; Korsog and Wolff, 1991; Lloyd et al., 1989; Davidson, 1993; Cox and Chu, 1993). Stoeckenius and Hudischewskyj (1990) used a classification method to group days into categories according to the magnitude of O_3 and the similarity of meteorological conditions within each defined group. Adjusted O_3 statistics for each year were computed from the meteorologically grouped data, and the yearly frequency of occurrence of each group relative to its long-term frequency was described. Wakim (1990) used standard regression analysis to quantify the effect of daily meteorology on O_3. Adjusted O_3 statistics were calculated by adding the expected O_3 statistic for a year with typical meteorology to the average of the regression residuals obtained for the adjusted year. Shively (1991) described a model in which the frequency of exceedance of various O_3 thresholds was modeled as a nonhomogeneous Poisson process where the parameter is a function of time and meteorological variables. Kolaz and Swinford (1990) categorized O_3 days as "conducive" or "nonconducive", based on selected meteorological conditions within the Chicago, IL, area. Within these categories, the meteorological intensity of days conducive to daily exceedances of the NAAQS for O_3 was calculated and used to establish long-term trends in the annual exceedance rate.

Cox and Chu (1993) modeled the daily maximum O_3 concentration using a Weibull distribution with fixed-shape and scale parameters, the logarithm of which varies as a linear function of several meteorological variables and a yearly index. The authors tested for a statistically significant trend term to determine if an underlying meteorologically adjusted trend could be detected. Overall, the measured and modeled predicted percentiles tracked closely in the northern latitudes but performed less adequately in southern coastal and desert areas. The results suggested that meteorologically adjusted upper percentiles of the distribution of daily maximum 1-h O_3 are decreasing in most urban areas over the period 1981 through 1991. The median rate of change was −1.1% per year, indicating that O_3 levels have decreased approximately 11% over this time period. The authors reported that trends estimated by ignoring the meteorological component appear to underestimate the rate of improvement in O_3 primarily because of the uneven year-to-year distribution of meteorological conditions favorable to O_3 formation.

Lefohn et al. (1993a) focused on a potentially useful method for identifying monitoring sites whose improvement in the level of O_3 concentrations may be attributed more to the implementation of abatement control strategies than meteorological changes. As has been pointed out previously, meteorology plays an important role in affecting the O_3 concentrations that are contained in the tail of the 1-h distributions, as indicated by the

successful predictive application of the exponential-tail model to distributions (California Air Resources Board, 1992). Because meteorology plays such an important role in affecting the tail of the 1-h distribution at a specific site, changes in "attainment" status are not expected to affect changes in the entire distribution pattern and, thus, the average diurnal pattern. Lefohn et al. (1993b) investigated the change in the annual average diurnal pattern as changes in O_3 levels occurred. The authors reported that, although the amplitude of the diurnal patterns changed, there was little evidence for consistent changes in the shape of the annual diurnal patterns (Figure 4-2). In a follow-up to this analysis, Lefohn et al. (1993a) reported that 25 of the 36 sites that changed compliance status across years showed no statistically significant change in the shape of the average diurnal profile (averaged by O_3 season). In addition, the authors reported that for 71% (10 of 14) of the sites in Southern California and Dallas-Fort Worth, TX, that showed improvement in O_3 levels (i.e., reductions in the number of exceedances over the years), but still remained in "nonattainment," a statistically significant change in the shape of the seasonally averaged diurnal profile occurred (e.g., Figure 4-3). Thus, the authors noted that, for the Southern California and Dallas-Fort Worth sites, changes were observed in the seasonally averaged diurnal profiles, whereas for the sites moving between attainment and nonattainment status, such a change in shape generally was not observed. Lefohn et al. (1993a) pointed out that it was possible that meteorology played a more important role in affecting attainment status than did changes in emission levels.

Historically, the long-term O_3 trends in the United States characterized by EPA have emphasized air quality statistics that are closely related to the NAAQS. A report by the National Academy of Sciences (NAS) (National Research Council, 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 also 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 EPA in tracking trends in the quality of the air that 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 (1991). 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 exceeded 0.080 or 0.105 ppm (Stoeckenius, 1991), or the number of days in California when the O_3 concentration exceeded 0.2 ppm (Zeldin et al., 1991). Several other O_3 concentration measures are described in this report.

As an alternative to the way in which EPA historically has implemented its trends analysis, U.S. Environmental Protection Agency (1992a) used percentiles in the range of the 50th percentile (or median) to the 95th percentile. The U.S. Environmental Protection Agency (1992a) reported that the pattern for the 10-year trends (1982 to 1991), using the various alternative O_3 summary statistics, were somewhat similar. There was a tendency for the curves to become flatter in the lower percentiles. The peak years of 1983 and 1988 were still evident in the trend lines for each indicator. The increase of 8% recorded in the annual

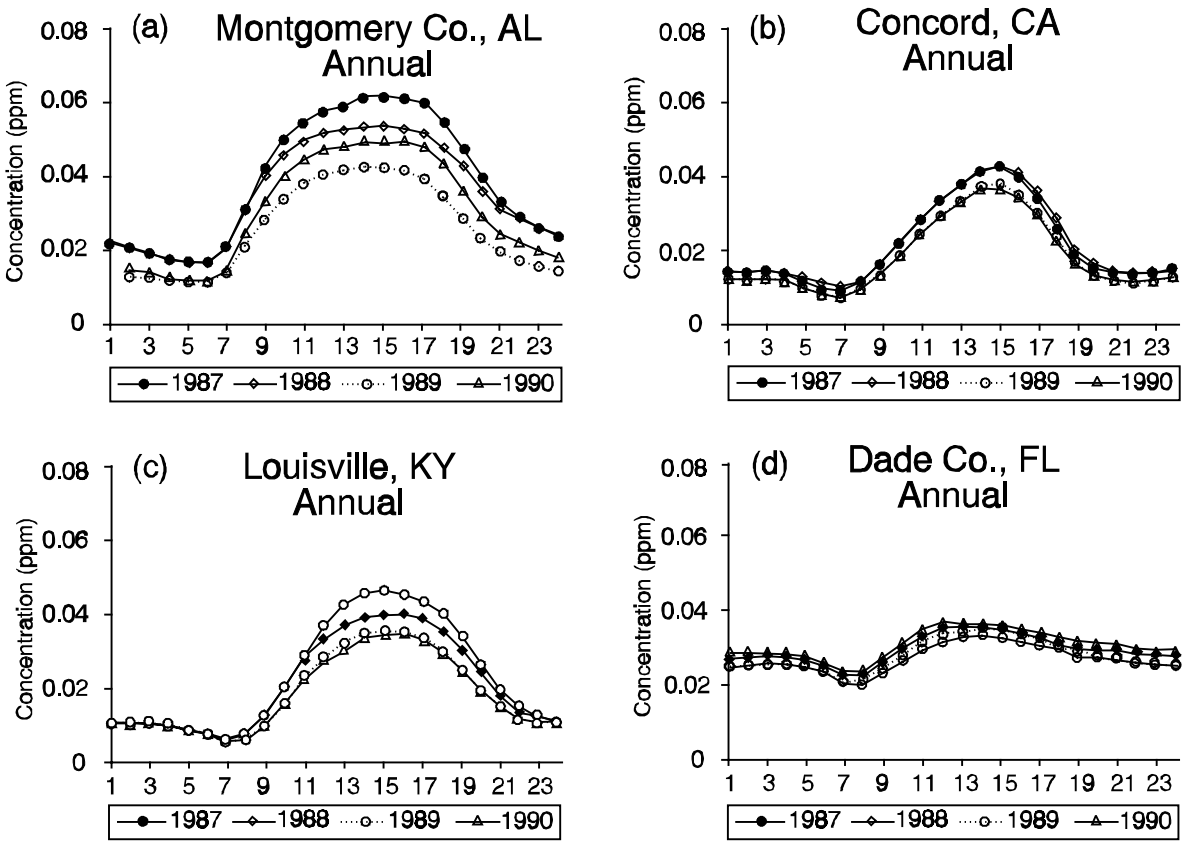


Figure 4-2. The annually averaged composite diurnal curves for the following sites that changed from nonattainment to attainment status: (a) Montgomery County, AL; (b) Concord, CA; (c) Louisville, KY; and (d) Dade County, FL; for the period 1987 to 1990. The darkened curve in each figure identified the year in which the greatest number of daily maximum 4-h average concentrations ≥0.08 ppm occurred.

Source: Lefohn et al. (1993b).

second-highest daily maximum 1-h concentration from 1987 to 1988 also was seen in the 95th and 90th percentile concentrations. The lower percentile indicators had smaller increases of 3 to 4%. The percent change between 1982 and 1991 for each of the summary statistics follows: annual daily maximum 1-h concentration, −11%; annual second daily maximum 1-h concentration, −8%; 95th percentile of the daily maximum 1-h concentrations, −5%; 90th percentile, −4%; 70th percentile, −1%; 50th percentile, or median of the daily maximum 1-h concentrations, +1%; and the annual mean of the daily maximum 1-h concentrations, −1%.

Besides EPA, additional investigators have assessed trends at several locations in the United States (e.g., Kuntasai and Chang, 1987; Gallopoulos et al., 1988; Korsog and Wolff, 1991; Lloyd et al., 1989; Rao et al., 1992; Davidson, 1993). For example, Kuntasai and Chang (1987) performed a basin-wide air quality trend analysis for the South Coast Air

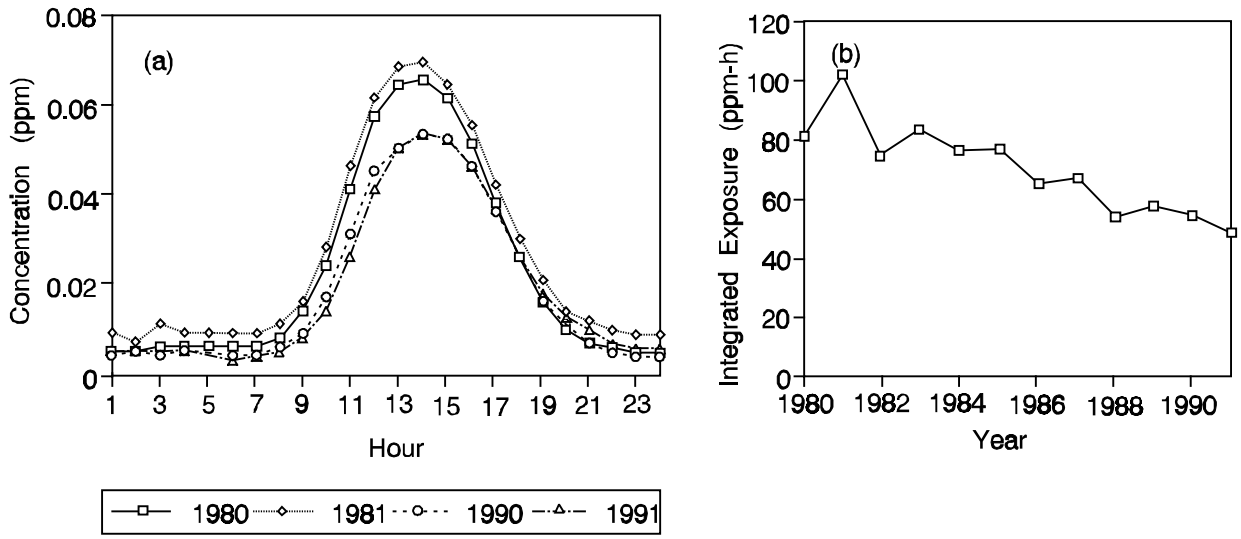


Figure 4-3. A summary of the (a) seasonal (January to December) averaged composite ozone diurnal curve and (b) integrated exposure W126 index for the Los Angeles, CA, site for the period 1980 to 1991.

Source: Lefohn et al. (1993a).

Basin of California using multistation composite daily maximum 1-h average ambient concentrations for the third quarter from 1968 to 1985. Basin-wide ambient O_3 concentrations appeared to show downward trends for the period 1970 to 1985, but because of high fluctuations, it was difficult to delineate trends for shorter periods. The meteorology-adjusted O_3 showed a more consistent downward trend than did unadjusted O_3. Korsog and Wolff (1991) examined trends from 1973 to 1983 at eight major population centers in the northeastern United States, using a robust statistical method. The 75th percentile was used by the authors in determining trends. The data were collected over a 3-mo (June through August) period. The surface temperature and upper air temperature variables were found to be the best predictors of O_3 behavior. Two regression procedures were performed to remove the variability of meteorological conditions conducive to high O_3 (i.e., O_3 concentrations >0.08 ppm). The results of the analysis showed that there had been a decrease of a few ppb on a yearly basis for the majority of the sites investigated by the authors.

Lloyd et al. (1989) investigated the improvement in O_3 air quality from 1976 to 1987 in the South Coast Air Basin. The authors reported that when the trend in total exceedance hours of a consistent set of basin air monitoring stations was considered, the improvement over the period of investigation was substantial. The authors reported that the number of station hours at or above the Stage I Episode Level (0.2 ppm, 1-h average) had decreased by about two-thirds over the period 1976 to 1987. Davidson (1993) reported on the number of days on which O_3 concentrations at one or more stations in the South Coast Air Basin exceeded the federal standard and the number of days reaching Stage I episode levels, for the months of May through October in the years 1976 to 1991. The author reported that the number of basin days exceeding the federal standard declined at an average annual rate of

2.27 days/year over the period. In addition, the number of basin days with Stage I episodes declined at an average annual rate of 4.70 days/year over the period 1976 to 1991. Rao et al. (1992) demonstrated the use of some statistical methods for examining trends in ambient O_3 air quality downwind of major urban areas. The authors examined daily maximum 1-h O_3 concentrations measured over New Jersey, metropolitan New York City, and Connecticut for the period 1980 to 1989. The analyses indicated that although there has been an improvement in O_3 air quality downwind of New York City, there has been little change in O_3 levels upwind of New York City during this 10-year period.

Lefohn and Runeckles (1987) proposed a sigmoidal weighting function that was used in developing a cumulative integrated exposure index (W126):

$$w_i = \frac{1}{[1 + M \times \exp^{(-A \times c_i)}]}, \qquad (4\text{-}1)$$

where: w_i = weighting factor for concentration i,
M and A are positive arbitrary constants, and
c_i = concentration i.

Lefohn et al. (1988b) reported the use of the sigmoidally weighted index with constants, M and A, 4,403 and 126 ppm^{-1}, respectively. The authors referred to the index as W126. The values were subjectively determined to develop a weighting function that (1) included hourly average concentrations as low as 0.04 ppm, (2) had an inflection point near 0.065 ppm, and (3) had an equal weighting of one for hourly average concentrations at approximately 0.10 ppm and above. To determine the value of the index, the sigmoidal weighting function at c_i was multiplied by the hourly average concentration, c_i, and summed over all relevant hours. The index included the lower, less biologically effective concentrations in the integrated exposure summation. The weighting function has been used to describe the relationship between O_3 exposure and vegetation response (e.g., Lefohn et al., 1988b, 1992a).

Lefohn and Shadwick (1991), using the W126 sigmoidally weighted exposure index, assessed trends in O_3 exposures at rural sites in the United States over 5- and 10-year periods (1984 to 1988 and 1979 to 1988, respectively) for forestry and agricultural regions of the United States. Although the statistical analysis did not explore the effects on trends of the lower O_3 exposure period 1989 to 1992, the analysis did reflect the effect of the higher O_3 exposure years (1983 and 1988). The hot, dry summer of 1988 was associated with the highest O_3 exposures in both the forest and agricultural regions of the eastern United States. To compare the exposure index values across years, a correction for missing data was applied for each pollutant. The corrections were determined for each site on a monthly basis. The Kendall's K statistic (Mann-Kendall test) was used to identify linear trends. Estimates of the rate of change (slope) for the index were calculated. Table 4-2 summarizes the results of the analysis. For sites distributed by forestry regions, there were more positive than negative slope estimates for the 5-year analysis of sites in the southern, midwestern, and Mid-Atlantic regions. For the 10-year analysis, the above was true except for the Mid-Atlantic seasonal analysis, where there was one positive and one negative significant trend. In the southern region, 38% of the sites showed significant trends. For the sites in

Table 4-2. Summary by Forestry and Agricultural Regions for

Ozone Trends Using the W126 Exposure Parameter Accumulated on a Seasonal Basis[a]

	Forestry						
	5-Year Trends				10-Year Trends		
			Significant			Significant	
Region	Not Significant[b]		−	+	Not 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						
	5-Year Trends				10-Year Trends		
			Significant			Significant	
Region	Not Significant[b]		−	+	Not 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

[a]See Appendix A for abbreviations and acronyms.
[b]Numbers in parentheses in the "Not Significant" column under "5-Year Trends" are the number of sites with exactly 3 years of data.

Source: Lefohn and Shadwick (1991).

the northeastern region, few sites showed a significant trend. There were considerably fewer sites in the remaining regions than in the four forestry regions above. Hence, for these regions, no significance was assigned to the differences in the number of negative and positive slope estimates in the tables. Similar to the results reported for the forestry regions, most of the sites in the agricultural regions showed no O_3 trends. However, in the Appalachian agricultural region, as many as 50% of the sites showed a pronounced indication of a trend. A predominance of positive significant trends for both the 5- and 10-year analyses was observed. In the other agricultural regions, there were approximately an equal number of positive and negative significant 5- and 10-year trends. The O_3 results produced patterns that were not pronounced enough to draw more than tentative conclusions for the 10-year analysis. For the 5-year analysis, there was still not a strong indication of an O_3 trend. However, when significant trends were observed, they were almost always positive. This can be attributed to eastern O_3 levels that were generally higher in 1988 than in previous years.

4.3 Surface Ozone Concentrations

4.3.1 Introduction

Ozone is measured at levels above the minimum detectable level at all monitoring locations in the world (Lefohn et al., 1990a). As dicussed earlier in Chapter 3, the concept of a "natural" background of O_3 is complex. Concentrations of background O_3 can vary with temperature, wind speed and direction, vertical motion, geographic location including latitude and altitude, and season of the year. This background O_3 can be attributed the following sources: (1) downward transport of stratospheric O_3 through the free troposphere to near ground level; (2) in situ O_3 production from methane emitted from swamps and wetlands reacting with natural NO_x emitted from soils, lighting strikes, and from downward transport of NO from the stratosphere into the troposphere; and (3) in situ production of O_3 from the reactions of biogenic VOCs with natural NO_x (National Research Council, 1991). A fourth source to be considered is the O_3 production resulting from long range transport of O_3 from distant pollutant sources (see Chapter 3).

The occasional occurrence of stratospheric injection of O_3, at specific times and in certain locations, is accepted and may be responsible for some of the rare occurrences of elevated levels that have been observed at some high- and low-elevation remote sites. A summer season average contribution of approximately 5 to 10 ppb for surface-level O_3 concentration from stratospheric intrusion has been estimated (Altshuller, 1989).

For purposes of comparing how O_3 levels have changed over time, it would be interesting to know how current levels compare to previous, historical natural background levels. However, estimations of background O_3 concentrations are difficult to make. The definition of background and the use of O_3 measurements are subject to much uncertainty. It is difficult, if not impossible, to determine whether any geographic location on earth is free from human influence (Finlayson-Pitts and Pitts, 1986). The natural precursor emissions can be responsible for the production of the O_3 concentrations observed at remote sites (Chameides et al., 1988; Zimmerman, 1979; Trainer et al., 1987). Citing indirect evidence for the possible importance of natural emissions, Lindsay et al. (1989) have emphasized that additional research is required to assess the role that natural hydrocarbons might play in urban and regional O_3 episodes.

It is possible for urban emissions, as well as O_3 produced from urban area emissions, to be transported to more rural downwind locations. This can result in elevated O_3 concentrations at considerable distances from urban centers (Wolff et al., 1977; Husar et al., 1977; Wight et al., 1978; Vukovich et al., 1977; Wolff and Lioy, 1980; Pratt et al. 1983; Logan, 1985; Altshuller, 1986; U.S. Environmental Protection Agency, 1986; Kelly et al., 1986; Pinkerton and Lefohn, 1986; Lefohn et al., 1987a; Logan, 1989; Lefohn and Lucier, 1991; Taylor and Hanson, 1992). For example, on over 40% of the 98 days that the maximum 1-h O_3 concentrations exceeded 0.12 ppm, the highest value was measured downwind of St. Louis at one of the rural sites, which was located approximately 50 km from downtown St. Louis (Altshuller, 1986). Urban O_3 concentration values often are depressed because of titration by NO_x (Stasiuk and Coffey, 1974). Reagan (1984) and Lefohn et al. (1987a) have observed this phenomenon where O_3 concentrations at center-city sites were lower than some rural locations. Because of the absence of chemical scavenging, O_3 tends to persist longer in nonurban than in urban areas (U.S. Environmental Protection Agency, 1986; Coffey et al., 1977; Wolff et al., 1977; Isaksen et al., 1978).

The distribution of O_3 or its precursors at a rural site near an urban source is affected by wind direction (i.e., whether the rural site is located up- or downwind from the source) (Kelly et al., 1986; Lindsay and Chameides, 1988). Thus, it may be difficult to apply land-use designations to the generalization of exposure regimes that may be experienced in urban versus rural areas. Because of this, it is difficult to identify a set of unique O_3 distribution patterns that adequately describe the hourly average concentrations experienced at monitoring sites in rural locations (Lefohn et al., 1991).

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 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 of O_3 also occur in the Texas Gulf Coast, the Northeast Corridor, and other heavily populated regions of the United States, but with a much lower frequency.

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 only a few episodes. Monitoring sites in polluted regions tend to experience frequent hourly average O_3 concentrations at or near minimum detectable levels. 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 and Madison, CT; Baton Rouge, LA; Bayonne, NJ; New York City and Babylon, NY; Harris County, 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 >0.125 ppm is important, Table 4-4 illustrates that, for most of the sites listed (except for several sites in California), such high hourly average concentrations occur less than 1% of the time and are associated with occasional episodes.

As indicated in Section 4.1, interest has been expressed in characterizing O_3 exposure regimes for sites experiencing daily maximum 8-h concentrations above specific

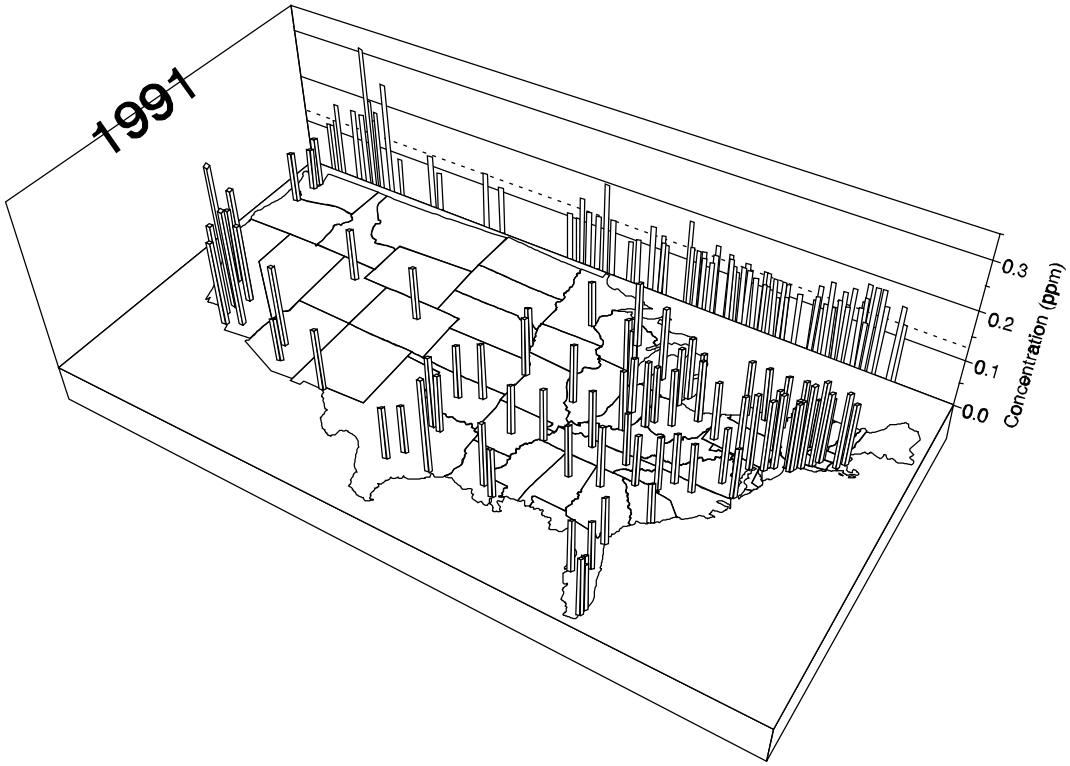


Figure 4-4. United States map of the highest second daily maximum 1-h average ozone concentration by Metropolitan Statistical Area, 1991.

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

thresholds (e.g., 0.08 or 0.10 ppm). Table 4-5 summarizes the highest second daily maximum 8-h average O_3 concentrations by MSA for the years 1989 to 1991. The data have been reported for the O_3 season as summarized in Table 4-1. In some cases, high concentrations occur in the fall and winter periods as well as in the summertime. Analyses documented the occurrence, at some sites, of multihour periods within a day of O_3 at levels of potential health effects. Although 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 O_3 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 O_3 concentrations showing only moderate peaks but exhibiting multihour levels above 0.10 ppm. Lefohn et al. (1993b) 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, but 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 O_3 levels may produce distributions of 1-h O_3 that result in a broader diurnal profile than those seen in

Table 4-3. The Highest Second Daily Maximum One-Hour Ozone Concentration (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991

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 (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991

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
Pascogoula, 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 (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991

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				

high-oxidant urban areas where O_3 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 O_3 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 O_3 exposure with an effect. For example, using O_3 ambient air quality data, McCurdy (1988) compared the number of exceedances of 0.12 ppm and the number of occurrences of the daily maximum 8-h average concentrations ≥0.08 ppm and reported that a positive correlation (r = 0.79) existed between the second-highest 1-h daily maximum in a year and the expected number of days with an 8-h daily maximum average concentration >0.08 ppm O_3. In this case, the predictive strength of using one O_3 exposure index to predict another is not strong.

Similar to analysis performed by McCurdy (1988), all of the hourly averaged data from rural agricultural and forested sites in the AIRS database were summarized into maximum 3-mo SUM06, second highest daily maximum hourly average concentration, and second highest daily maximum 8-h average concentration exposure indices per year for the period 1980 to 1991. For the rural agricultural sites, the correlation coefficients between the 3-mo SUM06 and the second highest daily maximum hourly average concentration and the second highest daily maximum 8-h average concentration were 0.650 and 0.739, respectively (Figure 4-5). For the rural forested sites, the correlation coefficients between the 3-mo SUM06 and the second highest daily maximum hourly average concentration and the second highest daily maximum 8-h average concentration were 0.585 and 0.683, respectively (Figure 4-6).

Table 4-4. Summary of Percentiles of Hourly Average Concentrations (ppm) for the April-to-October Period[a]

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
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

Table 4-4 (cont'd). Summary of Percentiles of Hourly Average Concentrations (ppm) for the April-to-October Period[a]

AIRS Site	Name	Year	Min.	10	30	50	70	90	95	99	Max	Number of Observations
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

[a]See Appendix A for abbreviations and acronyms.

Table 4-5. The Highest Second Daily Maximum Eight-Hour Average Ozone Concentration (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991

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 (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991

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-Millvile-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 (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991

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

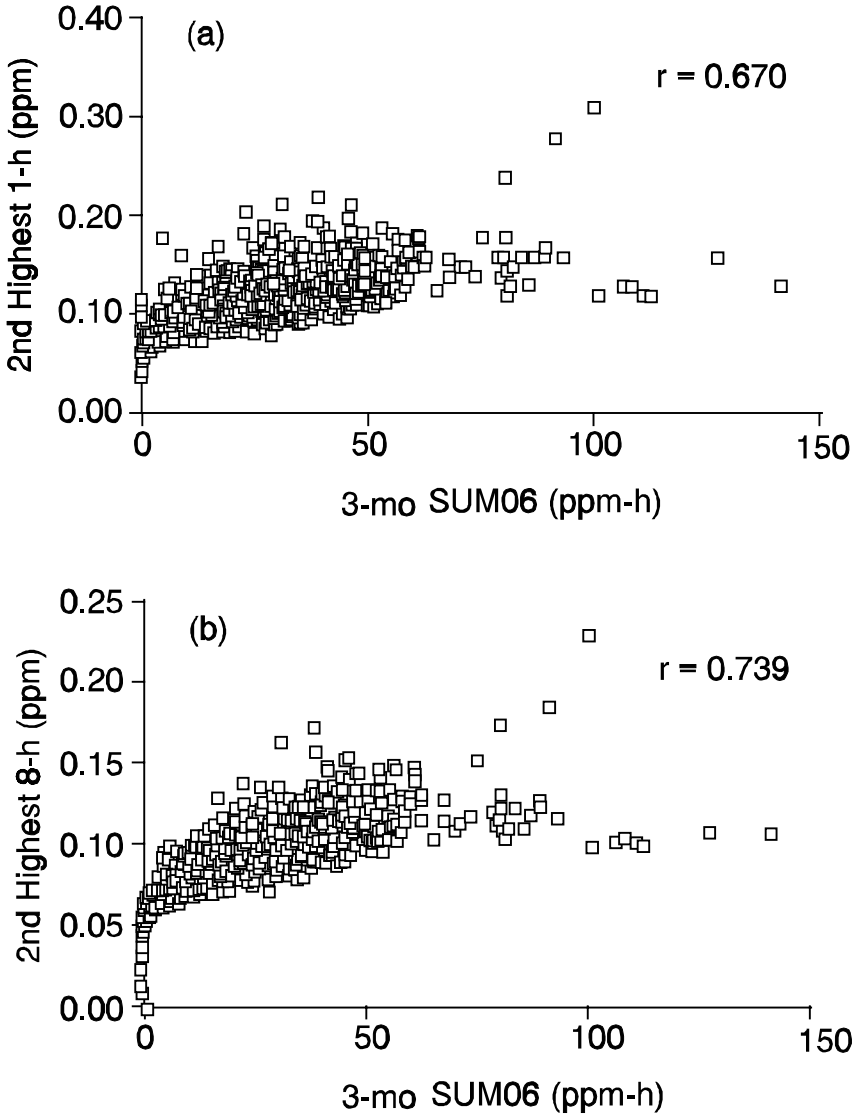


Figure 4-5. The relationship between (a) the second highest daily maximum hourly average ozone (O_3) concentration and the maximum 3-mo SUM06 value and (b) the second highest daily maximum 8-h average O_3 concentration and the maximum 3-mo SUM06 value for specific site years at rural agricultural sites for the 1980-to-1991 period.

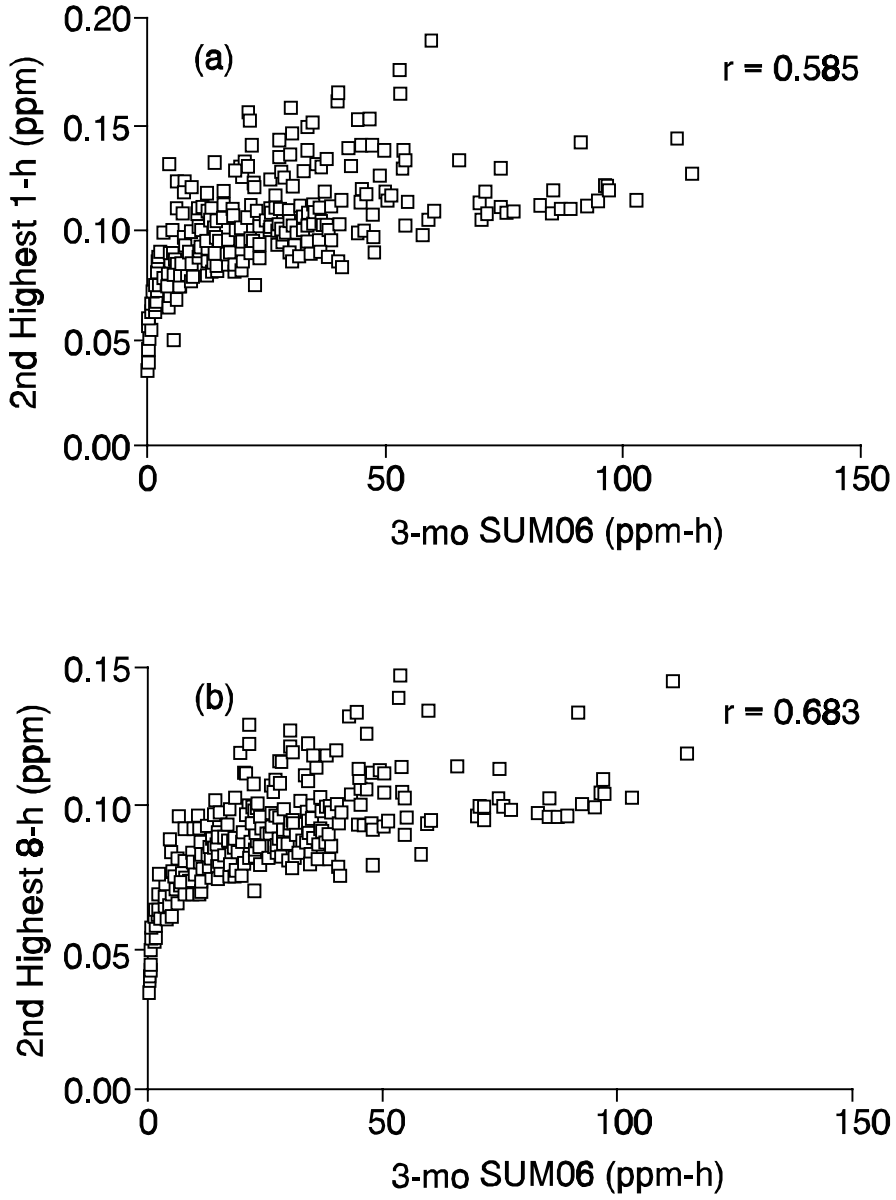


Figure 4-6. The relationship between (a) the second highest daily maximum hourly average ozone (O_3) concentration and the maximum 3-mo SUM06 value and (b) the second highest daily maximum 8-h average O_3 concentration and the maximum 3-mo SUM06 value for specific site years at rural forested sites for the 1980-to-1991 period.

One of the difficulties in attempting to use correlation analysis between indices for rationalizing the substitution of one exposure index for another to predicting an effect (e.g., SUM06 versus the second highest daily maximum hourly average concentration) is the introduction of the error associated with estimating levels of one index from another. Lefohn et al. (1989) have recommended that if a different exposure index (e.g., second highest daily maximum hourly average concentration) is to be compared to, for example, the SUM06 for

adequacy in predicting crop loss, then the focus should be on how well the two exposure indices predict crop loss using the effects model that is a function of the most relevant index, and not on how well the indices predict one another. Using data from both urban and rural O_3 monitoring sites in the midwestern United States that were located near agricultural or forested areas, Lefohn et al. (1989) reported a large amount of scatter between the second highest daily maximum hourly average concentration and the SUM06 indices. This large scatter indicated considerable uncertainty when attempting to predict a value for SUM06, given a specific second highest daily maximum hourly average concentration value. The authors reported that for a given second highest daily maximum hourly average concentration, the SUM06 values varied over a large range. Lefohn et al. (1989) concluded that such large uncertainty would introduce additional uncertainty when attempting to use the predicted exposure index to estimate an effect. The authors concluded that less error would be introduced if either of the two indices were used directly in the development of an exposure-response model.

As pointed out by the U.S. Environmental Protection Agency (1986), a familiar measure of O_3 air quality is the number or percentage of days on which some specific concentration is equalled or exceeded. This measure, however, does not shed light on one of the more important questions regarding the effects of O_3 on both people and plants: what is the possible significance of high concentrations lasting 1 h or longer and then recurring on 2 or more successive days?

The recurrence of high O_3 concentrations on consecutive days was examined in four cities (one site in each city) by the U.S. Environmental Protection Agency (1986). The numbers of multiday events were tallied by length of event (i.e., how many consecutive days) using data for the daylight hours (0600 to 2000 hours) in the second and third quarters of 1979 through 1981. These sites were selected because they included areas known to experience high O_3 concentrations (e.g., California), and because they represent different geographic regions of the country (west, southwest, and east).

Because of the importance of episodes and respites, the U.S. Environmental Protection Agency (1986) commented on the occurrences of the length of episodes and the time between episodes. The agency concluded that its analysis showed variations among sites in the lengths of episodes as well as the respite periods. In its discussion, the U.S. Environmental Protection Agency (1986) defined a day or series of days on which the daily 1-h maximum reached or exceeded the specified level as an "exposure"; the intervening day or days when that level was not reached was called a "respite". Four O_3 concentrations were selected: 0.06, 0.12, 0.18, and 0.24 ppm. At the Dallas site, for example, the value equalled or exceeded 0.06 ppm for more than 7 days in a row. The Pasadena site experienced 10 such exposures, but these 10 exposure events spanned 443 days; in Dallas, the 11 exposures involved only 168 days. At the lowest concentration (≥0.06 ppm), the Dallas station recorded more short-term (≤7 days) exposures (45) involving more days (159) than the Pasadena station (14 exposures over 45 days) because the daily 1-h maximum statistic in Pasadena remained above 0.06 ppm for such protracted periods. At concentrations ≥0.12 ppm, the lengthy exposures at the Pasadena site resolved into numerous shorter exposures, whereas in Dallas the exposures markedly dwindled in number and duration.

4.3.3 Nonurban Area Concentrations

4.3.3.1 Sites That Experience Low Maximum Hourly Average Concentrations

It is important to establish reference points that can be used to describe the distribution of hourly average concentrations at monitoring sites experiencing low maximum concentrations. Doing so will make it possible to confirm that the hourly average concentrations in control chambers utilized for research experiments associated with human health and vegetation effects are similar to those experienced under ambient conditions. For example, there has been concern expressed that O_3 concentrations in charcoal-filtration chambers used by NCLAN did not simulate the levels in those areas of the United States that experience low maximum O_3 concentrations (see Chapter 5, Section 5.5). Heuss (1982) expressed concern that the O_3 levels in the charcoal-filtration chambers were lower than those at sites experiencing low maximum hourly average concentrations, and that the resulting agricultural loss estimates derived from the NCLAN models may have been too high.

Two possible approaches for establishing reference points have been discussed (Lefohn et al., 1990a). One method is to estimate, using mathematical models and historical data, unpolluted background levels prior to disturbance by human influence. However, there are difficulties with this approach. Background can be defined as the unpolluted conditions in preindustrial times (i.e., absolutely unpolluted air in which there was no human interference). Alternatively, a background also can be defined as the condition *currently* existing at any location that is presently free from human influence. However, almost all geographic locations on the earth have been impacted by human influences (e.g., Finlayson-Pitts and Pitts, 1986; Hong et al., 1994) (see Section 4.3.1).

It is unlikely that a single value or even a fixed range of O_3 background values can apply uniformly across North America or elsewhere in the northern or southern hemispheres. Any attempt to quantify the historical background is subject to much uncertainty for the following reasons:

1. Little is known with certainty about the nature of past unpolluted conditions.
2. Even if all anthropogenic emissions of O_3 precursors were eliminated, it is unlikely that O_3 in, for example, eastern North America, would return to preindustrial levels. Since preindustrial times, major land use changes have occurred. Because substantial amounts of natural emissions of O_3 precursors are derived from soils and vegetation, especially during the warmer months, it is probable that these land use changes have modified the emissions of O_3 precursors and, thus, changed the concentrations of O_3.

Although not representing natural O_3 background, attempts have been made, using historical data, to estimate O_3 concentrations in the late 1800s and early 1900s. Model simulations and limited observations suggest that tropospheric O_3 has increased in the northern hemisphere since the preindustrial times and future increases may be possible (Bojkov, 1986; Volz and Kley, 1988; Thompson, 1992). However, several investigators have discussed the possible confounding influences that led to a great deal of uncertainty associated with characterizing the O_3 concentrations measured in the late 1800s and early 1900s (Lisac and Grubisic, 1991; Lefohn et al., 1992c; Cartalis and Varotsos, 1994). Using data collected over the past 30 years, consistent trends in tropospheric O_3 have not been observed across the

northern hemisphere (World Meteorological Organization/United Nations Environment Program, 1994). Using ozonesonde data, observations show that tropospheric O_3 has increased above some locations in the northern hemisphere. However, in the 1980s, the trends were variable and either small or nonexistent (Logan, 1994). European measurements at some surface sites indicate an increase in O_3 concentration since earlier this century. Because of the uncertainty associated with measurements taken in the late 1880s and early 1990s, it is difficult to compare O_3 concentration levels experienced in the United States with today's levels. However, it can be concluded that O_3 levels measured around 100 years ago were lower than the values observed today at most sites in the United States, and that consistently increasing trends in O_3 concentration measured at surface levels have not been observed annually at sites monitoring O_3 in the United States.

An alternative approach (adopted by Lefohn et al., 1990a, to establish reference points) is to examine O_3 hourly average concentration data from those monitoring sites in the world that experienced low maximum hourly average values. When data from these sites, including several in North America, were characterized, and the range of hourly average concentrations compared, it was found that the distributions of hourly average concentrations for sites with the lowest hourly average concentrations were similar. The authors believed the data from these sites could be used for establishing reference points that could be compared with more polluted areas.

Is it appropriate to use sites that experience the lowest hourly average concentrations in the United States today as reference levels, or should O_3 background levels that may have existed 100 years ago be used? Although it might be argued that all sites in the United States have been affected to such a level that today's values are not relevant because an increase in O_3 concentrations has occurred since the late 1800s, two key points argue against this line of reasoning. First, as indicated above, although O_3 levels have increased since the last century, consistent trends in tropospheric O_3 have not been observed across the northern hemisphere. Thus, at some monitoring sites, O_3 levels may not show increasing trends. Second, all the increases in background levels of O_3 may not necessarily be associated with changes in anthropogenic emissions. Since preindustrial times, major land use changes, resulting from human-induced activities, have occurred. Changes in natural emissions of O_3 precursors associated with soils and vegetation in the last 100 years may be associated with these land use changes, with the result that some of the increased levels in O_3 concentrations may be attributed to sources other than anthropogenic emissions. Thus, using historical data that contain large uncertainties in the estimation of O_3 concentrations as a reference point, may yield unrealistically low hourly average concentrations.

Based on a review of available data, the U.S. Environmental Protection Agency (1989) has indicated that a reasonable estimate of O_3 background concentration near sea level in the United States today, for an annual average, is from 0.020 to 0.035 ppm. This estimate included a 0.005- to 0.015-ppm contribution from stratospheric intrusions and a 0.01-ppm contribution from photochemically affected biogenic nonmethane hydrocarbons. In addition, the U.S. Environmental Protection Agency (1989) estimated that an additional 0.010 ppm is possible from the photochemical reaction of biogenic methane. A more conservative approach would be to associate the sum of O_3 concentrations from these two processes with the differences between 0.020 to 0.035 ppb and the stratospheric intrusion contribution.

For calculating annual average concentrations, the estimate made by the U.S. Environmental Protection Agency (1989) may be valid. Pratt et al. (1983), using data from low-elevation rural sites in Minnesota and North Dakota, reported that annual average

concentrations for an O_3 monitoring site in LaMoure County, ND (400 m), for 1978 through 1981, ranged from 0.030 to 0.035 ppm, whereas an O_3 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 O_3 concentration of 0.031 ppm.

The U.S. Environmental Protection Agency (1989) has estimated that background O_3 concentrations for a 1-h daily maximum at sea level in the United States during the summer are in the range of 0.03 to 0.05 ppm. However, the actual value may vary from site to site. Using measurements at a remote site in South Dakota, Kelly et al. (1982) estimated the background O_3 in air masses entering the midwestern and eastern United States to be 0.03 to 0.05 ppm. Lefohn and Foley (1992) reported that hourly average O_3 concentration data available for sites that experience low maximum hourly average values in the western United States indicate that, in almost all cases, the maximum hourly average concentrations were in the range of 0.060 to 0.075 ppm, and, at some of the sites, there were infrequent occurrences of hourly average concentrations below 0.02 ppm (i.e., lack of scavenging). These observations were similar to those reported for several O_3 monitoring sites experiencing low maximum hourly average O_3 concentrations for other locations in the world (Lefohn et al., 1990a; Pedersen and Lefohn, 1994).

Some vegetation researchers have used the seasonal average of the daily 7-h (0900 to 1559 hours) average as the exposure parameter in exposure-response models (Heck et al., 1982). For quantifying the effects of air pollution on crops and trees, some investigators have used controlled environment and field methods with charcoal-filtration systems (Olszyk et al., 1989). In both the design of the experiments and the analysis of the data, the 7-h (0900 to 1559 hours) seasonal mean reference point for O_3 was assumed to be 0.025 ppm. The 0.025 ppm concentration was used to estimate crop loss across the United States (Adams et al., 1985, 1989). For sites experiencing low maximum hourly average concentrations in the western United States, except for several years of O_3 measurements at Olympic National Park (Table 4-6), the 7-mo (April to October) average of the 7-h daily average concentrations ranged from 0.025 to 0.045 ppm (Altshuller and Lefohn, 1996).

Ozone hourly average concentrations were characterized at several sites located in both the western and south-central United States that experienced low maximum hourly average concentrations (Table 4-6). Redwood National Park, CA; Olympic National Park, WA; Glacier National Park, MT; Denali National Park, AK; Badlands, SD; Great Sand Dunes National Monument, CO; Theodore Roosevelt National Park, ND; and Quachita National Forest, AR, experienced no hourly average concentration ≥0.08 ppm for the period April to October (Altshuller and Lefohn, 1996). Except for 1988, the year in which Yellowstone National Park, WY, experienced a major forest fire, the Wyoming site experienced no hourly average concentrations ≥0.08 ppm. Logan (1989) has noted that O_3 hourly average concentrations above 0.08 ppm rarely are exceeded at remote western sites. In almost all cases for the above sites, the maximum hourly average concentration was ≤0.075 ppm. There have been some questions raised to whether the distributions experienced at those sites exhibiting low maximum hourly average concentrations in the western United States were representative of sites in the eastern and midwestern United States because of differences in biogenic precursors. The O_3 monitoring site in the

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, W126, and SUM06 Values for Sites Experiencing Low Hourly Average Concentrations with Data Capture ≥75% (Concentrations in ppm)[a]

				Percentiles								No. of	Hours		Seasonal	W126	SUMO6
Location	Site/AIRS ID	Year	Min.	10	30	50	70	90	95	99	Max	Obs.	≥0.08	≥0.10	7-h	(ppm-h)	(ppm-h)
Redwood, CA	Redwood NP	1988	0.002	0.011	0.018	0.023	0.029	0.038	0.041	0.046	0.060	4,825	0	0	0.026	1.8	0.1
	060150002	1989	0.000	0.010	0.017	0.022	0.027	0.034	0.038	0.042	0.047	4,624	0	0	0.024	1.0	0.0
		1990	0.000	0.011	0.018	0.023	0.028	0.035	0.038	0.043	0.053	4,742	0	0	0.025	1.2	0.0
		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	0.0
		1992	0.000	0.010	0.017	0.021	0.026	0.035	0.039	0.045	0.055	4,679	0	0	0.023	1.1	0.0
		1993	0.000	0.010	0.017	0.022	0.027	0.035	0.038	0.042	0.054	4,666	0	0	0.025	1.1	0.0
Olympic, WA	Olympic NP	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	0.1
	530090012	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	0.0
		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	0.1
		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	0.1
		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	0.3
		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	0.0
		1993	0.000	0.004	0.010	0.016	0.021	0.029	0.034	0.041	0.064	4,595	0	0	0.022	0.7	0.3
Glacier, MT	Glacier NP	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	1.8
	300298001	1990	0.000	0.003	0.014	0.026	0.035	0.044	0.047	0.052	0.066	5,092	0	0	0.036	4.1	1.3
		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	0.7
		1992	0.000	0.001	0.013	0.025	0.033	0.043	0.048	0.055	0.077	4,909	0	0	0.033	4.1	1.0
Yellowstone, WY	Yellowstone NP	1988	0.002	0.020	0.029	0.037	0.044	0.054	0.058	0.070	0.098	4,257	17	0	0.043	14.0	8.9
	560391010	1989	0.002	0.018	0.027	0.036	0.044	0.052	0.057	0.063	0.071	4,079	0	0	0.042	11.0	6.7
		1990	0.000	0.015	0.023	0.029	0.036	0.043	0.046	0.053	0.061	4,663	0	0	0.034	3.8	0.5
		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	1.2
		1992	0.001	0.018	0.029	0.036	0.042	0.051	0.056	0.064	0.075	4,384	0	0	0.042	10.7	6.3
		1993	0.000	0.018	0.028	0.036	0.042	0.047	0.050	0.054	0.060	4,399	0	0	0.041	6.5	0.2
	022900003	1990	0.003	0.017	0.024	0.029	0.034	0.040	0.043	0.048	0.050	3,978	0	0	0.030	2.1	0.0
		1991	0.005	0.018	0.024	0.028	0.034	0.041	0.043	0.047	0.057	4,809	0	0	0.030	2.7	0.0
		1992	0.003	0.016	0.023	0.028	0.034	0.044	0.047	0.050	0.054	4,800	0	0	0.031	3.7	0.0
		1993	0.002	0.017	0.023	0.028	0.033	0.041	0.043	0.048	0.055	4,773	0	0	0.030	2.6	0.0

Table 4-6 (con't). Seasonal (April to October) Percentile Distribution of Hourly Ozone Concentrations, Number of Hourly Mean Ozone Occurrences ≥00.08 and ≥0.10, Seasonal Seven-Hour Average Concentrations, W126, and SUM06 Values for Sites Experiencing Low Hourly Average Concentrations with Data Capture ≥75% (Concentrations in ppm)[a]

				Percentiles								No. of	Hours		Seasonal	W126	SUMO6
Location	Site/AIRS ID	Year	Min.	10	30	50	70	90	95	99	Max	Obs.	≥00.08	≥0.10	7-h	(ppm-h)	(ppm-h)
Badlands, SD	Badlands NP	1988	0.005	0.022	0.032	0.038	0.045	0.053	0.056	0.061	0.072	4,791	0	0	0.043	13.3	5.2
	460711010	1989	0.007	0.020	0.028	0.034	0.041	0.049	0.053	0.060	0.071	4,840	0	0	0.040	9.2	3.1
		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	4.8	0.8
		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	0.7
Great Sand Dunes, CO	Sand Dunes NM	1988	0.010	0.028	0.035	0.039	0.044	0.050	0.053	0.058	0.076	4,827	0	0	0.043	11.1	1.9
	080030002	1989	0.011	0.031	0.037	0.041	0.045	0.050	0.052	0.057	0.063	4,436	0	0	0.044	10.8	1.2
		1990	0.010	0.030	0.037	0.041	0.045	0.052	0.055	0.062	0.070	4,624	0	0	0.044	13.6	5.1
		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	9.0
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	2.8
		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	0.1
		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	0.4
		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	11.0
		1992	0.005	0.019	0.027	0.033	0.039	0.047	0.050	0.056	0.063	4,332	0	0	0.040	6.1	0.8
		1993	0.004	0.018	0.025	0.031	0.037	0.045	0.048	0.055	0.064	4,281	0	0	0.038	4.6	0.7
Point Reyes, CA	Point Reyes NP	1989	0.007	0.021	0.026	0.031	0.036	0.042	0.045	0.058	0.080	4,577	1	0	0.033	4.8	2.5
	060410002	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	0.4
		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	0.6
		1992	0.007	0.018	0.024	0.028	0.033	0.041	0.045	0.050	0.066	4,794	0	0	0.031	3.0	0.3
Arches, UT	Arches NP	1989	0.000	0.031	0.040	0.045	0.050	0.057	0.059	0.065	0.084	4,260	2	0	0.048	21.2	12.6
	490190101	1990	0.000	0.020	0.025	0.028	0.031	0.036	0.039	0.045	0.056	4,639	0	0	0.030	1.7	0.0
Montgomery Co., AR	Quachita NF	1991	0.000	0.002	0.010	0.016	0.023	0.035	0.041	0.051	0.064	4,835	0	0	0.027	1.6	0.1
	050970001	1992	0.000	0.005	0.015	0.024	0.030	0.041	0.045	0.053	0.067	4,902	0	0	0.033	3.0	0.9
		1993	0.000	0.008	0.019	0.027	0.035	0.047	0.052	0.061	0.070	4,844	0	0	0.036	6.7	3.7

[a]See Appendix A for abbreviations and acronyms.

Quachita National Forest in Arkansas experienced distributions of hourly average concentrations similar to some of the western sites.

Evans et al. (1983) summarized O_3 hourly averaged data collected at eight stations located in eight national forests across the United States. The first three stations began operations in 1976 (Green Mountain National Forest, VT; Kisatchie National Forest, LA; and Custer National Forest, MT); the second three in 1978 (Chequamegon National Forest, WI; Mark Twain National Forest, MO; and Croatan National Forest, NC); and the last two in 1979 (Apache National Forest, AZ; and Ochoco National Forest, OR). For the period 1979 to 1983, hourly maximum average concentrations at the sites (Custer, Ochoco, and Apache national forests) were similar to the hourly average concentrations determined for six of the seven sites characterized by Lefohn and Foley (1992). In almost all cases, none of the sites experienced hourly average concentrations ≥0.08 ppm, and the maximum hourly average concentrations were in the range of 0.060 to 0.075 ppm. Table 4-7 summarizes the percentile distributions for the three national forest sites.

Several sites experiencing low maximum hourly average concentrations were characterized by Lefohn et al. (1990a), using various exposure indices. One of the indices used was W126 (see Section 4.1); the W126 values, calculated over an annual period, are provided in Table 4-8. The W126 values for Theodore Roosevelt National Park were in the range of 6.48 to 8.03 ppm-h. The maximum hourly average concentration reported at the site was 0.068 ppm. The W126 values at the Custer and Ochoco national forests sites ranged from 5.79 to 22.67 ppm-h. The maximum hourly average concentrations measured at each site were 0.075 and 0.080 ppm, respectively. The W126 values calculated for the Custer and Ochoco national forest sites showed greater variability from year to year than the values calculated for the South Pole, Barrow, and Theodore Roosevelt National Park sites.

As the W126 values increased, the magnitude of the year-to-year variability also increased. For 2 years of data, the W126 values calculated for the White River U-4 Oil Shale, UT, site were 19.98 and 32.10 ppm-h. The maximum hourly concentration recorded was 0.079 ppm. The W126 values calculated for the Apache National Forest site ranged from 10.24 to 81.39 ppm-h. The highest hourly average concentration was 0.090 ppm.

The 7-h (0900 to 1559 hours) average concentration has been used by vegetation researchers to characterize O_3 exposures experienced in plant chamber experiments (see Chapter 5). Because O_3 concentrations are highest during the warm-season months and, at many low-elevation sites, during daylight hours, the 7-mo seasonal, 7-h (0900 to 1559 hours) average concentration is higher than annual average values. Most remote sites outside North America experience seasonal 7-h averages of 0.025 ppm (Table 4-9) (Lefohn et al., 1990a). The seasonal average of the daily 7-h average values for the South Pole, Antarctica, range from 0.024 to 0.027 ppm. The values range from 0.022 to 0.026 ppm at Barrow, AK. In the continental United States and southern Canada, values range from approximately 0.028 to 0.050 ppm (Lefohn et al., 1990a). At an O_3 monitoring site at the Theodore Roosevelt National Park, the range of the 7-mo (April to October) average of the 7-h daily average concentrations was from 0.038 to 0.046 ppm (Table 4-6). These 7-mo seasonal averages appear to be representative of values that may occur at other sites located in the United States and other locations in the northern hemisphere. In earlier investigations, Lefohn (1984) reported 3-mo (June to August), 7-h averages of 0.048, 0.044, and 0.059 ppm at remote sites at Custer, Ochoco, and Apache national forests, respectively.

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 ≥75% (Concentrations in ppm)[a]

				Percentiles								No. of	Hours		Seasonal	W126
Site	AIRS ID	Year	Min.	10	30	50	70	90	95	99	Max	Obs.	≥0.08	≥0.10	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

[a]See Appendix A for abbreviations and acronyms.

Table 4-8. The Value of the W126 Sigmoidal Exposure Parameter Calculated Over the Annual Period (Units in ppm-h)[a]

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[b]	
Custer NF, MT	1,006				14.08	22.67			12.18				
Ochoco NF, OR	1,364					19.54	5.79	9.10	8.02				
Birch Mountain, Alberta, Canada	850				19.73								
White River Oil Shale Project, UT	1,600							19.98	32.10				
Fortress Mountain, Alberta, Canada	2,103											25.04	83.89
Apache NF, 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

[a]See Appendix A for abbreviations and acronyms.
[b]Collection did not occur during the months of October, November, and December.

Source: Lefohn et al. (1990a).

Table 4-9. The Value of the Ozone Season (Seven-Month) Average of the Daily Seven-Hour (0900 to 1559 Hours) Concentration (ppm)[a]

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[b]	
Custer NF, MT	1,006				0.043	0.044			0.042				
Ochoco NF, OR	1,364					0.043	0.035	0.038	0.038				
Birch Mountain, Alberta, Canada	850				0.036								
White River Oil Shale Project, UT	1,600							0.045	0.045				
Fortress Mountain, Alberta, Canada	2,103											0.041	0.050
Apache NF, 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	

[a]See Appendix A for abbreviations and acronyms.
[b]Collection did not occur during the months of October, November, and December.

Source: Lefohn et al. (1990a).

4.3.3.2 Urban-Influenced Nonurban Areas

It is difficult to identify a set of unique O_3 distribution patterns that adequately describes the hourly average concentrations experienced at monitoring sites in nonurban locations because, as indicated earlier, many nonurban sites in the United States are influenced by local sources of pollution or long-range transport of O_3 or its precursors. Unlike the clean sites characterized by Lefohn and Jones (1986), Lefohn et al. (1990a), and Lefohn and Foley (1992), 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 0.1 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 O_3. For example, Evans et al. (1983) reported that the Green Mountain (VT) and Mark Twain national forest (MO) sites were influenced by long-range transport of O_3. The U.S. Environmental Protection Agency (1986) reported that the maximum hourly average concentrations at Green Mountain (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 O_3 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), O_3 measurements were made by the chemiluminescence method from 1977 through 1979 at nine "nonurban" Sulfate Regional Experiment (SURE) Program sites and Eastern Regional Air Quality Study 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", and the other four were classed as "rural". The O_3 data from these nine stations are summarized in Table 4-11. The sites are influenced either by local sources or by transport of O_3 or its precursors. The maximum hourly average concentrations generally are 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 included 41 in the eastern United States and 9 in the western United States, that routinely recorded hourly average O_3 concentrations. Figure 4-7 shows the locations of the NDDN sites. Edgerton and Lavery (1992) have summarized the O_3 concentrations at some of the sites for the period 1988 to 1990. Table 4-12 summarizes the 7-h (0900 to 1559 hours) growing season average concentration (May to September) for selected sites in the Midwest and the East. Fifty-nine percent of the monitoring sites listed in the table have been classified as agricultural and 36% as forested; one site was classified as commercial. As noted by the U.S. Environmental Protection Agency (1992a), 1988 was an exceptionally high O_3 concentration year, when compared with 1989 and 1990. The number of hourly O_3 concentrations ≥0.08 ppm is presented in Table 4-12. Edgerton and Lavery (1992) have summarized O_3 hourly average concentration data for several sites using the cumulative

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) (Concentrations in ppm)[a]

AIRS Site	Name	Min.	10	30	50	70	90	95	99	Max	Number of Hourly Values	Number of Occurrences ≥0.10	Max Uncorrected 3-mo SUM06 Value (ppm-h)
						Percentiles (ppm)							
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	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	.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	Shenandoah NP (Dickey Ridge), 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

[a]See Appendix A for abbreviations and acronyms.

Table 4-11. Summary of Percentiles of Hourly Average Concentrations for Electric Power Research Institute Sulfate Regional Experiment (SURE) Program Sites/Eastern Regional Air Quality Study (ERAQS) Ozone Monitoring Sites (Units in ppm)

SURE/ERAQS Name	Year	Min.	Percentiles 10	30	50	70	90	95	99	Max	Number of Observations
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

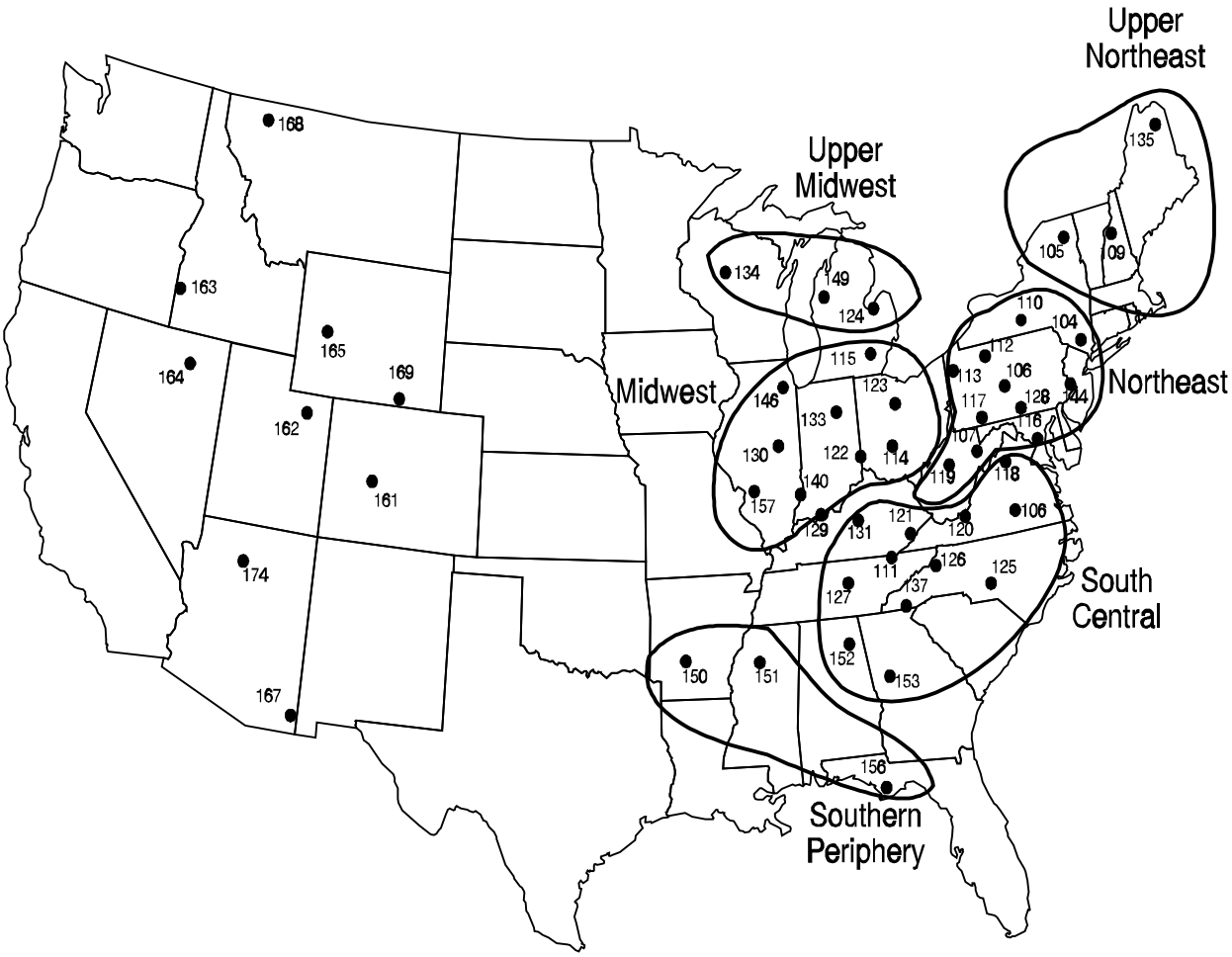


Figure 4-7. The location of National Dry Deposition Network monitoring sites as of December 1990.

Source: Edgerton and Lavery (1992).

integrated exposure index, W126, as proposed by Lefohn and Runeckles (1987). Based on evidence presented in the literature relating O_3 exposure with agricultural yield reduction, the index was proposed as a way to weight the higher hourly average concentrations greater than the lower values. The data in the table illustrate the large differences in cumulative exposure between those that occurred in 1988 and those that were experienced in 1989 and 1990. The percentile of the hourly average concentrations is summarized in Table 4-13. Although several of the monitoring sites are located in fairly remote locations in the eastern United States (based on land use characterization) the maximum hourly average concentrations reflect the transport of O_3 or its precursors into the area.

Taylor et al. (1992) have summarized the O_3 concentrations that were experienced at 10 EPRI Integrated Forest Study sites in North America. The authors reported that in 1988 all sites experienced maximum hourly average concentrations ≥0.08 ppm. In almost all cases, the sites experienced multiple occurrences above 0.08 ppm. This implies that,

Table 4-12. Seven-Hour Growing Season Mean, W126 Values, and Number of Hourly Ozone Concentrations ≥80 ppb for Selected Eastern National Dry Deposition Network Sites[a]

				7-h Mean (ppb)			W126 (ppm-h)			SUM06 (ppm-h)			SUM08 (ppm-h)		
Subregion	State	Site	Land Class[b]	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
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

[a]See Appendix A abbreviations for and acronyms.
[b]RA = Rural agricultural; RF = Rural forest; RC = Rural commercial; — = No data or insufficient data.

Source: Edgerton and Lavery (1992).

Table 4-13. Summary of Percentiles for National Dry Deposition Network Monitoring Sites (Units in ppm)

Site No.	Name	Year	Min.	10	30	50	70	90	95	99	Max	Number of Observations
			Percentiles									
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
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

Table 4-13 (cont'd). Summary of Percentiles for National Dry Deposition Network Monitoring Sites (Units in ppm)

Site No.	Name	Year	Min.	10	30	50	70	90	95	99	Max	Number of Observations
			Percentiles									
RURAL AGRICULTURAL SITES (cont'd)												
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
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

although the sites were located in remote forested areas, the sites experienced elevated O_3 concentrations that were more than likely due to long-range transport of O_3 or its precursors.

Ozone concentrations on a seasonal basis in the Shenandoah National Park exhibit some features in common with both urban and rural areas. During some years, maximum hourly average concentrations exceed 0.12 ppm, although some sites in the park exhibit a lack of hourly average concentrations near minimum detectable level. Taylor and Norby (1985) have characterized O_3 episodes, which they defined as any day in which a 1-h mean O_3 concentration was >0.08 ppm. Based on a 4-year monitoring period in the park, the probability was 80% that any given episode during the growing season would last 2 or more days, whereas the probabilities of episodes lasting for periods greater than 3, 4, and 5 days were 30, 10, and 2%, respectively. Single-day O_3 episodes were infrequent. Taylor and Norby (1985) noted that, given the frequency of respites, there was a 50% probability that a second episode would occur within 2 weeks.

Because of a lack of air quality data collected at rural and remote locations, it has been necessary to use interpolation techniques to estimate O_3 exposures in nonurban areas. In the absence of actual O_3 data, interpolation techniques have been applied to the estimation of O_3 exposures across the United States (Reagan, 1984; Lefohn et al., 1987a; Knudsen and Lefohn, 1988). "Kriging", a mathematical interpolation technique, has been used to provide estimates of seasonal O_3 values for the NCLAN for 1978 through 1982 (May to September of each year) (Reagan, 1984). These values, along with updated values, coupled with exposure-response models were used to predict agriculturally related economic benefits anticipated by lower O_3 levels in the United States (Adams et al., 1985; Adams et al., 1989).

Kriging is a statistical tool developed by Matheron (1963) and named in honor of D.G. Krige. Although originally developed specifically for ore reserve estimation, kriging has been used for other spatial estimation applications, such as analyzing and modeling air quality data (Grivet, 1980; Faith and Sheshinski, 1979). At its simplest, kriging can be thought of as a way to interpolate spatial data much as an automatic contouring program would. In a more precise manner, kriging can be defined as a best, linear unbiased estimator of a spatial variable at a particular site or geographic area. Kriging assigns low weights to distant samples and vice versa, but also takes into account the relative position of the samples to each other and the site or area being estimated.

Figure 4-8 shows the average for the 1985 through 1987 period for the seasonal (April to October) average of the daily maximum 7- and 12-h values across the United States. The estimates made for the Rocky Mountain region had large uncertainties associated with them because of a lack of monitoring sites.

Because of the importance of the higher hourly average concentrations in eliciting injury and yield reduction for agricultural crops (U.S. Environmental Protection Agency, 1992b), kriging was used to predict O_3 exposures in the eastern United States. The sigmoidally weighted W126 exposure index was used as described earlier in this section. Lefohn et al. (1992b) used the W126 index in its kriging to characterize the O_3 exposures that occurred during the period 1985 to 1989. Figure 4-9 illustrates the integrated O_3 exposure for the 1988 and 1989 periods (data derived from work described in Lefohn et al., 1992b). Using the kriged data in the East, the 1988 exposures were the highest for the 5-year period, whereas 1989 exhibited the lowest exposures. The O_3 gradient pattern analyses described by Lefohn et al. (1992b) identified contiguous areas of persistent,

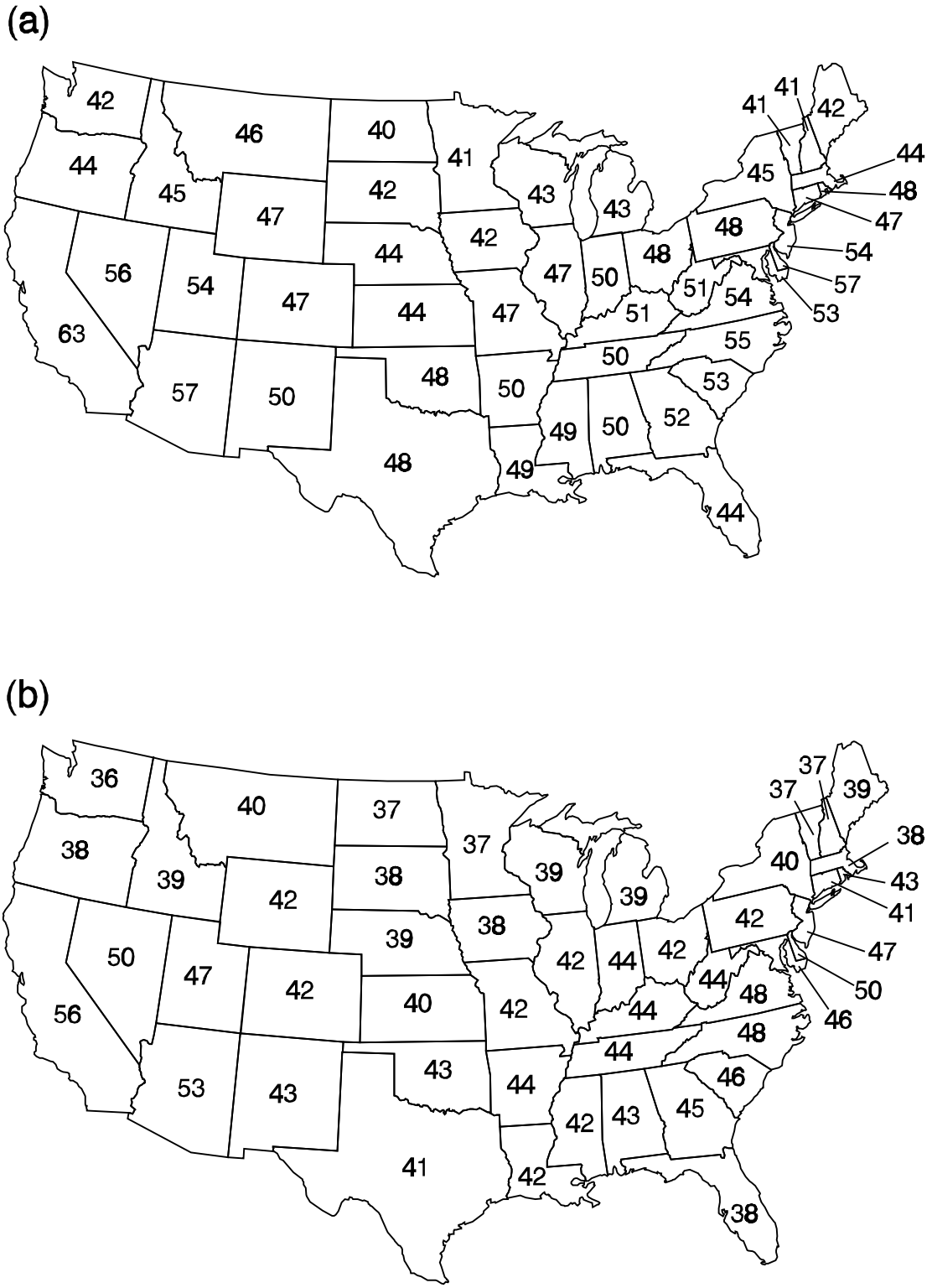


Figure 4-8. The kriged 1985 to 1986 maximum (a) 7-h and (b) 12-h average concentrations of ozone across the United States.

Source: Lefohn et al. (1991).

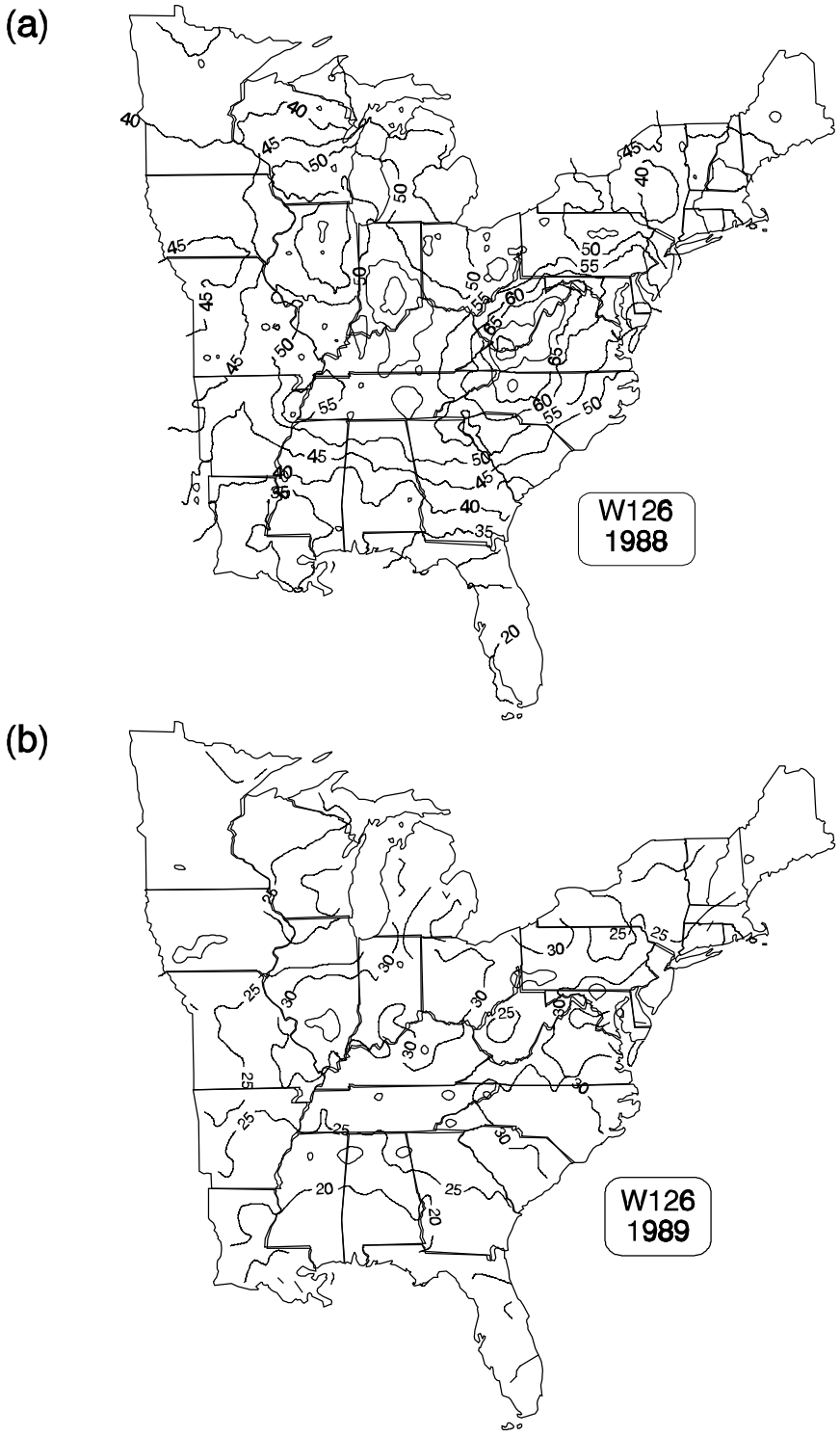


Figure 4-9. The kriged estimates of the W126 integrated ozone exposure index for the eastern United States for (a) 1988 and (b) 1989.

Source: Lefohn et al. (1992b).

relatively high seasonal O_3 values. The largest area extended from New Jersey south to northern Georgia and South Carolina. This area was roughly bounded on the west by the Appalachian Mountains. A second area, which exhibited persistent relatively high seasonal O_3 exposures, was centered over the Ohio River Valley in the region near the Kentucky-Indiana-Ohio borders. Relatively low O_3 exposures were found in Minnesota, Iowa, Wisconsin, Maine, Vermont, New Hampshire, and Florida. On a year-to-year basis, the analysis by Lefohn et al. (1992b) showed that regions that tended to be high for a specific year continued to experience O_3 exposures that were higher when compared to other regions.

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 (NO) 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 and destruction effects at various sites (Lefohn, 1992b). Nontransport 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. (1991) 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 identify adequately, at most sites, the presence of high hourly average concentrations and, thus, may not adequately 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 inversion layer, do not necessarily experience this depletion (Stasiuk and Coffey, 1974). Taylor and Hanson (1992) reported similar findings using data from the Integrated Forest Study. For the low-elevation sites, the authors reported that intraday variability was most significant due to the pronounced daily amplitude in O_3 concentration between the predawn minimum and midafternoon-to-early evening maximum. The authors reported that the

interday variation was more significant in the high-elevation sites. Ozone trapped below the inversion layer is depleted by dry deposition and chemical reactions if other reactants are present in sufficient quantities (Kelly et al., 1984). Above the nocturnal inversion layer, dry deposition generally does not occur, and the concentration of O_3 scavengers generally is lower, so O_3 concentration remains fairly constant (Wolff et al., 1987). A flat diurnal pattern is usually interpreted as indicating a lack of efficient scavenging of O_3 or a lack of photochemical precursors, whereas a varying diurnal pattern is taken to indicate the opposite. With the composite diagrams alone, it is difficult to quantify the daily or long-term exposures of O_3. For example, the diurnal patterns for two such sites are illustrated in Figure 4-10. The Jefferson County, KY, site is urban-influenced and experiences elevated levels of O_3 and NO_x. The Oliver County, ND, site is fairly isolated from urban-influenced sources and hourly average O_3 concentrations are mostly below 0.09 ppm. The flat diurnal pattern observed for the Oliver County site is usually interpreted as indicating a lack of efficient scavenging of O_3 or a lack of photochemical precursors, whereas the varying diurnal pattern observed at the Jefferson County site may be interpreted to indicate the opposite. Logan (1989) has described the diurnal pattern for several rural sites in the United States (Figure 4-11) and noted that average daily profiles showed a broad maximum from about 1200 hours until about 1800 hours at all the eastern sites, except for the peak of Whiteface Mountain, NY. Logan (1989) noted that the maximum concentrations were higher at the SURE sites than at the Western National Air Pollution Background Network sites in the East, because the latter were situated in more remote or coastal locations.

There is concern that the highest hourly average concentrations observed at rural agricultural and forested sites occur outside the most biologically active period of the day. To address this concern, a review of the hourly average data collected at all rural agricultural and forested sites in EPA's AIRS database for 1990 to 1992 was undertaken to evaluate the percentage of time hourly average concentrations ≥0.1 ppm occurred during the period 0900 to 1559 hours in comparison with the 24-h period. Each rural site for each of the 3 years that experienced a 3-mo SUMO6 ≥26.4 ppm-h (see Chapter 5, Section 5.6 for more details concerning the use of a 3-mo SUMO6 exposure index) was characterized. It was found that 70% of the rural agricultural and forested sites used in the analysis experienced at least 50% of the occurrences ≥0.1 ppm during the period 0900 to 1559 hours when compared to the 24-h period (Figure 4-12). When O_3 monitoring sites in California were eliminated, approximately 73% of the remaining sites experienced at least 50% of the occurrences ≥0.10 ppm during the daylight 7-h period when compared with the 24-h period (Figure 4-13). Reviewing Figures 4-12 and 4-13, for most rural agricultural and forested sites that experience 3-mo SUMO6 ≥26.4 ppm in the United States, most of the hourly average concentrations ≥0.1 ppm occur during the 0900 to 1559 hours period.

4.4.2 Urban Area Diurnal Patterns

The U.S. Environmental Protection Agency (1986) has discussed diurnal patterns for urban sites. Figure 4-14, reproduced from the previous document, shows the diurnal pattern of O_3 concentrations on July 13, 1979, in Philadelphia, PA. On this day a peak 1-h average concentration of 0.20 ppm, the highest for the month, was reached at 1400 hours, presumably as the result of meteorological factors, such as atmospheric mixing and local

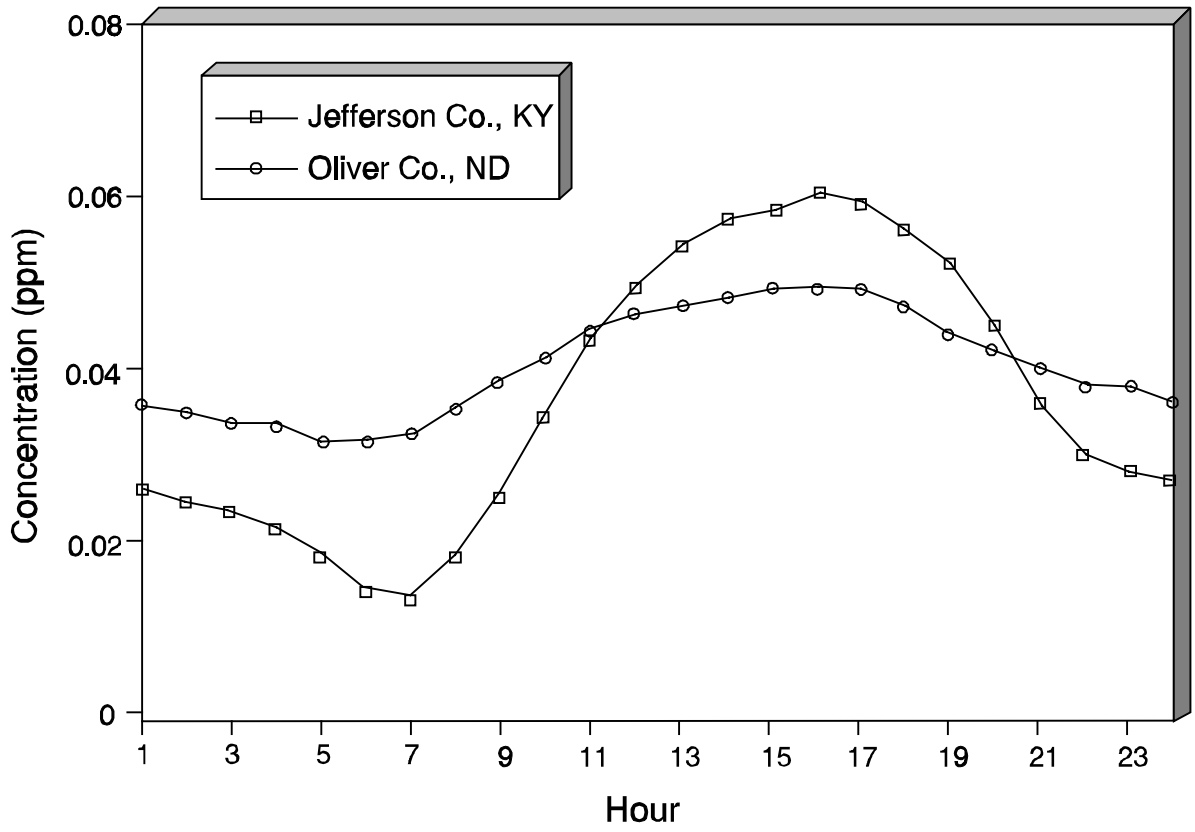


Figure 4-10. The comparison of the seasonal diurnal patterns using 1988 data for Jefferson County, KY, and Oliver County, ND.

photochemical processes. The severe depression of concentrations to below detection limits (less than 0.005 ppm) between 0300 and 0600 hours usually is explained as resulting from the scavenging of O_3 by local NO 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 4-15 through 4-17 (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: (1) center city-commercial (Washington, DC), (2) rural-near urban (St. Louis, MO), and (3) suburban-residential (Alton, IL). Several obvious points of interest present themselves in these figures: 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; some sites may be exposed to multiple peaks during a 24-h period; and 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.

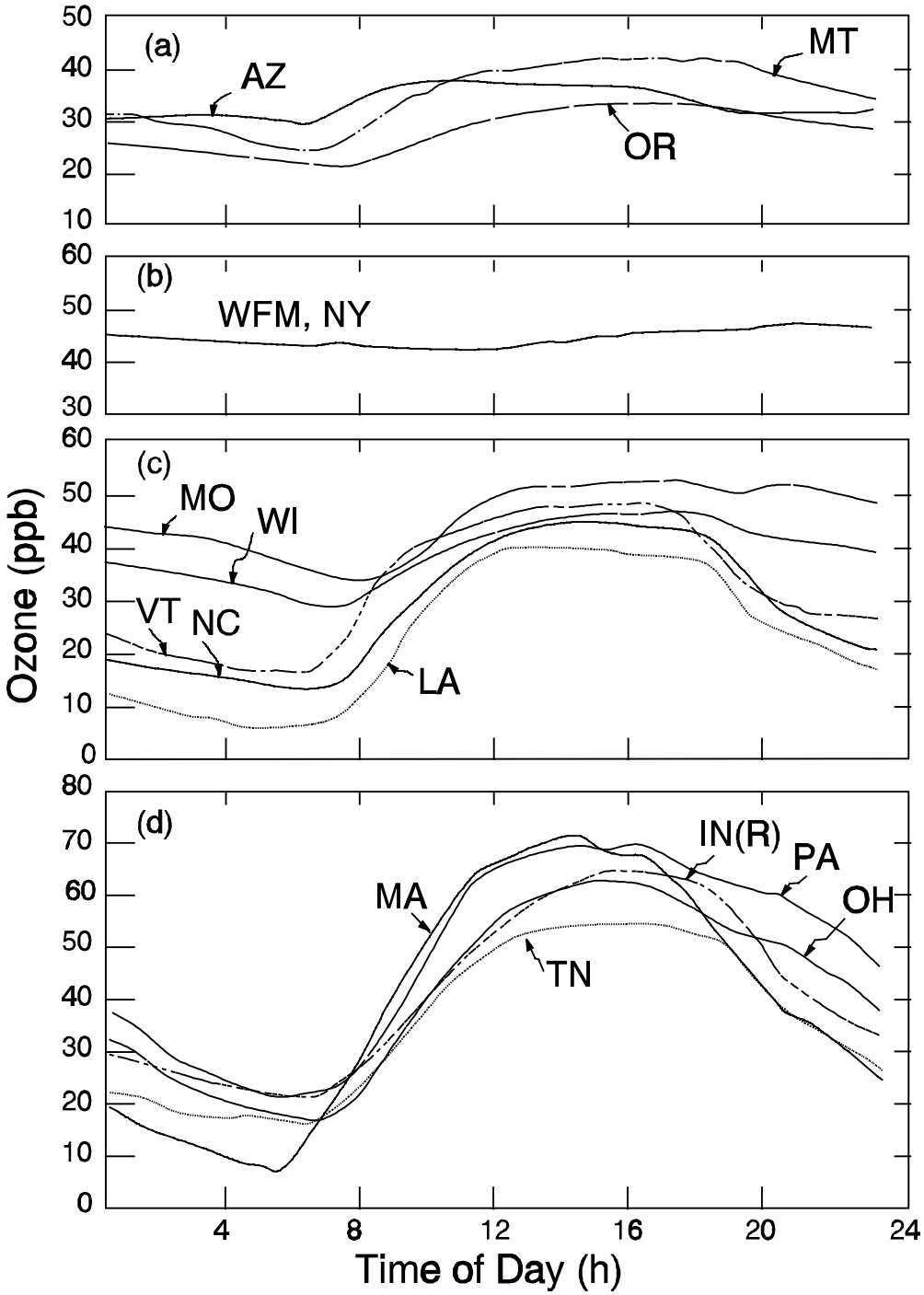


Figure 4-11. Diurnal behavior of ozone at rural sites in the United States in July. Sites are identified by the state in which they are located. (a) Western National Air Pollution Background Network (NAPBN); (b) Whiteface Mountain (WFM) located at 1.5 km above sea level; (c) eastern NAPBN sites; and (d) sites selected from the Electric Power Research Institute's Sulfate Regional Air Quality Study. IN(R) refers to Rockport.

Source: Logan (1989).

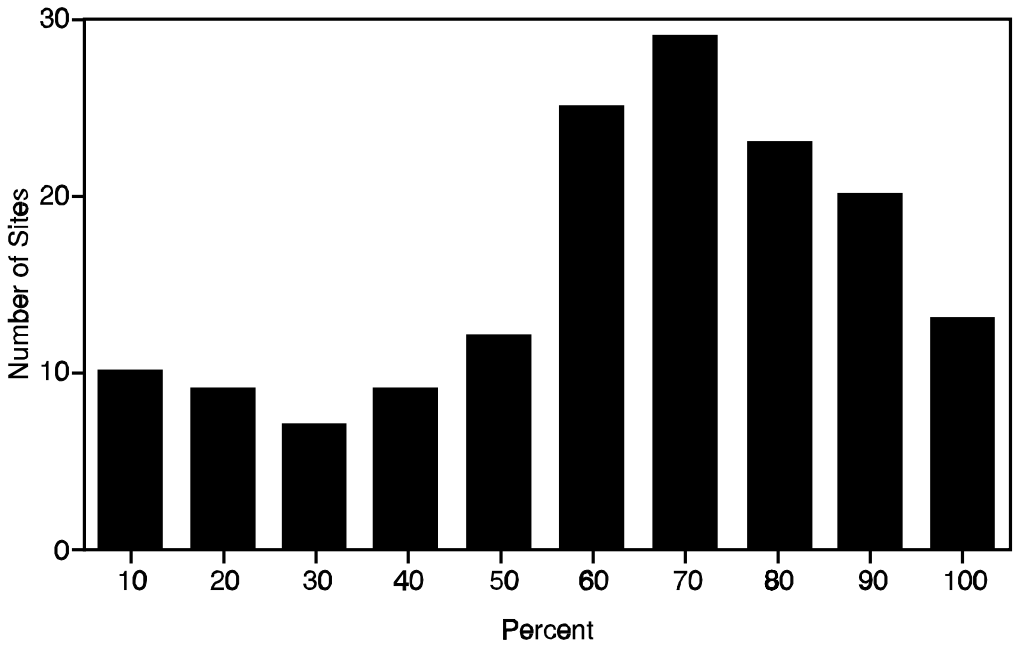


Figure 4-12. Percent of time hourly average concentrations ≥0.1 ppm occurred between 0900 and 1559 hours in comparison to 24-h period for all rural agricultural and forested sites with 3-mo SUM06 ≥26.4 ppm-h.

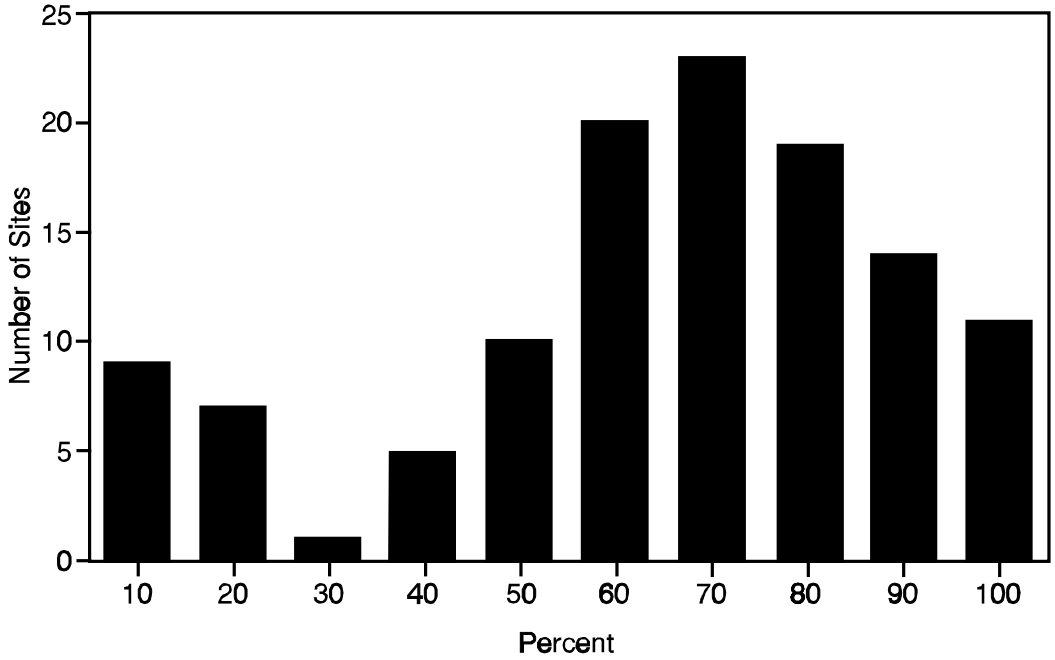


Figure 4-13. Percent of time hourly average concentrations ≥0.1 ppm occurred between 0900 and 1559 hours in comparison to 24-h period for all non-California rural agricultural and forested sites with 3-mo SUM06 ≥26.4 ppm-h.

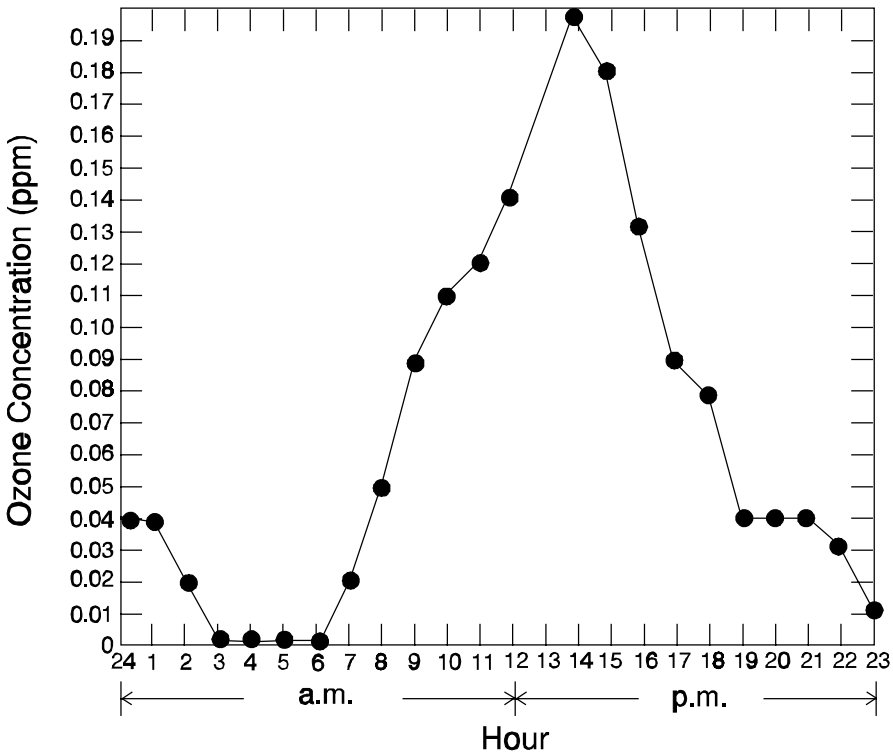


Figure 4-14. Diurnal pattern of 1-h ozone concentrations on July 13, 1979, Philadelphia, PA.

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 4-1 demonstrates the effects of lengthening the period of time over which values are averaged. This figure shows a composite diurnal pattern calculated on the basis of 3 mo. Although seasonal differences are observed, the comparison of 3-mo (Figure 4-18) with 1-mo composite diurnal concentrations (Figure 4-17) 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, 1986), 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.

4.4.3 Nonurban Area Diurnal Patterns

Nonurban 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.

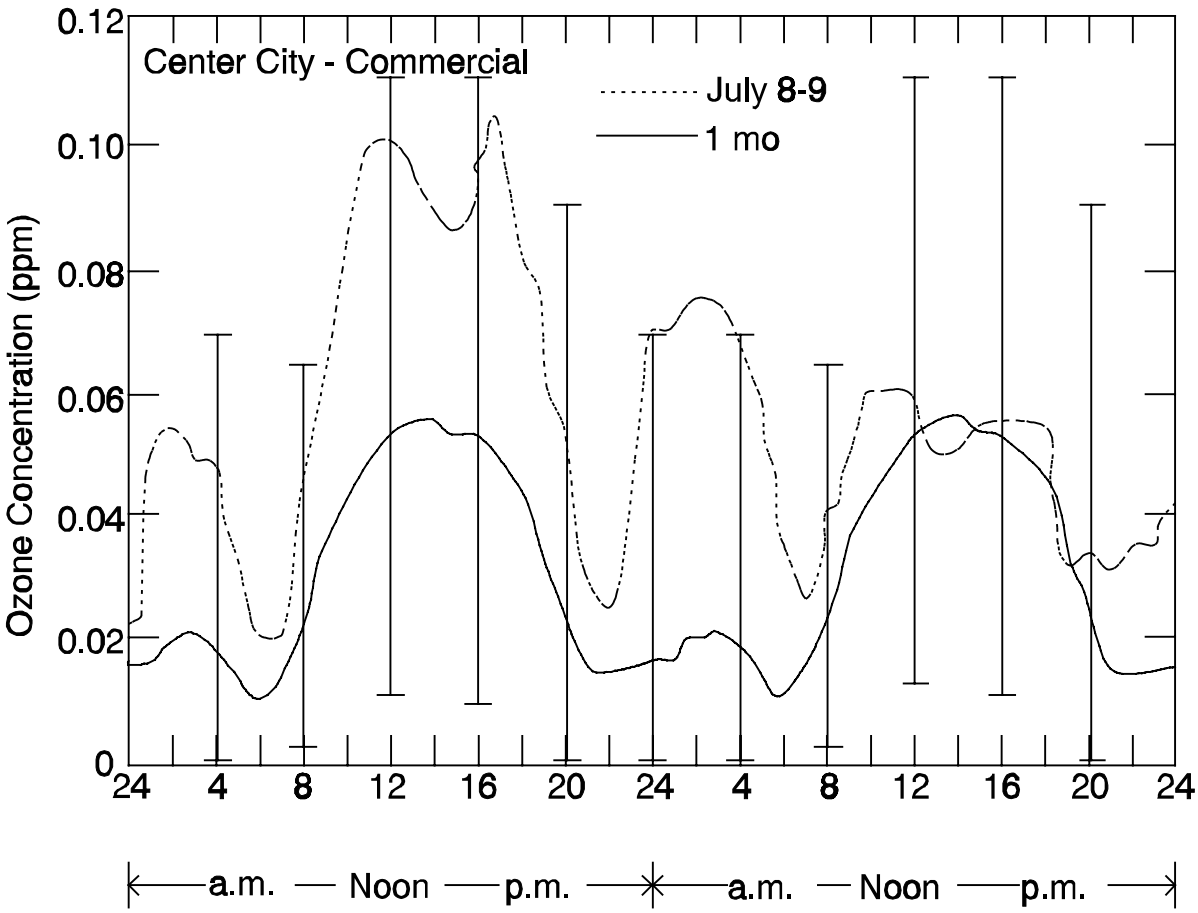


Figure 4-15. Diurnal and 1-mo composite diurnal variations in ozone concentrations, Washington, DC, July 1981.

Source: U.S. Environmental Protection Agency (1986).

The diurnal patterns for several agricultural sites have been characterized (U.S. Environmental Protection Agency, 1986). Figures 4-19 and 4-20 show some typical patterns of exposure. As discussed by U.S. Environmental Protection Agency (1986), the six sites, whose diurnal patterns are illustrated in Figure 4-18, 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.

Remote forested sites experience unique patterns of O_3 concentrations (Evans et al., 1983; Lefohn, 1984). These sites tend to experience a weak diurnal pattern, with

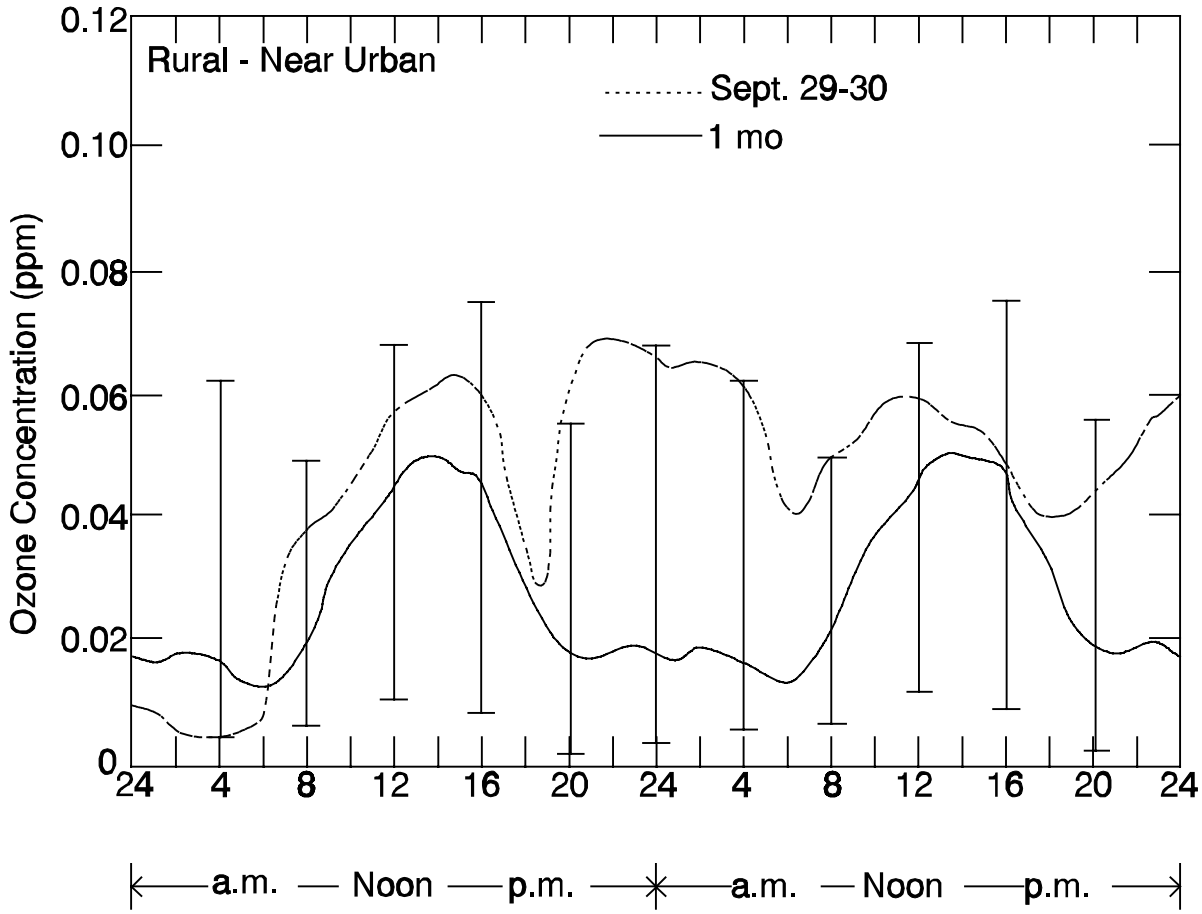


Figure 4-16. Diurnal and 1-mo composite diurnal variations in ozone concentrations, St. Louis County, MO, September 1981.

Source: U.S. Environmental Protection Agency (1986).

hourly average O_3 concentrations that occur frequently in the range of 0.04 to 0.05 ppm. Figure 4-21 shows diurnal patterns for several sites in the NDDN network that are located in forested areas. Several of the NDDN sites analyzed by Edgerton and Lavery (1992) exhibit fairly flat average diurnal patterns. Such a pattern is based on average concentrations calculated over an extended period. On a daily basis, some variation in O_3 concentration does occur from hour to hour, and, in some cases, high hourly average concentrations are experienced either during daytime or nighttime periods (Lefohn and Mohnen, 1986; Lefohn and Jones, 1986; Logan, 1989; Lefohn et al., 1990b; Taylor et al., 1992).

Lefohn et al. (1990b) characterized O_3 concentrations at high-elevation monitoring sites. The authors reported that a fairly flat diurnal pattern for the Whiteface Mountain summit site (WF1) was observed (Figure 4-22a), 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

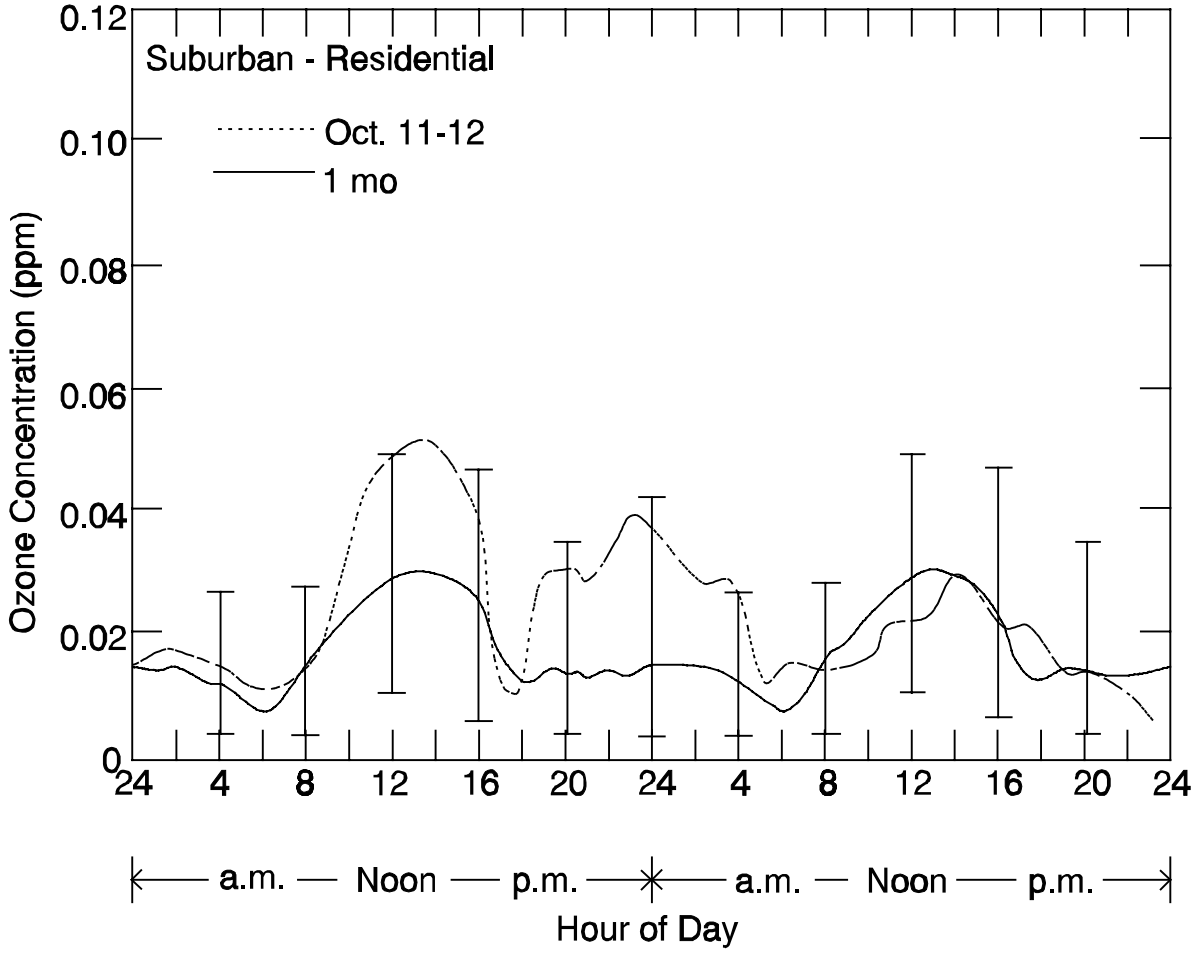


Figure 4-17. Diurnal and 1-mo composite diurnal variations in ozone concentrations, Alton, IL, October 1981 (fourth quarter).

Source: U.S. Environmental Protection Agency (1986).

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 4-22b). Aneja and Li (1992), in their analysis of the five high-elevation Mountain Cloud Chemistry Program (MCCP) 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 patterns over the period May to October (1986 to 1988) for the five sites occurred between 1800 and 2400 hours, whereas the minimum was observed between 0900 and 1200 hours. However, it is important to note that, as indicated by Lefohn et al. (1990b), the flat diurnal pattern is not observed for all high-elevation sites.

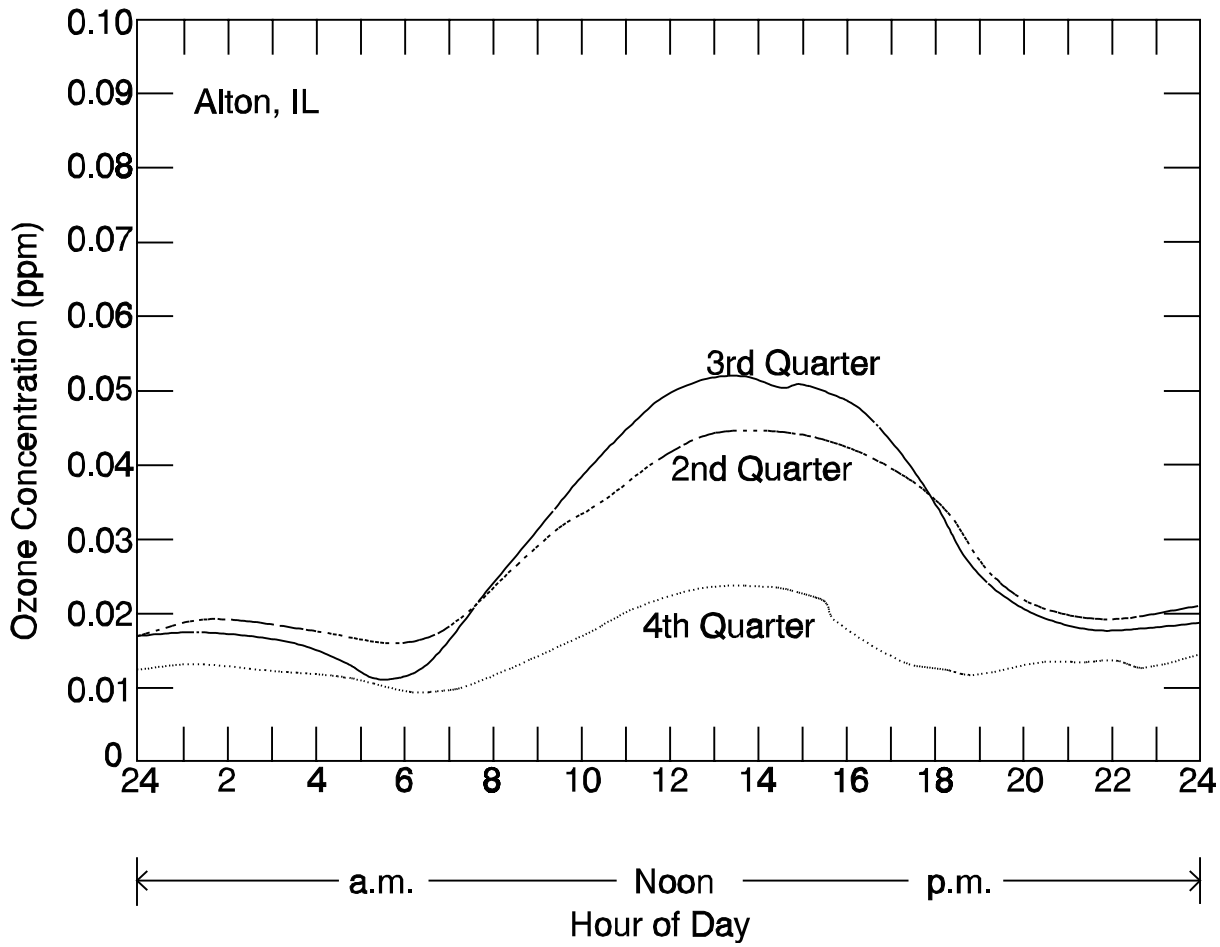


Figure 4-18. Composite diurnal patterns of ozone concentrations by quarter, Alton, IL, 1981.

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. Environmental Protection Agency (1986). The current form of the standard focuses on the highest hourly average concentrations. The description that follows uses the highest hourly average concentration as an indication of exposure. Figure 4-23 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, CA (Figure 4-23c), and Denver, CO (Figure 4-23d), show summer maxima. Tampa, FL, shows a late spring maximum but with concentrations in the fall (i.e., October) approaching those of spring (June) (Figure 4-23f). Dallas data also tend to be skewed toward higher spring concentrations; but note that November concentrations are also relatively high (Figure 4-23h). Because of seasonal humidity and storm tracks from year to year, the general weather conditions in a

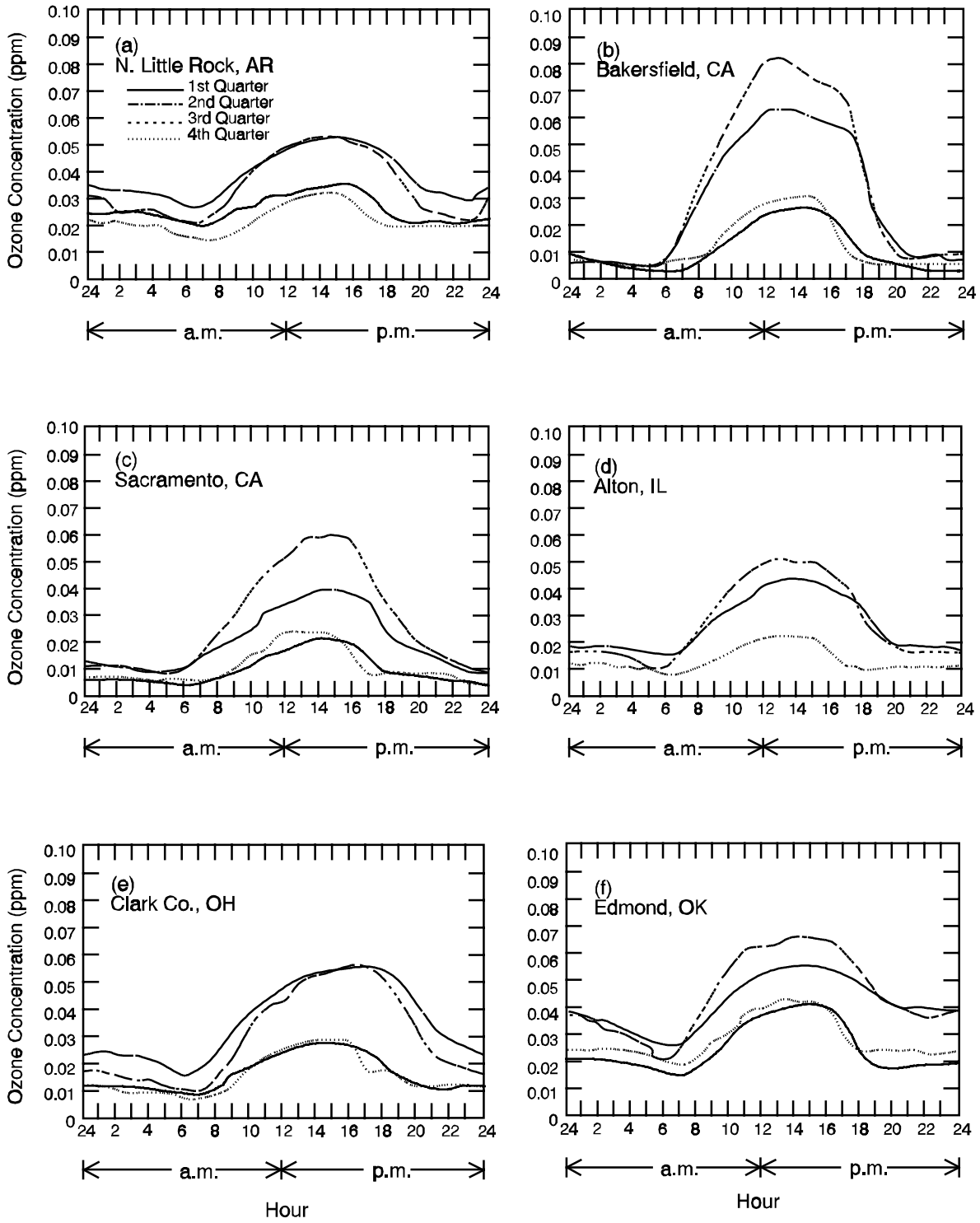


Figure 4-19. Quarterly composite diurnal patterns of ozone concentrations at selected sites representing potential for exposure of major crops, 1981.

Source: U.S. Environmental Protection Agency (1986).

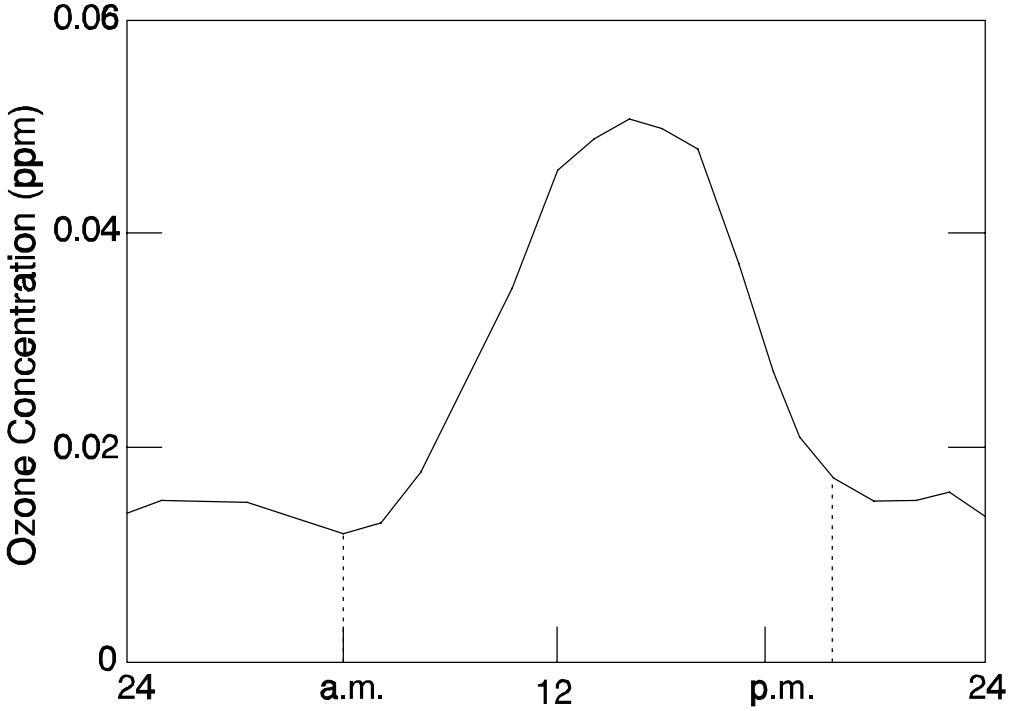


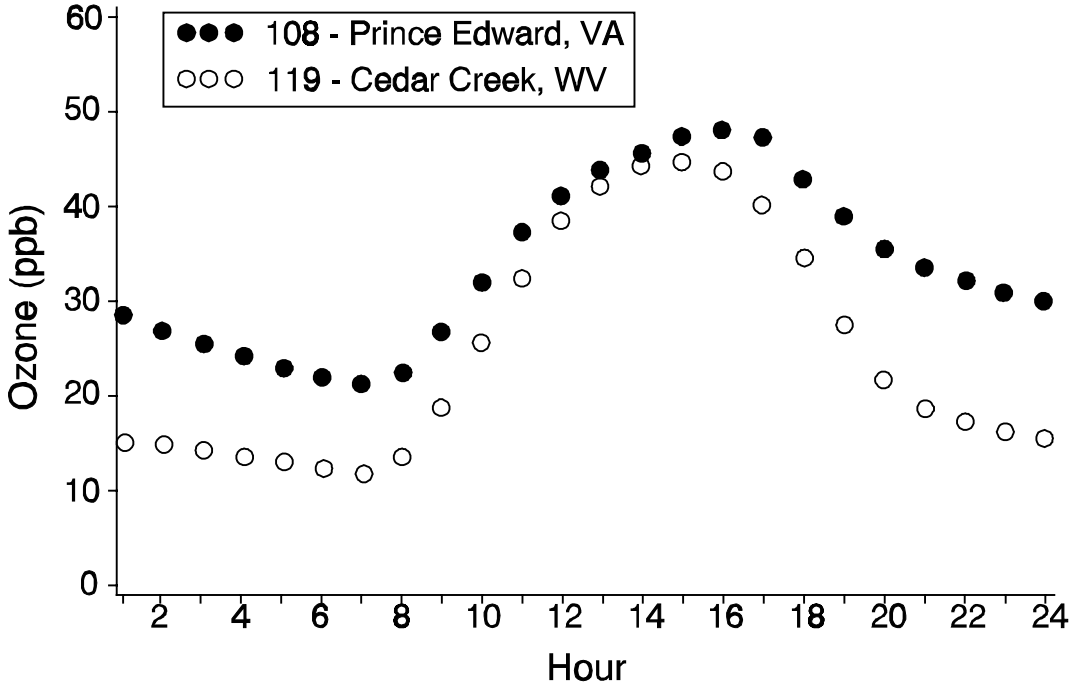
Figure 4-20. Composite diurnal ozone pattern at a rural National Crop Loss Assessment Network site in Argonne, IL, August 6 through September 30, 1980.

Source: U.S. Environmental Protection Agency (1986).

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, whereas 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 either to stratospheric intrusions or to an increasing frequency of slow-moving, high-pressure systems that promote the formation of O_3. Lefohn et al. (1990a) reported that for several clean sites, the highest values of exposure indices 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. (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



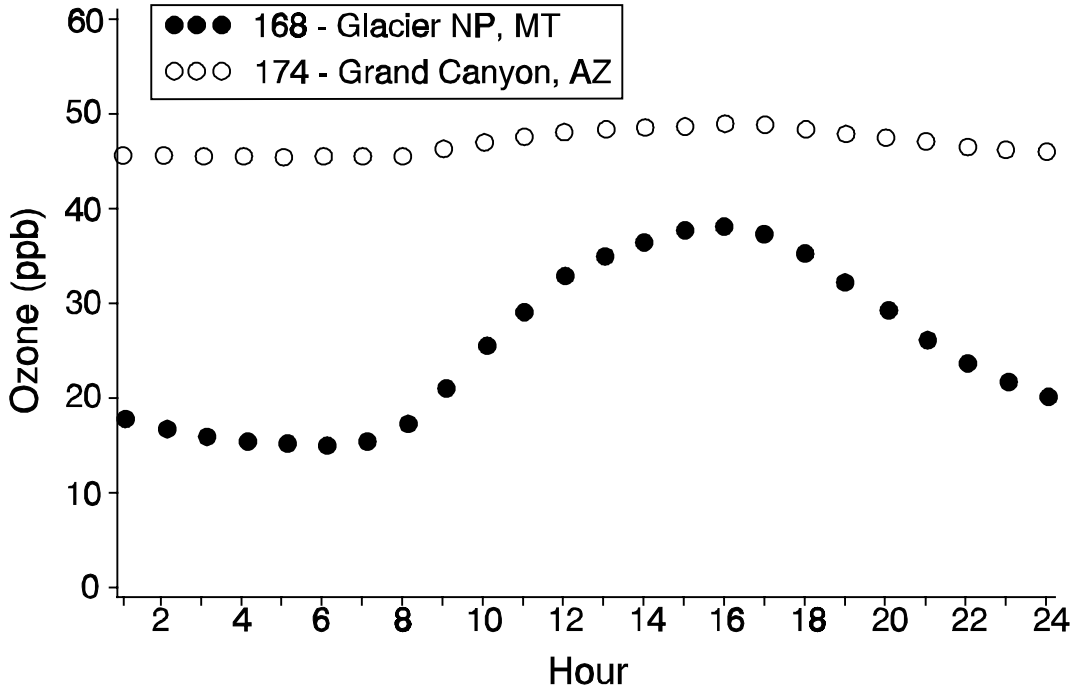


Figure 4-21. Composite diurnal ozone pattern at selected National Dry Deposition Network sites.

Source: Edgerton and Lavery (1992).

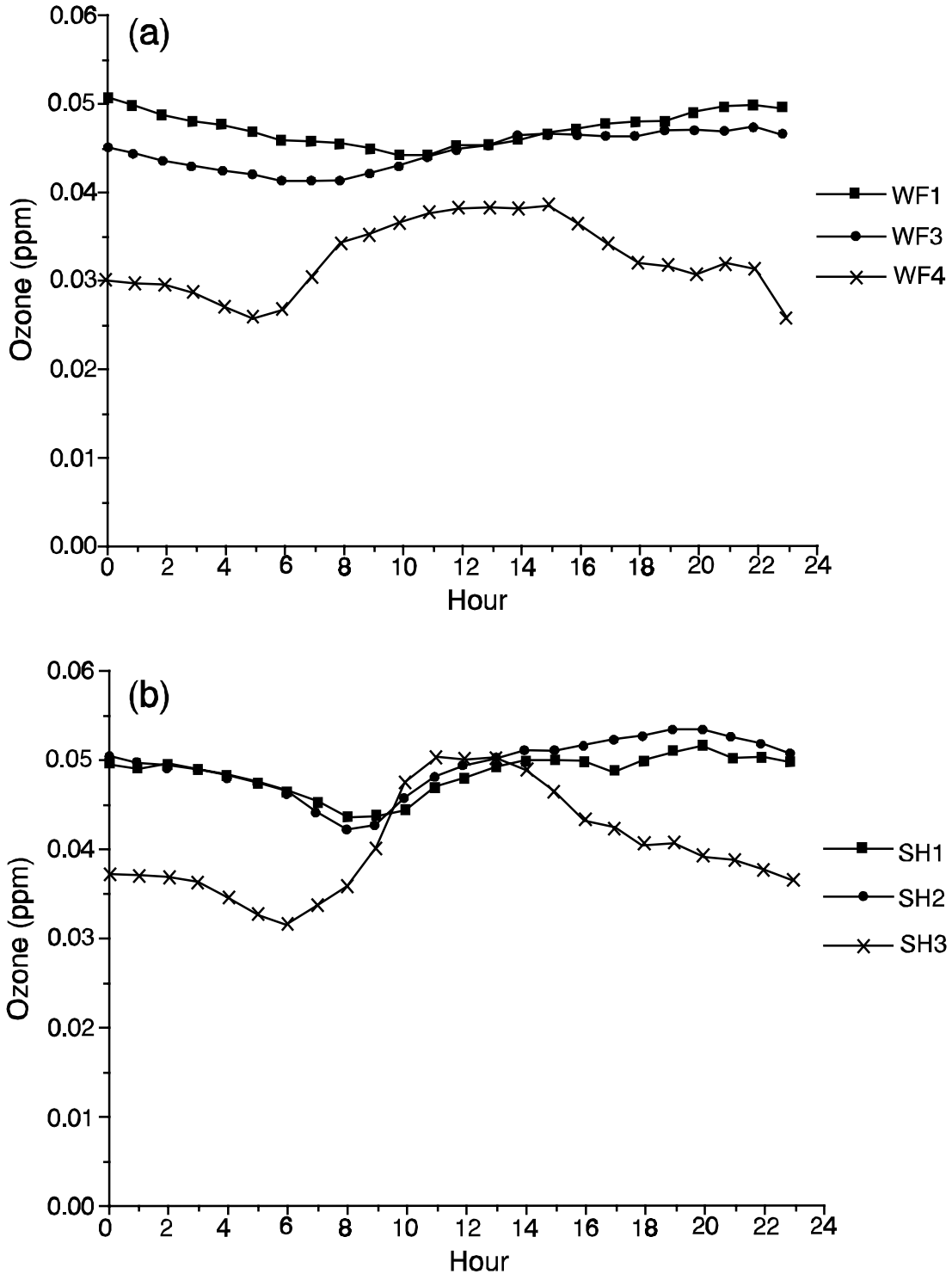


Figure 4-22. Composite diurnal pattern at (a) Whiteface Mountain, NY, and the (b) Mountain Cloud Chemistry Program Shenandoah National Park site for May to September 1987.

Source: Lefohn et al. (1990b).

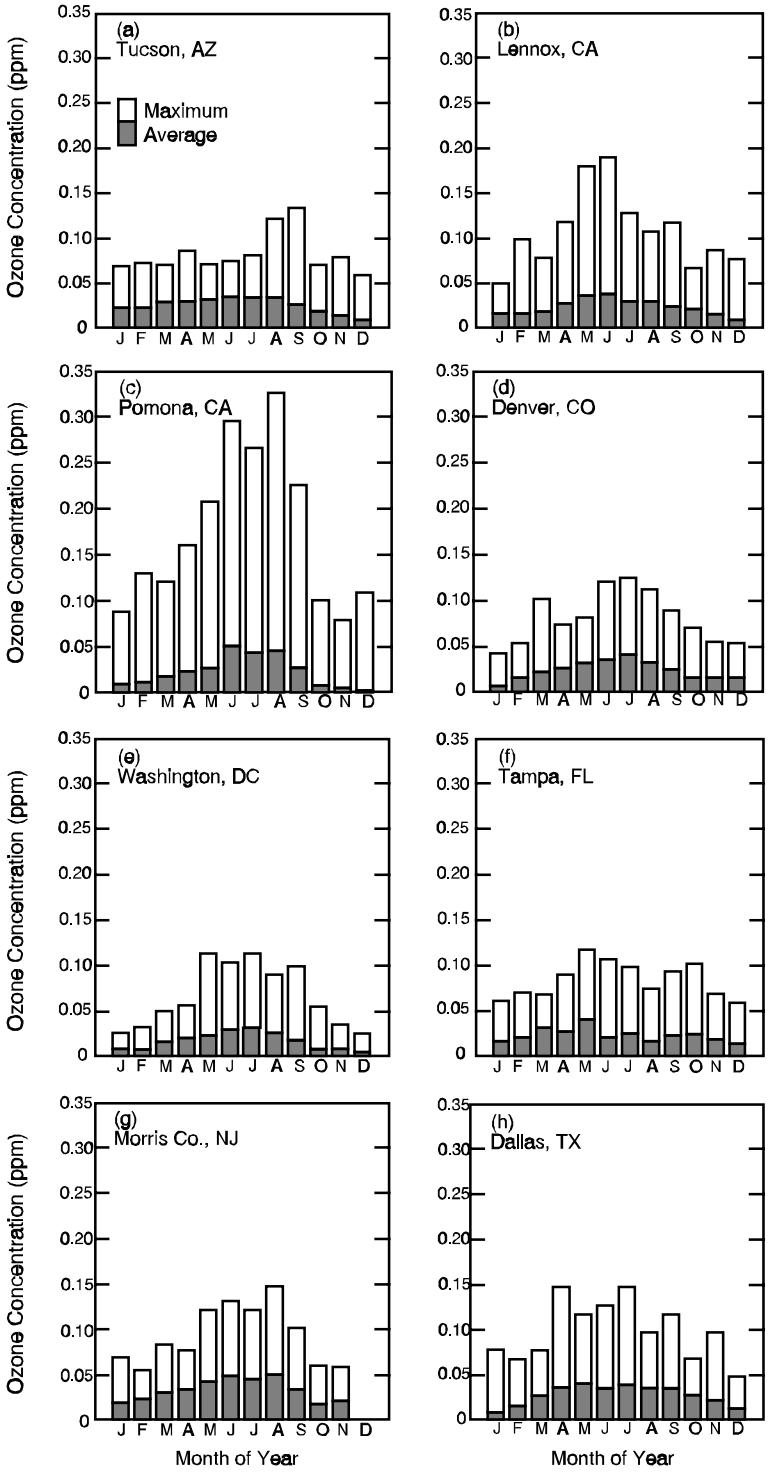


Figure 4-23. Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-h maximum in each month at selected sites, 1981.

Source: U.S. Environmental Protection Agency (1986).

used. Other species concentrations at the boundaries, as well as all species at the top of the modeling domain, are set to tropospheric clean-air concentrations.

Meteorological data are assimilated by the first stage of preprocessors. These data contain regular hourly observations from U.S. National Weather Service surface stations (and from similar stations in Canada as necessary), including wind speed and direction, air temperature, dew point, atmospheric pressure, and cloud amounts and heights. Twice-daily sounding data, from the upper-air observation network also are included in the meteorological database. Upper-air meteorological parameters include atmospheric pressure, wind speed and direction, and air temperature, dew point. Finally, both buoy and Coastal Marine Automated Station data are used. The parameters that typically are reported include wind speed and direction and air and sea temperatures.

Emissions data for the primary species are input to the ROM system as well. Originally these data were provided from the 1985 emissions inventory of NAPAP, with 18.5-km spatial resolution. Most recently, the interim regional inventory has been used widely to support current applications of the ROM. It represents an update and improvement of the NAPAP inventory and is being used to support SIP modeling until state inventories are approved (U.S. Environmental Protection Agency, 1993a,b). Species included are CO, NO, NO_2, and 10 hydrocarbon reactivity categories. Natural hydrocarbons also are input, including isoprene explicitly, monoterpenes divided among the existing reactivity classes, and unidentified hydrocarbons. The chemical mechanism in ROM is the CBM-IV.

Land-use input data consist of 11 land-use categories in 1/4° longitude by 1/6° latitude grid cells. The data are more than 20 years old and represent a weakness. New land-use data slowly are being collected and released. Changes in land use over the last 20 years may change significantly the estimates of biogenic hydrocarbon emissions for large regions of the United States. Data are provided for the United States and Canada as far as 55° N. The land-use categories are (1) urban land, (2) agricultural land, (3) range land, (4) deciduous forests, (5) coniferous forests, (6) mixed-forest wetlands, (7) water, (8) barren land, (9) nonforested wetland, (10) mixed agricultural land and range land, and (11) rocky, open places occupied by low shrubs and lichens. Land-use data are used to obtain biogenic emissions estimates, as a function of the area of vegetative land cover, and for the determination of surface heat fluxes.

Topography input data consist of altitude matrices of elevations in a 7.5° × 7.5° grid. The data are obtained from the GRIDS database operated by EPA's Office of Information Resources Management. Topography data are used in the calculation of layer heights.

The ROM does have its limitations, including the large grid size, relatively crude wind fields, and highly empirical vertical mixing assumptions (Wolff, 1993).

3.6.3.3 The Regional Acid Deposition Model

The RADM initially was developed at the NCAR for EPA and subsequently was refined and improved at the State University of New York at Albany. The model is an Eulerian transport, transformation, and removal model that includes a treatment of the relevant physical and chemical processes leading to acid deposition and the formation of photochemical oxidants. As summarized in Tables 3-21 through 3-25, these processes include atmospheric transport and mixing, gas-phase and aqueous-phase chemical transformations, dry deposition, and cloud mixing and scavenging.

Chemical trace species are transported and diffused through the three-dimensional RADM grid using externally specified meteorological data. The RADM uses hourly three-dimensional fields of horizontal winds, temperature, and water vapor mixing ratio calculated by the meteorological model MM4 with FDDA. In addition, RADM requires two-dimensional, hourly fields of surface temperature, surface pressure, and precipitation rates over the model domain. Kuo et al. (1985) found that in order to calculate accurate mesoscale trajectories, at least 3-h temporal resolution is desirable, and the 12-h resolution of upper air observations is inadequate. Recent verification studies with 30 meteorological episodes by Stauffer and Seaman (1990) further support the use of MM5 data with FDDA. Using meteorology generated from a dynamically consistent meteorological model can introduce errors caused by simulation errors associated with the meteorological model. These uncertainties can be quantified through objective verification studies with observed data (Anthes et al., 1985; Stauffer and Seaman, 1990).

The RADM2 chemical mechanism has been described by Stockwell et al. (1990), Chang et al. (1991b), Carter and Lurmann (1990), and Stockwell and Lurmann (1989). For RADM2, the VOCs are aggregated into 12 classes of reactive organic species. Each category of VOC is represented by several model species that span the required range for reaction with the OH radical. Most emitted organic compounds are lumped into surrogate 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 intermediate and stable species. During the aggregation of organic species, the principle of reactivity weighting is followed to attempt to account for differences in reactivity.

A major part of the SARMAP program described earlier is the extension of the RADM. The SARMAP is the modeling and data analysis component of a multi-year collaboration between two projects— SJVAQS and AUSPEX. In the near term, the objective of SARMAP is to produce a model that can be used to examine scenarios for control of O_3 precursor emissions as required under the CAAA for the 1994 planning cycle. The goals of the SARMAP modeling program can be summarized as follows:

- Development of a comprehensive state-of-the-science three-dimensional modeling system (consisting of emissions, meteorological, and air quality models) suitable for the simulation of O_3 concentrations, PM_{10} concentrations, visibility degradation, and acid deposition;
- Evaluation of the modeling system and its individual components against experimental data collected during the SJVAQS/AUSPEX field program; and
- Application of the model to estimate the effect of changes in emission levels on O_3 concentrations, PM_{10} concentrations, visibility degradation, and acid deposition.

The general attributes of the SARMAP modeling system are listed below.

- Integrated system of individual modules, including air quality, meteorological, emissions, and emissions projection; full compatibility of gridding system among all models.
- Ozone estimation capability; capability for efficiently incorporating modules for simulating aerosols, visibility, and acid deposition.
- Applicability at urban, subregional, and regional scales, embodying a full range of anticipated physical, chemical, and terrain characteristics.

- Capability of being driven by larger meteorological models, if desired (for generating initial and boundary conditions).
- Capability of generating as output a full complement of chemical species concentrations and meteorological parameters.
- Variable horizontal grid size.
- Variable number of vertical layers.
- Variable depth of vertical layers.
- Capability of nested grid application.
- Capability of varying the number of vertical layers with time of day. Selection of number of layers and timing of changes to be model-driven.
- Improved treatment of emissions injection aloft, including placement of plumes in the vertical, treatment of inversion penetration, proper vertical dilution of plumes, and proper treatment of chemistry.
- Inclusion of plume-in-grid capability.
- Capability for use of "computational tracers" for a variety of tests.
- Capability of simulating the O_3-VOC-NO_x system alone or in tandem with the aerosol system.
- Capability of simulating aerosols for the O_3-VOC-NO_x system.

The following modifications to the RADM2 gas-phase chemical mechanism have been made:

- Updating the rate constants, product parameters, and absorption cross sections and quantum yields for consistency with current recommendations;
- Improving the treatment of isoprene chemistry;
- Adapting the SAPRC emissions processing scheme to the RADM2 mechanism; and
- Adding extra species (acetaldehyde, PAN, and an additional aromatic) and their associated reactions and products.

The Smolarkiewicz scheme currently used in RADM will be replaced with the Bott scheme. This scheme is more accurate than the Smolarkiewicz scheme for continuous plumes and at low grid resolutions. The RADM cloud module will be replaced with the ADOM module. The RADM dry deposition module currently underestimates dry deposition velocities under stable conditions. This can result in unrealistically high O_3 concentrations at night.

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 O_3 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 O_3 concentrations and temporal and spatial O_3 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 evaluated independently, 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.

Compilations of the performance of photochemical models in the South Coast Air Basin of California and in other urban areas indicate a general tendency toward the underprediction of O_3 concentrations and particularly O_3 maxima. It should be noted that different areas of the country are characterized by different controlling factors in O_3 generation, so the reasons for O_3 underprediction in one area may not be the same as in another. A case in point is the possibility of anthropogenic ROG emissions underestimation in urban areas versus biogenic ROG emissions underestimation in rural and regional areas. It is well-recognized that urban and regional photochemical models have a number of uncertain input quantities, so it is possible, by adjusting these quantities within their ranges of uncertainty, to improve O_3 predictions. This process, which is inherent in any modeling exercise because of the uncertainty associated with many of the input quantities, can lead to getting the right answer for the wrong reason. Because the modeling of an O_3 episode usually is carried out to establish a "base case" against which to evaluate the effects of VOC and NO_x emissions changes, the accuracy of the base case is vital for obtaining a valid assessment of the effects of emissions perturbations. Due to the nonlinear response of the O_3/VOC/NO_x system, conclusions drawn about the effect of VOC and NO_x emissions changes may not reflect actual atmospheric response if the base case simulation is inaccurate. For this reason, it is important to understand the reasons why the base case simulation may not agree with observations. Several more or less equivalent alternate base cases may exist due to the fact that it often is possible to vary inputs within their ranges of uncertainties to achieve comparable model performance. Unfortunately, the O_3 responses to identical VOC/NO_x controls may be rather different depending on which base case is used.

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 (Tesche et al., 1990b). The recommended methods 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 (Tesche et al., 1990b): (1) the paired peak prediction accuracy, (2) the unpaired peak prediction accuracy, (3) the mean normalized bias, and (4) the mean absolute normalized gross error.

Accurate matching of O_3 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 O_3 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 O_3, 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, NO, NO_2, PAN, O_2, H_2O_2, HNO_2, 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, in order to include HNO_3 and nitrate aerosol in the data set for model comparisons, the model should include an adequate description of the HNO_3 depletion process associated with aerosol formation.

Adequate model performance for several reactive species increases the assurance that correct O_3 predictions are not a result of chance or fortuitous cancellation of errors introduced by various assumptions. Multispecies comparisons could be the key in discriminating among alternative modeling approaches that provide similar predictions of O_3 concentrations.

As noted above, photochemical models have the potential to produce nearly the right O_3 concentrations when performance is evaluated, but do so because two or more flaws were compensating each other. The existence of compensating errors in many modeling applications is suspected because most applications have used emission inventories whose validity is now in question (National Research Council, 1991). Underestimation of VOC emissions from motor vehicles may be responsible for the lack of agreement between inventories and ambient concentration data (Baugues, 1986; Lawson et al., 1990; Pierson et al., 1990; Fujita et al., 1992). Underestimation of emissions from other sources is also a possibility. One potentially underestimated VOC source is vegetation, which naturally emits VOCs. An underestimation of VOC emissions could be compensated for by underestimation of mixing height or wind speed, by overestimation of boundary concentrations of O_3 or precursors, or by inaccurate chemistry modules. Boundary concentrations (which can be obtained from measurements or regional models or by assuming background concentrations, often are poorly defined.

If only a routine database is available for modeling O_3 in an urban area, then there are four areas of concern that require attention (Roth, 1992).

(1) Air Quality Aloft. These data most likely will not be available. These measurements are important and are instrumental for diagnostic analysis of model simulations.
(2) Boundary Conditions. If the possibility of significant transport into the region exists, but the data are not available, the boundary conditions become a variable that allows the introduction of compensatory errors if the emissions estimates are inaccurate. An approach to circumventing this problem is to define the region in such a way that the boundaries become a much less significant issue.
(3) Ambient VOC Data. These generally are not routinely available. In their absence, evaluation of model performance is hampered.
(4) 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 planned to minimize the possibility of compensatory errors.

3.6.4.2 Performance Evaluation of Ozone Air Quality Models

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., 1993, Table 6-2). Thus, there is a growing body of information concerning the accuracy of the model's predictions; UAM itself is continuing to undergo revision. Evaluations of UAM's performance have been carried out for a number of geographic areas. Evaluations conducted since 1985 have indicated mean discrepancies between predicted and measured O_3 values of 20 to 40% of the observations, when paired in space and time (Roth et al., 1990). The prediction of peaks exhibits relative errors that are smaller than the average error, with a tendency toward underprediction (Roth et al., 1990). The discrepancies between predicted and measured NO_2 in UAM applications are on the order of 30 to 50%, with no improvement over the history of modeling applications (Roth et al., 1990). Underprediction of NO_2 by UAM has been typical, generally on the order of 20 to 40% (Roth et al., 1990).

As a result of the discovery of significantly underestimated mobile source VOC emissions (in the late 1980s), this emissions underestimation is the leading cause of O_3 underprediction in urban areas.

Regional Oxidant Model

A primary role of the ROM is to estimate boundary conditions for use by UAM in evaluating hydrocarbon and NO_x reduction strategies for urban areas in the eastern United States. This is especially the case in areas where transport is a significant element (U.S. Environmental Protection Agency, 1990d). Analysis of regional O_3 abatement strategies also is a major role of the ROM (Possiel et al., 1990).

The ROM has been used in the EPA program, the Regional Ozone Modeling for Northeast Transport (ROMNET) program, to assess the effectiveness of various regional emission control strategies in lowering O_3 concentrations to nationally mandated levels for the protection of human health, forests, and crops (Meyer et al., 1991b). As part of the ROMNET program, the ROM also is being used to provide regionally consistent initial and upwind boundary conditions to smaller-scale urban models for simulations of future-year scenarios.

The most complete testing of ROM2.0 was accomplished in an evaluation with the 50-day (July 12 to August 31, 1980) Northeastern Regional Oxidant Study database (Schere and Wayland, 1989a,b). The model underestimated the highest values and overestimated the lowest. It produced an overall 2% overprediction in predicting maximum daily O_3 concentrations averaged over aggregate groups of monitoring stations. A key indicator of model performance on the regional scale is the accuracy of simulating the spatial extent and location, as well as the magnitude, of the pollutant concentrations within plumes from significant source areas. In ROM2.0 performance analyses, plumes from the major metropolitan areas of the Northeast Corridor, including Washington, DC; Baltimore, MD; New York; and Boston, could be clearly discerned in the model predictions under episodic conditions. Generally, the plumes were well characterized by the model, although there was evidence of a westerly transport bias and underprediction of O_3 concentrations near the center

of the plume. Using aircraft data, ROM2.0 was found to underpredict the regional tropospheric burden of O_3.

The evaluation of ROM2.1 (Pierce et al., 1990), unlike that of ROM2.0, was based on routinely archived data from state and local agency monitoring sites rather than on an intensive field-study period. The evaluation consisted of the comparison of observed and predicted O_3 concentrations during selected episodes (totaling 26 days) of high O_3 observed during the summer of 1985. Evaluation showed that ROM2.1 underestimated the highest values and slightly overestimated the lowest; underestimates of the upper percentiles tended to be more prevalent in the southern and western areas of the ROMNET domain (Table 3-26). The model exhibited an overall 1.4% overprediction in predicting maximum daily O_3 concentrations averaged over aggregate groups of monitoring stations, and it appears to correct for the westerly transport bias of high-O_3 plumes in the Northeast Corridor seen in ROM2.0. As with ROM2.0, model performance degraded as a function of increasingly complex mesoscale wind fields.

In a recent evaluation of ROM (Systems Applications International, 1993), ROM2.2 overestimated observed O_3 maxima by 20 to 30 ppb over the period of July 4 through 6, 1988, and predicted an episodic peak of 242 ppb on July 9, 1988, when the observed peak was 138 ppb. The ROM2.2 performance for hourly O_3 concentrations in the New York region exceeded the range of EPA acceptable performance by a factor of two 90% of the time during the July 1988 episode. The Systems Applications International (1993) report concluded that "the patchiness of the ROM2.2 predictions compared to the observations raises serious questions as to whether the model will respond correctly to emission control strategies." The major conclusions of that report were:

- Model performance downwind of New York City is "unacceptable". The model significantly overpredicts peak O_3 levels, and the predicted diurnal variation of O_3 occurs too late in the afternoon.
- Model performance for the Philadelphia and Baltimore/Washington urban plumes is "poor" with "unpaired peak estimation accuracy at the outer edge of the acceptable range."
- Elsewhere, the model seems to give good results, although it produces O_3 spatial distributions that are too "patchy" when compared to observations.
- There is a systematic westerly bias in the ROM2.2 wind fields.
- The model performance for NO_x is "extremely poor" indicating that ROM2.2 may be overestimating the VOC/NO_x ratios across the region.

3.6.4.3 Database Limitations

As previously mentioned, the use of routine air quality and meteorological data requires that a number of assumptions be made about key model inputs. Although intensive field studies are desirable during O_3 episodes to acquire the full set of data required, three key problems arise: (1) such studies are expensive and, therefore, are limited in number; (2) the time required to carry out field studies usually exceeds the time available; and (3) most field studies have not captured the worst O_3 episodes. Because EPA guidance emphasizes planning to meet worst-case conditions, field data often must be manipulated to approximate highest O_3 concentrations. Such adjustments invariably increase uncertainty in model projections.

Studies that have, or will, provide data for model evaluation include the St. Louis, MO, RAPS, conducted in 1975 and 1976; the Northeast Corridor Regional Modeling Project,

conducted in 1979 and 1980; the South Central Coast Cooperative Aerometric Monitoring Program, conducted in 1985; SCAQS conducted in 1987; studies in Sacramento and San Diego, CA, in 1990; SJVAQS/AUSPEX conducted in 1990; LMOS conducted in 1990 and 1991; SOS conducted in 1991 and 1992; and a Gulf Coast study for 1993.

In most cases, field studies have not coincided with periods in which ozone concentrations have attained values as high as that on which the SIP must be based. Given the low probabilities of occurrence of the most adverse meteorological conditions and the fact that field studies typically acquire data for two or three ozone episodes, obtaining a design value concentration during the course of a field study is unlikely.

The EPA recommends that the five highest daily maximum O_3 concentrations at a design-value site, selected from the three most recent years, be modeled if EKMA is used for a SIP (U.S. Environmental Protection Agency, 1989b). Because EKMA's data requirements are minimal, it can be applied to the worst cases. In contrast, the number of episodes available for grid-based modeling is less than desirable in all areas. In addition, any available intensive databases often do not include the worst-case meteorology; intensive databases typically restrict modeling to two or three O_3 episodes having a duration of 2 to 3 days each. Moreover, the intensive databases never encompass the full range of meteorological conditions of interest (if O_3 exceedances occur in an area under different meteorological conditions, the relative effectiveness of different control strategies might vary with the different meteorological conditions). The EPA specifies procedures for episode selection for use with grid-based models (U.S. Environmental Protection Agency, 1991b).

Because the number of intensive databases is limited both in terms of episodes and regions, EPA has investigated the feasibility of applying UAM without conducting intensive field studies (Scheffe and Morris, 1990, 1991). These studies, known as the Practice for Low-cost Application in Nonattainment Regions (PLANR), were conducted for New York; Philadelphia; Atlanta; Dallas-Fort Worth, TX; and St. Louis. Of the five cities studied, St. Louis, New York, and Philadelphia had intensive databases available. Simulations were carried out using both routine and intensive databases for St. Louis and Philadelphia. Model performance using routine data was much better for St. Louis than for Philadelphia (Scheffe and Morris, 1990, 1991). Scheffe and Morris (1990, 1991) cautioned that the differing results may be complicated by the quality of the databases, but they speculate that model performance using routine databases for Philadelphia might have been poorer because of regional transport. Performance statistics for all four applications using routine data were consistent with other UAM applications (Scheffe and Morris, 1990, 1991); however, the paucity of data in the routine databases precluded any investigation of the possibility that compensating errors occurred.

Scheffe and Morris (1990, 1991) note that the PLANR lack of air quality data was addressed by extending the length of the simulations and expanding the upwind boundary, which, in effect, increased the need for accurate emissions inventories (boundary conditions could also be obtained through use of ROM). For PLANR applications, gridded emissions were created from routine county-level emission inventories by utilizing an emissions program that made use of surrogate information, such as population distribution. The PLANR study represents an interesting start on the problem of model application to areas without intensive databases; however the results were not sufficiently definitive for drawing conclusions of a broad, general nature.

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 in the model inputs and in assessing the effects of these reductions on O_3 in the region. Ozone concentrations can be decreased by reducing either VOC or NO_x concentrations to sufficiently low levels. The effects of NO_x emissions reductions on O_3 concentrations vary because NO_x is an atypical precursor (i.e., although it is necessary for O_3 formation, fresh NO emissions remove O_3, and high concentrations of NO_x retard the rate of O_3 formation by removing radicals). Control of NO_x tends to accelerate the rate of O_3 formation; however, its effects on peak O_3 concentration depend on the location and timing of the control and on ambient concentrations of VOCs and NO_x, which vary widely in time and space, even within a single urban area during 1 day.

At a given VOC level, as the initial NO_x is increased, O_3 first increases, then peaks, and then decreases. The reduction in peak O_3 with increasing NO_x is a well-established chemical phenomenon. The peak in O_3 formation occurs at an initial VOC/NO_x ratio of about 10/1 (i.e., 10 ppbC/1 ppb). At fixed NO_x level, as VOC is increased, O_3 formation increases but then levels off. As a result of this behavior, at VOC/NO_x ratios below about 10/1, VOC reduction has been the preferred strategy for O_3 reduction. In this region NO_x reductions speed up O_3 formation and lead to higher peak O_3 values. At VOC/NO_x ratios exceeding about 10/1, both VOCs and NO_x will reduce O_3, but less than proportionally. The reason the reduction in O_3 is less than proportional is because equal reductions of VOCs and NO_x at intermediate ratios tend to keep O_3 production at its maximum. The nonlinear chemical behavior of the VOC/NO_x system, discussed earlier in this chapter, is at the heart of the controversy over the role of NO_x in O_3 control (Heuss and Wolff, 1993).

As noted in Section 3.6.1.2, the concept that a region is characterized by a single VOC/NO_x ratio is oversimplified and may actually lead to incorrect conclusions concerning the optimal approach to O_3 reduction (Milford et al., 1989). The VOC/NO_x ratio in a region is a function of location and time of day; the source-rich center city area may be characterized by a lower ratio than that in downwind, suburban areas at any given time of day. Because of the complex spatial and temporal dependence of O_3 formation, grid-based photochemical air quality models are necessary to evaluate the effect of emission reduction strategies for a region.

Moreover, location-specific studies need to be performed to ascertain whether a given area is in the VOC- or NO_x-controlled regime. Research is being conducted into the relationship between O_3 and NO_y to determine whether NO_y is a better indicator of the O_3-forming potential than the VOC/NO_x ratio (Shepson et al., 1992b; Trainer et al., 1993; Kleinman et al., 1994; Milford et al., 1994).

In most modeling applications, inputs are adjusted within their range of uncertainty to improve performance. A key test of quality of performance is to evaluate the model predictions for other episodes without adjustments, using the same procedures for establishing inputs as for the original episode.

Grid modeling applications are currently underway by or for state agencies for approximately 20 areas within the United States to support regional O_3 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 O_3 levels.
An inherent question in using a less adverse episode to develop control strategies is how do

these strategies extrapolate to a more severe set of conditions? There is no clear answer to this question. At present, control strategies, evaluated by 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 O_3 concentration achieved. Another issue is that the form of the NAAQS for O_3 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 O_3 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 indicate that O_3 has been underestimated, most likely because VOC emissions from motor vehicles have been seriously underestimated. The underestimation was hidden by adjusting other model inputs within their range of uncertainty. In Atlanta, it has been estimated that approximately 60% of the VOC inventory is of biogenic origin, and the variation of anthropogenic emissions reductions required to achieve O_3 attainment within the uncertainty range of the biogenic emissions is on the order of 20%. The uncertainty range of the biogenic VOC emissions needs to be reduced to obtain tighter control strategy estimates.

The eastern United States poses special problems in regional-scale photochemical modeling. Boundary conditions typically contribute 40 to 70% of pollutant loading in many urban areas east of the Mississippi River. Regional-scale models are often either not available or not sufficiently reliable to use in estimating upwind boundary conditions. Furthermore, data are rarely available. If data are available, their use is limited to estimation of present conditions. If models are used in control strategy assessment and 40 to 70% of pollutant loading originates outside of the modeling region, major questions arise as to just how control strategies are to be determined. If uncertainties at the regional scale are significant and if regional-scale modeling is inaccurate, the limits of accuracy for urban-scale control strategy determination need to be carefully assessed.

An essential question is, given the inevitable uncertainties associated with O_3 air quality model predictions, can the effect of VOC and NO_x emissions changes on O_3 levels be unambiguously determined? The best approach to answering this question is a combination of sensitivity/uncertainty studies. Given the estimated uncertainties in model inputs and parameters for a particular application, the proposed VOC and NO_x emissions change scenarios should be examined for the full range of model inputs and parameters to determine how sensitive conclusions about the effect on O_3 levels are to the inherent uncertainties.

3.6.6 Conclusions

The 1990 CAAA (U.S. Congress, 1990) have mandated the use of photochemical grid models for demonstrating how most O_3 nonattainment areas can attain the NAAQS. Predicting O_3 is a complex problem. There are still many uncertainties in the models; nonetheless, models are useful for regulatory analysis and constitute one of the major tools for attacking the O_3 problem. These models have developed considerably in the past 10 years. However, their usefulness is constrained by having limited databases for use in model evaluation and from having to rely on hydrocarbon emissions data that may be inaccurate.

Table 3-27. Applications of Photochemical Air Quality Models to Evaluating Ozone[a]

Investigators	Region/Episode	Model Used	Strategies Evaluated
Chu et al. (1993) Chu and Cox (1993) Roselle et al. (1992) Mathur and Schere (1993)	Eastern United States; July 2-10, 1988	ROM2.2	Across-the-board NO_x/VOC reductions
Possiel et al. (1993) Possiel and Cox (1993)	Northeastern United States; July 1-12, 1988	ROM2.2	Estimate O_3 reductions per 1990 CAAA
Milford et al. (1992)	Northeastern United States; 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 (1990, 1991)	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 United States; July 2-17, 1988	ROM	Ozone control strategies in Northeast
Roselle and Schere (1990) Roselle et al. (1991)	Northeastern United States; July 12-18, 1980	ROM2.1	Sensitivity of O_3 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 O_3 levels
Milford et al. (1989)	South Coast Air Basin	CIT	Effects of systematic VOC and NO_x reductions
Middleton et al. (1993)	Eastern United States and southeastern Canada	RADM	2010 emissions projections

[a]See Appendix A for abbreviations and acronyms.

Primary issues and limitations associated with the use of photochemical air quality models are described below.

- High noise-to-signal ratios. Model imprecision for ozone predictions typically ranges from 25 to 40%, and inaccuracy (bias) ranges from 5 to 20%. These uncertainties are often of the same order as the percentage of reduction in the peak O_3 concentration for an area (from 160 to 120 ppb). Reasons for these inaccuracies include uncertainties in emissions inventories.
- Inadequacies of supporting databases in most geographical areas. Most areas are lacking or are deficient in data needed to estimate boundary conditions and

meteorological and air quality conditions aloft. There are few areas where speciated VOC concentrations are measured; surface NO_x data may be inaccurate. Where important data gaps exist, modeling accuracy suffers, and the prospects for reducing or eliminating the presence of compensating errors are diminished.

- Continuing need for improvements. Examples include the introduction of prognostic meteorological modeling in the mid-1980s, the discovery of underestimation of VOC emissions in the late 1980s, the inclusion of NO_x emissions from soils in 1993, and major adjustment of the emissions rates of isoprene in 1994.
- Presence of compensating errors. It appears that compensating errors have been present in many past applications, introducing the potential for bias into the estimation of the impacts of emissions control strategies.

Comparison of model predictions against ozone measurements, although necessary, is not a robust test of a model's accuracy. Ideally, one should evaluate performance against more extensive sets of species such as individual VOCs, NO_x, and NO_y. Compensating errors in input information to a model and within the model formulation can cause an O_3 model to generate correct O_3 predictions for the wrong reasons. Therefore, model evaluation indicators are needed to demonstrate the reliability of a prediction before the model can be used effectively in making control strategy decisions.

It is important to stress that, in O_3 modeling, a modeling system also is at issue, not just the air quality model itself. The modeling system includes a meteorological model, an emissions representation (where an emissions model is preferred to the traditional "inventory" approach), the air quality model, and a comprehensive supporting database. Where a problem exists, the entire modeling system must be evaluated.

Models can be used effectively in a relative sense to rank different control alternatives in terms of their effectiveness in reducing O_3 and to indicate the approximate magnitude of improvement in peak O_3 levels expected under various control strategies. To do so, there must be a sound emissions model and data and an adequate database on which to construct the modeling. Grid-based O_3 air quality modeling is superior to the available alternatives for O_3 control planning, but results can be misleading if the model is not evaluated sufficiently. The goal is to minimize the chances of incorrect use of the model.

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 PBL of the earth's atmosphere. In the stratosphere, 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 CH_4, CO, and NO_x. These processes contribute to the background O_3 in the troposphere.

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 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 many relatively "clean" areas of the PBL, CH_4 is the chief organic precursor to in situ photochemical production of O_3 and related oxidants. Exceptions can include clean forested or vegetated areas emitting biogenic organics. The major tropospheric removal process for CH_4 is by reaction with OH radicals. In the complex cyclic reactions that result in oxidation of CH_4, there can be a net increase in O_3 or a net loss of O_3, depending mainly on the NO concentration.

3.7.1.2 Ozone Formation in the Polluted Troposphere

The same basic processes by which CH_4 is oxidized occur in the atmospheric oxidative degradation of other, even more reactive and more complex VOCs. The only significant initiator of the photochemical formation of O_3 in the troposphere is the photolysis of NO_2, yielding NO and a ground-state oxygen atom that reacts with molecular oxygen to form O_3. The O_3 thus formed reacts with NO, yielding O_2 and NO_2. These cyclic reactions attain equilibrium in the absence of VOCs. In the presence of VOCs, however, the equilibrium is upset, resulting, from a complex series of chain reactions, in a net increase in O_3.

The key reactive species in the troposphere is the OH radical, which is responsible for initiating the oxidative degradation reactions of almost all VOCs. As in the CH_4 oxidation cycle, the conversion of NO to NO_2 during the oxidation of VOCs is accompanied by the production of O_3 and the efficient regeneration of the OH radical. The O_3 and PANs formed in polluted atmospheres increase with the NO_2/NO concentration ratio.

At night, in the absence of photolysis of reactants, the simultaneous presence of O_3 and NO_2 results in the formation of the NO_3^- radical. The reaction with NO_3^- radicals appears to constitute a major sink for alkenes, cresols, and some other compounds, although alkyl NO_3^- chemistry is not well characterized.

Most inorganic gas-phase processes, that is, the nitrogen cycle and its interrelationships with O_3 production, are well understood; the chemistry of the VOCs in ambient air, however, is not. The chemical loss processes of gas-phase VOCs, with concomitant production of O_3, include reaction with OH, NO_3, O_3, and photolysis.

The major classes of VOCs in ambient air are alkanes, alkenes (including alkenes from biogenic sources), aromatic hydrocarbons, carbonyl compounds, alcohols, and ethers. A wide range of lifetimes in the atmosphere, from minutes to years, characterize the VOCs.

The only important reaction of alkanes is with OH radicals. For alkanes having carbon-chain lengths of four or less ($\leq C_4$), the chemistry is well understood and the reaction rates are slow. For $\geq C_5$ alkanes, the situation is more complex because few reaction products have been found. Branched alkanes (e.g., isobutane) have rates of reaction that are highly dependent on structure. It is difficult to represent reactions of these VOCs satisfactorily in the

chemical mechanisms of air quality models. Stable products of alkane photooxidation are known to include carbonyl compounds, alkyl nitrates, and -hydroxycarbonyls. Major uncertainties in the atmospheric chemistry of the alkanes concern the chemistry of alkyl nitrate formation; these uncertainties affect the amount of NO-to-NO_2 conversion occurring and, hence, the amounts of O_3 formed during photochemical degradation of the alkanes.

Alkenes react in ambient air with OH and NO_3^- radicals and with O_3. All three processes are important atmospheric transformation processes, and all proceed by initial addition to the >C=C< bonds. Products of alkene photooxidation include carbonyl compounds, hydroxynitrates and nitratocarbonyls, and decomposition products from the energy-rich biradicals formed in alkene-O_3 reactions. Major uncertainties in the atmospheric chemistry of the alkenes concern the products and mechanisms of their reactions with O_3, especially the radical yields (which affect the O_3 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, -dicarbonyls (e.g., glyoxal), and unsaturated carbonyl or hydroxycarbonyl compounds. 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 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 certain higher molecular weight VOCs can lead to the formation of significant yields of organic particulates in ambient air. The chemical processes involved in the formation of O_3 and other photochemical pollutants lead to the formation of OH radicals and oxidized VOC reaction products that are of low enough volatility to be present as organic particulate matter. Hydroxyl radicals that oxidize VOCs also react with NO_2 and SO_2 to form HNO_3 and H_2SO_4, respectively, which can become incorporated into aerosols as particulate nitrate and sulfate. Controls aimed at reducing O_3 will also impact acid and secondary aerosol formation in the atmosphere.

3.7.2 Meteorological Processess Influencing Ozone Formation and Transport

3.7.2.1 Meteorological Processes

The surface energy (radiation) budget of the earth strongly influences the dynamics of the PBL and, in combination with synoptic winds, provides the forces for the vertical fluxes of heat, mass, and momentum. The redistribution of energy through the PBL creates

thermodynamic conditions that influence vertical mixing. Energy balances require study so that more realistic simulations can be made of the structure of the PBL.

Day-to-day variability in O_3 concentrations depends heavily on day-to-day variations in meteorological conditions. For example, the concentration of an air pollutant depends significantly on the degree of mixing that occurs between the time a pollutant, or its precursors, is emitted and the arrival of the pollutant at the receptor. Inversion layers (layers in which temperature increases with height above ground level) are prominent determinants of the degree of atmospheric vertical mixing and, thus, the degree to which O_3 and other pollutants will be dispersed or accumulate. Ozone left in a layer aloft, as the result of reduced turbulence and mixing at the end of daylight hours, can be transported through the night, often to areas far removed from pollution sources. Downward mixing on the subsequent day can result in increases in local concentrations from the transported O_3.

Growing evidence indicates that the conventional use of mixing heights in modeling is an oversimplification of the complex processes by which pollutants are redistributed within urban areas. In addition, it is necessary to treat the turbulent structure of the atmosphere directly and to acknowledge the vertical variations in mixing.

Geography can significantly affect the dispersion of pollutants along the coast or shore of oceans and lakes. Temperature gradients between bodies of water and land masses influence the incidence of surface conditions. The thermodynamics of water bodies may play a significant role in some regional-scale episodes of high O_3 concentrations.

An "air mass" is a region of air, usually of multistate dimension, that exhibits similar temperature, humidity, and stability characteristics. Episodes of high O_3 concentrations in urban areas often are associated with high concentrations of O_3 in the surroundings.

The transport of O_3 and its precursors beyond the urban scale (50 km) to neighboring rural and urban areas has been well documented and was described in the 1986 EPA criteria document for O_3. Areas of O_3 accumulation are characterized by synoptic-scale subsidence of air in the free troposphere, resulting in development of an elevated inversion layer; relatively low wind speeds associated with a weak horizontal pressure gradient around a surface high pressure system; a lack of cloudiness; and high temperatures.

3.7.2.2 Meteorological Parameters

Ultraviolet radiation from the sun plays a key role in initiating the photochemical processes leading to O_3 formation and affects individual photolytic reaction steps. There is little empirical evidence in the literature, however, linking day-to-day variations in observed UV radiation levels with variations in O_3 levels.

An association between tropospheric O_3 concentrations and tropospheric temperature has been demonstrated. Plots of daily maximum O_3 concentrations versus maximum daily temperature for the summer months of 1988 to 1990 for four urban areas, for example, show an apparent upper bound on O_3 concentrations that increases with temperature. A similar qualitative relationship exists at a number of rural locations.

The relationship between wind speed and O_3 buildup varies from one part of the country to another. Research done during the SOS (in the "Atlanta intensive" field study) indicates that measurements of variations in wind speed among methods at a particular level above ground must be larger than about 3 m/s to be considered statistically significant.

3.7.2.3 Normalization of Trends

Statistical techniques (e.g., regression techniques) can be used to help identify real trends in O_3 concentrations, both intra-annual and inter-annual, by normalizing meteorological variability. In the SOS, for example, regression techniques were used successfully to forecast O_3 levels to ensure that specialized measurements were made on appropriate days.

3.7.3 Precursors

3.7.3.1 Volatile Organic Compound Emissions

Hundreds of VOCs, 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, 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 area sources, deviations of emission rates from individual sources from assigned average factors can result in error for the entire area 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.

According to recent studies, vegetation emits significant quantities of VOCs into the atmosphere, chiefly monoterpenes and isoprene, but also oxygenated VOCs. 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.

3.7.3.2 Nitrogen Oxides Emissions

Anthropogenic NO_x is associated with combustion processes. The primary pollutant emitted is NO, formed at high combustion temperatures from the nitrogen and oxygen in air and from nitrogen in combustion fuel. Emissions of NO_x in 1991 in the United States totaled 21.39 Tg. The two largest NO_x emission sources are electric power generation plants and highway vehicles. Emissions of NO_x therefore are 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, whereas 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 than that 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.

3.7.3.3 Concentrations of Volatile Organic Compounds in Ambient Air

The VOCs most frequently analyzed in ambient air are 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 in 19 cities in 1985 produced NMHC measurements that showed median values ranging from 0.39 to 1.27 ppmC for 1984 and 0.38 to 1.63 ppmC in 1985. Overall median values from all urban sites were about 0.72 ppmC in 1984 and 0.60 ppmC in 1985.

Comparative data over two decades (the 1960s through the 1980s) 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 ppmC and terpenes from 0.001 to 0.030 ppmC.

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 a.m. 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 a.m. 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 a.m. 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 O_3 concentrations, however, was weak in a recent analysis.

3.7.3.5 Ratios of Concentrations of Nonmethane Organic Compounds to Nitrogen Oxides

The ratios of NMOC/NO_x vary substantially between cities and within a given city. With certain exceptions, urban NMOC/NO_x ratios have been in the range of 10 and below. In contrast, ratios of NMOC/NO_x in rural areas tend to equal or exceed 20. Discrepancies have been found between ambient NMOC/NO_x ratios and emission inventory NMOC/NO_x ratios, with ambient ratios of NMOC/NO_x significantly exceeding emission ratios of NMOC/NO_x.

Trends in ratios of NMOC/NO_x have shown downward trends to well below 10 during the 1980s, both for the South Coast Air Basin and for cities in the eastern United States. Based on these low ratios, hydrocarbon control should be more effective than NO_x control within a number of cities.

3.7.3.6 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 C_{10}: 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, where 14% was 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 CL, 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 O_3 with an alkene (C_2H_4) 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 O_3 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. Because the measurement is absolute, UV photometry also is used to calibrate other 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 MnO_2 scrubber used in UV O_3 photometers) will be positive interferences 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. An interference from water also appears to occur from condensation of moisture in sampling level. Results from collocated UV and CL instruments indicated positive biases in the UV data of 20 to 40 ppb on hot, humid days.

Differential optical absorption spectrometry has been used to measure ambient O_3, but further intercomparisons with other methods and interference tests are recommended. Passive sampling devices permit acquisition of personal human exposure data and of O_3 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 GPT of O_3 with NO. Ultraviolet photometry is the reference calibration method approved by EPA. Ozone is unstable and must be generated in situ at time of use to produce calibration mixtures.

Two methods generally have been employed to measure atmospheric PAN and its higher homologues: IR and GC using an ECD. A third method, less often used, couples GC with a molybdenum converter that reduces PAN to NO in the gas phase and subsequently measures the NO with a CL analyzer. Peroxyacetyl nitrate and the higher PANs are normally measured by GC-ECD. Detection limits have been extended to 1 to 5 ppt, using cryogenic enrichment of samples and specified desorption procedures that limit losses associated with cryosampling. Because PAN is unstable (explosive, and subject to surface-related decomposition), the preparation of reliable calibration standards is difficult. Methods devised to generate calibration standards include photolysis of static concentrations of gases, nitration of peracetic acid in single hydrocarbons, and analysis of PAN as NO under specified conditions of the dissociation of PAN into its precursors.

Early measurements of 10 to 80 ppb H_2O_2 reported in the 1970s have been found to be in error because of artifact formation of H_2O_2 from reactions of absorbed gaseous O_3. Modeling results also indicate that lower levels of H_2O_2, on the order of 1 ppb, occur in the atmosphere.

In situ measurement methods for H_2O_2 include FTIR and TDLAS. The FTIR method is specific for H_2O_2 but has a high detection level of 50 ppb (using a 1-km path

length). The TDLAS method also is specific and has a detection level of 0.1 ppb over averaging times of several minutes. Four frequently used wet chemical methods for measurement of H_2O_2 are available. All involve the oxidation of a substrate followed by instrumental detection and quantification of the resulting CL or fluorescence. Detection limits are comparable to those of FTIR and TDLAS, but interferences are common and must be obviated or minimized with specified procedures.

Calibration of methods for gaseous H_2O_2 measurement requires the immediate use of standard mixtures prepared by one of several wet chemical methods.

3.7.4.2 Volatile Organic Compounds

Increased monitoring of VOCs is required under Title I, Section 182, of the CAAA of 1990 because of the role of VOCs as precursors to the formation of O_3 and other photochemical oxidants. Volatile organic compounds are those 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}.

Traditionally, NMHCs have been measured by methods that employ a 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 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 HPLC method employing 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 O_3 scrubber has been recommended to prevent interference in this method by O_3 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 of photochemical oxidation and also from the inclusion of many of these compounds on the list of hazardous air pollutants in the 1990 CAAA. Measurement of these PVOCs is difficult because of their reactivity and water solubility. Methods are still in development.

3.7.4.3 Oxides of Nitrogen

Nitric oxide and NO_2 comprise the NO_x involved as precursors to O_3 and other photochemical oxidants.

The most common method of NO measurement is the gas-phase CL reaction with O_3. The CL method is essentially specific for NO. Commercial NO monitors have detection limits of a few parts per billion by volume in ambient air. Commercial NO analyzers may not

have sensitivity sufficient for surface measurements in rural or remote areas or for airborne measurements. Direct spectroscopic methods for NO exist that have very high sensitivity and selectivity for NO. Major drawbacks of these methods are their complexity, size, and cost, which restrict these methods to research applications. No PSDs exist for measurement of NO.

Chemiluminescence analyzers are the method of choice for NO_2 measurement, even though they do not measure NO_2 directly. Minimum detection levels for NO_2 have been reported to be 5 to 13 ppb, but more recent evaluations have indicated detection limits of 0.5 to 1 ppbv. Reduction of NO_2 to NO is required for measurement. In practice, selective measurement of NO_x by this approach has proved difficult. Commercial instruments that use heated catalytic converters to reduce NO_2 to NO measure not NO and NO_x, but more nearly NO and total NO_y. Thus, the NO_2 value inferred from such measurements may be significantly in error, which may in turn affect the results of modeling of ambient O_3.

Several spectroscopic approaches to NO_2 detection have been developed. As noted above for NO, however, these methods have major drawbacks that include their complexity, size, and cost, which, at present, outweigh the advantages of their sensitivity and selectivity. Passive samplers for NO_2 exist but are still in the developmental stage for ambient air monitoring.

Calibration of methods for NO measurement is done using standard cylinders of NO in nitrogen. Calibration of methods for NO_2 measurement include the use of cylinders of NO_2 in nitrogen or air, the use of permeation tubes, and gas-phase titration.

3.7.5 Ozone Air Quality Models

3.7.5.1 Definitions, Descriptions, and Uses

Photochemical air quality models are used to predict how O_3 concentrations change in response to prescribed changes in source emissions of NO_x and VOCs. They are mathematical descriptions of the atmospheric transport, diffusion, removal, and chemical reactions of pollutants. They operate on sets of input data that characterize the emissions, topography, and meteorology of a region and produce outputs that describe air quality in that region.

Two kinds of photochemical models are recommended in guidelines issued by EPA: (1) the grid-based UAM is recommended for modeling O_3 over urban areas, and (2) EKMA is identified as an acceptable approach under certain circumstances. The 1990 CAAA mandate the use of three-dimensional (grid-based) air quality models such as UAM in developing SIPs for areas designated as extreme, severe, serious, or multistate moderate.

In grid-based air quality models, the region to be modeled (the modeling domain) is subdivided into a three-dimensional array of grid cells. Pertinent atmospheric processes and chemical reactions are represented for each cell.

In trajectory models, such as EKMA, a hypothetical air parcel moves through the area of interest along a path calculated from wind trajectories. Emissions are injected into the air parcel and undergo vertical mixing and chemical transformations. Trajectory models provide a dynamic description of atmospheric source-receptor relationships that is simpler and less expensive to derive than that obtained from grid models, but meterological processes are highly simplified in trajectory models

The EKMA-based method for determining O_3 control strategies has some limitations, the most serious of which is that predicted emissions reductions are critically dependent on the initial NMHC/NO_x ratio used in the calculations. This ratio cannot be

determined with any certainty because it is expected to be quite variable in time and space 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 O_3 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 ROM use the CMB-IV. The CBM-IV and the SAPRC and RADM mechanisms 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 O_3 on both urban and regional scales; and is included in all urban- and regional-scale models. Wet deposition (the removal of gases and particles from the atmosphere by precipitation events) generally is not included in urban-scale photochemical models, because O_3 episodes do not occur during periods of significant clouds or rain.

Concentration fields of all species computed by the model must be specified at the beginning of the simulation; these concentration fields are called the initial conditions. These initial conditions are determined mainly with ambient measurements, either from routinely collected data or from special studies, but interpolation can be used to distribute the surface ambient measurements.

3.7.5.3 Evaluation of Model Performance

Air quality models are evaluated by comparing their predictions with ambient observations. An adequate model should give accurate predictions of current peak O_3 concentrations and temporal and spatial O_3 patterns. It also should 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. Likewise, multispecies comparisons could be the key in discriminating among alternative modeling approaches that provide similar

predictions of O_3 concentrations. Adequate model performance for several reactive species increases the assurance that correct O_3 predictions are not a result of chance or fortuitous cancellation of errors introduced by various assumptions.

If only a routine database is available for modeling O_3 in an urban area, then several concerns require attention relative to model performance evaluation: air quality aloft, boundary conditions, ambient VOC data, and meteorological data aloft. 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.

3.7.5.4 Use of Ozone Air Quality Model 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 simulated adequately and then reducing hydrocarbon or NO_x emissions, or both, in the model inputs and assessing the effects of these reductions on O_3 in the region. The adequacy of control strategies based on grid-based models depends, in part, on the nature of input data for simulations and model validation, on input emissions inventory data, and on the relationship between model output and the current form of the NAAQS for O_3.

Grid-based models that have been widely used to evaluate control strategies for O_3 or acid deposition, or both, are the UAM, the CIT model, the ROM, the ADOM, and the RADM.

3.7.5.5 Conclusions

Urban air quality models are becoming readily available for application and have been applied in recent years in several urban areas. Significant progress also has been made in the development of regional models and in the integration of state-of-the-art prognostic meteorological models as drivers.

There are still many uncertainties in photochemical air quality modeling. Prime among these are emission inventories. However, models are essential for regulatory analysis and constitute one of the major tools for attacking the O_3 problem. Grid-based O_3 air quality modeling is superior to the available alternatives for O_3 control planning, but the chances of its incorrect use must be minimized.

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standards are available commercially, the vendors do not guarantee long-term stability and accuracy.

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

For the higher molecular weight carbonyl species, liquid solutions can be evaporated, or pure vapor can be generated in dynamic gas-flow systems (permeation tubes, diffusion tubes, syringe delivery systems, etc.). These test atmospheres are then passed through the appropriate collection system and analyzed. A comparison of these data, with the direct spiking of liquid carbonyl species into the particular collection system, provides a measure of the overall collection efficiency.

3.5.2.4 Polar Volatile Organic Compounds

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

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

Two approaches have been utilized in developing analytical methods for PVOCs. One approach has incorporated the use of cryogenic trapping techniques similar to those discussed earlier for the nonpolar hydrocarbon species; the second approach has utilized adsorbent material for sample preconcentration. To be effective for sensitive parts-per-billion measurement of PVOCs, both approaches require some type of water management system to mitigate the adverse effects that water has on the chromatography and detector sensitivity and reliability. Several researchers have reported the use of cryogenic trapping with two-dimensional chromatography to selectively remove water vapor from the analytical process (Pierotti, 1990; Cardin and Lin, 1991). Although this column "heart cutting" technique has been successful for selected compounds, additional studies are needed to determine its potential use for the wide range of PVOCs. Ogle et al. (1992) developed a novel water management system based on the condensation of moisture from the saturated carrier gas stream during thermal desorption of a cryogenic trap. The moisture management system was found to be effective for reducing the amount of water delivered to the column during laboratory analyses of spiked mixtures. However, the system has not yet been extended to field monitoring. Gordon and Miller (1989) have used cryogenic trapping and

GC/MS spectrometry techniques to demonstrate the potential of chemical ionization (CI) within an ion trap to detect PVOCs. The water vapor present in the sample served as the CI reagent gas and appeared to be an effective reagent gas; however, deleterious chromatography results were also encountered. The authors concluded that further laboratory work is needed before this methodology can be applied to ambient air monitoring. Martin et al. (1991) also reported the use of cryogenic trapping with a GC-FID system to measure ambient levels of isoprene and two of its oxidation products, methacrolein and methylvinyl ketone (detection level of 0.5 ppb). The water vapor was selectively removed by using a potassium carbonate (K_2CO_3) trap ahead of the cryogenic trap. Frequent replacement of the K_2CO_3 trap was required.

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

3.5.3 Sampling and Analysis of Nitrogen Oxides

3.5.3.1 Introduction

The measurement of NO_x in ambient air is of interest because of the role that certain of those compounds play as precursors to O_3 and because NO_2 has been shown to impact health effects. Most of the NO_x emitted from combustion sources are NO and NO_2. Collectively these two compounds are called NO_x. They contribute to O_3 formation by means of reactions discussed in Section 3.2. As a result, measurement of NO_x is important in efforts to understand and control O_3 and NO_2 in ambient air.

The atmospheric photochemistry that produces O_3 also results in conversion of NO and NO_2 to products such as HNO_3, nitrous acid (HNO_2), organic nitrates such as PAN ($CH_3C(O)O_2NO_2$), and other species. The total of all of these labile nitrogen species in air, NO_x included, is termed NO_y. Such compounds may be labile via photolysis (e.g., HNO_2) or thermal decomposition (e.g., PAN), and may be toxic, irritating, or acidic. The organic nitrates can occur in the atmosphere as reservoirs for NO_2. However, in general, they do not play the same critical role that NO_2 and NO play as O_3 precursors. For that reason, this section focuses on measurement methods for NO and NO_2, as the primary O_3 precursors of NO_x. Nitrogen oxides other than NO_x may be important, however, as interferents in efforts to measure NO and NO_2. These non-NO_x species are considered in this section in that regard.

Measurements of NO_x may involve measurements of NO, of NO_2, or of the sum of NO_x. Nitrogen dioxide, but not NO, is a criteria air pollutant, and, thus, reference and equivalent methods are specified for NO_2 measurements. In this section, the current state of measurement methods for NO and NO_2 will be summarized separately. Such methods in some cases rely on measurements of total NO_x, or at least an approximation of NO_x. This

discussion focuses on current methods and on promising new technologies, but no attempt is made here to cover the extensive history of the development of these methods. More detailed discussions of such methods may be found elsewhere (U.S. Environmental Protection Agency, 1993c; National Aeronautics and Space Administration, 1983). Wet chemical methods are no longer commonly used and are not discussed here; a review of such methods is given by Purdue and Hauser (1980).

3.5.3.2 Measurement of Nitric Oxide

Gas-Phase Chemiluminescence Methods

By far the most common method of NO measurement is gas-phase CL with O_3. In this method, excess O_3 is added to air containing NO in a darkened, internally reflective chamber monitored by a photomultiplier tube. A small portion of the NO reactions with O_3 produce electronically excited NO_2 molecules that decay by emission of light of wavelengths longer than 600 nm. The emitted light is detected by a red-sensitive photomultiplier tube, through an optical filter that prevents passage of wavelengths shorter than 600 nm. This optical filtering minimizes interference from CL produced by O_3 reactions with other species (e.g., hydrocarbons). The excited NO_2 is readily quenched in air, so that, in typical instruments, air and O_3 are mixed at reduced pressure (i.e., at least 20 in. of Hg vacuum). The intensity of the emitted light is linearly proportional to the NO content of the sample air over several orders of magnitude in concentration.

Commercial CL instruments for continuous measurement of NO are available from several manufacturers. The chemiluminescence approach is also an EPA-designated measurement principle for measuring ambient NO_2; it requires a means of converting NO_2 to NO for detection. The complexities of this conversion are discussed in Section 3.5.3.3, on NO_2 methods. The commercial NO monitors typically are claimed to have detection limits of a few parts per billion by volume in air, with response time of a few minutes. Field evaluations of several commercial instruments have indicated that minimum levels of detection for NO_2 are 5 to 13 ppbv (Michie et al., 1983; Holland and McElroy, 1986). However, more recent evaluations have indicated better performance. Rickman et al. (1989) reported detection limits of 0.5 to 1 ppbv, and precision of ±0.3 ppbv, from laboratory and field evaluations of two commercial instruments operated on their 50 ppbv full-scale ranges. Commercial NO analyzers are portable and quite reliable and now are commonly used in ambient air monitoring networks.

Commercial NO analyzers may not have sensitivity sufficient for surface measurements in urban, rural, or remote areas, or for airborne measurements. As a result, several investigators have devised modifications to commercial instruments to improve their sensitivity and response time (Delany et al., 1982; Tanner et al., 1983; Dickerson et al., 1984; Kelly et al., 1986). Those modifications include operating at low pressure and high sample flow rate; using a larger, more reflective reaction chamber that promotes mixing of the reactants close to the photomultiplier tube; increasing the O_3 supply; for example, by use of oxygen in the O_3 source; cooling of the photomultiplier to reduce noise; adopting photon-counting techniques for light detection; and adding a prereactor to obtain a more stable and appropriate background signal. Commercial instruments modified in these ways are generally reported to have detection limits of 0.1 ppbv or less, with response times of 30 s or less.

Research-grade NO instruments specially designed for ultra-high sensitivity also have been built for use in remote ground-level or airborne applications (e.g., Ridley and

Howlett, 1974; Kley and McFarland, 1980; Kelly et al., 1980; Helas et al., 1981; Drummond et al., 1985; Torres, 1985; Kondo et al., 1987; Parrish et al., 1990). These instruments typically have detection limits of 10 ppt (i.e., 0.01 ppbv) or less, with response times from a few seconds to 1 min.

A number of studies indicate that the CL method is essentially specific for NO. Operation at reduced pressure prevents interference resulting from quenching by water vapor (Michie et al., 1983; Drummond et al., 1985). In air sampling, no significant interferences have been found in NO detection from sulfur-, chlorine-, and nitrogen-containing species (Joshi and Bufalini, 1978; Sickles and Wright, 1979; Grosjean and Harrison, 1985b; Fahey et al., 1985). However, H_2S and possibly other sulfur-containing compounds from seawater have been reported to give false NO signals (Zafiriou and True, 1986). This effect should not be important for ambient air measurements. Fahey et al. (1985) and Drummond et al. (1985) also reported no significant NO interference from a variety of other nitrogen-containing species, including NO_2, HNO_3, PAN, N_2O_5, NH_3, HCN, N_2O, and HO_2NO_2; as well as no interference from CH_4, propylene, and H_2O_2.

Several ambient air intercomparisons have been done of CL NO instruments (Walega et al., 1984; Hoell et al., 1987; Fehsenfeld et al., 1987; Gregory et al., 1990a). These studies have focused on high-sensitivity research instruments, rather than the commercial instruments used for widespread ambient air measurements. These studies have shown excellent agreement among the CL NO instruments, even at NO levels in the low ppt range (Hoell et al., 1987; Gregory et al., 1990a). These results support the validity of the CL approach for NO. Good agreement also has been found between CL measurements and spectroscopic NO measurements in these studies (see Section 3.5.3.2).

Spectroscopic Methods for Nitric Oxide

Direct spectroscopic methods for NO include two-photon laser-induced fluorescence (TPLIF), 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 ±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 in downtown Los Angeles air. Gregory et al. (1990a) 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.

Passive Samplers

At present, no passive sampler exists that directly measures NO. Instead, passive samplers developed for NO_2 have been adapted for NO measurement, using an oxidizing material that converts NO to NO_2. Palmes tubes (Palmes and Tomczyk, 1979) have been adapted for NO measurement by using two tubes in parallel. One tube collects NO_2 on a triethanolamine (TEA)-coated grid, whereas the other collects NO_2 on a TEA grid, plus NO oxidized by a chromic acid-coated surface. The grids are then extracted and analyzed for NO_2^- ion. Nitric oxide is determined by difference between the two results, after accounting for the different diffusivities of NO and NO_2. The sampling rates depend on temperature and air velocity. The tubes cannot be used for periods longer than 24 h and are intended for use at ppm NO levels important in the workplace (e.g., 2 to 200 ppm · h). Applicability to ambient NO levels has not been demonstrated.

A more sensitive passive sampler for NO has been reported (Yanagisawa and Nishimura, 1982) that uses the same TEA chemistry, with CrO_3 as the NO oxidizer. A detection limit of 70 ppbv-h has been reported. As with any currently available passive sampler, the disadvantages of the method are the potential for interferences, relatively poor precision, and low sensitivity for ambient air measurements.

3.5.3.3 Measurements for Nitrogen Dioxide

Gas-Phase Chemiluminescence Methods

In 1976, the gas-phase CL approach described above for NO detection was designated as the measurement principle on which EPA reference methods for ambient NO_2 must be based. The CL method thus filled the vacancy left by withdrawal of the Jacobs-Hochheiser method, because of technical problems, in 1973. To be designated as a reference method, an NO_2 detection method must use the CL approach and be calibrated by the specified methods (gas-phase titration of NO with O_3, or use of an NO_2 permeation device). In addition the instrument must meet the performance specifications shown in Table 3-18. An equivalent method, either manual or automated, must meet certain requirements for comparability with a reference method when measuring simultaneously in a real atmosphere. Those comparability requirements are shown in Table 3-19. An automated equivalent method must also meet the performance requirements shown in Table 3-18.

The selection of the O_3-CL method as the reference measurement principle for ambient NO_2 was the result of comparison tests of CL and wet chemical methods. Chemiluminescence analyzers were found superior to the wet chemical methods in response time, zero and span drift, and overall operation, although agreement among all the methods tested was good, at the NO_2 spike levels provided (Purdue and Hauser, 1980). Table 3-20 lists the methods currently designated (as of August 1, 1994) by EPA as reference and equivalent methods for ambient NO_2. Three wet chemical methods are shown as equivalent methods, but these rarely are used for ambient air measurements.

The O_3 CL method does not measure NO_2 directly, because the CL is produced by reaction of NO with O_3. As a result, NO_2 must first be reduced to NO for detection. In principle, such a reduction should readily result in measurement of NO + NO_2 (i.e.,

Table 3-18. Performance Specifications for Nitrogen Dioxide Automated Methods[a]

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_2O)	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

[a]See Appendix A for abbreviations and acronyms.

Source: Code of Federal Regulations (1987), 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

NO_x), and allow indirect measurement of NO_2 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 NO_2 to NO, including catalytic reduction with heated molybdenum or stainless steel, reaction with CO over a gold catalyst surface, reaction with ferrous sulfate ($FeSO_4$) at room temperature, reaction with carbon at 200 °C, and photolysis of NO_2 at wavelengths of about 320 to 400 nm (Kelly et al., 1986). It has been found in many separate investigations that the heated converters reduce NO_2 to

Table 3-20. Reference and Equivalent Methods for Nitrogen Dioxide Designated by U.S. Environmental Protection Agency[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

[a]As of August 1, 1994.
[b]Triethanolamine-guaiacol-sulfite with 8-amino-1-naphthalene-sulfonic acid ammonium salt.

NO effectively, but also reduce other NO_y species as well (e.g., Winer et al., 1974; Cox, 1974; Joseph and Spicer, 1978; Grosjean and Harrison, 1985b; Fahey et al., 1985). Efficiencies of conversion near 100% are reported in these studies for NO_2 and for NO_y species such as HNO_3, HNO_2, PAN, and organic nitrates. This finding is particularly important for widespread monitoring networks that use commercial instruments, because such instruments without exception use heated catalytic converters (typically molybdenum). Thus, such instruments measure not NO and NO_x, but more nearly NO and total NO_y. Although NO_x is the predominant NO_y species during early morning hours, other NO_y species constitute a substantial percent of the NO_y later in the day, especially in rural areas. The NO_2 value inferred from such measurements may be significantly in error (see below), and may in turn affect the results of models of ambient O_3. The completeness of the measured NO_y value is also questionable because, for example, HNO_3 is readily lost to surfaces, and, in ambient sampling, may be removed within the sampling system before reaching the heated converter.

Other conversion methods for NO_2 have been tried in an effort to achieve higher selectivity. Ferrous sulfate has been used for ambient NO_2 measurements using high-sensitivity research grade CL instruments (e.g., Kelly et al., 1980; Helas et al., 1981; Dickerson et al., 1984). This material is an efficient reducer of NO_2, but also has been found to convert a portion of PAN, and possibly a portion of HNO_2 and organic nitrates (Fehsenfeld et al., 1987). Memory effects and reduction in efficiency can occur because of humidity effects (Fehsenfeld et al., 1987). As a result of these characteristics, use of $FeSO_4$ has given high readings in comparison with spectroscopic instruments and the photolytic NO_2 converter, and its use likely results in overestimating ambient NO_x by a significant amount (Fehsenfeld et al., 1987; Ridley et al., 1988a; Gregory et al., 1990b). Ferrous sulfate has never been used in commercial NO_x instruments and is no longer used in research measurements.

The most specific method for converting NO_2 to NO is photolysis (Kley and McFarland, 1980). In the most common approach, ambient NO_2 is photolyzed to NO by light of 350 to 410 nm from a xenon arc lamp. The method does not produce NO from the major potential interferents present in air (i.e., HNO_3, PAN, and organic nitrates), but less abundant NO_y species such as HNO_2 or HO_2NO_2 may interfere. A detailed description of steps to minimize such interferences is given by Ridley et al. (1988b). As currently used, the photolytic converter appears to be essentially specific for NO_2. However, it does not provide complete conversion of NO_2. Conversion efficiencies are 50 to 60% with a new lamp but may decline to 20% over the course of several weeks (Parrish et al., 1990). Thus, the conversion efficiency must be calibrated repeatedly. This approach has not been implemented with commercial NO detectors but has been implemented with research-grade CL NO instruments for studies of NO_x and NO_y chemistry at a variety of locations (e.g., Buhr et al., 1990; Parrish et al., 1990; Trainer et al., 1991; Parrish et al., 1992, 1993). The photolytic method compares well with other techniques, including spectroscopic methods, even at NO_2 levels as low as 0.05 ppbv (Gregory et al., 1990b). Further improvement of the photolytic converter approach is continuing. Bradshaw et al. (1994) reported on plans to minimize wall effects in the photolytic converter and to use a metal halogen lamp in place of the xenon arc lamp. The metal halogen lamp emits strongly in the proper wavelength region and is much less expensive than the xenon arc lamp, allowing more frequent replacement of the lamp and consequently higher long-term photolytic efficiency.

As noted above, the commercial CL analyzers used for most ambient air NO and NO_x measurements actually measure NO and NO_y. The magnitude of the resulting overestimation of NO_2, determined by difference, obviously depends on the portion of NO_y that is NO_x. The smaller the portion of NO_y that is NO_x, the greater will be the error in the NO_2 determined by difference. In rural/remote areas, where NO_x has undergone extensive conversion to other products during transport from a source region, NO_x may contribute a small fraction of NO_y. In urban areas, close to sources, NO_x may comprise nearly all of NO_y. For example, in measurements at Point Arena, Parrish et al. (1992) report NO_x/NO_y ratios averaging 0.3 in air of marine origin and 0.75 in air subject to continental influence. Buhr et al. (1990) and Parrish et al. (1993) reported measurements at rural sites in eastern North America that indicate NO_x/NO_y ratios ranging from about 0.25 to 0.75, varying with the time of day, with the lowest ratios occurring during daytime, photochemically active periods. Clearly, although the commercial CL instruments are designated as reference methods for NO_2, the great majority of existing ambient air data for NO_2 or NO_x are biased high, due to the inclusion of some portion of other NO_y species. The magnitude of this bias may not be large in urban areas, but, in any case, it is essentially unknown at this time.

Luminol Chemiluminescence Method

This approach is based on the CL reaction of gaseous NO_2 with the surface of an aqueous solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione). Emission occurs primarily between 380 and 520 nm. In commercial instruments, luminol solution flows down a fabric wick that lies vertically on a clear window viewed by a photomultiplier tube. Nitrogen dioxide in sample air passing over the wick produces light, the intensity of which is proportional to the NO_2 concentration. Commercial instruments using this approach are compact, light, and relatively inexpensive and can provide detection limits as low as 0.01 ppbv, with response times below 30 s. The instrument has the advantage of detecting NO_2 directly. However, several difficulties have had to be dealt with in developing the method.

Original reports of the approach (Maeda et al., 1980) indicated positive interferences from O_3 and SO_2 and a negative one from CO_2. Reformulation of the luminol reagent solution has minimized, although not fully eliminated, those interferences (Wendel et al., 1983; Schiff et al., 1986). Reported effects include a slight negative response from NO, and sensitivity to PAN, HNO_2, and O_3 (Wendel et al., 1983; Schiff et al., 1986; Rickman et al., 1989; Kelly et al., 1990; Spicer et al., 1991). Response to NO_2 may be nonlinear at low concentrations (Kelly et al., 1990), although recent reformulation of the reagent apparently has reduced this behavior (Busness, 1992). Evaluation of the luminol NO_2 monitor indicates that great care must be taken in using and calibrating the instrument in order to achieve good precision and accuracy in ambient measurements (Kelly et al., 1990). The monitor has been used widely as a research tool, but has not been used widely in ambient air monitoring nor has it been designated an equivalent method for NO_2.

An O_3 scrubber is available to eliminate the O_3 interference noted above, but it also was found to remove a portion of the NO_2 (Kelly et al., 1990). The luminol approach also has been modified to measure NO, by using a CrO_3 converter that oxidizes NO to NO_2 for detection. Thus NO is detected by difference. This method has the potential for measurement of total NO_x; however, evaluations of the CrO_3 converter are still underway at several laboratories. Given the known interferences in the luminol approach, careful evaluation of this method must be completed before it gains acceptance as an NO measurement method.

An adaptation of the commercial luminol NO_2 detector has been reported to provide measurements of total NO_y, NO_2, and NO_x (Drummond et al., 1992). This adaptation, called the LNC-3M, uses a commercial luminol instrument for NO_2 detection, with a CrO_3 converter for NO_x detection. The NO_x measurement must be corrected for the few percent of the ambient NO_2 that is lost in the CrO_3 converter (Drummond et al., 1992). The NO_y measurement is achieved using a stainless steel converter maintained at 400 °C. Tests indicate that this converter provides a more complete conversion of alkyl nitrates, and consequently a more complete measurement of NO_y, than is provided by either the heated molybdenum converters used in commercial O_3 CL NO_x detectors or the gold converters with CO addition used in research instruments (Drummond et al., 1992). The LNC-3M adds a small amount of NO_2 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 it is in continuous use (Drummond et al., 1992).

Spectroscopic Methods

Several spectroscopic approaches to NO_2 detection have been developed; TDLAS, TTFMS, DOAS, and differential absorption lidar (DIAL) are absorption methods that have been used. The TDLAS method is probably the most commonly used spectroscopic NO_2 method. It can provide high selectivity for NO_2, with a detection limit of 0.1 ppbv, accuracy of ±15%, and a response time on the order of 1 min because of the White cell (Mackay and Schiff, 1987b). The DOAS method is an open-path, long-pathlength system. The detection limit for NO_2 with a 0.8-km pathlength and 12-min averaging time has been reported as 4 ppbv, with measurement accuracy reported as ±10% (Biermann et al., 1988). However, recent improvements have resulted in a commercial DOAS instrument capable of an NO_2 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 NO_2 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 NO_2 detection limit of 0.3 ppt, but is not fully proven for ambient measurements.

Fluorescence methods also have been used for NO_2, 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 NO_2 to NO for detection. Thus NO_2 is ultimately measured, by difference, as NO, but the NO is formed directly by photolysis of NO_2. With a 2-min integration time, an NO_2 detection limit of 12 ppt is reported. The method is highly selective for NO_2, because 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 largely have restricted the use of these NO_2 methods to specific research applications or as reference methods in intercomparisons. In such intercomparisons, absorption measurements have been used most commonly. The TDLAS method has been used in ground-level comparisons with O_3 CL and luminol instruments to provide specific NO_2 measurements (Walega et al., 1984; Sickles et al., 1990; Fehsenfeld et al., 1990) and in an airborne comparison with PF/TPLIF and O_3 CL instruments (Gregory et al., 1990b). A finding of these studies was that the TDLAS consistently read higher than other established methods at very low NO_2 levels (i.e., <0.4 ppbv) (Fehsenfeld et al., 1990; Gregory et al., 1990b).

The spectroscopic NO_2 method most fully developed beyond the research stage is the DOAS technique. Stevens et al. (1993) report testing of a commercial DOAS instrument in North Carolina over 17 days in the fall of 1989. The DOAS measured NO_2 using wavelengths between 400 and 460 nm and achieved a detection limit of 0.6 ppbv, as noted above. Simultaneous measurements of O_2, SO_2, HCHO, and HNO_2 also were provided by the DOAS instrument. Comparison of the DOAS NO_2 results to those from a commercial CL detector showed (DOAS NO_2) = 1.14 × (CL NO_2) + 2.7 ppbv, with an r^2 of 0.93, at NO_2 levels up to 50 ppbv (Stevens et al., 1993). The sensitivity, stability, response time, and multicomponent capability are the primary advantages of the DOAS approach. Further intercomparisons and interference tests are recommended (Stevens et al., 1993).

Passive Samplers

Passive samplers are attractive, inexpensive, and simple means to obtain long-term or personal exposure data for NO_2 or NO_x. The simplest passive sampler for NO_2 is the nitration plate, which is essentially an open dish containing filter paper impregnated with TEA. Nitrogen dioxide diffuses to the paper and is extracted later as NO_2^- for analysis. No diffusion barrier exists in this approach or in a similar approach using a candle-shaped absorber (Kosmus, 1985). Consequently, results are very much subject to ambient conditions and give, at best, a qualitative indication of NO_2 or NO_x.

Addition of a diffusion barrier to the nitration plate concept has led to badge-type passive samplers for NO_2 (e.g., Mulik and Williams, 1986, 1987; Mulik et al., 1989, 1991). In general, such devices use perforated screens, plates, or filters as diffusion barriers on the chemically reactive material, which may be exposed on one or both sides, depending on the application. Extraction of the sorbent then allows measurement of the NO_2 collected, typically as NO_2^- ion. Such a device using TEA as the active material gave very good agreement relative to a CL analyzer in laboratory tests with NO_2 at 10 to 250 ppbv (Mulik and Williams, 1987). However, interferences from PAN and HNO_2 (the latter in both outdoor and indoor air) are expected (Sickles and Michie, 1987). Comparison of ambient NO_2 results in the 5 to 25 $\mu g/m^3$ range (i.e., about 2.5 to 12.5 ppbv) from the passive device to those from TDLAS showed good agreement on average values, but a correlation coefficient (r) of only 0.47 on daily values (Mulik et al., 1989).

Badge-type personal samplers for NO_2 also have been developed by Yanagisawa and Nishimura (1982) (YN) and by Cadoff and Hodgeson (1983) (CH). Triethanolamine is used as the active collecting medium in both samplers, and both use colorimetry as the analytical method for detection of NO_2^-. The samplers differ in that the YN device uses TEA-coated on a cellulose filter, with a Teflon® filter as a diffusion barrier; whereas the CH sampler uses TEA-coated on a glass fiber filter, with a polycarbonate filter as a diffusion barrier. Detection limits are reported to be 0.07 ppm·h (Yanagisawa and Nishimura, 1982) and 0.06 ppm·h (Cadoff and Hodgeson, 1983) for the YN and CH samplers, respectively. Interferences from PAN and HNO_2 are expected (Sickles and Michie, 1987); likewise, the devices are sensitive to the speed of ambient air movement.

Palmes tubes have been developed for NO_2 measurement and adapted to NO measurement as described above. The device has been used for workplace and personal exposure monitoring (Wallace and Ott, 1982) and for ambient air measurements (U.S. Environmental Protection Agency, 1993c). A detection limit of 0.03 ppm·h can be achieved if IC is used to determine the extracted NO_2^- (Mulik and Williams, 1986). Adsorption of NO_2 to the tube walls may raise this limit considerably (Miller, 1988), but this effect can be counteracted by use of stainless steel tubes. The device is sensitive to temperature and wind speed, and PAN and HNO_2 are likely interferences (Sickles and Michie, 1987). In a comparison with two commercially produced NO_2 passive samplers, the Palmes tube showed reasonable accuracy and precision at loadings of 1 to 80 ppm·h. However, the commercial devices were designed for use at relatively high loadings; therefore, this comparison does not support the use of Palmes tubes for ambient air monitoring.

3.5.3.4 Calibration Methods

Calibration of NO measurement methods is done using standard cylinders of NO in nitrogen. Typical NO concentrations in such cylinders are 1 to 50 ppmv. Dilution of such standards with clean air using mass flow controllers can accurately provide NO concentrations in the ambient (i.e., 1 to 100 ppbv) range for calibration. Nitric oxide standards are available

as SRMs from NIST and as commercially available Certified Reference Standards. Commercially available certified NO standards have been shown to be stable and accurate for the specified concentrations.

Standard cylinders of NO_2 in nitrogen or air are sometimes used for NO_2 calibration. These standards are commercially available and are readily diluted to parts-per-billion-volume levels in the same manner as for NO standards. However, instability of the NO_2 levels in such standards has been reported, and caution must be used in relying on NO_2 standards as the primary means of calibration.

Two calibration methods for NO_2 are specified in the Code of Federal Regulations (1987) for calibration of ambient NO_2 measurements: (1) permeation tubes and (2) gas-phase titration.

An NO_2 permeation tube is an inert enclosure, generally of Teflon®, glass and Teflon®, or stainless steel and Teflon®, that contains liquid NO_2. As long as liquid NO_2 is present, NO_2 will permeate through the Teflon® at a rate that depends on the temperature of the tube. Maintaining the permeation tube at a constant temperature (i.e., ±0.1 °C) results in permeation of NO_2 at a constant rate. Dilution of the emitted NO_2 with a flow of dry air or N_2 results in known low NO_2 concentrations for calibration. Nitrogen dioxide permeation tubes are supplied as SRMs by NIST, and tubes are commercially available with a wide range of permeation rates. Permeation tubes are small, simple, reliable, and relatively inexpensive, although constant temperature ovens and dilution systems are required to obtain good results. Nitrogen dioxide permeation tubes are susceptible to moisture, and changes in permeation rate or emission of other species (HNO_3, HNO_2, NO) may occur if they are not kept dry. As with NO_2 cylinder standards, the NO_2 permeation tube requires care as a calibration method for NO_2.

Gas-phase titration uses the rapid reaction of NO with O_3 to produce NO_2 with 1:1 stoichiometry. In practice, excess NO generated from a standard cylinder containing 50 to 100 ppmv NO is reacted with O_3 from a stable source. The resultant decrease in NO concentration, usually measured on the NO channel of a CL NO_x analyzer, equals the concentration of NO_2 generated. Varying amounts of NO_2 can be produced by varying the amount of O_3.

3.6 Ozone Air Quality Models

To plan control strategies to achieve compliance with the NAAQS for O_3 at some future date, it is necessary to predict how O_3 concentrations change in response to prescribed changes in source emissions of precursor species (NO_x and VOCs). This assessment requires an air quality model, which in the case of O_3 prediction is often called a photochemical air quality model. The model, in effect, is used to determine the emission reductions needed to achieve the O_3 air quality standard. For at least a decade, EPA has offered guidelines on the selection of air quality modeling techniques for use in SIP revisions, new source reviews, and studies aimed at the prevention of significant deterioration of air quality.

It is worth noting the interrelated nature of O_3 and other air quality issues. Ozone, PM_{10}, visibility, and acid deposition are all connected as a result of similar sources and complex chemical mechanisms. Consequently, strategies for O_3 abatement that involve reductions of VOC and NO_x emissions also will impact particulate matter, visibility, and acid deposition.

Ozone air quality models provide the ability to address "what if" questions, such as, what if emissions of VOCs or NO_x are reduced? The model can be used as an experiment that cannot be run in the atmosphere. Sensitivity questions can be asked, such as, how important is emissions change A relative to emissions change B? or what is the effect of an X% uncertainty in a particular chemical reaction rate constant on the predicted O_3 levels?

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

Models can be verified by the demonstration of agreement between observations and predictions, but confirmation is inherently partial. Verification of mathematical models of natural systems is always incomplete because complete information on the natural system is never available. Furthermore, model results always include some degree of nonuniqueness because model inputs and parameters are never precisely known. Ozone air quality model applications are most reliable in the domain and conditions where model predictions have been evaluated by extensive, valid data and the comparisons of observations and predictions fall within accepted guidelines.

Historically, the primary measure of model performance has been degree of agreement between observed and predicted O_3 concentrations during simulated episodes, although it now is recognized that comparisons of observations and predictions for other compounds, such as organics and NO_y components, are also important in assessing model performance.

The purpose of Section 3.6 is to review briefly the main elements of O_3 air quality models, to describe several of the current models, to discuss the performance evaluation of these models, and to present examples of the use of the models for determining VOC and NO_x control strategies.

3.6.1 Definitions, Description, and Uses

Air quality models are mathematical descriptions of the atmospheric transport, diffusion, removal, and chemical reactions of pollutants. These models operate on sets of input data that characterize the emissions, topography, and meteorology of a region and produce outputs that describe air quality in that region. Mathematical models for photochemical air pollution first were developed in the early 1970s and have been improved, applied, and evaluated since that time. Much of the history of the field is described in reviews by Tesche (1983), Seinfeld (1988), and Roth et al. (1990).

Photochemical air quality models include treatments of the important physical and chemical processes that contribute to O_3 formation in and downwind of urban areas. In particular, such models contain a representation of the following phenomena (Roth et al., 1990):

- Precursor emissions. The spatial and temporal characteristics of reactive hydrocarbon, CO, and NO_x emissions sources must be supplied as inputs to the model. Hydrocarbon emissions generally are apportioned into groups (e.g., alkanes, alkenes, aromatics, etc.) according to the speciation requirements of the chemical kinetic mechanism embedded in the model.

- Pollutant transport. Once the O_3 precursors are emitted into the atmosphere, they are transported by the wind. When O_3 is formed, it also is subject to transport by the wind. Grid-based models require the preparation of three-dimensional, time-varying fields of wind speed and direction. These values must be specified for each grid cell. Cloud venting and mixing processes that are important on the regional scale also can be included in the pollutant transport description.
- Turbulent diffusion. Ozone and its precursors also are subject to turbulence-related dispersion processes that take place on a subgrid scale. These turbulent diffusion effects usually are represented in grid-based models by the so-called gradient transport hypothesis, where the pollutant flux is assumed to be proportional to the spatial gradient in the concentration field. The turbulent 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 EPA (U.S. Environmental Protection Agency, 1986b) identify two kinds of photochemical model: (1) the grid-based UAM is the recommended model for modeling O_3 over urban areas, and (2) the trajectory model EKMA is identified as an acceptable approach. The 1990 CAAA (U.S. Congress, 1990) mandate that three-dimensional, or grid-based, air quality models, such as UAM, be used in SIPs for O_3 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 that 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 O_3 problem, including the distribution of emissions in the region, the meteorological conditions, and, to some extent, the computational resources available. This space then is 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 vary, depending on the number of vertical layers and the vertical extent of the region being modeled. Increasing the vertical resolution in the computation should be accompanied by increased vertical resolution of the physical parameters used. A compromise generally must

be reached between the better vertical resolution afforded by the use of more vertical layers and the associated increase in computing time. Although aerometric data, such as the vertical temperature profile, which are needed to define the vertical structure of the atmosphere, are generally lacking, it is still important to use enough vertical layers so that vertical transport processes are represented accurately.

There are practical and theoretical limits to the minimum horizontal grid cell size. Increasing the number of cells increases computing and data acquisition effort and costs. In addition, the choice of the dimension of a grid cell implies that the input data information about winds, turbulence, and emissions, for example, are resolved to that scale. The spatial resolution of the concentrations predicted by a grid-based model corresponds to the size of the grid cell. Thus, effects that have spatial scales smaller than those of the grid cell cannot be resolved. Such effects include the depletion of O_3 by reaction with NO near strong sources of NO_x like roadways and power plants. Ozone predictions are sensitive to the choice of grid cell size. The use of a larger grid tends to smooth out VOC and NO_x precursor concentrations, affecting the computed chemical production of O_3. Multigrid models, in which a region with a finer grid resolution is embedded within a larger grid, are an approach to obtain a better resolution of O_3 formation processes in regions of intense source emissions (Odman and Russell, 1991).

Jang (1992) has examined the sensitivity of O_3 predictions to model grid resolution in regional air quality models. A high-resolution version of the Regional Acid Deposition Model (RADM) was used to simulate O_3 formation over the northeastern United States at different grid resolutions. The high-resolution version of RADM, with horizontal grid cell sizes of 20, 40, and 80 km, was operated within the 80-km RADM domain. Coarser grid sizes were found to result in lower resolved emission intensities of NO_x and VOCs. Because of the smearing effect of the large grid sizes, the coarser grid model tended to underpredict the O_3 highs in the areas downwind of cities and overpredict the O_3 lows in the intense NO_x emissions areas. It was found that the impact of model grid resolution on the chemistry of NO_x is more important than that on the chemistry of VOCs, and that model grid resolution has no significant impact on the total amount of odd oxygen ($O_x = O_3 + NO_2$) produced in the models but has great impact on the interactions of chemistry and transport processes that control the balance of O_x. As a result, the coarser grid model tends to predict higher O_3 and lower NO_2 than does the finer grid model, and the coarser grid tends to transport O_x more in the form of O_3, whereas the finer grid model tends to transport the O_x more in the form of NO_2.

Uncertainties arise in photochemical modeling from the basic model components (chemical mechanism and numerical techniques in solving the governing equations) and from inputs to the simulations that reflect the particular episode (boundary and initial conditions, emission inventory, wind field, and mixing depth). Sensitivity studies aim to determine the range of uncertainty in model predictions corresponding to ranges of uncertainty in the basic model components and input quantities. Such studies are valuable in pinpointing those quantities to which model predictions are most sensitive and, therefore, in directing future efforts in reducing the uncertainty in key parameters. These studies are also valuable in assessing the sensitivity of future air quality changes to uncertainties in the base case episode. It is not possible to state general, widely applicable levels of uncertainty for photochemical model inputs and parameters. These will depend on the particular region being modeled, and, in the case of meteorological and emissions inputs, may even depend on the time of day

during the simulation. All model application exercises should include, to the extent possible, an analysis of the uncertainties in model inputs and parameters.

Several grid-based photochemical air quality models have been developed to simulate O_3 production in urban areas or in larger regions. They differ primarily in their treatment of specific atmospheric processes, such as chemistry, and in the numerical procedures used to solve the governing system of equations. These models will be reviewed in Section 3.6.3.

3.6.1.2 Trajectory Models

In the trajectory model approach, a hypothetical air parcel moves through the area of interest along a path calculated from wind trajectories. Emissions are injected into the air parcel and undergo vertical mixing and chemical transformations. The data requirements for trajectory models include: (1) initial concentrations of all relevant pollutants and species; (2) rates of emissions of VOC and NO_x precursors into the parcel along its trajectory; (3) meteorological characteristics, such as wind speed and direction, needed to define the path of the air parcel through the region; (4) mixing depth; and (5) solar ultraviolet radiation.

The key assumption inherent in the trajectory model is that a hypothetical air parcel maintains its integrity along the trajectory. Almost certainly, the parcel assumption fails at night, when flows drift and the atmosphere stratifies; for hilly or mountainous terrain; and under convergence conditions. Thus, the trajectory model concept does not apply in many areas and under a variety of conditions (Liu and Seinfeld, 1975).

Trajectory models provide a dynamic description of atmospheric source-receptor relationships that is simpler and less expensive to derive than that obtained from grid models. Trajectory models are designed to study the photochemical production of O_3 in the presence of sources and vertical diffusion of pollutants; otherwise the meteorological processes are highly simplified.

A simple trajectory model is used in EKMA (Dodge, 1977a). This modeling approach relates the maximum level of O_3 observed downwind of an urban area to the levels of VOCs and NO_x observed in the urban area. It is based on the use of a simple, one-cell moving box model. As the box moves downwind, it encounters emissions of organics and NO_x that are assumed to be uniformly mixed within the box. The height of the box is allowed to expand to account for the breakup of the nocturnal inversion layer. As the height of the box increases, pollutants above the inversion layer are transported into the box. The model is first used to generate a series of constant O_3 lines (or isopleths) as depicted in Figure 3-25. The isopleths show the downwind, peak 1-h O_3 levels as a function of the concentrations of VOCs and NO_x for a hypothetical urban area. These isopleths were generated by carrying out a large number of model simulations in which the initial concentrations and anthropogenic emissions of VOCs and NO_x were varied systematically, whereas all other model inputs were held constant. When it was first conceived, EKMA employed a very simple, highly empirical chemical mechanism and the isopleths generated were for a hypothetical situation in Los Angeles. As understanding of the chemical processes responsible for O_3 formation increased, the EKMA model was updated to include more complete representations of atmospheric chemistry. Although EKMA has employed the CBM-IV mechanism, the same mechanism that is currently being used in several grid-based models, the most recent version allows the input of any mechanism. The EKMA method is

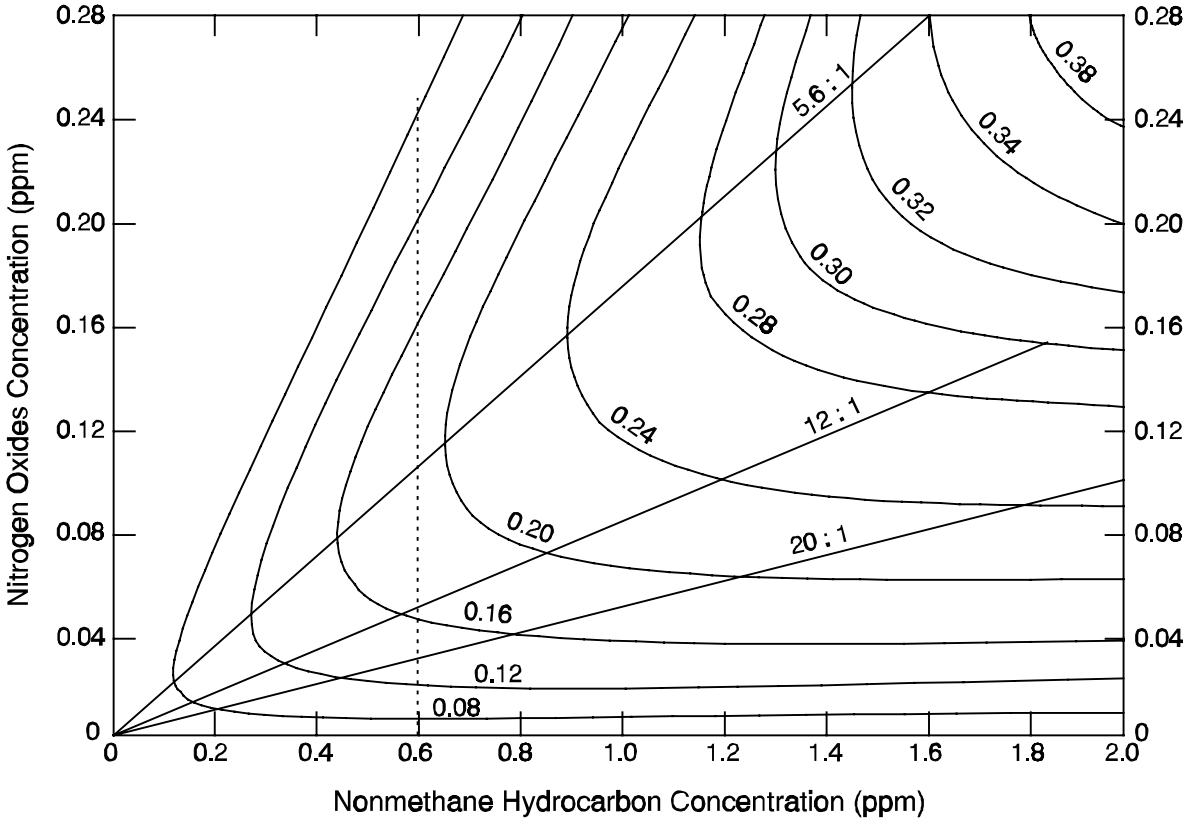


Figure 3-25. Example of Empirical Kinetic Modeling Approach diagram for high-oxidant urban area.

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

now used to generate city-specific isopleth diagrams using information on emissions, transport, and dilution that are appropriate to the particular city being modeled.

City-specific O_3 isopleths can be used to estimate the reduction in NMHC or NO_x levels needed to achieve the NAAQS for O_3 in a specific urban area. The first step is to determine the early-morning NMHC/NO_x ratio for the urban area in question and the maximum 1-h downwind O_3 concentration. Both the NMHC/NO_x ratio and the peak O_3 concentration are obtained from air monitoring data. These two values define a point on the isopleth surface and, from this point, the percentage reductions in NMHC or NO_x, or both, needed to achieve the O_3 NAAQS can be determined.

As examination of Figure 3-25 reveals, for an NMHC concentration of 0.6 ppmC, for example, increasing NO_x leads to increased O_3 until NMHC/NO_x ratios of about 5:1 to 6:1 are reached; further NO_x increases, leading to lower NMHC/NO_x ratios, inhibit O_3 formation. Thus, in this example, there is a "critical" ratio (in the range of 5:1 to 6:1) at which the NO_x effect on O_3 changes direction. Besides this "critical" ratio, an "equal control" NMHC/NO_x ratio also exists, above which the reduction of NO_x is more beneficial in terms of O_3 reduction than an equal percentage reduction in NMHC. This ratio, for the isopleths

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

The EKMA-based method for determining control strategies has some limitations, the most serious of which is that predicted emissions reductions are critically dependent on the initial NMHC/NO_x ratio used in the calculations. This ratio cannot be determined with any certainty because it is expected to be quite variable in time and space in an urban area. Another limitation is that trajectory models have limited spatial and temporal scopes of application. They are generally 1-day models, simulating only one cell at a time. Another problem with the use of morning NMHC/NO_x ratios is the failure to account for photochemical evolution as urban emissions are carried downwind. As demonstrated in simulations by Milford et al. (1989) and in smog chamber studies by Johnson and Quigley (1989), an urban plume that is in the VOC-controlling regime (low NMHC/NO_x ratio) near city center can move increasingly into the NO_x-controlling regime (high NMHC/NO_x ratio) as the air parcels age and move downwind. This progression occurs because NO_x is photochemically removed from an aging plume more rapidly than VOCs, causing the VOC/NO_x ratio to increase. As demonstrated by Milford et al. (1989), the implication of this evolution is that different locations in a large urban area can show very different O_3 sensitivities to VOC and NO_x changes. Because of this and other drawbacks, the 1990 CAAA (U.S. Congress, 1990) require that grid-based models be used in most O_3 nonattainment areas.

3.6.2 Model Components

3.6.2.1 Emissions Inventory

The spatial and temporal characteristics of VOC and NO_x emissions must be supplied as inputs to a photochemical air quality model. Emissions from area and point sources are injected into ground-level grid cells, and emissions from large point sources are injected into upper level cells. Total VOC emissions generally are apportioned into groups of chemically similar species (e.g., alkanes, alkenes, aromatics, etc.) according to the requirements of the chemical mechanism. This apportionment may be accomplished using actual emission sampling and analysis or be based on studies of similar emission sources. Recognition of potential undercounting in existing inventories has spurred efforts to improve the accuracy of emissions inventories. In fact, at present, the emissions inventory is the most rapidly changing component of photochemical models. It has been recognized that both mobile and stationary source components have been highly uncertain and that there is significant ongoing effort to improve the accuracy of emissions inventories.

Some emissions terminology is as follows (Tesche, 1992):

- Emissions data—the primary information used as input to emissions models.
- Emissions model—the integrated collection of calculational procedures, or algorithms, properly encoded for computer-based computation.
- Emissions estimates—the output of emissions models; used as input to photochemical models.

- Emissions inventory—the aggregated set of emissions estimate files.
- Emissions model evaluation—the testing of a model's ability to produce accurate emissions estimates over a range of source activity and physicochemical and meteorological conditions.

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

- Spatial allocation of precursor emissions (VOCs, NO_x, CO):
  - Actual location of individual point sources;
  - Spatial allocation by gridding surrogates;
  - Assignment of surrogates to other categories.
- Stack parameters for point sources:
  - Temperature, height, diameter, and exit velocity.
- Speciation of VOC emissions for CBM-IV mechanism:
  - Region-specific speciation profiles;
  - EPA default speciation profiles.
- Temporal allocation of precursor emissions:
  - Operating schedules for individual point sources;
  - 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), 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). The consistency of existing inventories was improved in 1990 when EPA released the Emissions Preprocessor System (EPS) as a component of the UAM (U.S. Environmental Protection Agency, 1992b). 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 that are needed by a photochemical grid model.

A step beyond the EPS is the Emissions Modeling System (EMS)[1] (Tesche, 1992). The EMS 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 for use in 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.

As a result of a variety of independent studies, it recently has been determined that urban VOC emissions inventories, particularly motor vehicle emissions, have been significantly understated. These studies include tunnel studies (Pierson et al., 1990) and comparisons of ambient and emission inventory VOC/NO_x ratios (Fujita et al., 1992).

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

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 (Tesche, 1987; Kessler, 1988):

(1) Objective analysis procedures that interpolate observed surface and aloft wind speed and direction data throughout the modeling domain;
(2) Diagnostic methods in which the mass continuity equation is solved to determine the wind field;
(3) 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; or
(4) Hybrid methods that embody elements from both diagnostic and prognostic approaches.

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.

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).

In recent years, attempts have been made to combine the best features of objective analysis and pure diagnostic wind modeling. The current release of EPA's UAM-IV includes the Diagnostic Wind Model (DWM) as the suggested wind-field generator for this urban-scale photochemical model. The DWM (U.S. Environmental Protection Agency, 1990c) is representative of this class of hybrid objective-diagnostic models. The DWM combines the features of the Complex Terrain Wind Model (CTWM) (Yocke, 1981) and the objective wind interpolation code developed at the California Institute of Technology (Goodin et al., 1980). In the DWM, a two-step procedure normally is followed. First, a "domain-scale" wind is

estimated from available surface and upper-air synoptic data. This initial field consists of a single wind vector (e.g., horizontal homogeneity) for each elevation. The domain-scale wind is adjusted using procedures derived from the CTWM for the kinematic effects of terrain such as lifting, blocking, and flow acceleration. Thermodynamically generated influences such as mountain-valley winds are parameterized. This first step produces a horizontally varying field of wind speed and direction for each vertical layer within the DWM modeling domain. Typically, 10 to 12 vertical layers are used. In the second step, available hourly surface and upper air measurements are combined objectively with the step 1 hourly diagnostic flow fields to produce a resultant wind field that matches the observations at the monitoring points and obeys the general constraints of topography in regions where data are absent. The DWM contains a number of user-specified options whereby different final flow fields may be produced, depending on selection of various smoothing and weighting parameters. The final output of the DWM is a set of hourly averaged horizontal wind fields for each model layer.

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

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

Prognostic Modeling

In prognostic meteorological modeling, atmospheric fields are computed based on numerical solutions of the coupled, nonlinear conservation equations of mass, momentum, energy, and moisture. Derivations of these equations are presented extensively in the literature (Haltiner, 1971; Pielke, 1984; Seinfeld, 1986; Cotton and Anthes, 1989). Many prognostic models have been developed for computing mesoscale wind fields, as shown in the

recent survey by Pielke (1989), and they have been applied to a variety of problems, including the study of land-sea and land-lake circulations. Available prognostic models range from relatively simple one-dimensional representations to complex three-dimensional codes.

Prognostic wind models are attractive because they explicitly address the various 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).

Three ongoing regional O_3 modeling programs in the United States are using prognostic models to drive regional O_3 models. These include LMOS; SARMAP; and a regional O_3 modeling program in Southeast Michigan, Northern Ohio, and Southwest Ontario. Part of EPA's long-range plan (in the Office of Research and Development [ORD]) for model development is to construct a "third" generation modeling framework referred to as MODELS 3 (Dennis and Novak, 1992). 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 EPA for this purpose.

Activities are currently underway in LMOS to supply prognostic model fields to EPA's ROM for use in simulating regional O_3 distributions in four multiple-day O_3 episodes extensively monitored during the 1991 field program in the midwest. The EPA will be utilizing ROM2.2 (version 2.2) with fields obtained from CAL-RAMS (Lyons et al., 1991) to examine whether prognostic model output gives improved regional O_3 estimates (Guinnup and Possiel, 1991).

The SARMAP program is the modeling and data analysis component of a multiyear collaboration between two projects, SJVAQS and AUSPEX. The major near-term objective of SARMAP is to understand the processes that lead to high O_3 concentrations in the San Joaquin Valley of California. An overview of the regional meteorological and air quality modeling approach of SARMAP is described by Tesche (1993). For SARMAP, the MM5 model was chosen as the "platform" prognostic meteorological model because of its broad application history; its demonstrated reliability on large domains, requiring spatially and temporally varying boundary conditions; and its capability for four-dimensional data

assimilation (FDDA)—needed for longer-range simulations (see Section 3.6.2.2). All of these attributes are crucial to the success of mesoscale meteorological modeling.

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. However, the meteorological fields generated by a prognostic model do not always agree with observational data. Numerical approximations, physical parameterizations, and initialization problems are among the potential sources of error growth in model forecasts that can cause model solutions to deviate from actual atmospheric behavior. Methods that have been devised over the past 20 years to mitigate these problems are described below.

"Post-processing" refers to methods whereby output fields from prognostic models are selectively adjusted through a series of objective techniques with the aim of improving the realism of the resultant fields. Examples of this procedure (sometimes referred to as objective combination) are given by Cassmassi et al. (1991) in the Los Angeles Basin, Kessler and Douglas (1989) in the South Central Coast Air Basin, and Moore et al. (1987) in the San Joaquin Valley.

Ideally, a prognostic model should be initialized with spatially varying, three-dimensional fields (i.e., wind, temperature, moisture) that represent the state of the atmosphere at the initial simulation time. A prognostic model that is initialized with such fields, however, can generate large nonmeteorological "waves" when the initial conditions do not contain a dynamic balance consistent with the model formulation (Hoke and Anthes, 1976; Errico and Bates, 1988). The objective of an initialization procedure is to bring the initial conditions into dynamic balance so that the model can integrate forward with a minimum of noise and a maximum of accuracy (Haltiner and Williams, 1980). Dynamic initialization makes use of a model’s inherent adjustment mechanism to bring the wind and temperature into balance prior to the initial simulation time. In this technique, a "presimulation" integration of the model equations produces a set of dynamically balanced initial conditions. By allowing the simulation to begin with a balanced initial state, this technique reduces the generation of meteorological noise and thus improves the quality of the simulation.

Four-Dimensional Data-Assimilation Techniques

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

A recent example of the use of FDDA in regional-scale applications with the MM4/RADM model is given by Stauffer and Seaman (1990). Attempts to apply FDDA in

support of urban-scale photochemical grid modeling are described by Tesche et al. (1990b) and McNally (1990) for the San Diego Air Basin and by Stauffer et al. (1993) for the Grand Canyon region of Arizona. Currently, FDDA is being used in the CAL-RAMS simulations in the LMOS program (Lyons et al., 1991) and in the MM5 simulations for SARMAP (Seaman, 1992).

3.6.2.3 Chemical Mechanisms

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.

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

No single chemical mechanism is currently considered "best". Both UAM-IV and ROM utilize the carbon-bond mechanism (CBM-IV), which, along with the SAPRC (Statewide Air Pollution Research Center, University of California, Riverside) and RADM mechanisms, is considered to represent the state of the science (Tesche et al., 1993; National Research Council, 1991). Agreement among mechanisms is better for O_3 than for other secondary pollutants (Dodge, 1989, 1990; National Research Council, 1991), raising concern that the mechanisms may suffer from compensating errors. These mechanisms are at least 5 years old and often are tested on much older smog chamber data.

The chemical mechanisms used in existing photochemical O_3 models contain uncertainties that may limit the accuracy of the model predictions. The reactions that are included in these mechanisms generally fall into one of three categories.

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

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

- The *n*-alkanes comprise approximately one-half of the major carbon emissions in urban areas. Reaction rates are relatively slow. The only important reaction is with the hydroxyl radical. For alkanes C_4 or below, the chemistry is well understood and the reaction rates are slow. For C_5 and higher alkanes the situation is more complex because few reaction products have been found.
- Branched-chain alkanes have rates of reaction that are highly dependent on structure. Rate constants have been measured for only a few of the branched alkanes, and reaction products for this class of organics are not well characterized.
- Alkenes are reactive with OH, O_3, and the NO_3 radical. Most rate constants of these reactions are known. Alkenes make up ≤15% of the emitted carbon and constitute about 25% of the hydrocarbon reactions in urban areas. Ozone reaction products are not well characterized, and the mechanisms are poorly understood. Mechanisms for the NO_3 radical are also uncertain.
- Aromatics constitute about 15 to 20% of the carbon compounds emitted and 25% of the hydrocarbons reacting in urban areas. Aromatics have been studied frequently, but only a few reaction products have been well characterized. Aromatics act as strong NO_x sinks under low NO_x conditions.

Mechanisms used in photochemical air quality models thus have uncertainties, largely attributable to a lack of fundamental data on products and product yields. The missing information necessitates that assumptions be made. Current mechanisms provide acceptable overall simulation of O_3 generation in smog chamber experiments. Specific VOCs may, however, be simulated poorly, and products other than O_3 may not be simulated accurately. Existing mechanisms are mostly applicable to single-day, high NO_x conditions because those are the conditions of almost all smog chamber experiments. Low NO_x condition simulations are verified less thoroughly. Fundamental kinetic data are needed on the photooxidation of aromatics, higher alkanes, and higher alkenes to fill in areas of uncertainty in current mechanisms. Whereas these uncertainties are important and require continued research to remove, the uncertainties are likely not such that general conclusions about the relative roles of hydrocarbons and NO_x in O_3 formation will be changed by new data.

3.6.2.4 Deposition Processes

Species are removed from the atmosphere by interaction with ground-level surfaces, so-called dry deposition, and by absorption into airborne water droplets followed by transport of the water droplets, wet deposition. Dry deposition is an important removal process for ozone and other species on both the urban and regional scales and is included in all urban and regional scale models as a contribution to the ground-level flux of pollutants. Wet deposition is a key removal process for gaseous species on the regional scale and is included in regional scale acid deposition models. Urban-scale photochemical models generally have not included a treatment of wet deposition as O_3 episodes do not occur during periods of significant clouds or rain.

Dry Deposition

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

It is customary to interpret the dry deposition process in terms of the electrical resistance analogy, where transport of material to the surface is assumed to be governed by three resistances in series: (1) the aerodynamic resistance (r_a), (2) the quasi-laminar layer resistance (r_b), and (3) the surface or canopy resistance (r_s) (Wu et al., 1992). The aerodynamic resistance characterizes the turbulent transport through the atmosphere from reference height z_r down to a thin layer of stagnant air very near the surface. The molecular-scale diffusive transport across the thin quasi-laminar sublayer near the surface is characterized by r_b. The chemical interaction between the surface and the pollutant of interest once the gas molecules have reached the surface is characterized by r_c. The total resistance (r_t) is the sum of the three individual resistances, and is, by definition, the inverse of the deposition velocity, $1/v_d = r_t = r_a + r_b + r_s$. Note that the deposition velocity is small when any one of the resistances is large. Hence, either meteorological factors or the chemical interactions on the surface can govern the rate of dry deposition.

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

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

<u>McRae and Russell (1984):</u>
$HNO_3 > SO_2 > NO_2 \approx O_3 > PAN > NO$;
<u>Derwent and Hov (1988):</u>
$HNO_3 > SO_2 = O_3 > NO_2 > PAN$;
<u>McRae et al. (1982b):</u>
$O_3 > NO_2 > PAN > NO > CO$; and
<u>Chang et al. (1987):</u>
$HNO_3 > H_2O_2 > NH_3 > HCHO > O_3 = SO_2 = NO_2 = NO > RCHO$.

There is general agreement that HNO_3 is removed at the highest observed rates, which is consistent with the relative deposition rates observed by Huebert and Robert (1985). Most of the surveys are roughly consistent with the relative deposition velocity ordering seen in the experiments of Hill and Chamberlain (1976): diffusion-limited acids > $SO_2 > NO_2 \approx O_3 > PAN > NO > CO$. This suggests surface resistance values should be ordered approximately as $CO > NO > PAN > O_3 \approx NO_2 > SO_2 > HNO_3 = 0$. However, there is still a substantial range of variability in reported deposition velocities. For example, McKeen et al.

(1991) calculated dry deposition velocities for HNO_3, O_3, and PAN of 10, 0.5, and 0.3 cm s^{-1}, respectively. Note that a large deposition velocity for HNO_3 will limit the lifetime of HNO_3 relative to O_3 in photochemically aged air.

There are a significant number of other gases for which there are no surface resistance data and for which values must be estimated using expert judgment. The values should be consistent with the existing experimental values for vegetative surfaces and should preserve the apparent rank ordering among the pollutant species (discussed above). For O_3, surface resistance values by land-use type and season recommended by Sheih et al. (1986) and Wesely (1988) are appropriate. For NO, NO_2, NH_3, H_2O_2, HCHO, and CH_3CHO, the surface resistance values for each land use can be estimated from that for SO_2 (Wesely, 1988), except different proportionality factors should be used for NO and NO_2.

The treatment of dry deposition is perhaps the most primitive of the scientific modules in photochemical air quality models. Knowledge of deposition rates is limited, and uncertainties in deposition velocities are high. For travel times of one to several days, the quantities of pollutants that are predicted to be removed by dry deposition can be substantial for those species with appreciable deposition velocities. Setting all species deposition velocities to zero in a model provides an indication of the importance of dry deposition relative to other processes influencing pollutant dynamics. Further effort to describe the dynamics of deposition are needed, together with evaluation against available data that can be used to test deposition modules.

Wet Deposition

Wet deposition refers to the removal of gases and particles from the atmosphere by precipitation events, through incorporation of gases and particles into rain, cloud, and fog water followed by precipitation at the earth's surface. Removal of gases and particles during snow falls is also wet deposition. Wet removal of gases arises from equilibrium partitioning of the chemical between the gas and aqueous phases (Bidleman, 1988; Mackay, 1991). This partitioning can be defined by means of a washout ratio, Wg, with Wg = [C]rain/[C]air, where [C]rain and [C]air are the concentrations of the chemical in the aqueous and gas phases, respectively. Because Wg is the inverse of the air/water partition coefficient, K_{aw}, then Wg = RT/H, where R is the gas constant, T is the temperature, and H is the Henry's Law constant (Mackay, 1991).

Particles and particle-associated chemicals are efficiently removed from the atmosphere by precipitation events, and the washout ratios for particles, Wp, are typically in the range 10^4 to 10^6 (Eisenreich et al., 1981; Bidleman, 1988). Wet deposition is important for particles (and particle-associated chemicals) and for those gas-phase compounds with washout ratios of $Wg \geq 10^4$. Examples of such gaseous chemicals are HNO_3, H_2O_2, phenol, and cresols, all of which are highly soluble in water. Formaldehyde is present in the aqueous phase as the glycol, $H_2C(OH)_2$, and has an effective washout ratio of 7×10^3 at 298 K (Betterton and Hoffmann, 1988; Zhou and Mopper, 1990). Note that the importance of wet deposition may depend on whether the chemical is present in the gas phase or is particle-associated. For example, the gas-phase alkanes have low values of Wg and are inefficiently removed by wet deposition, whereas the particle-associated alkanes are efficiently removed by wet deposition (Bidleman, 1988), through removal of the host particles.

3.6.2.5 Boundary and Initial Conditions

When a grid-based photochemical model is applied to simulate a past pollution episode, it is necessary to specify the concentration fields of all the species computed by the model at the beginning of the simulation. These concentration fields are called the initial conditions. Throughout the simulation, it is necessary to specify the species concentrations, called the boundary conditions, in the air entering the three-dimensional geographic domain.

Three general approaches for specifying boundary conditions for urban-scale applications can be identified: (1) use the output from a regional-scale photochemical model, (2) use objective or interpolative techniques with ambient observational data, or (3) use default regional background values and expand the area that is modeled for urban areas sufficiently isolated from significant upwind sources.

In the ideal case, observed data would provide information about the concentrations for all the predicted species at the model's boundaries. An alternative approach is to use regional models to set boundary and initial conditions. This is, in fact, preferred when changes in these conditions are to be forecast. In any event, simulation studies should use boundaries that are far enough from the major source areas of the region that concentrations approaching regional values can be used for the upwind boundary conditions. Boundary conditions at the top of the area that is being modeled should use measurements taken from aloft whenever they are available. Regional background values often are used in lieu of measurements. An emerging technique for specifying boundary conditions is the use of a nested grid, in which concentrations from a larger, coarse grid are used as boundary conditions for a smaller, nested grid with finer resolution. This technique reduces computational requirements compared to those of a single-size, fine-resolution grid.

Initial conditions are determined mainly with ambient measurements, either from routinely collected data or from special studies. Where spatial coverage with data is sparse, interpolation can be used to distribute the surface ambient measurements. Because few measurements of air quality data are made aloft, it generally is assumed that species concentrations are initially uniform in the mixed layer and above it. To ensure that the initial conditions do not dominate the performance statistics, model performance should not be assessed until the effects of the initial conditions have been swept out of the grid.

3.6.2.6 Numerical Methods

The core of a grid-based O_3 air quality model is the numerical solution of the three-dimensional atmospheric diffusion equation (McRae et al., 1982c). The central numerical schemes involve horizontal advection and simultaneous vertical mixing, advection, and chemistry. A possible source of model inaccuracy is the numerical method used to solve the governing equations. The solution of chemical kinetics is generally the most computationally intensive step in O_3 air quality models. To compute the rate of chemical reaction one essentially must solve a system of stiff nonlinear ordinary differential equations. The desirable characteristics of the integration routine are speed and stability, at a certain prescribed level of accuracy. The chemistry integration routines used in several ozone air quality models are based on the implicit, hybrid, exponential scheme developed by Young and Boris (1977). The integration is stable, efficient, and sufficiently accurate. It has been concluded from several studies that the numerical solution of the vertical/chemical portion of the model is less likely to be a source of O_3 prediction inaccuracy (Odman et al., 1992) than the horizontal advection, numerical method (McRae et al., 1982; Chock, 1985, 1991; Dabdub and Seinfeld, 1994). Although the horizontal transport computations typically consume only a small fraction of the total computer time, it is well known that numerical diffusion and

dispersion degrade the computed solution and that available methods differ greatly in their numerical performance in this regard (Chock, 1985, 1991; Dabdub and Seinfeld, 1994). Continued work on optimizing the numerical methods used in O_3 air quality models is necessary.

3.6.3 Urban and Regional Ozone Air Quality Models

Several grid-based models have been widely used to evaluate O_3 and acid deposition control strategies.

- The Urban Airshed Model, developed by Systems Applications, Inc., has been, and continues to be, applied to urban areas throughout the country. It is described in Section 3.6.3.1. The current EPA-approved version is UAM-IV. The UAM-V, which has been developed for LMOS, is a nested regional-scale model.
- The California Institute of Technology (CIT) model has been applied to California's South Coast Air Basin (McRae et al., 1982a,b; McRae and Seinfeld, 1983; Milford et al., 1989; Harley et al., 1993).
- The ROM, developed by EPA, has been applied to the northeastern and southeastern United States (Schere and Wayland, 1989a,b). It is described in Section 3.6.3.2.
- The Acid Deposition and Oxidant Model (ADOM) was developed by ENSR Consulting and Engineering for the Ontario Ministry of the Environment and Environment Canada (Venkatram et al., 1988) and the German Umweltbundesamt. Its primary application has been to acidic deposition.
- The RADM was developed by NCAR and the State University of New York for 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 based nominally 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 nondivergent wind field, are employed in each model. The regional models, ROM, RADM, ADOM, and STEM-II, address the vertical redistribution of pollutants resulting from the presence of cumulus clouds.

Table 3-21. Grid-Based Urban and Regional Air Pollution Models: Overview of Three-Dimensional Air Quality Models[a]

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) Tesche et al. (1992) U.S. Environmental Protection Agency (1990a,b,c; 1992b) Scheffe and Morris (1993)	Tesche et al. (1993)
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. (1991b)
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)

[a]See Appendix A for abbreviations and acronyms.

Table 3-22. Grid-based Urban and Regional Air Pollution Models: Treatment of Emissions and Spatial Resolution[a]

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

[a]See Appendix A for abbreviations and acronyms.

Table 3-23. Grid-based Urban and Regional Air Pollution Models: Treatment of Meteorological Fields, Transport, and Dispersion[a]

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.

[a]See Appendix A for abbreviations and acronyms.

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 also are influenced by cloud thickness. At present, only RADM, ADOM and STEM-II treat wet deposition. The treatment of dry deposition in the models also is summarized in Table 3-25.

Regional-scale modeling is an important contributor to the development of boundary conditions for urban-scale models. In recent years, regional-scale modeling has been receiving increased attention as the need for addressing interlinked air quality problems at broader scales is increasing. At the expanded spatial and temporal scales of regional-scale models, the simulation of certain dynamic processes becomes more critical. For example, in regional-scale models the treatment of biogenic VOC emissions and removal by dry and wet deposition generally require greater attention and accuracy than at the urban scale. On the other hand, the exact mechanistic details of the oxidation of some highly reactive VOCs may be somewhat less important.

More detailed descriptions now will be presented for UAM, ROM, and RADM. The UAM is described, as it is specified officially by EPA, as a grid-based model for urban-scale O_3 control strategy determination. The regional-scale O_3 model, ROM, is being used by EPA to evaluate O_3 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 O_3/acid deposition model, RADM has been used to evaluate combined O_3 and acid deposition abatement strategies for the northeastern United States and Canada.

The EPA 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 (1990a,b,c; 1992b) and a comprehensive evaluation by Tesche et al. (1993). 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 horizontally.

The original UAM developed by Reynolds et al. (1973) simulated the dynamic behavior of six pollutants: (1) reactive and (2) unreactive hydrocarbons, (3) NO, (4) NO_2, (5) O_3, and (6) CO. Since 1977, the UAM has employed various versions of the CBM. Currently, the model utilizes the CBM-IV Mechanism (Gery et al., 1988, 1989), which treats

Table 3-24. Grid-based Urban and Regional Air Pollution Models: Treatment of Chemical Processes[a]

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 and 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 and 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 and 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 and 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

[a]See Appendix A for abbreviations and acronyms.

Table 3-25. Grid-based Urban and Regional Air Pollution Models: Treatment of Cloud and Deposition Processes[a]

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 precipitating cumulus clouds, precipitating stratus clouds, and 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 cumulus clouds and 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.

[a]See Appendix A for abbreviations and acronyms.

36 reacting species. Reactive organic compounds include alkanes, alkenes, aromatics, and aldehydes, and nitrogen-bearing species include HNO_2, HNO_3, and PAN.

Under development at the time of writing of the present document is version V of UAM (Morris et al., 1991, 1992). This version (UAM-V) contains the following features: the ability to treat two-way interactive nested grids; the use of state-of-the-science treatment of atmospheric, meteorological, and chemical processes; the treatment of subgrid-scale plume processes using a plume-in-grid algorithm; and the use of structured programming techniques to take advantage of computational speed enhancement opportunities offered by the current and next generation of computers.

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 O_3 over regional domains and for episodes of up to 15 days in duration. These processes include horizontal transport; atmospheric chemistry and subgrid-scale chemical processes; nighttime wind shear and turbulence associated with the low-level nocturnal jet; the effects of cumulus clouds on vertical mass transport and photochemical reaction rates; mesoscale vertical motions induced by terrain and the large-scale flow; terrain effects on advection, diffusion, and deposition; emissions of natural and anthropogenic O_3 precursors; and dry deposition. The processes are simulated mathematically 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 model objectively both regional winds and diffusion. The three model layers of ROM are prognostic (predictive) and are free to expand and contract locally in response to changes in the physical processes occurring within the layers. During an entire simulation period, horizontal advection and diffusion and gas-phase chemistry are modeled in the 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 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, the thermal internal boundary layer that often exists over large lakes or near sea coasts, and 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 O_3-concentration periods; the base of Layer 3 is typically 1 to 2 km above the ground. Relatively clean tropospheric air is assumed 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

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)	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 (NEROXA) 89.00 W to 67.00 W Longitude 35.00 N to 47.00 N Latitude 88 × 72 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)
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)	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 (SEROXA) 98.75 W to 76.25 W Longitude 27.67 N to 37.67 N Latitude 90 × 60 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)

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 from the ground to well above the top of the mixed layer. These types of clouds are termed fair-weather cumulus because atmospheric conditions are such that the clouds do not grow to the extent that precipitation forms. The dynamic effects of this transport process and daytime cloud evolution can have significant effects on the chemical fate of pollutants. Within the ROM system, a submodel parameterizes the above-cloud flux process and the subsequent impact on mass fluxes among all layers of the model. In the current implementation of the chemical kinetics, liquid-phase chemistry is not included, and, thus, part of the effects from the cloud flux processes are not accounted for in the simulations. The magnitude of the mass flux proceeding directly from the surface layer to the cloud layer is modeled as being proportional to the observed amount of cumulus cloud coverage and inversely proportional to the observed depth of the clouds.

Horizontal transport within the ROM system is governed by hourly wind fields that are interpolated from periodic wind observations made from upper-air soundings and

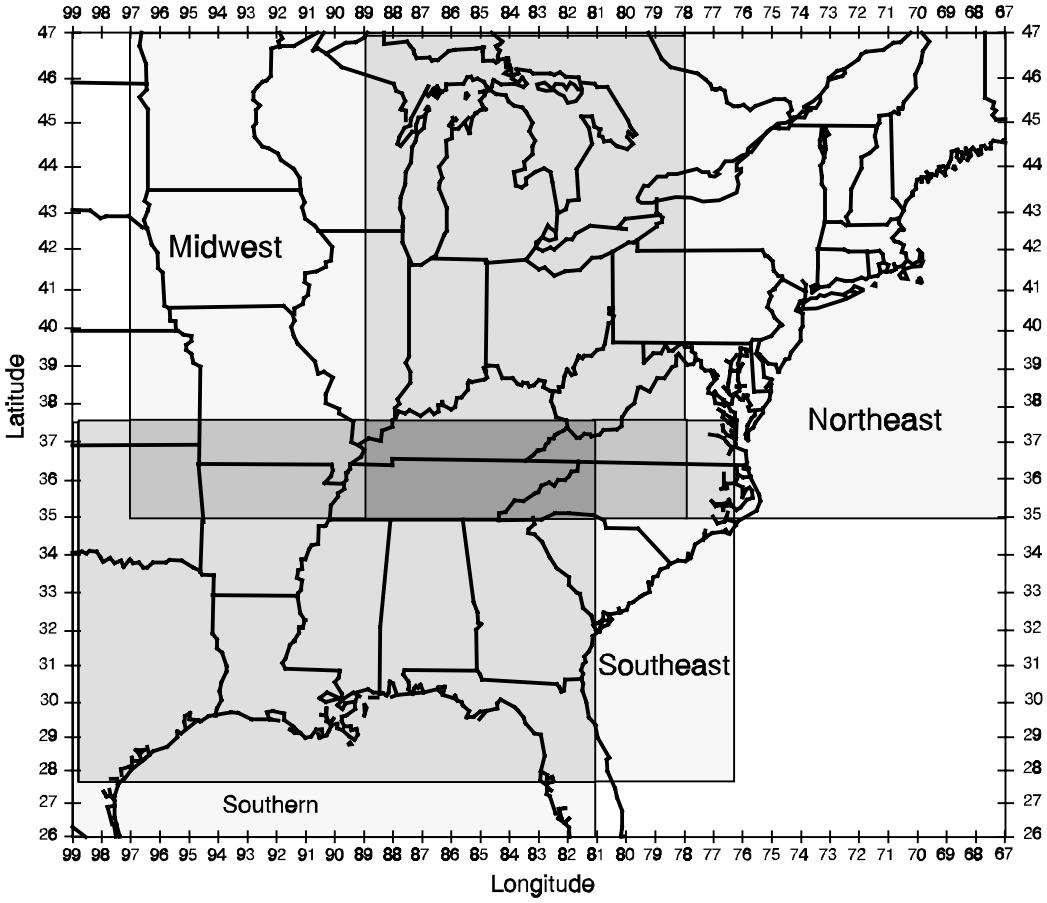


Figure 3-26. Regional oxidant model superdomain with modeling domains.

surface measurements. During the nighttime simulation period, the lowest few hundred meters of the atmosphere above the ground may become stable as a radiation inversion forms. Wind speeds increase just above the top of this layer, forming the nocturnal jet. This jet is capable of carrying O_3, other reaction products, and emissions injected aloft considerable distances downwind. This phenomenon is potentially significant in modeling regional-scale air quality and is implicitly treated by the model, where the definition of Layer 1 attempts to account for it.

The ROM system requires five types of "raw" data inputs: (1) air quality, (2) meteorology, (3) emissions, (4) land use, and (5) topography.

Air quality data required by the ROM include initial conditions and boundary conditions. The model usually is initialized 2 to 4 days before the start of the period of interest with clean tropospheric conditions for all species. This period of interest is called an "episode" and usually lasts around 15 days. Ideally, the initial condition field will have been transported out of the model domain in advance of the portion of the episode of greatest interest. Upwind lateral boundary conditions for O_3 are updated every 12 h based on measurements, except for the large superdomain, where tropospheric background values are

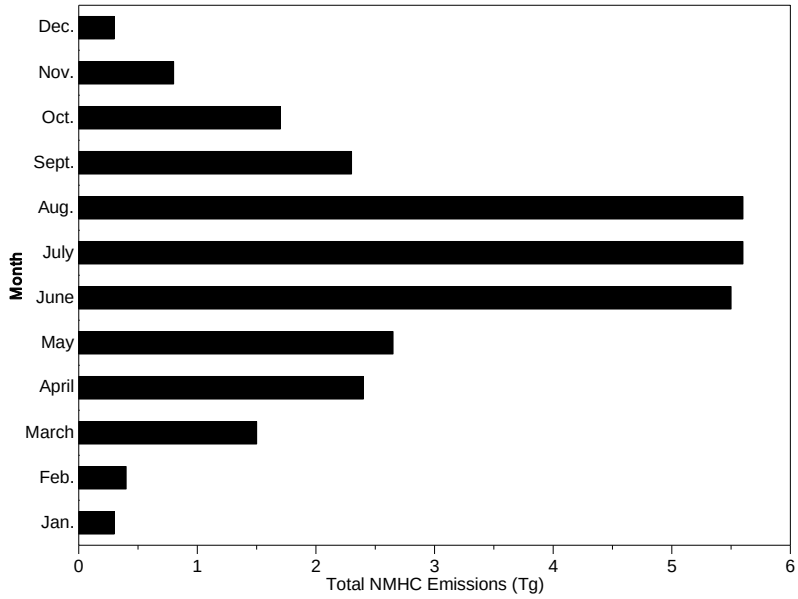


Figure 3-24. Estimated biogenic emissions of volatile organic compounds in the United States as a function of season.

Source: Fehsenfeld et al. (1992).

summertime anthropogenic VOC effect should be somewhat larger for southern regions. This is a very small change, however, relative to the uncertainty associated with VOC emission estimates. In an earlier discussion of the NAPAP inventory, VOC emissions from manmade sources were considered to be almost independent of season.

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 O_3. Larger summertime emissions of VOCs will enhance O_3 production in urban areas. Biogenic VOC sources in the vicinity of urban areas can contribute significant quantities of reactive hydrocarbons to the urban O_3 precursor mix (Cardelino and Chameides, 1990).

3.4.2 Concentrations of Precursor Substances in Ambient Air

The volatile organic compounds, excluding CH_4, often are referred to as 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 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 chemical reactions and increases in mixing depths and consequent increases in dilution volumes. Photochemical

atmospheric reactions also can rapidly convert NO to NO_2, 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 the Empirical Kinetics Modeling Approach (EKMA), most of the measurements available emphasize the 6 a.m. 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 O_3 and other photochemical products.

3.4.2.1 Nonmethane Organic Compounds

In earlier measurements based on GC analyses made during a number of different studies in urban areas between 1969 and 1983, the mean 6 a.m. to 9 a.m. NMHC concentrations were reported to range from 0.324 to 3.388 ppm carbon (ppmC) (U.S. Environmental Protection Agency, 1986a). The highest NMHC concentrations were those measured at sites in Los Angeles.

A program for analysis of NMOCs and NO_x in the months of June through September was conducted in a considerable number of U.S. cities during the 1980s. The results obtained from measurements made during the 6 a.m. to 9 a.m. period at sites in 22 cities in 1984 and 19 cities in 1985 have been subjected to statistical analysis and interpretation (Baugues, 1986). The total NMOC measurements throughout the June through September periods in these cities were obtained by the cryogenic preconcentration-direct flame ionization detection method (PDFID) (McElroy et al., 1986). In addition, during about 15% of the 6 a.m. to 9 a.m. periods, canister samples were collected for subsequent GC analysis (Seila et al., 1989). In 1984, the lowest median NMOC value obtained was 0.39 ppm C from measurements in Charlotte, NC, whereas the highest median NMOC value obtained was 1.27 ppmC from measurements in Memphis, TN. In 1985, the lowest median NMOC value obtained was 0.38 ppmC from measurements in Boston, MA, whereas the highest median NMOC value obtained was 1.63 ppmC in Beaumont, TX. The overall median values from all urban sites were approximately 0.72 ppmC in 1984 and 0.60 ppmC in 1985 (Baugues, 1986). The GC analyses made on samples collected in 1984, 1985, and 1986 have been reported (Seila et al., 1989). The more abundant individual hydrocarbons include C_2-C_6 alkanes, C_2-C_5 alkenes, C_6-C_9 aromatics, and acetylene. Based on the 48 most abundant concentrations, the overall median concentrations by class of hydrocarbon (NMHCs) were as follows: paraffins, 0.266 ppmC, 60% of total; aromatics, 0.166 ppmC, 26% of total; olefins, 0.047 ppmC, 11% of total; and acetylene, 0.013 ppmC, 3% of total (Seila et al., 1989). Additional individual NMHCs (totaling about 0.100 ppmC) were detected at concentrations □0.002 ppm C each. Most of these compounds were identified by class but not by structure.

Detailed hydrocarbon analyses for C_2-C_{10} NMHCs were obtained during the 17 intensive days of the Southern California Air Quality Study (SCAQS) in 1987 (Lonneman et al., 1989; Rasmussen, 1989; Stockberger et al., 1989). The average percentage ambient composition from eight Southern California sites during 11 intensive sampling days of the summer of 1987 by class of NMHCs were as follows: paraffins, 53.4; aromatics, 27.2; olefins, 12.1; carbonyls, 7.7 (Main and Lurmann, 1993).

In Atlanta, during the summer of 1990, hydrocarbon concentrations were measured at six sites with automated GCs. Results were reported on 54 hydrocarbons, with 24-h average concentrations ranging from 0.186 to 0.397 ppmC (Purdue et al., 1992).

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

Aldehydes and ketones occur in urban air as O_3-oxidant precursors from emissions such as vehicular exhaust and as products of reactions of OH radicals with NMHCs, reactions of alkenes with O_3, and, at night, reactions with NO_3 radicals. Early morning aldehyde concentrations have been predicted to result to a greater extent from atmospheric reactions of alkenes than from emission of vehicular exhaust (Altshuller, 1993). During the day, aldehydes and ketones are rapidly produced from reactions of OH radicals with aliphatic and aromatic hydrocarbons and of alkenes with O_3. Carbonyl concentrations tend to increase through the daytime hours (Grosjean, 1982, 1988; Grosjean et al., 1993b).

Measurements of ambient air concentrations of carbonyls indicate the total loading of aldehydes and ketones from all processes. Ambient urban air concentrations of HCHO and total aldehydes were tabulated for the 1960 to 1981 period (Altshuller, 1983a). Subsequent studies by 2,4-dinitrophenylhydrazine high-performance liquid chromatography (DNPH-HPLC) techniques (Section 3.5.2.3) have shown consistently that HCHO and acetaldehyde are the most abundant aldehydes; however, a number of other carbonyls (including propanal, acrolein, acetone, butanal, crotonaldehyde, methyl ethyl ketone, pentanal, hexanal, benzaldehyde, and tolualdehyde) also have been measured (Fung, 1989; Grosjean 1982, 1988, 1991; Kalabokas et al., 1988; Zweidinger et al., 1988). The ratios of HCHO to acetaldehyde concentrations (in parts per billion volume) can vary from less than 0.5 in 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 HCHO to acetaldehyde concentrations occur in the 1.0 to 3.0 range.

A compilation of the maximum, average range of HCHO concentrations from many studies in Southern California carried out between 1960 and 1989 is available (Grosjean, 1991). A downward trend in HCHO 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 HCHO concentrations decreased from above 100 ppbv in the 1960s to the 10- to 30-ppbv range during the last decade (Grosjean, 1991). In other U.S. cities in the early 1980s, the maximum HCHO 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 (Grosjean and Fung, 1984); Raleigh, NC (Zweidinger et al., 1988); and Atlanta (Shreffler, 1992; Grosjean et al., 1993b). The average percentage of carbonyls relative to total NMHCs were reported as follows: Los Angeles, 3%; Raleigh, 2%; and Atlanta, 2% (formaldehyde + acetaldehyde concentrations) at two different

sampling sites. In SCAQS, carbonyls were measured at eight sites in the summer and five in the fall of 1987 (Fung, 1989; Fujita et al., 1992). The average percentage of C_1 to C_6 carbonyls relative to NMHCs was 7.6% in the summer and 3.7% in the fall.

Compilations of NMHC concentrations of nonurban and remote locations are available (U.S. Environmental Protection Agency, 1986a; Altshuller, 1989a). Total NMHC concentrations reported ranged from less than 0.01 to 0.14 ppmC. At remote locations over the Pacific, NMHC concentrations generally were less than 0.01 ppmC. 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 O_3 production (Chameides et al., 1988; Roselle et al., 1991). Similar modeling of the effect of biogenic hydrocarbons on O_3 production within urban plumes over southeastern England predicted a 2- to 8-ppb increase in plume and background O_3 concentrations (MacKenzie et al., 1991). Because of lower emissions of biogenic and lower overall NMOC/NO_x ratios, O_3 production over southeastern England is predicted to be limited by the availability of anthropogenic hydrocarbons.

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

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

In two other recent studies in deciduous forests, the isoprene oxidation products were measured as well as isoprene itself (Pierotti et al., 1990; Martin et al., 1991). Both studies report the ambient concentrations of methacrolein and methyl vinyl ketone. In an investigation in a central Pennsylvania deciduous forest in the summer of 1988, average midday concentrations of isoprene were in the 0.005- to 0.010-ppmC range; whereas the corresponding concentrations of methacrolein and methyl vinyl ketone were in the 0.001- to 0.002-ppmC range (Martin et al., 1991). In the study conducted in California forests with samples collected between noon and 4:00 p.m. in late spring and summer, the upper quartile of isoprene concentrations was within the 0.010- to 0.025-ppmC range, whereas methacrolein concentrations were within the 0.001- to 0.003-ppmC range, and methyl vinyl ketone concentrations were within the 0.0005- to 0.0015-ppmC range (Pierotti et al., 1991).

Higher-molecular-weight semivolatile carbonyls have been measured in a number of rural-remote areas (Jüttner, 1986; Yokouchi et al., 1990; Nondek et al., 1992; Ciccioli et al., 1993). The compounds identified include C_5-C_{12} 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).

In an urban-scale study in Atlanta 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 ppmC. 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 a.m. 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; whereas the highest median NO_x concentration of 0.088 ppm was obtained from measurements in Memphis. In 1985, the lowest median NO_x concentration of 0.005 ppm was obtained from measurements in West Orange, whereas 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 a.m. 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 areas between 1980 and 1989 (U.S. Environmental Protection Agency, 1991a). In the 1990 Atlanta study, the average summer NO_x concentration values at the six study sites ranged from 0.011 to 0.026 ppm (Purdue et al., 1992).

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

concentrations are measured. Nitrogen oxide concentrations at or below 0.0001 ppm occur at other remote surface locations (Fehsenfeld et al., 1988).

3.4.2.3 Ratios of Concentrations of Nonmethane Organic Compounds to Nitrogen Oxides

The ratios of 6 a.m. to 9 a.m. NMOC/NO_x have been obtained from the measurements in the U.S. cities discussed above (Baugues, 1986). In 1984, the lowest median NMOC/NO_x ratio of 9.1 was obtained in Cincinnati, OH, and the highest median NMOC/NO_x ratio of 37.7 was obtained in Texas City, TX. In 1985, the lowest median NMOC/NO_x ratio of 6.5 was obtained in Philadelphia, PA, whereas the highest median NMOC/NO_x ratio of 53.2 was obtained in Beaumont, TX. The range in daily 6 a.m. to 9 a.m. NMOC/NO_x ratios within a given city is large, with 10th percentile to 90th percentile NMOC/NO_x ratios varying usually by factors of 2 to 4 and, at several sites, by factors of 5 to 10 (Baugues, 1986). There appears to be a tendency for higher NMOC/NO_x ratios in the cities included in the southeastern (9) and southwestern (15) United States than in the northeastern (7) and midwestern United States (7) (Altshuller, 1989b). The NMOC-to-NO_x ratios at rural sites tend to be higher than the mean NMOC-to-NO_x ratios in urban locations, with mean values at several rural sites ranging between 20 and 40 (Altshuller, 1989b).

In SCAQS, the ambient NMOC (NMHCs + carbonyl)/NO_x ratios averaged 8.8 in the summer and 6.9 in the fall of 1987 (Fujita et al., 1992). However, the 6 intensive days in the fall between November 11 and December 11 were not characterized by elevated O_3 concentrations (Zeldin, 1993). These ambient ratios were 2 to 2.5 times higher than the corresponding emission inventory ratios. Discrepancies as large or larger have been discussed previously for urban and rural NMHC/NO_x ambient-to-emission ratios in the eastern United States (Altshuller, 1989b).

A trend analysis of NMHC/NO_x ratios in the South Coast Air Basin is available for the 1976 to 1990 period (Fujita et al., 1992). The ratios were consistently higher in the summer than in the fall. These ratios started decreasing slowly during the 1980s, from maximum ratios of about 12 in the summer and 9 in the fall to 8.5 in the summer and 7 in the fall by 1990. The ambient-to-emission inventory ratios over this period ranged from as high as 3.4 in the summer to 1.7 in the winter (Fujita, 1993).

Interest in the 6 a.m. to 9 a.m. NMOC/NO_x ratios is associated with their use in the EKMA type of trajectory model (Section 3.6.1.2). The analysis at 10 eastern and midwestern sites of upper-quartile O_3 days relative to other O_3 days indicated a significant difference (p 0.10) by the two-sample Wilcoxon Rank Sum test at four of the 10 sites with NMOC/NO_x ratios (Wolff and Korsog, 1992). However, the correlation of NMOC/NO_x ratios with maximum 1-h O_3 concentrations was very weak. It was concluded that the use of the 6 a.m. to 9 a.m. NMOC/NO_x ratio in EKMA will not provide sufficient information to distinguish among NMOC, NO_x, or combined VOC-NO_x strategies as optimum strategies for urban areas.

A compilation of VOC/NO_x ratios between 1981 and 1988 in 10 cities in the northeastern and midwestern United States presents ratios ranging from 5.8 to 11.5, but generally below 10 (Wolff, 1993). Trends between 1986 and 1991 in VOC/NO_x ratios in four of these cities; New York; Newark, NJ; Philadelphia; and Washington, DC, show downward trends towards VOC/NO_x ratios between 4 and 6 (Zalewsky et al., 1993; Wolff, 1993). For Philadelphia, and the other sites, the downward trend in VOC/NO_x is associated with decreasing VOC concentrations with little change in NO_x (Zalewsky et al., 1993; Wolff,

1993). It has been pointed out that, in the National Academy of Science report (National Research Council, 1991), hydrocarbon control is considered more effective for VOC/NO_x ratios of about 10 or less, whereas NO_x control is considered more effective for VOC/NO_x ratios of 20 or more. Based on these results, it may be concluded that, in many cities in the northeastern and midwestern United States, continued VOC control, rather than NO_x control, will be more effective in reducing O_3 (Wolff, 1993). It also has been concluded by Wolff (1993) that models with greater spatial resolution than the Regional Oxidant Model (ROM), such as the UAM, are more applicable than ROM for determining appropriate O_3 control strategies in urban areas.

3.4.3 Source Apportionment and Reconciliation

3.4.3.1 Source Apportionment

Source apportionment refers to determining the quantitative contributions of sources to ambient air pollutant concentrations. In principle, it includes two fundamentally different approaches: (1) source-oriented and (2) receptor-oriented. In the source-oriented approach, a mathematical dispersion model is applied to an emissions inventory and meteorological data to produce an estimate of ambient pollutant concentrations that can be expected at a specified point in space and time. In contrast, the receptor-oriented approach depends on simultaneous ambient concentration measurements of a variety of pollutant species and a knowledge of the relative amounts of the species (source profiles) that are present in the emissions of the sources that are potential contributors. A mathematical receptor model operates on the source profile and ambient species concentration information to deconvolute the ambient concentrations into their source contributions, without the need of emissions inventory or meteorological information. Indeed, the desire to avoid the latter two kinds of information, whose acquisition is often problematical, has been an important motivation in the development of the receptor-oriented approach.

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

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

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

Manmade Sources of Volatile Organic Compounds

A principal approach for receptor modeling of anthropogenic VOC sources is that of "mass balance". In this approach, a particular linear combination of source profiles is sought that best approximates (in a linear least-squares sense) the profile of VOC species

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

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

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

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

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

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

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

The source categories covered by these studies taken together include vehicle exhaust, gasoline evaporation (whole gasoline and headspace vapor), industrial emissions (refineries, coke ovens, and chemical plants), architectural coatings, dry cleaning, wastewater treatment, auto painting, industrial solvents/degreasers, graphic arts (printing), and natural

gas. Each study gives estimates for the percentage contributions to measured ambient VOCs (or related quantity) for a selected subset of these source categories. The one exception is the work of Sweet and Vermette (1992) that estimates the percentage source contributions to individual species, rather than to total VOCs. Such species apportionment is always available from the CMB calculations, but often is not reported explicitly.

Usually, the source profiles used were generic; that is, from compilations of source measurements taken elsewhere (U.S. Environmental Protection Agency, 1993d). The work of Lewis et al. (1993) is unique in the use of profiles extracted from the ambient air data themselves.

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

The results for gasoline evaporation contribution estimates are much less satisfactory. This is because the recent studies, with the exceptions of Harley et al. (1992) and Lewis et al. (1993), included a gasoline headspace vapor profile but not a whole gasoline profile in their calculations. The latter two studies suggest that this omission is a serious error. For example, Harley et al. (1992) found a remarkably large whole gasoline contribution (nearly the same as that of vehicle exhaust), and Lewis et al. (1993) find a whole gasoline contribution that is about 20% that of vehicle exhaust. Both, however, find a whole gasoline contribution about four times greater than the headspace contribution. Because vehicle exhaust and whole gasoline profiles are quite similar (except for the very light species that are absent in gasoline but present in exhaust as combustion products), excluding the whole gasoline profile will tend to overestimate the exhaust contribution. Although this error may not greatly affect the total mobile-source-related emissions estimate, it is misleading with regard to implied control strategies.

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

Biogenic Sources of Volatile Organic Compounds

The possible role of biogenic VOC emissions in O_3 formation is being considered much more seriously now (Chameides et al., 1988) than was the case a decade ago. Because of the severe experimental problems in accurately measuring biogenic emissions directly, receptor modeling approaches are of considerable interest. Compared with anthropogenic sources, however, the application of receptor modeling methodology to biogenic sources has been very limited. The principal reason is that it has not been possible to find VOC species that are simultaneously distinctive components of biogenic emissions, emitted in an approximately fixed proportion to the total VOC biogenic emissions, and relatively unreactive. Without these conditions, the construction of a credible stable biogenic source profile is not possible, and, consequently, the CMB approach is unusable.

In this situation, a crude form of receptor modeling has been used in which the ambient concentration of a VOC species, whose only source is thought to be biogenic, is divided by the estimated abundance of the species in the total VOC biogenic emissions. Typical candidates include isoprene (deciduous emission) and the terpenes α- and β-pinene (coniferous emission), δ-caranene, and limonene. Because these are all highly reactive, any

such estimate can be regarded only as a lower limit of the contribution that biogenic emissions make to total ambient VOC, if the loss resulting from atmospheric transformation is not taken into account. As an example, Lewis et al. (1993) used isoprene, the most prominent biogenic species measured in downtown Atlanta during the summer of 1990, to infer a lower limit of 2% (24-h average) for the biogenic percentage of total ambient VOC at that location. Isoprene emissions have a strong diurnal dependence. Lower limits for biogenic emissions at other hours, inferred from average isoprene concentrations, were 1% at 8:00 a.m., 5% at noon, 6% at 4:00 p.m., and 2% at 9:00 p.m.

The recent review article by Fehsenfeld et al. (1992) lists other prominent biogenic species and calls attention to the newly recognized importance of alcohols, such as methanol (CH_3OH), as biogenic primary emissions. Goldan et al. (1993) reported the C_5 alcohol, 2-methyl-3-buten-2-ol to be the most abundant VOC of biogenic origin present in a predominantly lodgepole pine forest in Colorado. Ciccioli et al. (1993) present data from sites in Germany and Italy showing substantial contributions from various aldehydes and argue that their dominant source is biogenic primary emissions, rather than photochemical oxidation products.

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

3.4.3.2 Source Reconciliation

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. Because concentrations and emission rates are specified in different units, the comparisons are done in terms of percentages: the percentage contribution of a source to ambient total VOCs as estimated by receptor modeling versus the emission rate of the source as a percentage of the total VOC emission rate of the inventory.

Nearly all the receptor modeling studies listed above have included such a percentage comparison. Typically, the agreement is quite good for vehicle exhaust, generally the dominant VOC source in urban airsheds. Gasoline evaporation comparisons are much less consistent, at least partly for the reasons already indicated. Typically, there is at least qualitative agreement for the other anthropogenic sources: they are small in the inventory, and the receptor-estimated contributions are small. An interesting exception is refinery emissions in Chicago (Scheff and Wadden, 1993), for which the receptor estimate was 7%, five times greater than the inventory estimate. Another is the significant (5 to 20%) natural gas/propane contribution estimated in Los Angeles, Columbus, and Atlanta but not reflected in their inventories. The few biogenic source estimates provided by receptor modeling are generally smaller than those given in emissions inventories, at least partly because of the previously

referred to reactivity problem. Credible ^{14}C measurements on VOC samples would be extremely helpful in validating the magnitude of the biogenic component of emissions inventories.

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

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

Introduction

The measurement of O_3 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 O_3 in the air of populated regions, widespread O_3 monitoring networks have been operated for many years, and the development of measurement and calibration approaches for O_3 has been reviewed extensively (e.g., U.S. Environmental Protection Agency, 1986a). This section focuses on the measurement of O_3 in the ambient atmosphere at ground level and summarizes the current state of ambient O_3 measurement and calibration. No attempt is made here to cover the full history of development of these methods because that has been documented elsewhere (e.g., U.S. Environmental Protection Agency, 1978, 1986a). Instead, this section concentrates on those methods currently used and on new developments and novel approaches to O_3 measurement.

Although no method is totally specific for O_3, current methods for O_3 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 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 O_3 are described.

Chemiluminescence Methods

Gas-Phase Chemiluminescence. The most common chemiluminescence method for O_3 is direct gas-phase reaction of O_3 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 measurements (Stevens and Hodgeson, 1970) followed soon after. Typically, an O_3 monitor based on this approach functions by mixing a constant flow of about 1 L/min of sample air with a small constant flow (□50 cm^3/min) of ethylene. Mixing occurs in a small inert reaction chamber fitted with a sealed window through which light can pass to the photocathode of a photomultiplier tube. Electronically excited formaldehyde molecules, generated by a small fraction of the O_3-ethylene reactions, produce a broad band of emission centered at 430 nm. The emission intensity is linearly proportional to the O_3 concentration over the range of 0.001 ppm to at least 1 ppm. Calibration of the monitor with a known O_3 source provides the relationship between monitor response and O_3 concentration. Detection limits of 0.005 ppm and a response time of less than 30 s are easily attained, and are typical of currently available commercial instruments.

Although no interference has been found from common atmospheric pollutants, a positive interference from atmospheric water vapor has been reported (California Air Resources Board, 1976; Kleindienst et al., 1993, and references therein) and has recently been confirmed (Kleindienst et al., 1993; Hudgens et al., 1994). The recent results indicate a positive interference of about 3% per percent H_2O by volume at 25 □C, based on tests at O_3 concentrations of 0.085 to 0.32 ppm, and at H_2O concentrations of 1 to 3% (i.e., dew point temperatures of 9 to 24 □C). It has been estimated that the interference of water in ethylene chemiluminescent measurements at 30 □C and 60% relative humidity could be as high as 13 ppbv of O_3, or 11% of the O_3 reading at 120 ppbv (Kleindienst et al., 1993). Calibration with known O_3 concentrations in air of temperature and humidity, similar to that of the sample air, can minimize this source of error.

A separate potential problem with the ethylene chemiluminescent method is leakage of the pure ethylene reagent gas. Because O_3 and hydrocarbon measurements are often co-located for monitoring purposes, leakage of ethylene could cause difficulty in obtaining valid measurements of total nonmethane hydrocarbons (TNMHC) in ambient air.

The measurement principle set forth by EPA for compliance monitoring for O_3 is the chemiluminescence method using C_2H_4 (Federal Register, 1971). Methods of testing and the required performance specifications that commercial O_3 monitors must meet to be designated a reference or equivalent method are documented (Federal Register, 1975). A monitor may be designated a reference method if it employs gas-phase chemiluminescence with C_2H_4 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 O_3 monitors. Note that ethylene chemiluminescence monitors typically have response times far superior to those required in Table 3-15.

The list of commercial O_3 monitors designated as reference or equivalent methods by EPA is shown in Table 3-16 (updated as of August 1, 1994). Details on three monitors not described in the 1986 EPA criteria document for O_3 and other oxidants are presented in Table 3-17. All of the reference methods are C_2H_4 chemiluminescence instruments, as required by the definition of a reference method. The equivalent methods are based on either gas-solid

chemiluminescence or UV-absorption measurements. Those methods are described below. A gas-liquid chemiluminescence analyzer for O_3, which may be submitted for EPA equivalency in the near future, also is described below.

Gas-Solid Chemiluminescence. The reaction of O_3 with Rhodamine-B adsorbed on activated silica gel produces chemiluminescence in the red region of the visible spectrum. This was the first chemiluminescence method ever developed for ambient O_3 measurement

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 (1994).

(Regener, 1960, 1964). The emitted light intensity is linearly related to the O_3 concentration, and the detection limit can be as low as 0.001 ppm. No direct interferences from other gas-phase pollutants are known; however, decay of the sensitivity because of surface aging can occur (Hodgeson et al., 1970). Addition of gallic acid to the surface stabilizes the response characteristics, apparently by allowing direct reaction of O_3 with the gallic acid, rather than with the Rhodamine-B (Bersis and Vassiliou, 1966). A commercial analyzer (Phillips Model PW9771) based on this approach has been designated an equivalent method for ambient O_3 (see Table 3-16), but gas-solid chemiluminescence currently is used rarely for ambient measurements.

Gas-Liquid Chemiluminescence. A recently developed commercial monitor uses the chemiluminescent reaction of O_3 with the dye eosin-Y in solution (Topham et al., 1992). The monitor functions by exposing a fabric wick, wetted with the eosin-Y solution, to a flow of sample air within view of a red-sensitive photomultiplier tube. The monitor, designated the LOZ-3, is compact, portable, and requires no reagent gases. The LOZ-3 provides very fast response: a lag time of 2 s, a rise time of 3 s, and a fall time of 2 s, all relative to a step change of 400 ppbv O_3, are reported (Topham et al., 1992). Instrument noise at zero and at 382 ppbv ozone is 0.05 ppbv or less, calculated as the standard deviation of 25 successive 2-min averages. The precision of the LOZ-3 is reported to be 0.80 ppbv at 100 ppbv O_3 and 1.87 ppbv at 400 ppbv O_3, both calculated as one standard deviation of six repeated measurements at these levels (Topham et al., 1992). The instrument provides linear response up to 200 ppbv, with a gradually decreasing slope of the response curve above that

Table 3-16. Reference and Equivalent Methods for Ozone Designated by the U.S. Environmental Protection Agency[a]

Principal Method	Designation Number	Method Code
Reference Methods		
(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
Equivalent Methods		
(UV Absorption)		
Advanced Pollution Instrument 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 Corporation LC-12	EQOA-0382-055	055
Thermo Electron 49	EQOA-0880-047	047
Equivalent Methods (Gas/Solid CL)		
Philips PW9771	EQOA-0777-023	023

[a]As of August 1, 1994; see Appendix A for abbreviations and acronyms.

level. Temperature and pressure sensitivity are corrected by internal circuitry (Topham et al., 1992). An initial large positive interference from SO_2 that becomes smaller and negative as the eosin solution ages is reported, and a positive interference from CO_2 is also present. Topham et al. (1992) report that a pretreatment technique applied to the eosin reagent solution minimizes both of these interferences. Several of the performance characteristics of the LOZ-3 are impressive, but verification of the reported interference levels and the effectiveness of temperature and pressure corrections appears to be needed.

Table 3-17. List of Designated Reference and Equivalent Methods for Ozone

Designation Number	Identification	Source	Manual or Auto	Ref. or Equiv.	Federal Register Vol.	Federal Register Page	Federal Register Notice Date
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 Temperature/Pressure 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	September 18, 1990
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-µm Teflon® 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	September 28, 1992

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.	Federal Register Page	Federal Register 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 *enabled* or *disabled*, at any temperature in the range of 15 to 35 °C, with a 5-µm Teflon® filter element installed in the filter assembly behind the secondary panel, the service switch on the second panel set to the *In* position; with the following menu choices selected: Calibration: *Manual* or *Timed*; Diagnostic Mode: *Operated*; Filter Type: *Kalman*; Pres/Temp/Flow Comp: *On*; Span Comp: *Disabled*; with the 50-pin I/O board installed on the rear panel configured at any of the following output range settings: Voltage, 0.1, 1, 5, and 10V; Current, 0-20, 2-20, and 4-20 mA; and with or without any of the following options: Valve Assembly for External Zero/Span (EZS) Rack Mount Assembly Internal Floppy Disk Drive	Lear Siegler Measurement Controls Corp. 74 Inverness Drive East Englewood, CO 80112-5189	Auto	Equiv.	58	6964	February 3, 1993

[a]Designated since publication of the 1986 EPA criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1986a).
[b]Users 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- to 0.5-ppm range. Thus, designation of any full-scale range lower than the 0- to 0.5-ppm range does not imply commensurably better performance than that obtained on the 0- to 0.5-ppm range.

This method is undergoing testing and is likely to be submitted for EPA certification as an equivalent method.

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 also was 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 O_3 (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 (MnO_2) 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, because the absorption coefficient and pathlength are accurately known, and the measured absorbance can be converted directly to a concentration.

Commercial UV photometers for ambient O_3 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. Because the measurement is absolute, UV photometry also is used to assay O_3 calibration standards as in Section 3.5.1.1. Ambient air monitors using UV photometry are generally calibrated with standard O_3 mixtures to account for losses of O_3 in sampling lines.

A potential disadvantage of UV photometry is that any atmospheric constituent that absorbs 254-nm light and is removed fully or partially by the MnO_2 scrubber will be a positive interference in O_3 measurements. Potential interferents include aromatic hydrocarbons, mercury vapor, and SO_2. A recent study (Kleindienst et al., 1993) demonstrated that toluene and possibly aromatic reaction products, such as benzaldehyde, produce positive interferences in UV photometric O_3 measurements. This result was found using photochemically reactive mixtures of toluene and NO_x, at concentrations at a factor of 2 to 5 higher than those expected in polluted urban air. Consideration of the relative absorption coefficients of O_3 and the aromatics indicated that, at higher humidities, toluene can cause an interference of 0.1 ppbv O_3 per ppbv of toluene, whereas benzaldehyde may cause an interference as high as 5 ppbv O_3 per

ppbv benzaldehyde (Kleindienst et al., 1993). This interference may be humidity dependent. In earlier work at very low humidities, no interference was observed with toluene, and only a very small interference was observed with benzaldehyde (Grosjean and Harrison, 1985b). However, even at very low humidities, these investigators observed significant interferences from styrene, cresols, and nitrocresols. Evaluation of aromatic interference is limited by a lack of appropriate absorption spectra in the 250-nm range and by a lack of ambient measurements of most of the aromatic photochemical reaction products. The use of C_2H_4 chemiluminescence monitors in areas where aromatic concentrations are substantial has been suggested (Kleindienst et al., 1993).

The same study found no consistent effect of ambient water vapor on measured O_3 concentrations using UV photometry, in contrast to the effect noted using C_2H_4 chemiluminescence (Kleindienst et al., 1993). However, short-term disturbances in UV photometric O_3 readings were observed when the humidity of the sample air was changed substantially within a few seconds. This finding corroborates the observations of Meyer et al. (1991a) in an earlier study that indicated microscopic irregularities in the UV cell windows as the cause of such disturbances. This effect should be absent in UV photometric measurements of ambient O_3 at the ground but could be important in other applications, such as measuring vertical O_3 profiles from an aircraft (Kleindienst et al., 1993).

A different approach to evaluating potential interferences in O_3 measurements was taken by Leston and Ollison (1993). These investigators examined ambient O_3 data from instruments of different measurement principles co-located at monitoring sites. The focus of their study was the O_3 "design value", the fourth highest daily maximum hourly value from a monitoring station within an urban area, which is established in the 1990 Clean Air Act Amendments (CAAA) (U.S. Congress, 1990) as the basis for classification of the area relative to attainment of the NAAQS for O_3. Leston and Ollison (1993) examined hourly O_3 concentration data from co-located UV and C_2H_4 chemiluminescence instruments, from 1989 and 1990 at a site in Madison, CT, and from shorter periods at sites in East Hartford, CT, and Mobile, AL. They also examined 11 winter days of simultaneous O_3 data from UV and Luminox LOZ-3 instruments, from Long Beach, CA. Leston and Ollison (1993) reported positive biases in the UV data of 20 to 40 ppbv O_3 during "hot, humid, hazy conditions typical of design value days." They proposed that most O_3 data and all design values are biased high by known and suspected interferences, and that those interferences are exacerbated by water vapor. Leston and Ollison (1993) argue that the interference in UV measurements from benzene derivatives (e.g., styrene, cresols, benzaldehyde, nitro-aromatics) is poorly accounted for. For example, of these compounds, only styrene is measured in the Photochemical Aerometric Monitoring Stations (PAMS) VOC monitoring network (Leston and Ollison, 1993).

An experimental study by Hudgens et al. (1994) attempted to address the issues raised by Leston and Ollison (1993) by evaluating several aspects of both UV and chemiluminescence O_3 measurements. This study confirmed the positive interference of water vapor in the chemiluminescence method as 3% per percent water by volume (Kleindienst et al., 1993) and also confirmed that no comparable interference exists with the UV method. However, Hudgens et al. (1994) also showed that some UV instruments give noisier response when operated under conditions in which condensation of moisture may occur in the sampling lines, as in an air conditioned enclosure during hot, humid weather. Hudgens et al. (1994) also tested several aromatic hydrocarbons for both absorbance at 254 nm and behavior in the

O_3 scrubber of UV instruments. Both positive and negative potential interferences were found; the former by adsorption of UV-absorbing aromatics in the scrubber, and the latter by release of those stored compounds on an increase in sample humidity. Transient O_3 breakthrough also was said to occur under humid conditions (Hudgens et al., 1994). The combined effects of adsorbed material and sample humidity may contribute to the anomalous behavior reported for a few scrubbers from field instruments, but that behavior could not be reproduced with new scrubbers, even after continuous sampling of a smog chamber mixture for up to 13 weeks (Hudgens et al., 1994). The aromatic compounds present at highest concentrations in ambient air (e.g., benzene, toluene, xylenes, benzaldehyde) are relatively weak UV absorbers and are not efficiently removed by the O_3 scrubber. As a result, those compounds are not significant interferences in the UV method (Hudgens et al., 1994). However, less common aromatics (e.g., styrene, nitrotoluene) were found to absorb 254-nm light as effectively as does O_3 and to be efficiently adsorbed in the O_3 scrubber (Hudgens et al., 1994). The importance of such compounds as interferents in the UV method will depend on their ambient concentrations.

Interferences of the magnitude suggested by Leston and Ollison (1993) clearly would have serious implications for monitoring of ambient O_3. It is difficult to estimate whether interferences in the UV method could be as high as suggested, in part, because data are lacking on the ambient levels of potential interferents. Many potential interferents are photochemically reactive, and it is questionable whether such compounds could co-exist with ozone in sufficient quantities to constitute a significant interference. The results of Hudgens et al. (1994) also suggest that periodic replacement of the O_3 scrubber may minimize any interferences in the UV method. In any case, full evaluation of interferences in UV and ethylene chemiluminescence methods may require simultaneous measurements of O_3, humidity, temperature, and speciated organic compounds, and perhaps of other meteorological parameters and potential interferents.

Spectroscopic Methods for Ozone

Spectroscopic methods have the potential to provide direct, sensitive, and specific 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 O_3 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 O_3, by DOAS, and various investigators have applied the technique since then (Stevens et al., 1993, and references therein). Stevens et al. (1993) described 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 O_3 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 O_3) = 0.90 × (UV O_3) □ 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, although further intercomparisons and interference tests are recommended (Stevens et al., 1993).

Personal and 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 O_3 are of value as a means of obtaining personal human exposure data for O_3 and as a means of obtaining long-term O_3 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 O_3 in remote areas are examples of the latter application. Passive sampling devices have the advantages of simplicity, small size, and low cost, but also may present disadvantages, such as poor precision, loss of effectiveness during use or storage, and interference from other atmospheric constituents. New designs for PSDs have been implemented to overcome some of these limitations and to make them more useful for short-term ambient and indoor studies, personal exposure assessments, and validation of exposure models. Passive samplers for measuring O_3 at ambient concentrations are now commercially available.

The Ogawa PSD for O_3 (Ogawa, Inc., Pompano Beach, FL) contains 0.1 mL of a solution of $NaNO_2$ and $NaCO_3$ in glycerine on glass fiber filter paper. The nitrite ion reacts with O_3 to form nitrate. Following exposure, the PSDs are analyzed by extraction of the nitrate with deionized water, followed by ion chromatographic (IC) analysis. In a comparative ambient O_3 study over 24 weeks, this PSD demonstrated agreement within about 10% with the weekly real-time measurements taken by a UV O_3 monitor (Mulik et al., 1991). Extension of these measurements to a full year produced similar results (Mulik et al., 1991). The standard deviation of weekly average measurements by three collocated PSD samplers ranged from about ± 1 to ± 6 ppb, at weekly average O_3 levels of 12 to 45 ppb (Mulik et al. 1991). The Ogawa PSD also was used in a study of personal exposure to indoor and outdoor O_3, showing a correlation of $r = 0.91$, and relative errors of 15% (daytime) and 25% (nighttime) relative to UV photometric data (Liu et al., 1992).

Another PSD for O_3 has been developed that is based on the use of a colorant that fades when exposed to O_3 (Grosjean and Hisham, 1992; Grosjean and Williams, 1992). The plastic, badge-type PSD contains a diffusion barrier and a colorant-coated filter as the O_3 trap. The colorant used is indigo carmine (5,5'-disulfonate sodium salt of indigo, $\lambda_{max} = 608$ nm). With a plastic grid or Teflon® filter as the diffusion barrier, detection limits of 30 ppb·day and 120 ppb·day, respectively, are achieved. Interferences from NO_2, HCHO, and PAN are 15, 4, and 16%, respectively, of the ambient interferent concentrations. For sampling ambient O_3 in most locations, these interferences are probably negligible (Grosjean and Hisham, 1992). Following sampling, the color change is measured by reflectance spectroscopy and no chemical analysis is required. The reported shelf life is 3 mo prior to O_3 exposure and 12 mo after O_3 exposure (Grosjean and Hisham, 1992).

Field tests of the indigo carmine PSD were conducted at five forest locations in California in the summer of 1990 (Grosjean and Williams, 1992). During these tests, ambient O_3 ranged up to 250 ppbv; 3-day average O_3 values at the sites ranged from 40 to 88 ppbv. The precision of the measurements was $\pm 12\%$ based on 42 sets of collocated samplers, over sampling durations of 3 to 30 days. The color change in the PSD was highly correlated ($r = 0.99$) with O_3 dose as measured by UV photometry. No effect of ambient temperature or

humidity variations was observed, and the total interference caused by other pollutants (NO_2, PAN, aldehydes) was less than 5%.

A third PSD for O_3 also has been developed recently; it is based on color formation from the reaction of O_3 with an aromatic amine (Kirollos and Attar, 1991). The ChromoSense™ direct-read passive dosimeter is a credit-card-sized device that changes color proportionally to the integrated dose of exposure of the specific toxic material for which it was designed (U.S. Patent 4,772,560). The dosimeter consists of an outer polyester pouch that encloses a polymeric plate with a sorbent and membrane. A filtering layer is coated on the membrane to reduce the sensitivity of the detection process to NO_2. The chromophoric layer, consisting of an aromatic amine that can react with O_3 and form color, is encapsulated so as to create a very high surface area. A polymeric barrier separates the chromophore from a UV-absorbing layer to reduce their interaction. The UV absorber (in a polymeric matrix) helps stabilize the chromophore toward intense light exposure when the device is used outdoors. The transparent polymeric plate keeps the wafer flat and allows uninterrupted optical viewing of the color of the reference and the sample area. An electronic reading device measures color on both the exposed (sample) and unexposed (reference) areas, and displays a digital reading that is proportional to the log of the O_3 dose. Visible color is formed at doses as low as 20 ppb h. No interference from NO_2 is observed at NO_2 concentrations up to 350 ppb, and only a small effect of ambient humidity has been reported (Kirollos and Attar, 1991). No data on precision have yet been reported.

A popularization of a PSD for O_3 has been achieved in the form of the EcoBadge®, which employs color formation by reaction of O_3 with an undisclosed reagent in a filter paper (Vistanomics, Inc., Glendale, CA). The EcoBadge is available through several scientific equipment catalogs, primarily as a tool for classroom instruction on environmental issues. The badge is said to indicate both a 1-h and an 8-h average O_3 concentration. Comparison of color development to a standard chart indicates O_3 concentrations up to about 350 ppbv, with a limit of resolution of about 20 ppbv or more. The badge is stated to be unaffected by air velocity, humidity, or temperature, with only a slight interference from NO_2. Test data apparently have not been published. The EcoBadge has been used in middle and high school programs promoting science and math and is included in the curriculum of the Global Thinking Project (1993), an international telecommunications and education network.

Calibration Methods for Ozone

Because it is an unstable molecule and cannot be stored, O_3 must be generated at the time of use to produce calibration mixtures. Electrical discharges in air or oxygen readily produce O_3, but at concentrations far too high for calibration of ambient monitors. Radiochemical methods are expensive and require the use of radioactive sources, with associated safety requirements. For calibration purposes, low levels of O_3 nearly always are generated by photolysis of oxygen at wavelengths <200 nm. Placing a mercury lamp near a quartz tube through which air is flowing produces small amounts of O_3 in the airstream. Commercial O_3 sources based on this approach typically adjust the lamp current to control the amount of light transmitted, and thus the O_3 produced.

Once a stable, low concentration of O_3 has been produced from a photolytic generator, that O_3 output must be established by measurement with an absolute reference method. The original reference calibration procedure promulgated by EPA in 1971 (Federal Register, 1971) was an iodometric procedure, employing 1% aqueous neutral buffered

potassium iodide (NBKI). A large number of studies conducted in the 1970s revealed several deficiencies with potassium iodide (KI) methods, the most notable of which were poor precision or interlaboratory comparability and a positive bias of NBKI measurements relative to simultaneous absolute UV absorption measurements.

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

The measurement principle of UV O_3 photometers used as reference standards is identical to that of O_3 photometers used for ambient measurements (see Section 3.5.1.1). A laboratory photometer used as a reference standard will typically contain a long-path cell (1 to 5 m) and employ sophisticated digital techniques for making effective double-beam measurements of small absorbances at low O_3 concentrations.

A primary reference standard is a UV photometer that meets the requirements set forth in the 1979 revision designating UV photometry as the reference method (Federal Register, 1979a). Commercially available O_3 photometers that meet those requirements may function as primary standards. The EPA and the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards [NBS]) have established a nationwide network of standard reference photometers (SRPs) that are used to verify local primary standards and transfer standards. A secondary or transfer standard is a device or method that can be calibrated against the primary standard and then moved to another location for calibration of O_3 monitors. Commercial UV photometers for O_3 often are used as secondary or transfer standards, as are commercial photolytic ozone generators and apparatus for the gas-phase titration of O_3 with NO.

The latter method, gas-phase titration (GPT) of O_3 with NO ($NO + O_3 \rightarrow NO_2 + O_2$), is a direct and absolute means of determining O_3, provided NO is in excess so that no side reactions occur. Under such conditions, GPT has the advantage that measurement of the NO or O_3 consumed or the NO_2 produced gives a simultaneous measurement of the other two species. All three modes have been used, and this method is often used for calibration of NO/NO_x analyzers. Gas-phase titration has been compared to UV photometry in several studies. The most detailed study is that of Fried and Hodgeson (1982), who used an NBS primary standard UV photometer, highly accurate flow measurements, photoacoustic detection of NO_2, and NBS (now NIST) Standard Reference Materials as sources of NO and NO_2. That study showed that decreases in O_3 as measured by the UV method averaged 3.6% lower than the corresponding decrease in NO and increase in NO_2 measured independently. Because of uncertainty about the origin of the small bias relative to UV photometry, GPT is used as a transfer standard but not as a primary reference standard.

3.5.1.2 Peroxyacetyl Nitrate and Its Homologues

During laboratory organic photooxidation studies, Stephens et al. (1956a,b) determined the presence of a number of alkyl nitrates and an unidentified species called "Compound X". The presence of Compound X in the atmosphere of Los Angeles was confirmed by Scott et al. (1957). In later work (Stephens et al., 1961), its structure was determined and Compound X was named peroxyacetyl nitrate, or PAN. Since the discovery of PAN, much effort has been directed toward its atmospheric measurement. In the following subsections PAN measurement and calibration techniques are described. The discussion on

measurement techniques includes a summary description and identifies limits of detection, specificity (interferences), reproducibility, and accuracy of each method. The relative merits of each method also are presented. The subsection on calibration techniques includes those methods most often employed during ambient air measurement studies.

Measurement Methods

Two methods generally have been employed to make atmospheric measurements of PAN. These methods are infrared spectroscopy (IR) and GC. Infrared spectroscopy permits the sampling and analysis to be conducted in real time. Because PAN is very reactive in the gas phase and exhibits surface adsorptive effects, the minimal contact time offered by IR makes this method very attractive. However, IR instrumentation is expensive and complex and requires a good deal of space. On the other hand, GC is inexpensive and requires minimal space and operator training. A GC can be set up to automatically sample and analyze air for PAN and PANs. Application of these methods for obtaining ambient concentrations of PAN and other organic nitrates recently has been reviewed by Roberts (1990).

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

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

Gas Chromatography-Electron Capture Detection. Peroxyacetyl nitrate is normally measured by using a GC coupled to an electron capture detector (GC/ECD). The method was originally described by Darley et al. (1963) and subsequently has been refined and employed by scientists over the years. Key features of the method remain unchanged. The column and detector temperatures are kept relatively low (50 and 100 °C, respectively) to minimize PAN thermal decomposition. Short columns of either glass or Teflon® generally are used (1 to 5 ft in length). Finally, column packing normally includes a Carbowax stationary phase coated onto a deactivated solid support. Using packed columns, detection limits of

10 ppt have been reported using direct sampling with a 20-mL sample loop (Vierkorn-Rudolph et al., 1985). Detection limits were further extended to 1 to 5 ppt using cryogenic enrichment of samples (Vierkorn-Rudolph et al., 1985; Singh and Salas, 1983). These studies have found only slight overall losses of PAN (10 to 20%) associated with cryosampling, provided samples are warmed only to room temperature during desorption.

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

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

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

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.

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 approach, 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 $\pm$ 0.3 ppm PAN.

Peroxyacetyl nitrate can be synthesized in the condensed phase by the nitration of peracetic acid in C_6H_{14} (Helmig et al., 1989), heptane (Nielsen et al., 1982), C_8H_{18} (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 signal measured upstream and downstream of an alkaline bubbler (Grosjean and Harrison, 1985a). Joos et al. (1986) coupled a chemiluminescence NO_x analyzer with a GC system to permit calibration of the ECD response by reference to the chemiluminescence NO_x analyzer that has been calibrated by traditional methods.

As noted previously, NO in the presence of PAN is converted to NO_2. Approximately four molecules of NO can react per molecule of PAN. Lonneman et al. (1982) devised a PAN calibration procedure based on the reaction of PAN with NO in the presence of benzaldehyde, which is added to control unwanted radical chemistry and to improve precision. Using this approach and an initial NO-to-PAN ratio between 10 and 20 to 1, the change in NO concentration is monitored with a chemiluminescence NO analyzer, the change in PAN GC-

ECD response is monitored, and the resulting ratio (i.e., NO/PAN) is divided by the stoichiometric factor of 4.7 to arrive at a calibration factor for the ECD.

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

3.5.1.3 Gaseous Hydrogen Peroxide

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

In the following section, the discussion focuses on those sampling and analytical methods most frequently used within the last decade to determine atmospheric levels of H_2O_2. The measurement techniques are described and limits of detection, specificity (interferences), reproducibility, and accuracy are discussed.

Measurement Methods

In situ measurement methods that have been employed for determining gaseous H_2O_2 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 also have been used frequently: (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 H_2O_2 recently has been reviewed by Sakugawa et al. (1990) and Gunz and Hoffmann (1990).

In Situ Methods. Fourier transform infrared spectroscopy was employed in the early 1980s for atmospheric measurements (Tuazon et al., 1980; Hanst et al., 1982). Even though the FTIR is very specific for H_2O_2, 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 H_2O_2 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, 1987a; Schiff et al., 1987).

Wet Chemical Methods. Numerous wet chemical techniques for measuring H_2O_2 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 H_2O_2. Copper^{2+} (Armstrong and Humphreys, 1965; Kok et al., 1978 a,b; Das et al., 1982) and hemin, a blood component (Yoshizumi et al.,

1984), have been reported as catalysts for the luminol-based H_2O_2 oxidation. Method sensitivity of 0.01 ppb has been achieved. Interference from O_3, SO_2, 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; Lazrus et al., 1985; Aoyanagi and Mitsushima, 1985; Hoshino and Hinze, 1987).

Peroxyoxalate Method. The peroxyoxalate chemiluminescence method also has 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 on return to the ground state. Method sensitivity of 0.01 ppb is achieved, and no interferences are observed from O_3 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: (1) a substrate that is oxidizable; (2) the enzyme, horseradish peroxidase (HRP); and (3) H_2O_2. The production or decay of the fluorescence intensity of the substrate or reaction product is measured as it is oxidized by H_2O_2, 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*-hydroxphenyl)propionic acid (HPPA) (Zaitsu 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. Because the chemical reaction is sensitive to both H_2O_2 and organic peroxides, a dual-channel system with a H_2O_2 removal step (use of catalase) is used to distinguish H_2O_2 from organic peroxides (Lazrus et al., 1985; Wei and Weihan, 1987; Dasgupta and Hwang, 1985; Kok et al., 1986).

The peroxidase-POPHA-fluorescence technique has been used by several groups to measure gas-phase H_2O_2 concentrations (Lazrus et al., 1986; Tanner et al., 1986; Heikes et al., 1987; Van Valin et al., 1987; Dasgupta et al., 1988; Olszyna et al., 1988; Meagher et al., 1990). Method detection levels range from 0.01 to 0.1 ppb. However, artifact formation does occur as a result of the reaction of dissolved O_3 in the collection devices (Staehelin and Hoigne, 1982; Heikes, 1984; Gay et al., 1988). To overcome the O_3 interference, researchers have used NO to eliminate O_3 (Tanner, 1985; Tanner et al., 1986; Shen et al., 1988).

Fenton Reagent-Isomeric Hydroxybenzoic Acids Method. This technique involves the formation of aqueous OH radicals from the reaction of Fenton reagent (Fe^{2+}) complex) with gaseous H_2O_2. The OH radicals, in turn, react with benzoic acid (hydroxyl radical scavenger) to form isomeric hydroxybenzoic acids (OHBA). The OHBA fluoresces weakly at the pH necessary to carry out the above reactions. Fluorescence is enhanced by adding NaOH to the product stream (Lee et al., 1990) or by using a low pH Al^{3+} fluorescence enhancing reagent (Lee et al., 1993).

Comparison of Methods

The above techniques have been shown to measure H_2O_2 in the atmosphere with detection levels of 0.1 ppb. Kleindienst et al. (1988) compared several of these techniques using three sources of H_2O_2: (1) zero air in the presence and absence of common interferences,

(2) steady-state irradiations of hydrocarbon-NO_x mixtures, and (3) ambient air. The measurements were conducted simultaneously from a common manifold. For pure samples in zero air, agreement within 23% was achieved among methods over a concentration range of 0.06 to 128 ppb. A negative SO_2 interference was caused with the luminol technique. During the irradiation experiment, significant concentrations of organic peroxides were generated, and the agreement among techniques for H_2O_2 was very poor. For ambient measurements, the methods agreed reasonably well with an average deviation of 30% from the mean values.

Atmospheric intercomparison studies also have been conducted as part of the Carbon Species Methods Comparison Study (Calif, 1986). The results of the study indicated that the wet chemical methods still suffer from sampling artifacts and interferences from other atmospheric constituents (Dasgupta et al., 1990; MacKay et al., 1990; Kok et al., 1990; Sakugawa et al., 1990; Tanner and Shen, 1990). Lee et al. (1991) showed that substantial loss of airborne H_2O_2 can occur when air is drawn through Teflon® tubing of inlet sampling devices. In addition to reducing the H_2O_2 in incoming ambient air, this line loss also compromises the use of aqueous standards to calibrate a gas-phase monitoring system. More recently, Lee et al. (1994) have demonstrated a surfaceless inlet system to eliminate line loss problems. It is clear from the above studies that further comparisons of techniques are needed to resolve questions of errors and to provide improved measurement techniques.

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 a standardized permanganate solution (Lee et al., 1991).

Gaseous H_2O_2 standards are not as easily prepared, and stability problems require the 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 also have 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* 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 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 VOCs. The revisions require states to establish VOC air monitoring stations in nonattainment areas 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 CAAA of 1990 (U.S. Congress, 1990). Several states have begun acquiring VOC data on 55 O_3 precursors at these PAMS, using methodology discussed in an EPA technical assistance document (U.S. Environmental Protection Agency, 1991c).

The term *nonmethane organic compounds* also is used frequently and refers to a subset of VOCs, because it excludes the compound CH_4. Numerous sampling, analytical, and calibration methods have been employed to determine NMOCs in ambient air. Some of the analytical methods utilize detection techniques that are highly selective and sensitive to specific functional groups or atoms of a compound (e.g., formyl group of aldehydes, halogen), whereas others respond in a more universal manner (i.e., to the number of carbon atoms present in the organic molecule). In this overview of the most pertinent measurement methods, NMOCs have been arranged into three major classifications: (1) NMHCs, (2) carbonyl species, and (3) polar volatile organic compounds (PVOCs). Measurement and calibration procedures are discussed for each classification.

3.5.2.2 Nonmethane Hydrocarbons

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

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

Nonspeciation Measurement Methods

The original EPA reference method for NMOC, which was promulgated in 1971, involves GC separation of CH_4 from the remaining organics in an air sample (Federal Register, 1971). A second sample is injected directly to the FID without CH_4 separation. Subtraction of the first value from the second produces a nonmethane organic concentration.

A number of studies of commercial analyzers employing the Federal Reference Method have been reported (Reckner, 1974; McElroy and Thompson, 1975; Harrison et al., 1977; Sexton et al., 1982). These studies indicated overall poor performance of the commercial instruments when either calibration or ambient mixtures containing NMOC concentrations <1 ppmC were used. The major problems associated with using these NMOC instruments have been reported in an EPA technical assistance document (Sexton et al., 1981). The technical assistance document also suggests ways to reduce the effects of existing problems. Other nonspeciation approaches to the measurement of nonmethane organics also

have been investigated. These approaches have been discussed in the 1986 EPA air quality criteria document (U.S. Environmental Protection Agency, 1986a). Again, these approaches also are subject to the same shortcomings as the EPA reference method (i.e., poor performance below 1 ppmC of NMHC).

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

A brief summary of the method is as follows. A whole air sample is drawn through a glass bead trap that is cooled to approximately □185 □C using liquid argon. The cryogenic trap collects and concentrates the NMOC, while allowing the CH_4, nitrogen, oxygen, etc., to pass through the trap without retention. After a known volume of air has been drawn through the trap, carrier gas is diverted to the trap first to remove residual air and CH_4. When the residual gases have been flushed from the trap, the cryogen is removed and the temperature of the trap is ramped to approximately 100 □C. The revolatilized compounds pass directly to a FID (no analytical column). The corresponding signal is integrated over time (several minutes) to obtain a total FID response from the NMOC species. Water vapor, which also is preconcentrated, causes a positive shift in the FID signal. The effect of this shift is minimized by optimizing the peak integration parameters.

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

Speciation Measurement Methods

The primary measurement technique utilized for NMOC speciation is GC. Coupled with FID, this analytical method permits the separation and identification of many of the organic species present in ambient air.

Separation of compounds is accomplished by means of both packed and capillary GC columns. If high resolution is not required and large sample volumes are to be injected, packed columns are employed. The traditional packed column may contain either a solid polymeric adsorbent (gas-solid chromatography) or an inert support, coated with a liquid (gas-liquid chromatography). Packed columns containing an adsorbent substrate normally are required to separate C_2 and C_3 compounds. The second type of column can be a support-coated or wall-coated open tubular capillary column. The latter column has been used widely for environmental analysis because of its superior resolution and broader applicability. The wall-coated capillary column consists of a liquid stationary phase coated or bonded (cross-linked) to the specially treated glass or fused-silica tubing. Fused-silica tubing is most commonly used because of its physical durability and flexibility. When a complex mixture is introduced into a GC column, the carrier gas (mobile phase) moves the sample through the

packed or coated capillary column (stationary phase). The chromatographic process occurs as a result of repeated sorption-desorption of the sample components (solute) as they move along the stationary phase. Separation occurs as a result of the different affinities that the solute components have for the stationary phase.

As described in the previous O_3 criteria document (U.S. Environmental Protection Agency, 1986a), the GC-FID technique has been used by numerous researchers to obtain ambient NMOC data. Singh (1980) drew on the cumulative experience of these researchers to prepare a guidance document for state and local air pollution agencies interested in obtaining speciation data. In general, most researchers have employed two gas chromatographic units to carry out analyses of NMOC species in ambient air. The more volatile VOCs (C_2 through C_5) generally are measured on one unit using packed-column technology, whereas the other GC separates the less volatile organics using a capillary column. In typical chromatograms of urban air, all major peaks are identified and, on a mass basis, represent from 65 to 90% of the measurable nonmethane organic burden.

Identification of GC peaks is based on matching retention times of unknown compounds with those of standard mixtures. Subsequent verification of the individual species is normally accomplished with gas chromatographic-mass spectrometric (GC/MS) techniques. Compound-specific detection systems, such as electron capture, flame photometry, and spectroscopic techniques, also have been employed to confirm peak identifications. The peak matching process is far from being a trivial task. Ambient air chromatograms are often very complex (>200 peaks/run) and require a good deal of manual labor to assure that the peak matching process is being carried out correctly by the resident peak identification/ quantification software. Efforts to improve on the accuracy of peak assignment and diminish the labor hours normally associated with the objective recently have been reported. Silvestre et al. (1988) developed an off-line spreadsheet program that is menu-driven and used to identify and edit a chromatogram containing 200 peaks within 15 min. The accuracy of peak assignment was typically better than 95%. Mason et al. (1992) developed a novel algorithm that is embedded within the Harwell MatchFinder software package and demonstrated the potential of the algorithm for enhancing peak identification in complex chromatograms. The authors indicate that the software could be used to batch-process large volumes of chromatographic data. A commercial software package from Meta Four Software, Inc., was recently employed during the Atlanta Ozone Precursor Monitoring Study to batch process chromatographic data from over 6,000 GC runs (Purdue et al., 1992). This software was also used to validate peak identities from two GC databases and was shown to improve peak identities from the originally processed data by 10 to 20% (Holdren et al., 1993).

Because the organic components of the ambient atmosphere are present at parts-per-billion levels or lower, sample preconcentration is necessary to provide sufficient material for the GC-FID system. The two primary techniques utilized for this purpose are the use of solid adsorbents and cryogenic collection. The more commonly used sorbent materials are divided into three categories: (1) organic polymeric adsorbents, (2) inorganic adsorbents, and (3) carbon adsorbents. Primary organic polymeric adsorbents used for NMOC analyses include the materials Tenax®-GC and XAD-2®. These materials have a low retention of water vapor, and, hence, large volumes of air can be collected. These materials do not, however, efficiently capture highly volatile compounds such as C_2 to C_5 hydrocarbons, nor certain polar compounds such as CH_3OH and C_3H_6O. Primary inorganic adsorbents are silica gel, alumina, and molecular sieves. These materials are more polar than the organic polymeric adsorbents and

are thus more efficient for the collection of the more volatile and polar compounds. Unfortunately, water also is collected efficiently, which in many instances leads to rapid deactivation of the adsorbent. Carbon adsorbents are less polar than the inorganic adsorbents and, as a result, water adsorption by carbon adsorbents is a less significant problem. The carbon-based materials also tend to exhibit much stronger adsorption properties than organic polymeric adsorbents; thus, lighter-molecular-weight species are more easily retained. These same adsorption effects result, however, in irreversible adsorption of many compounds. Furthermore, the very high thermal desorption temperatures required (350 to 400 °C) limit the use of carbon adsorbents and also may lead to degradation of labile compounds. The commonly available classes of carbon adsorbents include various conventional activated carbons, carbon molecular sieves (Spherocarb®, Carbosphere®, Carbosieve®), and carbonaceous polymeric adsorbents (Ambersorb® XE-340, XE-347, SE-348).

Although a number of researchers have employed solid adsorbents for the characterization of selected organic species in air, only a few attempts have been made to identify and quantitate the range of organic compounds from C_2 and above. Westberg et al. (1982) evaluated several carbon and organic polymeric adsorbents and found that Tenax®-GC exhibited good collection and recovery efficiencies for $\geq C_6$ organics; the remaining adsorbents tested (XAD-4®, XE-340®) were found unacceptable for the lighter organic fraction. The XAD-4® retained $\geq C_2$ organic gases, but it was impossible to desorb these species completely without partially decomposing the XAD-4®. Good collection and recovery efficiencies were provided by XE-340® only for organics of C_4 and above. Ogle et al. (1982) used a combination of adsorbents in series and designed an automated GC-FID system for analyzing C_2 through C_{10} hydrocarbons. Tenax-GC® was utilized for C_6 and above; whereas Carbosieve S® trapped C_3 through C_5 organics. Silica gel followed these adsorbents and effectively removed water vapor while passing the C_2 hydrocarbons onto a molecular-sieve, 5A adsorbent. More recently, Levaggi et al. (1992) used a combination of adsorbents in series for analyzing C_2 through C_{10} hydrocarbons. Tenax GR, Carbotrap, and Carbosieve S-III were evaluated. At room temperature collection, excellent recovery efficiencies were obtained for all species except acetylene (breakthrough begins after 220 cc). Smith et al. (1991b) evaluated a commercially available GC system (Chrompack, Inc.) and found that a Carbotrap C, Carbopack B, and Carbosieve S-III combination was effective for all C_2 and above species, if the trap temperature was maintained at ≤30 °C during collection (600 cc). The above researchers also caution that artifact peaks do occur during thermal desorption and recommend closely screening the resulting data.

The preferred method for obtaining NMOC data is cryogenic preconcentration (Singh, 1980). Sample preconcentration is accomplished by directing air through a packed trap immersed in either liquid oxygen (B.P. ≤183 °C) or liquid argon (B.P. ≤186 °C). For the detection of about 1 ppbC of an individual compound, a 250-cc air sample normally is processed. The collection trap generally is filled with deactivated 60/80 mesh glass beads (Westberg et al., 1974), although coated chromatographic supports also have been used (Lonneman et al., 1974). Both of the above cryogens are sufficiently warm to allow air to pass completely through the trap, yet cold enough to collect trace organics efficiently. The use of cryogenic preconcentration for collection of VOCs, in general, was automated to allow sequential hourly updates of GC data (McClenny et al., 1984), leading to the initial configuration of what are now referred to as automated GCs ("auto GCs") for O_3 precursor monitoring. The cryogenic collection procedure also condenses water vapor. An air volume

of 250 cc at 50% relative humidity and 25 °C contains approximately 2.5 mg of water that appears as ice in the collection trap. The collected ice at times will plug the trap and stop the sample flow; furthermore, water transferred to the capillary column during the thermal desorption step occasionally causes plugging and other deleterious column effects.
To circumvent water condensation problems, Pleil et al. (1987) have characterized the use of a Nafion® tube drying device to remove water vapor selectively during the sample collection step. Although hydrocarbon species are not affected, polar organics are partially removed when the drying device is used. Burns et al. (1983) also showed that partial loss or rearrangement of monoterpenes, or both (e.g., α-pinene, limonene), occurs when the Nafion® tube is used to reduce water vapor.

The EPA has recently provided technical guidance for measuring VOCs that is based on the above studies as well as emerging and developing technology (U.S. Environmental Protection Agency, 1991c). Guidance for the use of auto GC sampling and analysis for VOCs has been derived from experience gained from application of this technology during an O_3 precursor study conducted by EPA in Atlanta during the summer of 1990 (Purdue et al., 1992). For that study, an auto GC system developed and manufactured by Chrompack, Inc., and modified for O_3 precursor monitoring (McClenny et al., 1991b) was used to obtain hourly VOC measurements. The GC system was equipped with a preconcentration adsorption trap, a cryofocusing secondary trap, and a single analytical column. The study was focused on the identification and quantitation of 55 O_3 precursor compounds, and resulted in accounting for 65 to 80% of the total NMOC mass. Sample volumes of 600 cc were used and a detection level of 0.1 ppb C was reported. External auditing indicated accuracy of ±30% at challenge concentrations of 2 ppbC (17-component audit mixture).

The study also revealed several weaknesses. First of all, excessive amounts of liquid cryogen were consumed in carrying out the measurements. The inferior quality of the cryogen containers and poor delivery schedules resulted in reduced data capture. Secondly, because of the single-column approach, numerous target species either co-eluted or were poorly resolved. Thirdly, several significant artifact peaks co-eluted with the target species and, therefore, biased the reported concentrations of those species, as well as the total NMOC (by summation of peaks). Additionally, Shreffler (1993) reported results from analyses of canister samples collocated with the automated field GC systems. In general, good agreement between the systems was found when comparing the sum of the 55 identified O_3 precursors. However, regression analysis indicated that the average total NMOC concentrations found from the analyses of canister samples were 50% higher than those measured with the field GC systems.

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

In addition to direct sampling via preconcentration with sorbents and cryogenic techniques, collection of whole air samples is frequently used to obtain NMOC data. Rigid devices such as syringes, glass bulbs, or metal containers and nonrigid devices such as Tedlar®

and Teflon® plastic bags are often utilized during sampling. The primary purpose of whole-air collection is to store an air sample temporarily until subsequent laboratory analysis is performed. The major problem with this approach is assuring the integrity of the sample contents prior to analysis. The advantages and disadvantages of the whole air collection devices were summarized in the 1986 air quality criteria document (U.S. Environmental Protection Agency, 1986a).

The canister-based method is the preferred means for collecting VOCs and is described as part of the "EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" (Compendium Method TO-14). McClenny et al. (1991a) recently reviewed the canister-based method and discussed basic facts about the canisters, described canister cleaning procedures, contrasted the canister collection system versus solid adsorbents, and discussed the storage stability of VOCs in canisters. Although storage stability studies have indicated that many target VOCs can be stored with integrity over time periods of at least 7 days, there are still many VOCs for which there are no stability data (Pate et al., 1992; Oliver et al., 1986; Holdren and Smith, 1987; Westberg et al., 1982, 1984; Gholson et al., 1990). Coutant (1993) has developed a computer-based model for predicting adsorption behavior and vapor-phase losses in multicomponent systems, based on the potential for physical adsorption as well as the potential for dissolution in condensed water for canister samples collected at high humidities. At present, the database for the model contains relevant physicochemical data for 78 compounds (including water), and provisions for inclusion of up to 120 additional compounds are incorporated in the software.

Calibration Methods

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

As described in the previous O_3 criteria document (U.S. Environmental Protection Agency, 1986a), static systems generally are preferred for quantitating NMOCs. The most commonly used static system is a compressed-gas cylinder containing the appropriate concentration of the compound of interest. These cylinder gases also may be diluted with hydrocarbon-free air to provide multi-point calibrations. Cylinders of calibration gases and hydrocarbon-free air are available commercially. Also, some standard gases such as propane and benzene, as well as a 17-component ppb mixture, are available from NIST as certified standard reference materials (SRMs). Commercial mixtures generally are referenced against these NIST standards. In its recent technical assistance document for sampling and analysis of O_3 precursors, EPA recommended propane (or benzene)-in-air standards for calibration (U.S. Environmental Protection Agency, 1991c). Some commercially available propane cylinders have been found to contain other hydrocarbons (Cox et al., 1982), so that all calibration data should be referenced to NIST standards.

Because of the uniform carbon response of a GC-FID system ($\pm$10%) to hydrocarbons (Dietz, 1967), a common response factor is assigned to both identified and unknown compounds obtained from the speciation systems. If these compounds are oxygenated species, an underestimation of the actual concentrations will be reported. Dynamic calibration systems are employed when better accuracy is needed for these oxygenated hydrocarbon species. Dynamic systems normally are employed to generate in situ

concentrations of the individual compound of concern and include devices such as permeation 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 HCHO, the most abundant aldehyde, were subject to some interferences and lacked sensitivity at low parts-per-billion concentrations (Altshuller and Leng, 1963; Altshuller et al., 1961; Altshuller and McPherson, 1963). However, spectroscopic methods such as FTIR and DOAS also lack sensitivity for HCHO in the low parts-per-billion concentration range. The 1986 air quality criteria document described two methods frequently used: (1) the chromotropic acid (CA) method for HCHO and (2) the 3-methyl-2-benzothiazolone hydrazone (MBTH) technique for total aldehydes (U.S. Environmental Protection Agency, 1986a). However, spectroscopic methods, on-line colorimetric methods, and the HPLC method employing DNPH derivatization are the preferred methods currently used for measuring atmospheric levels of carbonyl species.

Spectroscopic Methods

Three spectroscopic methods have been used to make measurements for atmospheric levels of HCHO and were recently intercompared at an urban site in California (Lawson et al., 1990). The FTIR method used gold-coated 30-cm-diameter mirrors and a total optical path of 1,150 m. The 2,781.0-cm^{-1} "Q-branch" adsorption peak was used to measure HCHO. The limit of detection was 3 ppb, and the measurement errors were within $\pm$3 ppb. The DOAS method was operated at an 800-m pathlength, and an absorption peak at 339 nm was used to measure HCHO; NO_2 and HNO_2 spectral features were subtracted. The limit of detection was 4.5 ppb, and the experimental error was $\pm$30%. A 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 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 and Schiff (1987a).

On-Line Fluorescence Method

A wet chemical method based on the derivatization of HCHO in aqueous solution to form a fluorescent product was developed by Kelly et al. (1990) and recently tested (Kelly and Fortune, 1994). 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 with a response time of 1 min. The instrument is portable and highly selective for HCHO.

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 HPLC. This method takes advantage of the reaction of carbonyl compounds with DNPH to form a 2,4-dinitrophenylhydrazone:

$$C=O + NH_2NHC_6H_3(NO_2)_2 \rightarrow H_2O + RR'C=NNHC_6H_3(NO_2)_2 \quad (3\text{-}82)$$

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 initially was conducted with micro-impingers containing an organic solvent and an 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 a UV detection system (360 nm).

An improved procedure subsequently was 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 midget impinger containing a C_2H_3N solution of DNPH and an acid catalyst. After sampling, an aliquot of the original collection solution is injected directly into the liquid chromatograph. This approach eliminates the extraction step and several sample-handling procedures associated with the DNPH-aqueous solution and provides much better recovery efficiencies. This method has been formalized by EPA as Compendium Method TO-5 (Winberry et al., 1988). The TO-5 Method has been further modified to include the use of a DNPH-impregnated solid adsorbent, rather than DNPH impinger solutions, as the collection medium. This modification and associated sampling conditions are referred to as EPA Method TO-11. The methodology can be used easily for long-term (1 to 24 h) sampling of ambient air. Sampling rates of 500 to 1,200 cc/min can be achieved and detection levels of 1 ppbv can be attained with sampled volumes of 100 L. The method currently calls for the use of SepPak® silica gel material as the sorbent material. However, researchers have noted that O_3 present in ambient air reacted more easily with carbonyl compounds collected on DNPH-coated silica gel cartridges than on DNPH-coated C_{18}-bonded silica material. To eliminate this negative bias, these researchers used an O_3 scrubber (Arnts and Tejada, 1989). Smith et al. (1989) noted that artifact peaks occurred when O_3 was bubbled through impingers containing DNPH solution. These artifacts were identified as DNPH-O_3 reaction products and were shown to cause positive interferences unless they were chromatographically resolved from the HCHO-hydrazone derivative. Although the TO-11 Method has been included in EPA's *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (U.S. Environmental Protection Agency, 1991c), a KI-coated denuder tube also has been recommended to remove O_3 upstream of the DNPH-coated cartridges.

Although both the Sep-Pak® C_{18} and silica gel cartridges have been used by researchers (either with or without O_3 scrubbers), there is still considerable uncertainty as to which type of cartridge gives the most reliable carbonyl results. Experiments are currently underway at several laboratories to investigate the effect of O_3 on the performance of DNPH-coated cartridges. However, results have not yet been reported in the literature.

Calibration of Carbonyl Measurements

Because they are reactive compounds, it is extremely difficult to make stable calibration mixtures of carbonyl species in pressurized gas cylinders. Although gas-phase

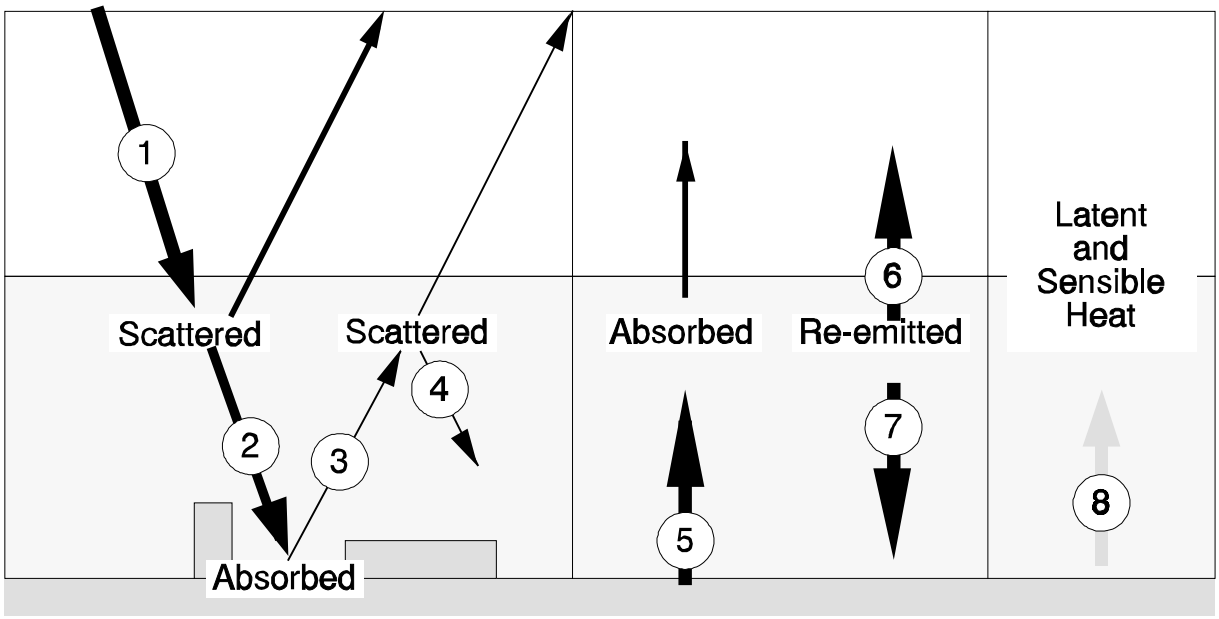


Figure 3-7. Surface radiation budget for short- and long-wave radiation. The surface radiation budget is driven by the input of short-wave radiation (1). This direct input is reduced by scatter (2) and absorption passing through the atmosphere. The amount that remains can be absorbed or reflected at the surface. The reflected light (3) also can 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).

3.3.1.2 Planetary Boundary Layer

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

As air is moved vertically through the atmosphere, as might happen in a convective thermal, its temperature will decrease with height as the result of adiabatic expansion. It is the comparison of how the temperature *should* change with height in the absence of external heating or cooling against the *actual* temperature change with height that is a measure of atmospheric stability. Those layers of the atmosphere where temperature increases with height (inversion layers) are the most stable as air, cooling as it rises, becomes denser than its new warmer environment. In an atmospheric layer with relatively low turbulence, pollutants do not redistribute vertically as rapidly as they do in an unstable layer.

Also, because a stable layer has a relatively low rate of mixing, pollutants in a lower layer will not mix through it to higher altitudes.

The stability of the atmosphere is often measured through computation of potential temperature as

$$\theta = \left(\frac{P}{P_o}\right)^{-R/c_p}, \tag{3-79}$$

where θ is the virtual potential temperature, P is the pressure of the air parcel, P_o 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 O_3 precursors are mixed uniformly through the layer below the mixing height. As this layer grows, it both entrains remnant O_3 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 2 or 3 h 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, 1964, 1972). 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 at which it is warmer than the rising and cooling underlying air. Because these circumstances are associated with specific synoptic conditions, they are less frequent than the ubiquitous nighttime radiation inversion. An elevated inversion is, nevertheless, a very significant air pollution feature, because it may persist throughout the day and, thus, restrict vertical mixing.

When compared to a source near the surface and the effects of a radiation (surface) inversion, the pollutant dispersion pattern is quite different for an elevated source plume trapped in a layer near the base of an elevated inversion. This plume will not be in contact with the ground surface in the early morning hours because there is no mixing through the surface radiation inversion. Thus, the elevated plume will not affect surface pollutant concentrations until the mixing processes become strong enough to reach the altitude of the plume. At that time, the plume may be mixed downward quite rapidly in a process called

fumigation. During fumigation, surface O_3 concentrations will increase if the morning O_3 concentration is higher aloft than at the ground and if insufficient scavenging by NO occurs at ground-level. In fact, the rapid rise in O_3 concentrations in the morning hours is often the result of vertical (downward) transport from an elevated reservoir of O_3. After this initial increase, surface concentrations can continue to increase as a result of photochemistry or transport of O_3-rich air to the receptor.

When surface heating decreases in the late afternoon and early evening, the surface inversion will form again under most conditions. The fate of the elevated inversion is less clear, however. Although O_3 and its precursors have been mixed vertically, the reduction of turbulence and mixing at the end of the daylight hours leaves O_3 in a remnant layer that is often without a well-defined thermodynamic demarcation. This layer is then transported through the night, often to regions far removed from pollution sources, where its pollutants can influence concentrations at remote locations the next morning, as mixing entrains the elevated remnant layer. This overnight transport can be aided by the development of a nocturnal jet that forms many nights at the top of the surface inversion layer.

Geography can have a significant impact on the dispersion of pollutants (such as along the coast of an ocean or one of the Great Lakes). Near the coast or shore, the temperatures of land and water masses can be different, as can the temperature of the air above these land and water masses. When the water is warmer than the land, there is a tendency toward reduction in the frequency of surface inversion conditions inland over a relatively narrow coastal strip (Hosler, 1961). This in turn tends to increase pollutant dispersion in such areas. The opposite condition also occurs if the water is cooler than the land, as in summer or fall. Cool air near the water surface will tend to increase the stability of the boundary layer in the coastal zone, and thus decrease the mixing processes that act on pollutant emissions. These conditions occur frequently along the New England coast (Hosler, 1961). Similarly, pollutants from the Chicago area have been observed to be influenced by a stable boundary layer over Lake Michigan (Lyons and Olsson, 1972). This has been observed especially in summer and fall when the lake surface is most likely to be cooler than the air that is carried over it from the adjacent land.

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

There is concern that the strict use of mixing height unduly simplifies the complex atmospheric processes that redistribute pollutants within urban areas. There is growing evidence that some O_3 precursors may not be evenly redistributed over some urban areas. These are cases where the sources are relatively close to the urban area and atmospheric mixing is not strong enough to redistribute the material over a short travel time. In these

cases, it is necessary to treat the turbulent structure of the atmosphere directly and acknowledge the vertical variations in mixing. Methods that are being used to investigate these processes include the use of a diffusivity parameter to express the potential for mixing as a function of height. A simple expression of how the mean concentration, $\overline{\chi}$, changes with time, t, in an air parcel, assuming all concentrations are homogeneous in the horizontal, is

$$\frac{d\overline{\chi}}{dt} = -\frac{\partial \overline{w'\chi'}}{\partial z} , \qquad (3\text{-}80)$$

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 O_3 and its precursors often is 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

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

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, 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.

The use of an eddy diffusivity approach to turbulent diffusion assumes local down-gradient diffusion, a situation not always realistic in the atmosphere. It is important to note that eddy diffusivity is not valid under convective conditions because counter-gradient flows occur (Sun, 1986). Eddy diffusivity also does not work in the presence of multiple stable layers. Moreover, the form of the eddy diffusivity used in the existing air quality models is rather arbitrary. More research will be needed to remove this arbitrariness.

Another method used for convective situations is a technique called "large-eddy simulation", employed to recreate the probability of redistribution within the mixing height. This method explicitly simulates the larger eddies occurring under convective situations. 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 O_3 field experiments.

3.3.1.3 Cloud Venting

Vertical redistribution of O_3 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 as chemical reactors for soluble pollutants, returning the "processed" air to the PBL. They also can result in physical redistribution of O_3 and its precursors from the

PBL if convection is sufficiently vigorous (Greenhut, 1986; Dickerson et al., 1987). Clouds also act to influence photolysis rates and chemical transformation rates.

Greenhut (1986) showed that the net O_3 flux in the cloud layer was a linear function of the difference in O_3 concentration between the boundary and cloud layers. Ozone fluxes between clouds were usually smaller than those found within clouds, but the slower rate is at least partially offset by the larger region of cloud-free air relative to cloudy air.

Large clouds, such as cumulonimbus, offer considerably more potential for redistribution of O_3 and its precursors. Additionally, the cumulonimbus clouds also are associated with precipitation, a scavenger of pollutants, and with lightning, a potential source for NO_x. Using CO as a tracer, Dickerson et al. (1987) and Pickering et al. (1990) have illustrated the redistribution potential of cumulonimbus cloud systems. Lyons et al. (1986) provided an illustration of the potential for groups of cumulonimbus clouds to vent the polluted boundary layer.

The role of cloud venting is thought to be largely a cleansing process for the boundary layer, although a portion of the material lifted into the free troposphere could be entrained back to the surface in subsequent convection. Aircraft observations frequently have documented the occurrence of relatively high O_3 concentrations above lower concentration surface layers (e.g., Westberg et al., 1976). This is a clear indication that O_3 is preserved essentially in layers above the surface and can be transported over relatively long distances, even when continual replenishment through precursor reactions is not a factor, such as at night.

3.3.1.4 Stratospheric-Tropospheric Ozone Exchange

The fact that O_3 is formed in the stratosphere, mixed downward, and incorporated into the troposphere, where it forms a more or less uniformly mixed background concentration, has been known in various degrees of detail for many years (Junge, 1963). The mechanisms by which stratospheric air is mixed into the troposphere have been examined by a number of authors, as documented previously by the U.S. Environmental Protection Agency (EPA) (U.S. Environmental Protection Agency, 1986a, and references therein).

Although the portion of background O_3 near the surface attributed to stratospheric-tropospheric O_3 can be in the 5 to 15 ppb range for a seasonal average, this amount of O_3 by itself cannot account for peak urban O_3 values or regional episodes of elevated O_3 levels (Johnson and Viezee, 1981; Ludwig et al., 1977; Singh et al., 1980; and Viezee et al., 1979). Johnson and Viezee (1981) concluded that the O_3-rich intrusions studied sloped downward toward the south. In terms of dimensions, the average crosswind width (north to south), at an altitude of 5.5 km (ca. 18,000 ft), for six spring intrusions, averaged 226 km, and, for four fall tropopause fold systems, averaged 129 km. Ozone concentrations at 5.5 km averaged 108 ppb in the spring systems and 83 ppb in the fall systems. From this and other research described in the previous criteria document for O_3 and other photochemical oxidants (U.S. Environmental Protection Agency, 1986a), Viezee and coworkers (Viezee and Singh, 1982; Viezee et al., 1983) concluded (1) that direct ground-level impacts by stratospheric O_3 may be infrequent, occurring <1% of the time; (2) that such ground-level events are short-lived and episodic; and (3) that they are most likely to be associated on a 1- to 4-h average with O_3 concentrations in the range 60 to 100 ppb.

The monthly stratospheric-tropospheric total O_3 flux from tropospheric folding events in the Northern Hemisphere has been estimated. These fluxes, in units of 10^{35} O_3 molecules per month per tropospheric folding event, increase from 1.0 in January to

2.1 in April and May, decline to 1.0 in August, and reach a minimum of 0.5 in October and November (Viezee et al., 1983). The spring-to-fall variation resembles the seasonal variations of O_3 near ground-level often observed at more remote sites (e.g., Logan, 1985). Four of the 10 episodes in which ground-level O_3 has been attributed to stratospheric O_3 transport occurred during March, but several such episodes during summer months have been reported (see below).

Using the ^{7}Be-to-O_3 ratio as an indicator of O_3 of stratospheric origin and SO_4^{2-} concentrations as a tracer for anthropogenic sources, Altshuller (1987) estimated stratospheric contributions of O_3 in the range 0 to 40 ppb (0 to 95% of observed O_3) at ground level at Whiteface Mountain, NY, for July 1975 and mid-June to mid-July 1977. Monthly average stratospheric contributions were estimated at 5 to 10 ppb. Extant ^{7}Be and O_3 data for a number of lower-elevation rural locations in the western, midwestern, and southeastern United States also were examined, and stratospheric or upper tropospheric contributions of 6 to 8 ppb were calculated. The author concluded that the calculated values for such contributions should be viewed with caution and regarded as probable upper limits because of scatter in the ^{7}Be and corresponding O_3 data that hindered definition of the ^{7}Be-to-O_3 ratio. Altshuller also concluded that removal and dilution processes result in the loss of most stratospheric O_3 before it reaches ground level. In other work performed in England, O_3 of stratospheric origin was estimated to contribute 10 to 15 ppb to the daily maximum hourly mean O_3 concentrations in an April through October period (Derwent and Key, 1988; United Kingdom Photochemical Oxidant Review Group, 1993).

3.3.2 Meteorological Parameters

This section focuses on analyses of data from previous and ongoing measurement programs to address two key questions: (1) are there meteorological parameters which are systematically associated with O_3 levels? and (2) are relationships between O_3 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 O_3 levels include ultraviolet radiation, temperature, wind speed, atmospheric mixing and transport, and surface scavenging. The following examines the theoretical basis for each of these factors and identifies to what degree empirical evidence supports the hypotheses.

3.3.2.1 Sunlight

Ultraviolet radiation plays a key role in initiating the photochemical processes leading to O_3 formation. Sunlight intensity (specifically the UV portion of sunlight) varies with season and latitude, but the latter effect is strong only during 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 systems 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 O_3 levels. Samson and Shi (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 peak in O_3 concentrations usually lags the peak in potential solar radiation that occurs at the Summer Solstice on or about June 23.

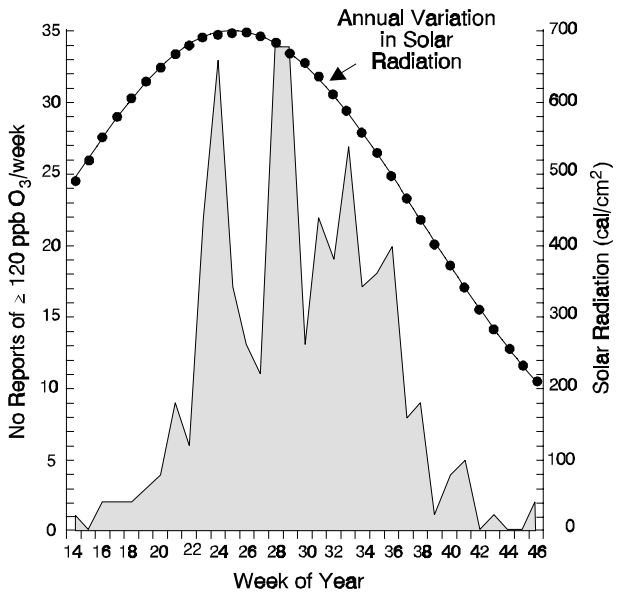
3.3.2.2 Temperature

There is an association between tropospheric O_3 concentration and tropospheric temperature that has been demonstrated from measurements in outdoor smog chambers and from measurements in ambient air. A linear relationship between maximum O_3 and temperature was obtained in the smog chambers with little scatter around the regression line (Kelly and Gunst, 1990). Numerous ambient studies done over more than a decade have reported that successive occurrences or episodes of high temperatures characterize seasonally high O_3 years (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), in New England (Wolff and Lioy, 1978; Atwater, 1984; Wackter and Bayly, 1988), and elsewhere.

Figures 3-9 and 3-10 show the daily maximum O_3 concentrations versus maximum daily temperature for summer months (May to October), 1988 to 1990, for Atlanta and New York City, NY, and for Detroit, MI, and Phoenix, AZ, respectively. There appears to be an upper-bound on O_3 concentrations that increases with temperature. Likewise, Figure 3-11 shows that a similar qualitative relationship exists between O_3 and temperature even at a number of rural locations.

The notable trend in these plots is the apparent upper-bound to O_3 concentrations as a function of temperature. It is clear that, at a given temperature, there is a wide range of possible O_3 concentrations because other factors (e.g., cloudiness, precipitation, wind speed) can reduce the O_3 production. The upper bound presumably represents the maximum O_3 concentration achieved under the most favorable conditions. These plots, based on ambient air measurements, show wide scatter in O_3 concentration with temperature because of the contributions to variations from several of these factors that do not influence the results from smog chamber studies (Kelly and Gunst, 1990). Table 3-4 lists the results of a statistical regression performed on the paired O_3-temperature data used in Figures 3-9 and 3-10 with separate slopes listed for temperatures above and below 30 °C. Results show that, for T > 30 °C, the O_3-temperature relationship is statistically significant at all sites. The rate of increase for T > 30 °C is 3 to 5 ppb/°C at eastern United States rural sites and ranges from 4 to 9 ppb/°C at the three eastern U.S. urban sites (New York, Detroit, and Atlanta). At two western sites, Williston, ND, and Billings, MT, there is a much weaker

Figure 3-8. The number of reports of ozone concentrations ≥120 ppb at the 17 cities studied in Samson and Shi (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 and Shi (1988).

dependence on temperature, possibly reflecting the lower level of anthropogenic activity. At a third western site, Medford, OR, the O_3-temperature relationship is comparable to that at rural eastern sites.

Relationships between peak O_3 and temperature also have been recorded by Wunderli and Gehrig (1991) for three locations in Switzerland. At two sites near Zurich, peak O_3 increased 3 to 5 ppb/°C for diurnal average temperatures between 10 and 25 °C, and little change in peak O_3 occurred for temperatures below 10 °C. At the third site, a high-altitude location removed from anthropogenic influence, much less variation of O_3 with temperature was observed.

The hypotheses for this correlation of O_3 with temperature include, but are not necessarily limited to:

1. Reduction in photolysis rates under meterological conditions associated with low temperatures;
2. Reduction in H_2O concentrations at low temperatures;
3. Thermal decomposition of PAN and its homologues;
4. Increased anthropogenic emissions of reactive hydrocarbons or NO_x, or both;
5. Increased natural emissions of reactive hydrocarbons; and
6. Relationships between high temperatures and stagnant circulation patterns.

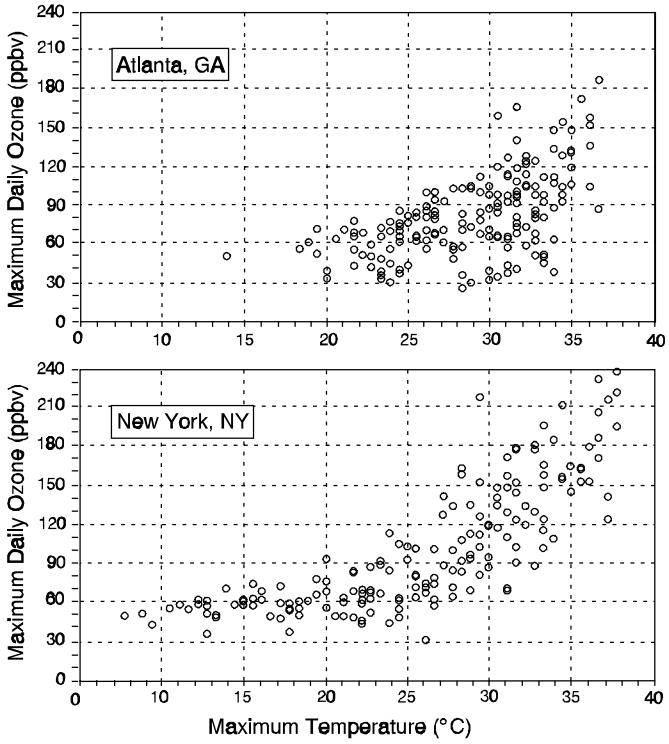


Figure 3-9. A scatter plot of maximum daily ozone concentration in Atlanta, GA, and New York, NY, versus maximum daily temperature.

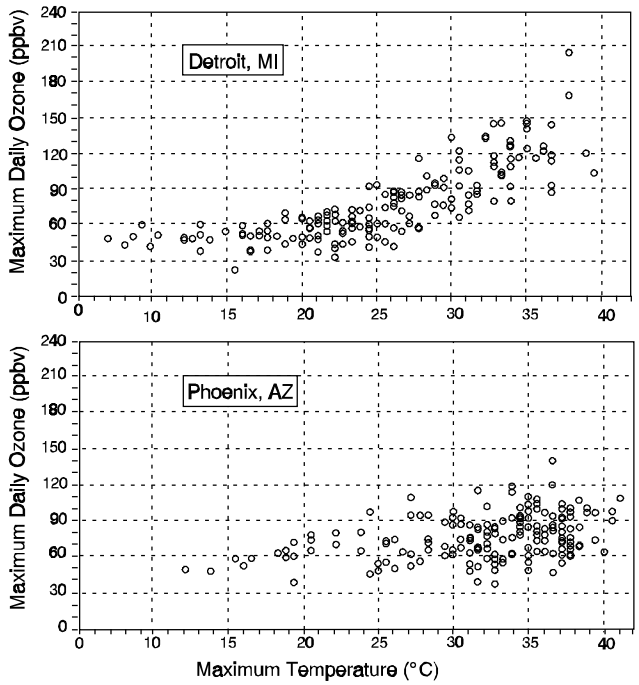


Figure 3-10. A scatter plot of maximum daily ozone concentration in Detroit, MI, and Phoenix, AZ, versus maximum daily temperature.

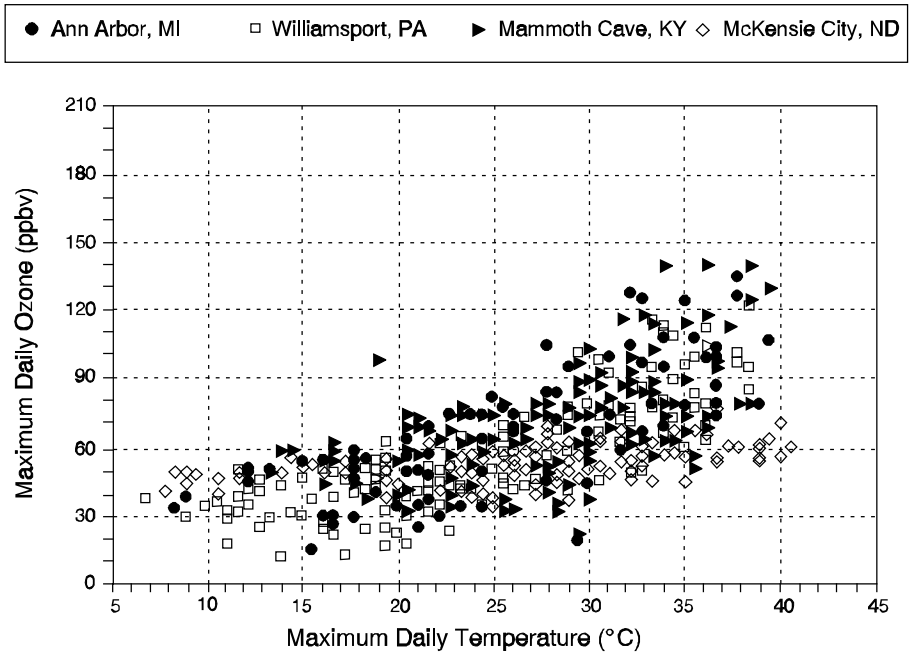


Figure 3-11. A scatter plot of maximum ozone concentration versus maximum daily temperature for four nonurban sites. The relationship with temperature is still apparent, although the slope is reduced from that of the urban areas.

Table 3-4. Rates of Increase of Peak Ozone with Diurnal Maximum Temperature (ppb/°C) for Temperature <300 K (27 °C) and Temperature >300 K, Based on Measurements for April 1 to September 30, 1988[a]

Location		T < 300 K		T > 300 K	
		$\Delta O_3/\Delta T$	T-Statistic	$\Delta O_3/\Delta T$	T-Statistic
Urbanized Regions					
	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	—	—
Nonurban Sites					
	Williamsport, PA	1.2	−5.0	4.0	−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	0.8	−3.7
	Billings, MT	0.1	−0.5	0.7	−2.2
	Medford, OR	0.5	−2.6	3.3	−13.7

[a]See Appendix A for abbreviations and acronyms.

The relationship with temperature is well known, but not yet reproduced by air quality models. Although it has been argued that this striking relationship with temperature is an indirect result of the stagnant synoptic meteorological conditions that lead to higher O_3 levels, the correlation is not strong with other parameters of stagnation, notably wind speed, which is discussed later.

Reduction in Photolysis Rates

It is possible that, on a seasonal scale, the correlation between temperature and O_3 may be an indirect correlation with UV radiation variability. This is insufficient, however, to explain the day-to-day correlation between the two variables.

Changes in photolysis rates and in H_2O concentrations are related in that both are linked to the supply of OH radicals, which determines the rate of O_3 production in clean atmospheres and contributes to O_3 production in polluted atmospheres. A reduction in either photolysis rates or H_2O would reduce the source of OH radicals. Calculations by Sillman and Samson (1995) showed that the difference between summer and fall photolysis rates (at 40° N latitude) has a significant impact on the rate of O_3 production in urban photochemical simulations, roughly equal to the impact of PAN thermal decomposition (discussed below). However the impact of photolysis rates and of water vapor was much lower in simulations for polluted rural environments. In the simulations by Sillman et al. (1993), O_3 production in urban environments was limited largely by the supply of OH radicals to react with hydrocarbons; whereas in rural environments the limiting factor was the source of NO_x. Consequently, photolysis rates and H_2O had less impact on O_3 production in rural environments.

Thermal Decomposition of Peroxyacetyl Nitrate

Temperature-dependent photochemical rate constants provide a link between O_3 and temperature (Sillman et al., 1990a; Cardelino and Chameides, 1990). The reason for the decline in O_3 in rural areas when the PAN decomposition rate decreases is that PAN represents a sink for NO_x in rural environments. When the rate of PAN decomposition is decreased, NO_x drops sharply, whereas OH and HO_2 remain largely unaffected. Consequently, the rate of the important HO_2 + NO reaction (see Section 3.2) shows a substantial decrease.

The photochemical response in an urban environment is fundamentally different, although the final result, a decrease in O_3 with temperature, is similar. The impact of PAN in urban environments is attributable to its role as a sink for odd hydrogen rather than to its effect on NO_x (Cardelino and Chameides, 1990). Sillman et al. (1990a) have shown that the well-known division of O_3 photochemistry into NO_x- and VOC-sensitive regimes is associated with the relative magnitude of odd-hydrogen sinks.

Sillman and Samson (1995) found that the thermal decomposition of PAN was enough to explain an increase of 1 to 2 ppb peak O_3/°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 O_3 with a rise in temperature (3 to 5 ppb/°C, Table 3-4).

Increased Anthropogenic Emissions

Emission rates for anthropogenic hydrocarbons (VOCs) also can increase with temperature (U.S Environmental Protection Agency, 1989; Stump et al., 1992). Increased

anthropogenic VOC emissions might be expected to cause increased rates of O_3 production in urban areas where O_3 is sensitive to VOC, but would be less likely to have impact on rural areas where biogenic VOC emissions can predominate. However, O_3 in rural areas is NO_x dependent. The NO_x-sensitive rural areas also would show increased O_3 production with a rise in temperature as biogenic NO_x emissions increase with temperature.

Increased Natural Emissions

Emissions of biogenic hydrocarbons increase sharply with a rise in 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 4. From coniferous trees, the increase was on the order of 1.5.

Recently, Jacob et al. (1993) found that the photochemistry of O_3 production in a polluted rural environment (Blue Ridge Mountains, VA) is significantly different in September and October, when natural emissions from deciduous forests have ceased. The difference in chemistry between summer and fall leaf production also may have an impact on the O_3-temperature correlation.

Correlation with Stagnation

Recently, Jacob et al. (1993b) found that model-simulated O_3 formation in the rural United States shows a tendency to increase with a rise in temperature, based solely on the difference in atmospheric circulation between relatively warm and relatively cool days. The model-simulated O_3-temperature correlation was less than observed but large enough to represent a significant component of the observed correlation. However, the temperature-meteorology correlation identified by Jacob et al. (1993b) was based on simulated meteorology from a General Circulation Model rather than on direct observations.

3.3.2.3 Wind Speed

Ozone is expected to be influenced by wind speed because lower wind speeds should lead to reduced ventilation and the potential for greater buildup of O_3 and its precursors. Abnormally high temperatures are frequently associated with high barometric pressure, stagnant circulation, and suppressed vertical mixing resulting from subsidence (Mukammal et al., 1982), all of which may contribute to elevated O_3 levels. However, in reality this relationship varies from one part of the country to another. Figure 3-12 shows the frequency of 24-h trajectory transport distances to Southern cities on days with resulting concentrations of $O_3 \geq 120$ ppb (Samson and Shi, 1988). The frequency for Southern cities is biased toward lower wind speeds. The same bias was shown for all 17 cities in the study. A similar plot for cities in the northeastern United States (Figure 3-13) shows an opposite pattern, in which the bias is toward higher wind speeds than normal. It is unclear how much meteorological information is needed in order to perform accurate urban-area O_3 simulations using advanced photochemical models. To understand the significance of variations between upper-air wind measurements during the Southern Oxidant Study (SOS), 1992, Atlanta, an intensive, intercomparison test of the precision of upper-air measurements was conducted. Collocated measurements were made at an SOS measurement site, using a boundary-layer lidar, a wind profiler, and a rawinsonde balloon. There was generally good agreement between the profiler and rawinsonde, although some large outliers existed. Figure 3-14 illustrates that the root-mean-square difference (RMSD) varied with altitude. The RMSD reached a minimum near 1,200 m above ground level (AGL) of about 2 m/s, rising to over

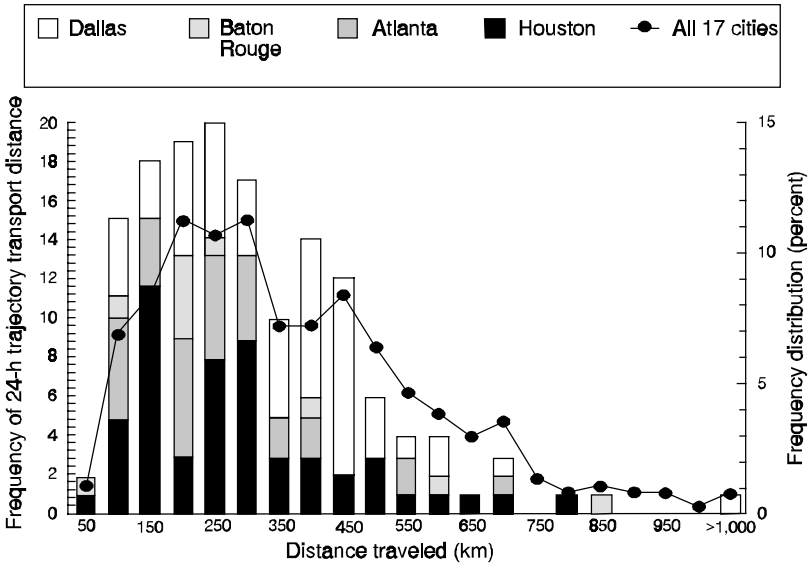


Figure 3-12. The frequency of 24-h trajectory transport distance en route to city when ozone was ≥120 ppb in four Southern U.S. cities, compared with the percent frequency distribution for all 17 cities (scale on right) of a nationwide study, 1983 to 1985.

Source: Samson and Shi (1988).

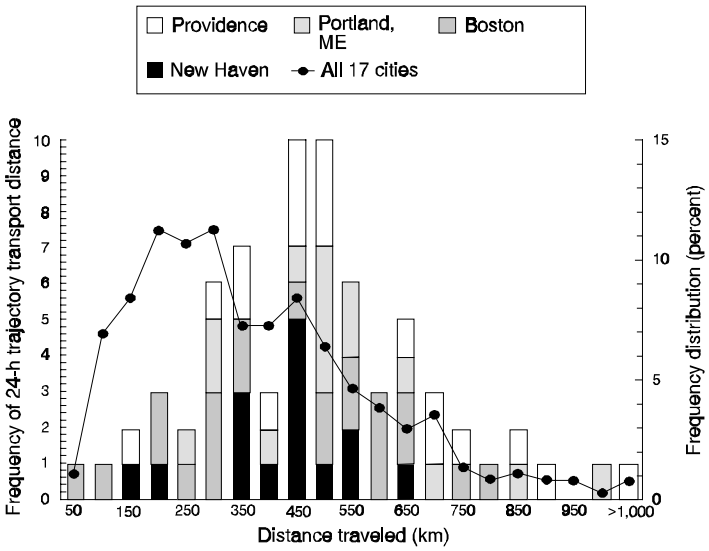


Figure 3-13. The frequency of 24-h trajectory transport distance en route to city when ozone was ≥120 ppb in four New England cities, compared with the percent frequency distribution for all 17 cities (scale on right) of a nationwide study, 1983 to 1985.

Source: Samson and Shi (1988).

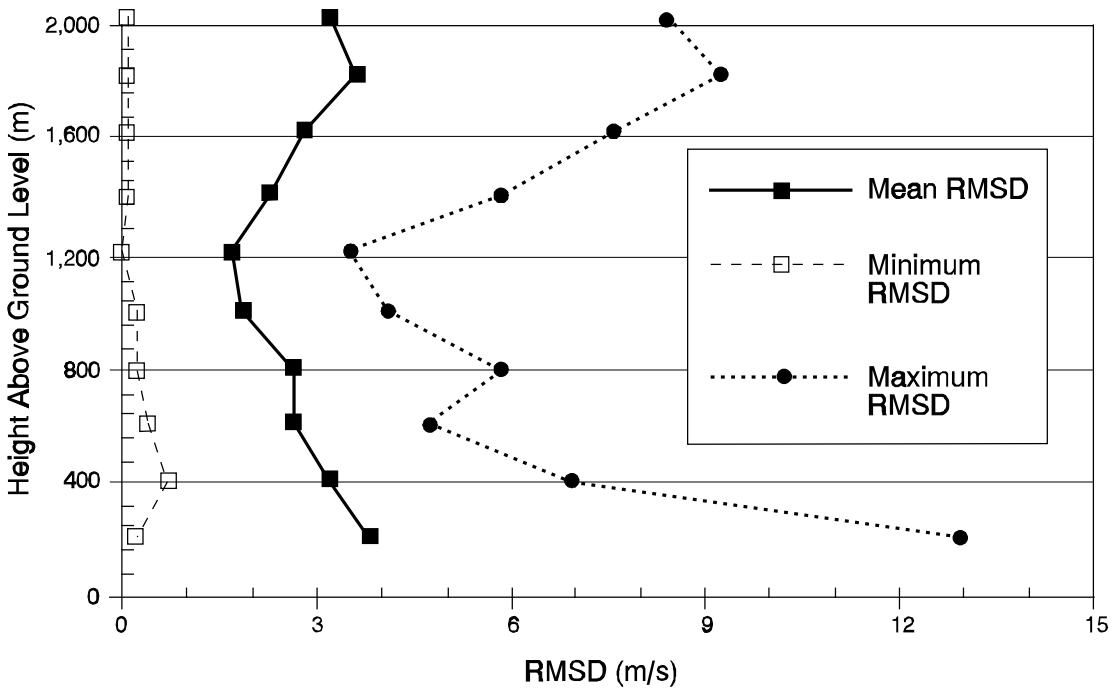


Figure 3-14. The root-mean-square difference (RMSD) between CLASS observations and profiler observations as a function of height above ground level.

3 m/s near the surface and above 1,200 m AGL. Figure 3-15 illustrates the RMSD for the lidar comparison with CLASS observations. There is slightly greater RMSD at all heights than for the profiler-rawinsonde comparison, with a relative minimum observed at about 1,200 m.

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. The profiler obtained values biased slightly higher than the CLASS system (+0.2 m/s), whereas 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 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, 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 is stagnant over, say, the center of Canada will exhibit relatively cold, dry conditions and will be relatively devoid of pollutants. Air that

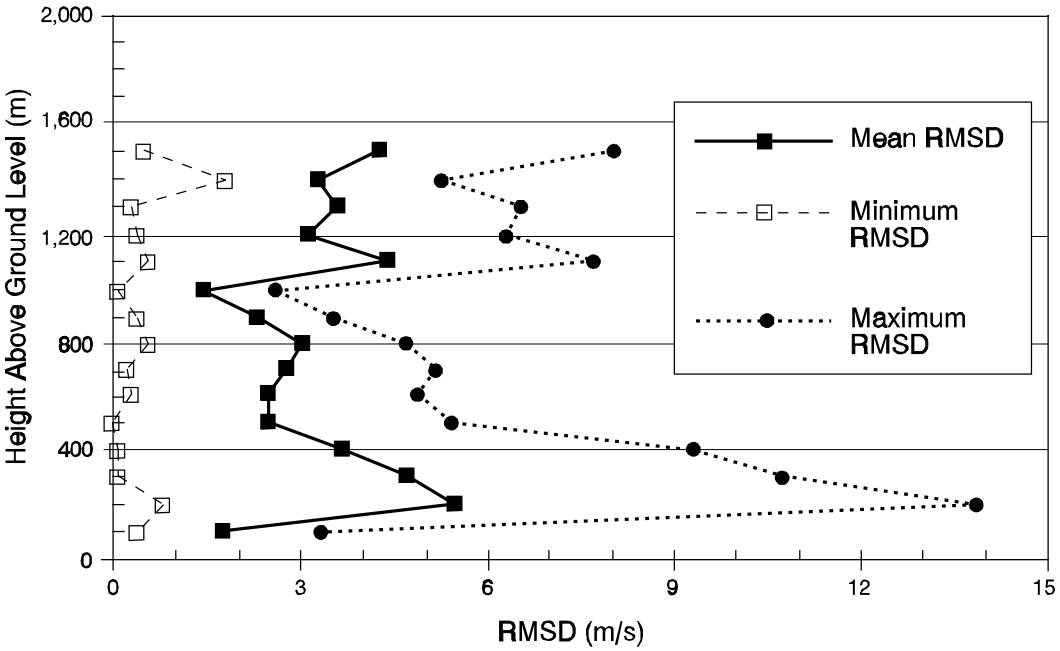


Figure 3-15. The root-mean-square difference (RMSD) between CLASS observations and lidar observations as a function of height above ground level.

resides over the industrial regions of the midwestern United States will exhibit low visibility and, often, high O_3 levels on a regional scale. Meteorological processes play an important role in determining the amount of "accumulation" of O_3 and its precursors that occurs under such stagnant conditions.

Episodes of high O_3 concentrations in urban areas often are associated with high concentrations of O_3 in the surroundings. This accumulated O_3 forms under the same atmospheric conditions that lead to high O_3 levels in urban areas and exacerbates the urban problem by supplying relatively high O_3 and precursor concentrations to the urban area from upwind. The transport of O_3 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, 1984; Sexton, 1982; Wolff et al., 1982; Altshuller, 1988). A summary of most of these reports was given in the 1986 O_3 criteria document (U.S. Environmental Protection Agency, 1986a) and will not be reiterated here. The phenomena of high nonurban O_3 levels was 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 O_3 accumulation are characterized by synoptic-scale subsidence of air in the free troposphere, resulting in development of an elevated inversion layer; relatively low wind speeds associated with the weak horizontal pressure gradient around a surface high pressure system; lack of cloudiness; and high temperatures.

On occasion, O_3 at levels greater than 120 ppb can occur in rural areas far removed from urban or industrial sources. Ozone levels at the summit of Whiteface Mountain exceeded this value during the summer of 1988 when O_3 accumulated across a

wide expanse of the eastern United States at levels ≥120 ppb. Nonetheless, even when the regional accumulation is at a level below the current O_3 NAAQS, the increment needed to bring the level above the NAAQS in an urban area is not large.

The identification and understanding of the transport of photochemical O_3 and other oxidants and their precursors by weather systems represent a significant advance in comprehending photochemical air pollution and the potential extent of its effects. Considerable progress has been made in the development of long-range photochemical modeling techniques so that the likely impact of synoptic systems can be anticipated. Such tools are very much in the research stage, however, because the local impact of O_3 and other oxidants results from a complex interaction of distant and local precursor sources, urban plumes, mixing processes, atmospheric chemical reactions, and general meteorology.

3.3.3 Normalization of Trends

The degree to which meteorological factors can be "normalized" out of the O_3 concentration and "trends" data depends in large part on the strength of the relationships between O_3 and meteorological components. As part of the SOS Atlanta intensive field campaign, an attempt was made to model statistically the O_3 levels in Atlanta to build a predictive tool for forecasting days of specialized measurement. Figure 3-16 shows the fit of the data used to create the model to the model simulations. Figure 3-17 shows the fit obtained from independent data collected in 1992.

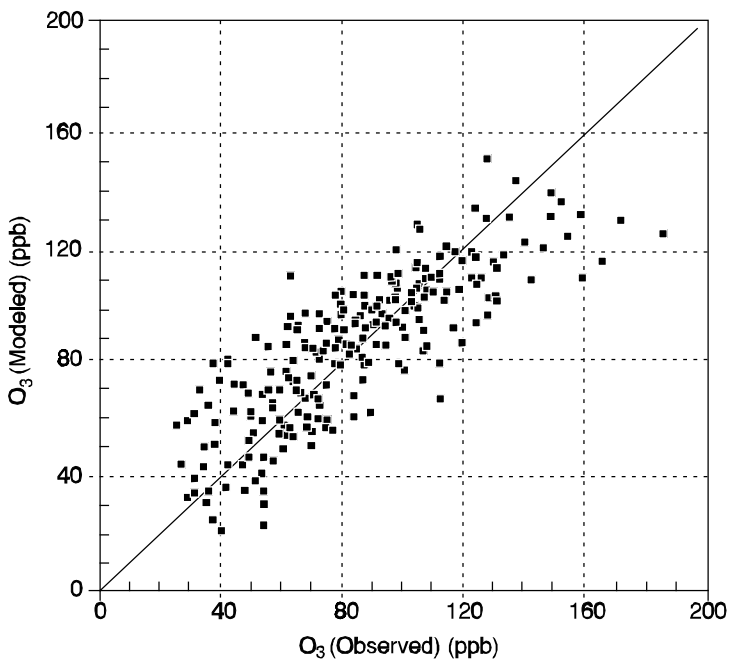


Figure 3-16. Model of ozone (O_3) levels using regression techniques. The use of wind speed, temperature, and previous-day ozone provided a means to forecast O_3 levels.

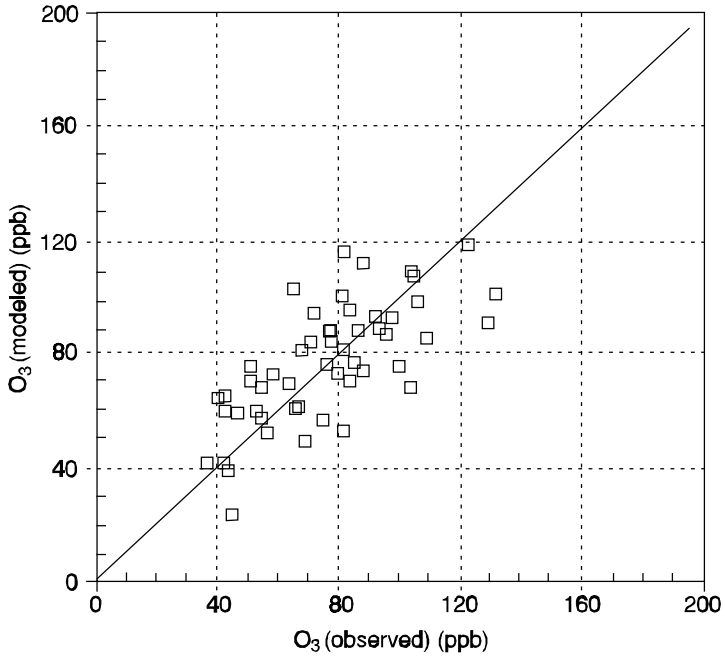


Figure 3-17. Simulated versus observed ozone levels using regression techniques on an independent data set obtained in the summer of 1992 in Atlanta, GA.

This model was used successfully to predict next-day O_3 levels in Atlanta. Ozone levels in a number of American cities should be analyzed using regression tools such as this in order to normalize meteorological variability. Through such analyses, it is possible that trends, if any, represented as systematic deviations from the model, may become observable. A summary of other techniques for removing meteorological variability is contained in the recent monograph from the National Research Council (1991). Table 3-5 lists a sample of studies aimed at evaluation of O_3 trends.

3.4 Precursors of Ozone and Other Oxidants

3.4.1 Sources and Emissions of Precursors

3.4.1.1 Introduction

As described elsewhere in this chapter, O_3 is formed in the atmosphere through a series of chemical reactions that involve VOCs and NO_x. Control of O_3 depends on reducing emissions of VOCs or NO_x or both. Thus, it is important to understand the sources and source strengths of these precursor species in order to devise the most appropriate oxidant control strategies. In the following sections, anthropogenic and biogenic NO_x and VOC sources will be described, and the best estimates of their current emission levels and trends will be provided. Confidence levels for the assigned source strengths will be discussed.

Both English and metric units have been utilized in emission inventories. Thousands or millions of short tons are the common scales in the English system. The metric unit most

Table 3-5. Recent Studies Examining Trends in Ozone Data After Removal of Variability Associated with Meteorological Factors

Study	Variables	Approach
Jones et al. (1989)	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, wind speed, 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, wind speed, 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, wind speed, 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).

often employed is millions of metric tons, which is equivalent to teragrams (Tg). To convert English tons to teragrams, multiply English tons by 0.907×10^{-6}. For consistency, teragrams have been employed throughout the ensuing discussion.

3.4.1.2 Nitrogen Oxides

Manmade Emission Sources

Anthropogenic NO_x sources are associated with combustion processes. The primary pollutant is NO, which is formed from nitrogen and oxygen atoms that are produced at high combustion temperatures when air is present. In addition, NO_x is formed from nitrogen contained in the combustion fuel. Major NO_x source categories include transportation, stationary source fuel combustion, industrial processes, solid waste disposal,

and some miscellaneous combustion-related activities. Table 3-6 provides a more detailed summary of each of these source categories. The transportation category includes gasoline- and diesel-powered motor vehicles, aircraft, railcars, vessels, and off-highway vehicles. Electric utilities, industrial and commercial/institutional boilers, industrial furnaces, and space heaters comprise the stationary source fuel combustion category. Industrial processes include petroleum refining and paper, glass, steel, cement, and chemical production. The incineration and open burning of waste leads to emissions of NO_x in the solid waste disposal category. The miscellaneous sources category includes prescribed forest slash burning, agricultural burning, coal refuse burning, and structure fires. It should be noted at this point that, even though NO is the pollutant emitted, NO_x emission inventories are quantified relative to NO_2 (mol wt = 46). Nitrogen dioxide is a secondary pollutant produced via oxidation of NO in the atmosphere.

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 EPA. 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: (1) highways, (2) rural roads, and (3) urban streets.

Table 3-7 provides a summary 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. About half of the emissions (10.69 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 are divided among 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. Local NO_x source apportionment may differ substantially from these national figures.

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 III, IV, V, and VI (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 3-6. 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	Forestries
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			
Railcars	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 (1992a).

Table 3-7. 1991 Emission Estimates for Manmade Sources of Nitrogen Oxides in the United States

Source Category	Emissions (Tg)	
Transportation		9.71
Highway vehicles	7.20	
Off-highway vehicles	2.51	
Stationary fuel combustion		10.69
Electric utilities	6.74	
Industrial	3.27	
Other	0.68	
Industrial processes		0.80
Solid waste disposal		0.07
Miscellaneous		0.12
Forest burning		
Other burning		
Miscellaneous organic solvents		
Total of all sources		21.39

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

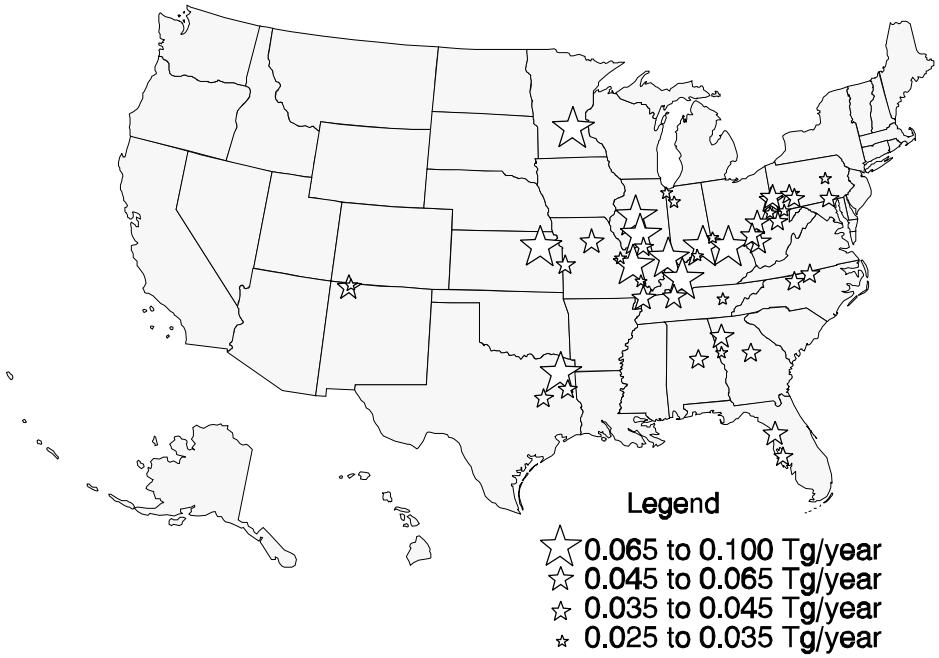


Figure 3-18. The 50 largest sources of nitrogen oxides (power plants) in the United States.

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

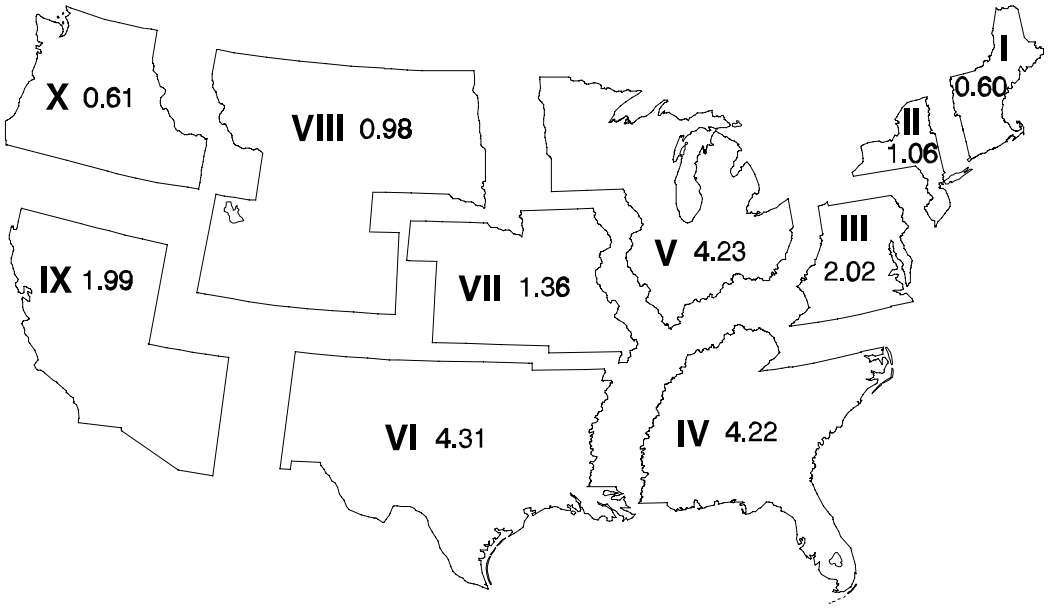


Figure 3-19. Nitrogen oxides emissions (Tg/year) from manmade sources in the 10 U.S. Environmental Protection Agency regions of the United States, 1991.

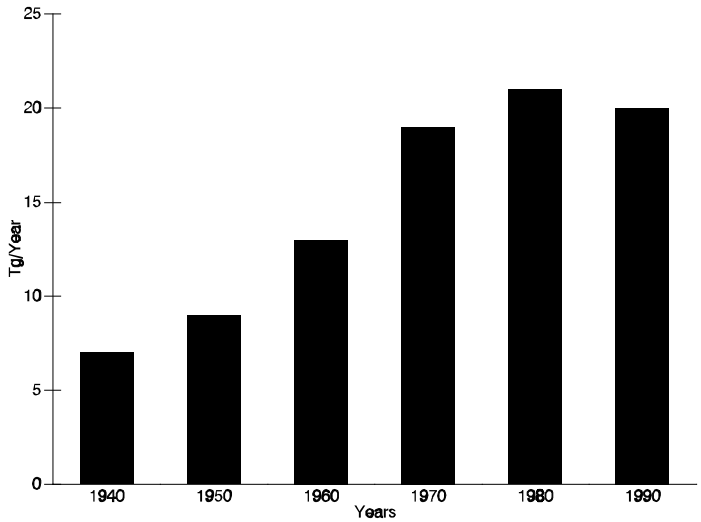
Source: U.S. Environmental Protection Agency (1993b).

Seasonal variations are available for the 1993 NO_x emissions from 14 source categories in the United States (U.S. Environmental Protection Agency, 1994). Very little seasonal variation occurred for categories contributing approximately three-quarters of the total annual NO_x emissions, including the categories of highway vehicles, electric utilities, and industrial combustion sources. For off-highway sources (comprising 20% of the total annual NO_x emissions), 29% of the off-highway NO_x emissions occur in the summer and 21% in the winter. In contrast, the category of other combustion sources (comprising 5% of the total annual NO_x emissions) emit 47% of the NO_x emissions in the winter and only 8% in the summer. An earlier inventory for 1985 (U.S. Environmental Protection Agency, 1989), which considered only total point and area anthropogenic NO_x emissions, indicated that very little variation occurred in NO_x emissions among the winter, spring, summer, and fall seasons. The contributions of these NO_x categories also were shown to vary seasonally by region of the United States.

Trends in Nitrogen Oxides Emissions

Estimates of NO_x emissions have been made back to 1900, when approximately 2.3 Tg were emitted into the atmosphere in the United States (U.S. Environmental Protection Agency, 1992a). 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

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 (1992a).

20 Tg/year. Currently, more 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. However, the recent trends in transportation-related NO_x emissions shown in Table 3-8 indicate no trend between 1987 and 1991. 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, transportation-related NO_x emissions have remained essentially constant, whereas the stationary source NO_x emissions have increased about 10%.

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 the provisions of the Clean Air Act, which was 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 O_3 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% between 1990 and 2000. Projections based on VMT and emission factors from the MOBILE model suggest nearly a 50% decrease in NO_x emissions from highway vehicles manufactured from 1990 to 2000 (U.S. Environmental Protection Agency, 1992a).

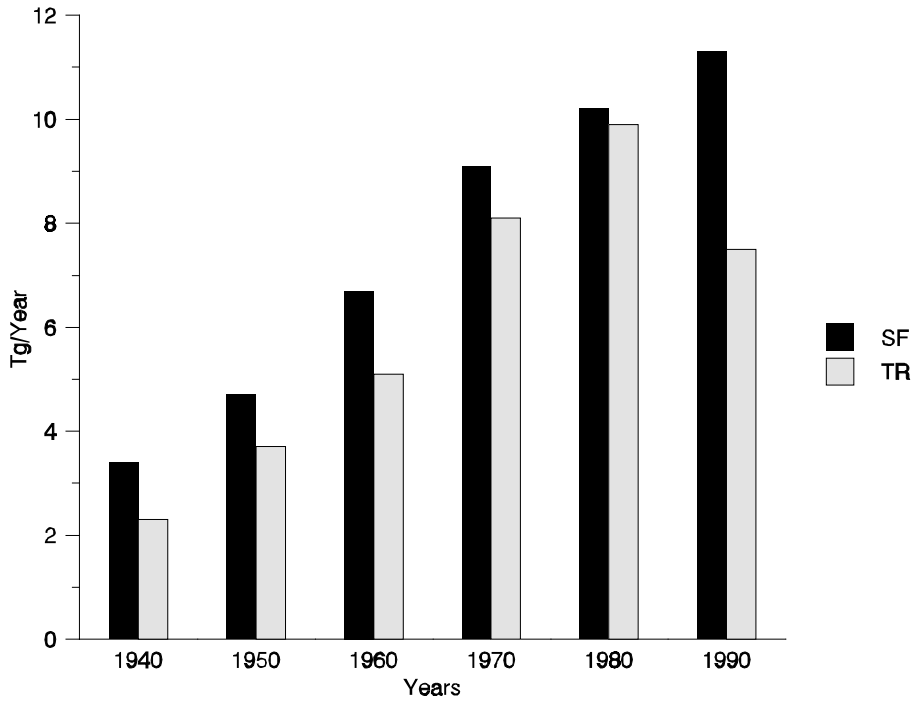


Figure 3-21. Changes in nitrogen oxides emissions from stationary source fuel combustion (SF) and transportation (TR) from 1940 through 1990.[a]

[a]The values for 1990 do not agree with those in Table 3-8 because different models were employed for deriving the short- and long-term trends.

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

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[a]	9.9	10.7
1989	9.7	10.7
1988	9.9	10.6
1987	9.7	10.1

[a]The values for 1990 do not agree with those in Figure 3-21 because different models were employed for deriving the short- and long-term trends.

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

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 generally is believed that published estimates are very reliable. For example, the National Acid Precipitation Assessment Program (NAPAP) NO_x inventory for U.S. emissions in 1985 (18.6 Tg) was assigned a 90% relative confidence interval in the range of 6 to 11% (Placet et al., 1991). This confidence level was based on judgments used to assign uncertainty to component inputs of emission models and on statistical assumptions used to aggregate uncertainty values.

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

Recent attempts to validate NO_x emission factors or inventories have involved comparing ambient NO_x concentrations with values predicted using emissions-based models. These generally have taken one of two forms: (1) comparisons between NO_x concentrations measured in a tunnel and those predicted from emission factors, activity levels, and dilution factors in the tunnel; or (2) whole-city integration procedures in which ambient NO_x concentrations are compared to ambient NO_x levels that have been predicted using a model such as the Urban Airshed Model (UAM). The latter approach has been applied in the South Coast Air Basin (Fujita et al., 1992). It was reported that measured and predicted NO_x concentrations agreed within 20% for a 2-day period in August 1987. Likewise, the results from tunnel studies (Pierson et al., 1990; Robinson et al., 1996) have shown reasonably good agreement between predicted and measured NO_x concentrations. It is important to keep in mind that ambient NO_x levels predicted using a modeling method cannot be assigned true value status. There could be as much or more uncertainty in the model outputs as there is in the emission inputs that are being tested. The fact, however, that an emissions-based model predicts ambient concentrations that are close to those measured tends to lend credence to the NO_x emission estimates. No systematic study of the effect of these uncertainties on model predictions has been published, but a limited summary of sensitivity analyses appears in Seinfeld (1988).

In addition, NO_x inventory validation has involved comparing annual emission estimates reported by different groups. Table 3-9 shows several annual U.S. NO_x emission estimates. In 1982, the estimates vary by less than 12% and this decreases to about 9% in the 1985 comparison.

Natural Emission Sources

Natural sources of NO_x include lightning, soils, wildfires, stratospheric intrusion, and the oceans. Of these, lightning and soils are the major contributors. The convention 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

Table 3-9. Comparison of Estimates of Nitrogen Oxides Emissions from Manmade Sources in the United States[a]

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

[a]See Appendix A for abbreviations and acronyms.

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

NO_x emitted from large wildfires can be significant on a regional scale, this source is overall 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 small NO_x emissions from sea water, transport of NO_x from oceans is thought to be a negligible source in the United States.

Lightning. Lightning produces high enough temperatures to allow N_2 and O_2 to be converted to NO. Two methods have been employed to estimate the NO_x source strength from lightning:

(1) Multiply the frequency of lightning flashes by the energy dissipated per flash and the NO production per unit of energy dissipated; or
(2) Relate NO_x production to NO_3^- deposition in remote areas where lightning-produced NO_x is thought to be the dominant NO_3^- precursor.

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

Soils. Both nitrifying and denitrifying organisms in the soil can produce NO_x. The relative importance of these two pathways is probably highly variable from biome to biome. Nitric oxide is the principal NO_x species emitted from soils, with emission rates depending mainly on fertilization levels and soil temperature. Several reports have noted a large increase in NO_x emissions from agricultural soils treated with NO_3^--containing fertilizers (Johansson and Granat, 1984; Kaplan et al., 1988; Johansson, 1984). Measurements of soil NO_x emissions have established that the relationship with temperature is exponential,

consisting of approximately a twofold increase for each 10 °C rise in temperature (Williams et al., 1992; Valente and Thornton, 1993).

Inventorying soil NO_x emissions is difficult because of the large temporal and spatial variability in emissions. The existing inventories have been developed using emission algorithms that are functions of soil temperature and land-use type. Two broad, land-use categories—natural and agricultural—have been assigned. The natural soils are broken down into biome types, and the agricultural soils subdivided according to fertilizer applications. 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 10 U.S. Environmental Protection Agency regions. Approximately 60% of this NO_x is emitted in Regions V, VII, and VIII (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 from Soils by U.S. Environmental Protection Agency Region[a]

U.S. Environmental Protection Agency Region	NO_x Emissions (Tg)
I, II, and III	0.05
IV	0.11
V	0.26
VI	0.18
VII	0.27
VIII	0.21
IX	0.04
X	0.01
Total	1.20[b]

[a]See Appendix A for abbreviations and acronyms.
[b]Values do not sum to total due to independent rounding.

Source: Placet et al. (1991).

Uncertainty in Estimates of Natural Nitrogen Oxides Emissions

As previously indicated, 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 4 (Placet et al., 1991).

Sources of uncertainty when inventorying NO_x emissions from soils include: land-use assignments, soil temperature, and emission algorithm development. Confidence levels assigned to categories 1 and 2 are about ±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 ±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 2 to 4.

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 the summer months of 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

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, aromatics), or substituted hydrocarbons that contain a functional group such as alcohol, ether, carbonyl, ester, or halogens. The emissions of methane have been ignored because of their largely natural origin and the fact that the importance of methane is limited primarily to global scale processes. In addition, the atmospheric oxidation rate of methane 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.

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

Table 3-11. Estimated 1991 Emissions of Volatile Organic Compounds from Manmade Sources in the United States

Source Category	Emissions (Tg)	
Transportation		7.87
Highway vehicles	6.00	
Off-highway vehicles	1.87	
Stationary fuel combustion		0.68
Electric utilities	0.03	
Industrial	0.26	
Other	0.39	
Industrial processes		9.97
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		2.01
Miscellaneous		0.51
Total all sources		21.04

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

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.

Seasonal variations are available for the 1993 anthropogenic VOC emissions from 14 source categories in the United States (U.S. Environmental Protection Agency, 1994). Very few seasonal variations occur for categories contributing approximately 85% of the total annual VOC emissions. The only category of VOC emissions that showed significant seasonal variation was off-highway sources, which comprises 13% of the total annual VOC emissions. These off-highway sources contribute 31% of their VOC emissions in summer and 19% in winter. An earlier inventory for 1985 (U.S. Environmental Protection Agency, 1989), which considered total point and area anthropogenic VOC emissions, indicated that very little variation in VOC emissions occurred between the winter, spring, summer, and fall seasons. The contribution of these VOC emissions also were shown to vary seasonally by region of the United States.

Trends in Emissions

Emissions of nonmethane VOCs peaked in the early 1970s and have decreased continually since then. 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, 1992a). Figure 3-22 illustrates these changes at 10-year intervals from 1940 to 1990. Until 1970, highway vehicles were the major source of VOC emissions. As automobiles have been equipped with more and better emission controls, however, emissions from the transportation sector have dropped below those from industrial processes, the category that 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 exhibited a decrease in emissions from 4.5 Tg in 1940 to a 1990 level estimated at 2.8 Tg/year.

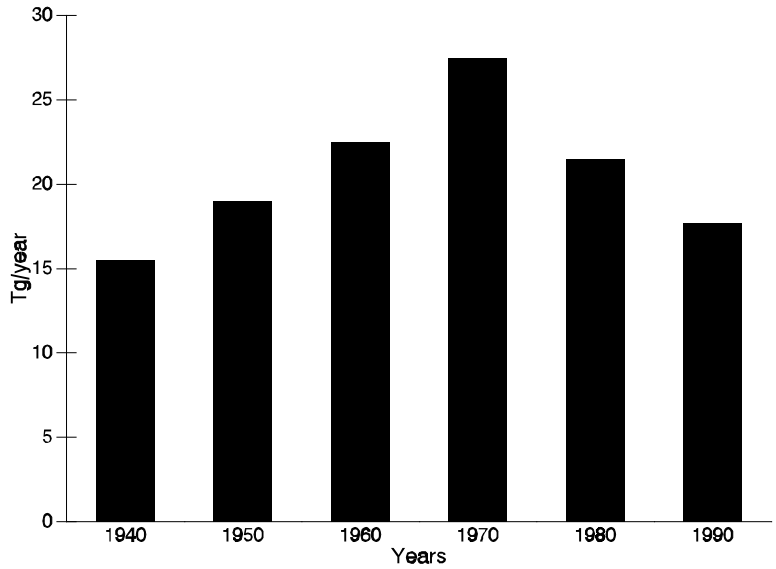


Figure 3-22. Changes in emissions of volatile organic compounds from major manmade sources in the United States, 10-year intervals, 1940 through 1990.

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

Trends for the dominant VOC emissions categories from 1987 through 1991 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 a predicted overall 25% decrease in total national VOC emissions between 1990 and 2000 (U.S. Environmental Protection Agency, 1992a).

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

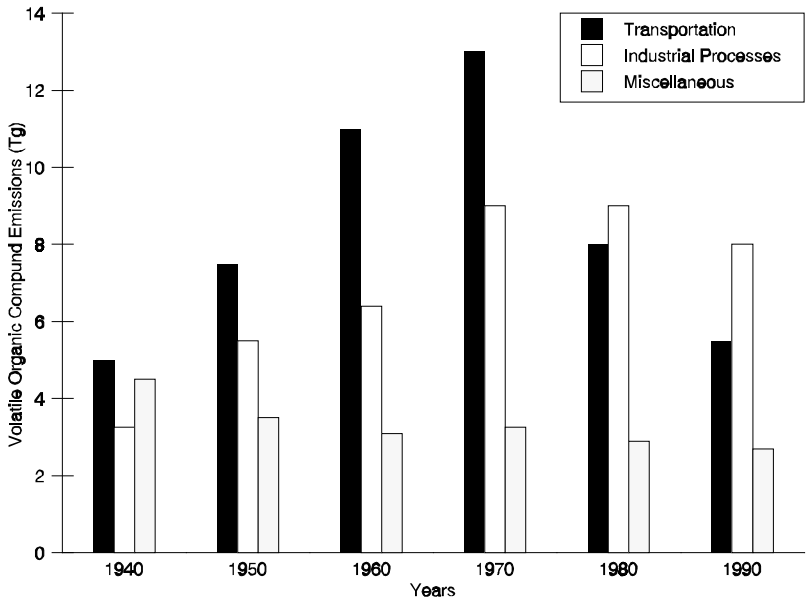


Figure 3-23. Changes in emissions of volatile organic compounds from major manmade sources, 1940 through 1990.[a]

[a]The values for 1990 do not agree with those in Table 3-12 because different models were employed for deriving the short- and long-term trends.

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

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[a]	8.07	9.96	2.05
1989	8.26	9.92	2.08
1988	9.15	10.00	2.10
1987	9.29	9.65	2.05

[a]The values for 1990 do not agree with those in Figure 3-23 because different models were employed for deriving the short- and long-term trends.

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

assigned for thousands of individual sources (e.g., valves, flanges, meters, processes), and emission estimates for each of these sources are summed to produce the emissions total. Because it would be impractical to determine an emission factor for each of these sources within a refinery individually, average emission factors for the various source categories are utilized. This can lead to substantial error if emissions from 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 on environmental factors such as temperature, which add to the difficulty in establishing reliable emission estimates. Such sources fall into a miscellaneous solvent evaporation category that includes emissions from processes such as dry cleaning, degreasing, printing, automobile body 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 are included in the inventorying process. The activity models assume that vehicles of the same age accumulate mileage at the same rate. This is most likely not correct; there is a need to assess the uncertainty in this assumption through a systematic collection of vehicle type, age, and mileage accumulation statistics.

Experiments carried out in tunnels have looked at the relationship between measured VOC emission factors and those derived from automotive emission models. In a study designed to verify automotive emission inventories for the South Coast Air Basin, measurements in the Van Nuys Tunnel indicated that automotive VOC emissions were a factor of 4 larger than predicted using emission models (Pierson et al., 1990). Results from two tunnel studies conducted in 1992 (Robinson et al., 1996) show much better agreement between VOC measurements and model predictions than those obtained in the Van Nuys Tunnel. Comparisons were made for the Tuscarora Tunnel on the Pennsylvania Turnpike in south-central Pennsylvania and at the Fort McHenry Tunnel under Baltimore Harbor. For Tuscarora, MOBILE4.1 gives 131% of the average measured VOC values and MOBILE5 gives 216% of the average measured VOCs. For Fort McHenry, MOBILE4.1 gives 53% of the average measured VOC values and MOBILE5 gives 81% of the average measured VOCs. Somewhat better agreement also was obtained from the Van Nuys Tunnel data when the updated California emission model EMFACTEP was used (Robinson et al., 1996). At the Cassier Tunnel in Vancouver, Canada, agreement within ±30% was obtained between the VOC measurements and the Canadian version of the MOBILE models (Gertler et al., 1994). The 1993 results from the Caldecott Tunnel in the San Francisco, CA, area show deviations between VOC measurements and model predictions similar to those obtained in the Van Nuys Tunnel, possibly because of similar urban/local fleets. Differences in test results between the newer tunnel studies and those obtained in the early Van Nuys Tunnel study are likely due to the better condition of the vehicles in the newer studies and the lack of power enrichment or other transients because of the steady-speed driving. However, it is important to appreciate that results from tunnel measurements do not necessarily predict equivalency of VOC

measurements with model predictions under highly transient urban/local driving and fleet conditions.

Recent developments in remote sensing have permitted more accurate measurement of hydrocarbon exhaust emissions from on-road vehicles (Stedman et al., 1991). These studies have demonstrated a highly skewed distribution, with the majority of VOC emissions coming from about 20% of the automobiles. Emission factors developed from laboratory dynamometer testing most likely do not properly account for the high-emitting vehicle contribution (Pitchford and Johnson, 1993). In many cases, these high emitters are older cars that are poorly maintained. In order to reduce this source of uncertainty, it may be necessary to reassess the life spans assigned to vehicles. Vehicles manufactured more than 25 years prior to 1993 are not included in the inventory. However, these older vehicles are likely to be high emitters, and, if they are underrepresented in the model, emissions will be underestimated. Activity models provide data in terms of national averages. This can contribute to inaccuracies in emissions estimates if a particular region varies from the national average in terms of vehicle types, age, or VMT.

Ambient measurements of VOCs and NO_x have been employed in order to better define uncertainty levels in VOC inventories. Some of the earliest work was carried out in the Atlanta area in the 1980s. Using a simple model and measured ambient VOC and NO_x concentrations, it was shown that ambient NO_x levels were consistent with the urban NO_x emission estimates. However, measured ambient VOC concentrations were as much as a factor of 6 greater than predicted (Westberg and Lamb, 1985). Improvements in mobile source emission models have resulted in somewhat higher emission estimates, so that the discrepancy between model estimates and ambient data has been reduced to about a factor of 2.5 (Fujita et al., 1992; Cadle et al., 1993). It is clear that the relationship between emission inventories and ambient concentrations of NO_x and VOCs warrants further study. In addition to improving the mobile source emission inventories, it will be necessary to place uncertainty bounds on stationary source inventories. Whether stationary source emissions of VOCs are underpredicted using current emission inventory methodology is not known (Finlayson-Pitts and Pitts, Jr., 1993).

Biogenic Emissions

Vegetation emits significant quantities of reactive VOCs into the atmosphere. Many of these biogenic VOCs may contribute to O_3 production in urban (Chameides et al., 1988) and rural (Trainer et al., 1987) environments. The VOC emissions of primary interest are isoprene and the monoterpenes (e.g., α-pinene, β-pinene, myrcene, limonene, etc.), which are hydrocarbons. Recent field measurements have shown that a variety of oxygenated organics also are emitted from plants (Winer et al., 1992). A thorough discussion of biogenic emissions and their implication for atmospheric chemistry has been published recently by Fehsenfeld et al. (1992), who reviewed the techniques used to measure VOC emissions from vegetation, laboratory emissions studies that have been used to relate emission rates to temperature and light intensity, development of emission models, and the use of emission models in the preparation of emission inventories.

Since the late 1970s, a number of regional and national biogenic emission inventories have been reported (Zimmerman, 1979; Winer et al., 1983; Lamb et al., 1985, 1987, 1993). These inventories are based on algorithms that relate VOC emissions from a particular vegetation class to ambient temperature, land-use, and, in the case of isoprene, photosynthetically active radiation. Most biogenic VOC emissions from vegetation increase

exponentially with temperature. Isoprene emissions are light-dependent, being minimal at night and increasing with solar intensity during the day. Deciduous vegetation is the dominant source of isoprene; whereas coniferous trees emit primarily monoterpenes. Other things being equal, isoprene is emitted at a much higher rate than the monoterpenes. For example, in a southern forest of mixed pine and hardwoods, the isoprene emission rate from an oak tree is about 10 times larger than the flux of α-pinene from an adjacent loblolly pine during the midday period.

The most recent biogenic VOC emissions estimate for the United States totals 29 Tg/year (Lamb et al., 1993). This estimate includes 5.9 Tg isoprene, 4.4 Tg α-pinene, 6.5 Tg other monoterpenes, and 12.3 Tg other VOCs. Table 3-13 provides a summary of the contributions from the various vegetation categories based on an inventory of monthly statewide data for eight land-cover types. In preparing this inventory, algorithms were developed that related VOC emissions to temperature and light for each of the biomass categories shown in the table. On a national scale, coniferous forests are the largest vegetative contributor because of their extensive land coverage. The category "Other VOCs" is the dominant biogenic hydrocarbon contributor to the national total. From the standpoint of inventory accuracy, this is somewhat unfortunate because the identities of most of the "Other VOCs" are uncertain. This classification has carried over from the extensive field-measurement program conducted by Zimmerman (1979) and coworkers in the mid-1970s. The category "Other VOCs", includes peaks that showed up in sample chromatograms at retention times that could not be matched to known hydrocarbons. It is likely that if the Zimmerman study were repeated today, most of the species making up this "Other VOCs" category could be identified. Recent field studies have made use of GC/MS techniques that were not available to Zimmerman in the 1970s.

Biogenic emissions, because of their dependence on temperature and vegetational growth, vary by season. In addition, the southern tier of states is expected to produce more biogenic emissions than those in the north because of higher average temperatures. Table 3-14 shows a spatial and temporal breakdown of U.S. biogenic emissions. Summertime emissions comprise 16.7 of the 29.1 Tg (or 57%) of the annual totals in all regions. The EPA Regions IV and VI in the southeastern and southcentral United States, respectively, have the highest summertime and annual biogenic VOC emission rates. Region IV contributes 16% of the summertime and 18% of the annual biogenic VOC emissions in the United States, whereas Region VI contributes 21% of the summertime and 23% of the annual biogenic emissions in the United States. Compared to Regions IV and VI, regions to the north have more rapid increases in biogenic VOC emissions in the spring and more rapid decreases in biogenic VOC emissions in the fall.

Uncertainty in Estimates of Biogenic Emissions

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

Table 3-13. Annual Biogenic Hydrocarbon Emission Inventory for the United States (Tg)[a]

	Land Use								
Compound	Oak Forests	Other Deciduous Forests	Coniferous Forests	Scrub-lands	Grass-lands	Crop-lands	Inland Waters	Urban Areas	U.S. Total
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	4.03	2.56	8.48	5.85	1.31	6.37	0.21	0.26	29.1
Percent of Total	13.9	8.8	29.2	20.1	4.5	21.9	0.7	0.9	

[a]See Appendix A for abbreviations and acronyms.

Source: Lamb et al. (1993).

Table 3-14. Annual Biogenic Hydrocarbon Emission Inventory by Month and by U.S. Environmental Protection Agency Region for United States Emissions (Tg)

	U.S. Environmental Protection Agency Region									
Month	III	IV	V	VI	VII	VIII	IX	X	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	0.020	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	0.018	0.080	0.004	0.073	0.007	0.022	0.060	0.043	0.3	1.1
Total	2.1	5.3	2.5	6.6	2.3	4.0	4.0	2.5	29.1	

Source: Lamb et al. (1993).

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

Comparison of Manmade and Biogenic Emissions

The most recent anthropogenic and biogenic VOC emissions estimates for the United States indicate that natural emissions (29 Tg) exceed manmade emissions (23 Tg). During the summer months in the United States, anthropogenic emissions constitute 25% of the annual anthropogenic VOC emissions, whereas biogenic emissions constitute 57% of the annual biogenic emissions. On a teragram basis, anthropogenic VOC emissions during the summer contribute 0.25 × 23 Tg = 5.75 Tg, whereas summer biogenic VOC emissions contribute 0.57 × 29 Tg = 16.5 Tg. Therefore, on a national basis, the ratio of biogenic to anthropogenic VOC emissions is approximately 2.9 for the United States. However, this ratio varies with region in the summer months. These calculations depend on the assumption that regional summertime anthropogenic VOC emissions are one-quarter of the annual VOC emissions. With this assumption, the ratios of biogenic to anthropogenic VOC emissions for three selected regions are as follows: 2.2 for Region IV, 1.6 for Region V, and 3.2 for Region VI (Lamb et al., 1993; U.S. Environmental Protection Agency, 1994). However, in a recent National Research Council review (1991), it was concluded that emissions from manmade sources are currently underestimated by a significant amount (60 to 80%). Because uncertainty in both biogenic and anthropogenic VOC emission inventories is large, it is not possible to establish whether the contribution of emissions from natural or manmade sources of VOCs is larger.

3.4.1.4 Relationship of Summertime Precursor Emissions and Ozone Production

Peak O_3 levels are recorded in most regions of the country during the months of June, July, and August. From the foregoing discussion, it is obvious that natural emissions of NO_x and VOCs peak during this same time frame. Biogenic emissions are very dependent on temperature; and, as ambient temperatures rise during the summer months, NO_x and VOC emissions reach a maximum. Figure 3-24 clearly demonstrates this for biogenic VOC emissions, and a plot of monthly biogenic NO_x emissions would show a similar pattern. Well over 50% of biogenic NO_x and VOC emissions occur during the period of maximum photochemical activity.

Seasonal changes in anthropogenic emissions of NO_x are believed to be relatively small. The transportation sector produces slightly less NO_x during the warmer months, but there is probably a small increase from the stationary source category because of higher summertime power demands. Because these are the major U.S. sources of NO_x and changes in seasonal 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 is a summertime increase. In 1993, 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, 1994). The

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, whereas 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 O_3 concentration year, for almost all of the five 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 Sites Experiencing Low Exposures

Lefohn et al. (1990a) have characterized the O_3 concentrations that occurred at several sites in the United States that experience low maximum hourly average concentrations. The Theodore Roosevelt National Park 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. (1990a), 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 River Oil Shale site in Colorado experienced its maximum monthly mean during the spring and summer months.

The W126 sigmoidal weighting function index was also used to identify the month of highest O_3 exposure. A somewhat more variable pattern was observed than when the maximum monthly average concentration was used. For some sites, the winter/spring pattern was represented; for others, it was not. In some cases, the highest W126 exposures occurred earlier in the year than was indicated by the maximum monthly concentration. For example, in 1979, the Custer National Forest site experienced its highest W126 exposure in April, although the maximum monthly mean occurred in August. In 1980, the reverse occurred.

There was no consistent pattern for those sites located in the continental United States. The Theodore Roosevelt and Ochoco national park sites, the Custer National Forest site, and the White River Oil Shale site experienced their maximum O_3 exposures during the spring and summer months. The sites experiencing their highest O_3 exposures in the fall-to-spring period did not necessarily experience the lowest O_3 exposures.

4.6 Spatial Variations in Ozone Concentrations

4.6.1 Urban-Nonurban Area Concentration Differences

Diurnal concentration data presented earlier indicate that peak O_3 concentrations can occur later in the day in rural areas than in urban, with the distances downwind from urban centers generally determining how much later the peaks occur. Meagher et al. (1987) reported that for five rural sites in the Tennessee Valley region of the southeastern United States, O_3 levels were found to equal or exceed urban values for the same region. Data presented in the 1978 criteria document demonstrated that peak concentrations of O_3 in rural areas generally are lower than those in urban areas, but that average concentrations in rural areas are comparable to or even higher than those in urban areas (U.S. Environmental Protection Agency, 1978). Reagan (1984) noted that O_3 concentrations measured near population-oriented areas were depressed in comparison with data collected in more isolated areas. As noted earlier, urban O_3 values are often depressed because of titration by NO (Stasiuk and Coffey, 1974). In reviewing the NCLAN's use of kriging to estimate the 7-h seasonal average O_3 levels, Lefohn et al. (1987a) found that the 7-h values derived from kriging for sites located in rural areas tended to be lower than the actual values because of the effect of using data from urban areas to estimate rural values. In addition to the occurrence of higher average concentrations and occasionally higher peak concentrations of O_3 in nonurban than in urban areas, it is well documented that O_3 persists longer in nonurban than in urban areas (Coffey et al., 1977; Wolff et al., 1977; Isaksen et al., 1978). The absence of chemical scavengers appears to be the main reason.

4.6.2 Concentrations Experienced at High-Elevation Sites

The distributions of hourly average concentrations experienced at high-elevation cities are similar to those experienced in low-elevation cities. For example, the distribution of hourly average concentrations for several O_3 sites located in Denver were similar to distributions observed at many low-elevation sites in the United States. However, as will be discussed in Section 4.6.3, for assessing the possible impacts of O_3 at high-elevation sites, the use of absolute concentrations (e.g., in units of micrograms per cubic meter) instead of mixing ratios (e.g., parts per million) may be an important consideration.

Lefohn et al. (1990b) summarized the characterization of gaseous exposures at rural sites in 1986 and 1987 at several MCCP high-elevation sites. Aneja and Li (1992) have summarized the ozone concentrations for 1986 to 1988. Table 4-14 summarizes the sites characterized by Lefohn et al. (1990b). Table 4-15 summarizes the concentrations and exposures that occurred at several of the sites for the period 1987 to 1988. In 1987, the 7- and 12-h seasonal means were similar at the Whiteface Mountain WF1 and WF3 sites (Figure 4-24a). The 7-h mean values were 0.0449 and 0.0444 ppm, respectively, and the 12-h mean values were 0.0454 and 0.0444 ppm, respectively. Note that, in some cases, the 12-h mean was slightly higher than the 7-h mean value. This resulted when the 7-h mean period (0900 to 1559 hours) did not capture the period of the day when the highest hourly mean O_3 concentrations were experienced. A similar observation was made, using the 1987

Table 4-14. Description of Mountain Cloud Chemistry Program Sites[a]

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 NP (SH1), VA	1,015	38°	37′	12″	78°	20′	48″
Shenandoah NP (SH2), VA	716	38°	37′	30″	78°	21′	13″
Shenandoah NP (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′	

[a]See Appendix A for abbreviations and acronyms.

data, for the MCCP Shenandoah National Park sites. The 7- and 12-h seasonal means were similar for the SH1 and SH2 sites (Figure 4-24b). Based on cumulative indices, the Whiteface Mountain summit (1,483-m) site (WF1) experienced a higher exposure than the WF3 (1,026-m) site (Figure 4-24c). Both the sum of the concentrations ≥0.07 ppm (SUM07) and the number of hourly concentrations ≥0.07 ppm were higher at the WF1 site than at the WF3 site. The site at the base of the mountain (WF4) experienced the lowest exposure of the three O_3 sites. Among the MCCP Shenandoah National Park sites, the SH2 site experienced marginally higher O_3 exposures, based on the index that sums all of the hourly average concentrations (i.e., referred to as "total dose" in the figure) and sigmoidal values, than the high-elevation site (SH1; Figure 4-24d). The reverse was true for the sums of the concentrations ≥0.07 ppm and the number of hourly concentrations ≥0.07 ppm.

When the Big Meadows, Dickey Ridge, and Sawmill Run, Shenandoah National Park, data for 1983 to 1987 were compared, it again was found that the 7- and 12-h seasonal means were insensitive to the different O_3 exposure patterns. A better resolution of the differences was observed when the cumulative indices were used (Figure 4-25). There was no evidence that the highest elevation, Big Meadows, site consistently had experienced higher O_3 exposures than the other sites. In 2 of the 5 years, the highest elevation site experienced lower exposures than the Dickey Ridge and Sawmill Run sites, based on the sum of all concentration or sigmoidal indices. For 4 of the 5 years, the SUM07 index yielded the same result.

Taylor et al. (1992) indicate that the forests they monitored experienced differences in O_3 exposure. The principal spatial factors underlying this variation were 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 10 EPRI Integrated Forest Study sites located in North America.

Table 4-15. Seasonal (April to October) Percentiles, SUM06, SUM08, and W126 Values for the Mountain Cloud Chemistry Program Sites[a]

Site	Elev. (m)	Year	Min.	10	30	50	70	90	95	99	Max	No. Obs.	SUM06	SUM08	W126
Howland Forest, ME	65	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
(HF1)		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	1,000	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
(MS1)		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	1,483	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
(WF1) (36-031-0002)		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	1,026	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
(WF3)															
Whiteface Mountain, NY	604	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
(WF4)															
Mt. Mitchell, NC	2,006	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
(MM1)		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	1,760	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
(MM2)		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	1,015	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
(SH1)		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	716	1987[b]	0.003	0.027	0.040	0.049	0.059	0.071	0.077	0.086	0.145	2,908	55.7	7.8	41.8
(SH2)														55.8	
Shenandoah Park, VA	524	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
(SH3)		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	1,689	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
(WT1)		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

[a]See Appendix A for abbreviations and acronyms.
[b]Calculations based on a May to September season.

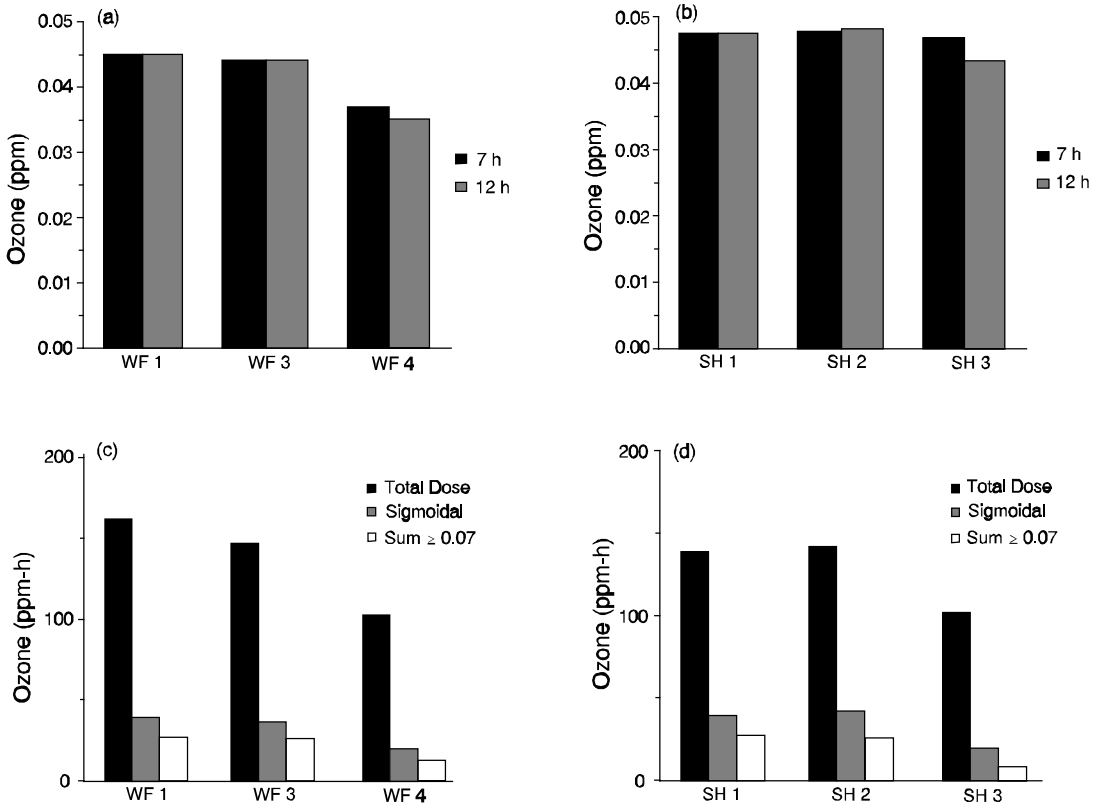


Figure 4-24. Seven- and 12-h means at (a) Whiteface Mountain and (b) Shenandoah National Park for May to September 1987 and integrated exposures at (c) Whiteface Mountain and (d) Shenandoah National Park for May to September 1987.

Source: Lefohn et al. (1990b).

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 data are presented in this section: (1) a case of relative homogeneity in a city with a population under 500,000 (New Haven, CT) and (2) a case of relative inhomogeneity 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, 1986), the percentiles of the hourly average concentrations for a New Haven site and two other monitoring stations that were operating at the time in the same county, one in Derby, 9 mi west of New Haven, and one in Hamden, 6 mi north of New Haven, generally are similar. Table 4-17 shows the monitoirng data and time of the maximum hourly concentrations by quarter at these three sites.

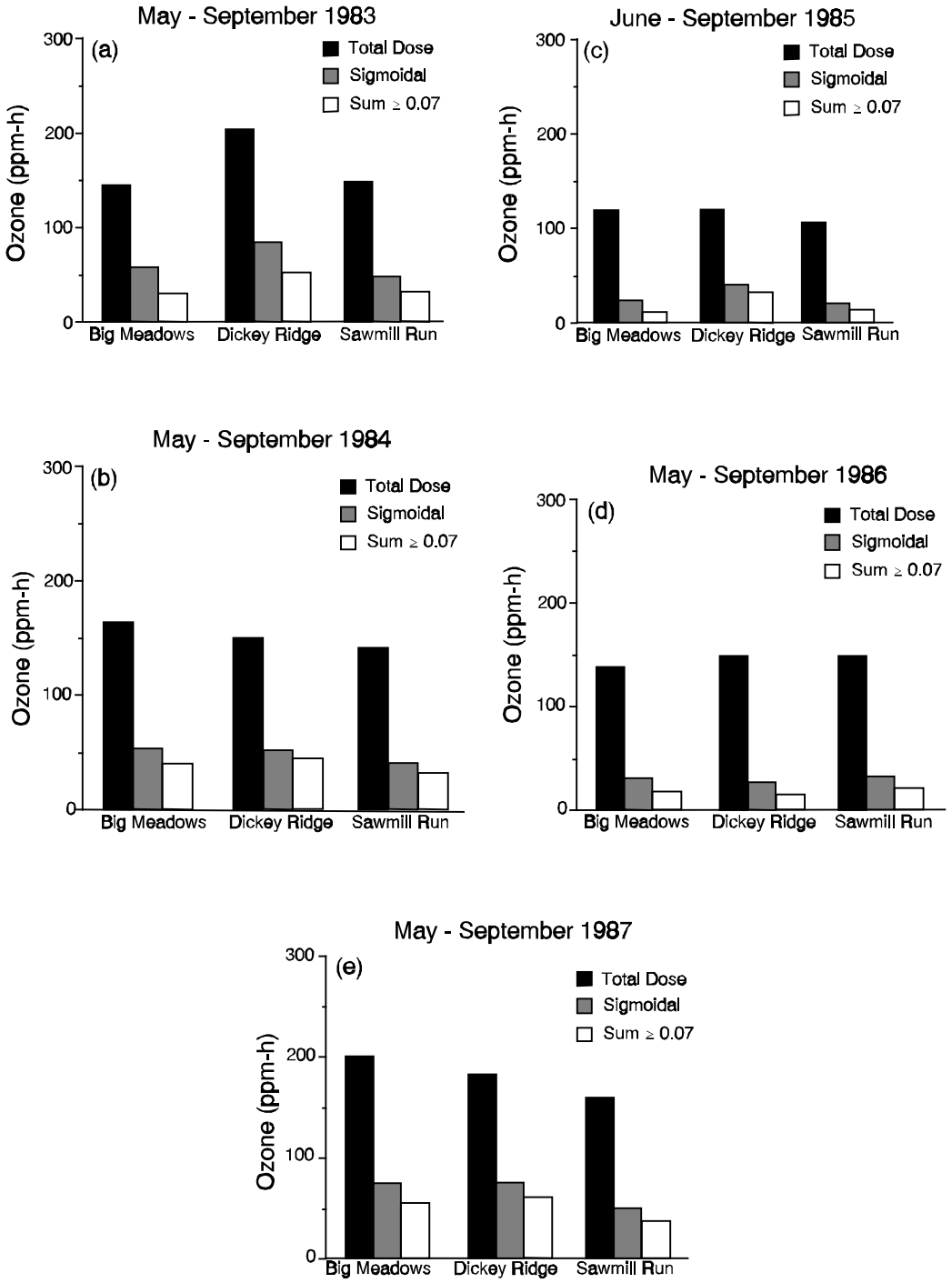


Figure 4-25. Integrated exposures for three non-Mountain Cloud Chemistry Program Shenandoah National Park sites, 1983 to 1987.

Source: Lefohn et al. (1990b).

Table 4-16. Summary Statistics for 11 Integrated Forest Study Sites[a]

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
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

Table 4-16 (cont'd). Summary Statistics for 11 Integrated Forest Study Sites[a]

Site	Year	Quarter	24-h (ppb)	12-h (ppb)	7-h (ppb)	1-h Max (ppb)	SUM06 (ppm-h)	SUM08 (ppm-h)
LOW ELEVATION SITES (cont'd)								
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
Gainesville, FL	1987	2	42	53	50	[b]	[b]	[b]
	1987	3	29	44	41	[b]	[b]	[b]
	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	[b]	[b]
	1988	2	54	69	75	115	[b]	[b]
	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

[a]See Appendix A for abbreviations and acronyms.
[b]Data were insufficient to calculate statistic.

Source: Adapted from Taylor et al. (1992).

Table 4-17. Quarterly Maximum One-Hour 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
Time of day	1100 hours	1400 hours	1400 hours	1000 hours
Date	March 29	June 24	August 12	October 3
Derby, CT				
No. measurements	11	2,140	2,187	1,360
Max 1-h, ppm	0.015	0.280	0.290	0.060
Time of day	2300 hours	1400 hours	1400 hours	1900 hours
Date	March 31	June 24	August 12	December 20
Hamden, CT				
No. measurements	56	2,065	1,446	286
Max 1-h, ppm	0.050	0.240	0.240	0.065
Time of day	2400 hours	1500 hours	1300 hours	1500 hours
Date	March 29	June 24	July 20	October 7

Source: U.S. Environmental Protection Agency (1986).

The source of much of the O_3 experienced in the New Haven area is the greater New York area (e.g., Wolff et al., 1975; Cleveland et al., 1976a,b). An urban plume transported over the distance from New York City to New Haven would tend to be relatively well-mixed and uniform, such that intracity variations in New Haven probably would be minimal.

As indicated in the previous version of the criteria document (U.S. Environmental Protection Agency, 1986), intracity differences in O_3 concentrations also have been reported by Kelly et al. (1986) for a 1981 study in Detroit, MI. Ozone concentrations were measured for about 3 mo at 16 sites in the metropolitan Detroit area and in nearby Ontario, Canada. Values at 15 sites were correlated with those at a site adjacent to the Detroit Science Center, about 3 km north of the central business district in Detroit. In general, the correlation decreased as distance from the Science Center site increased; and, in general, the actual concentrations increased with distance from that site toward the north-northeast. The highest O_3 concentrations were recorded at sites about 10 to 70 km north-northeast of the urban core. At greater distances or in other directions, O_3 maxima decreased.

Chicago is an example where O_3 concentrations increase as the distance from the inner city increases. Figure 4-26 shows, for a number of O_3 monitoring sites, the number of days in 1991 that the maximum hourly average concentration was greater than 0.1 ppm. The greatest number of exceedances of the daily maximum 1-h concentration of 0.1 ppm was to the north of the city.

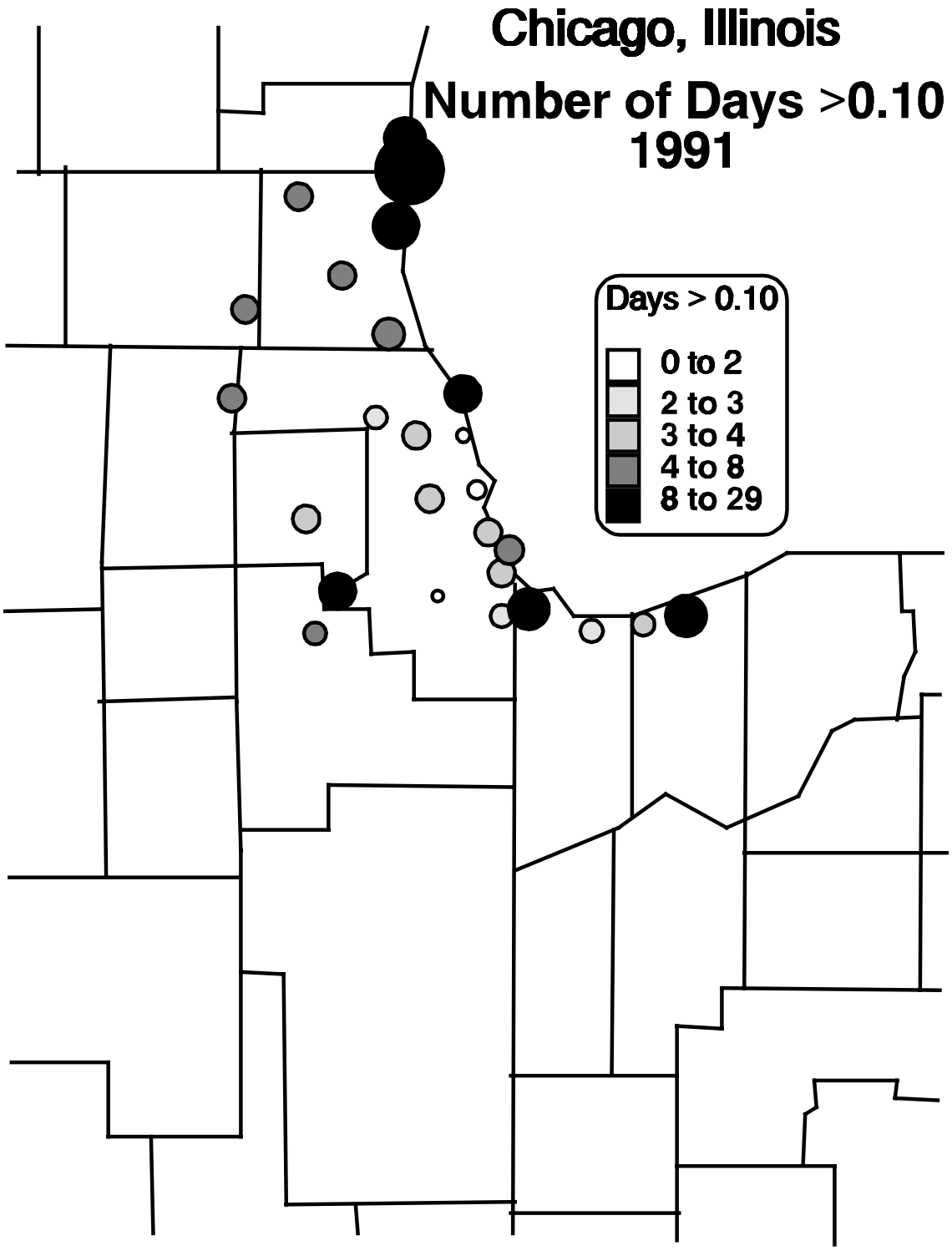


Figure 4-26. Number of days in 1991 for which the maximum hourly average ozone concentration was greater than 0.1 ppm at Chicago, IL.

Concentrations of O_3 vary with altitude and with latitude. Although a number of reports contain data on O_3 concentrations at high altitudes (e.g., Coffey et al., 1977; Reiter, 1977b; Singh et al., 1977; Evans et al., 1985; Lefohn and Jones, 1986), fewer reports are available that present data for different elevations in the same locality. There appears to be no consistent conclusion concerning the relationship between O_3 exposure and elevation.

Wolff et al. (1987) reported, for a short-term study at High Point Mountain in northwestern New Jersey, that both the daily maximum and midday O_3 concentrations were similar at different altitudes, but that the O_3 exposures increased with elevation. Wolff et al. (1987) conducted a study of the effects of altitude on O_3 concentrations at three sites located at three separate elevations on High Point Mountain in northwestern New Jersey. Data for several days indicate that in mid-July, when atmospheric mixing was good, vertical profiles were nearly constant, with concentrations increasing only slightly with elevation. Likewise, the daily O_3 maxima were similar at different elevations. At night, however, O_3 concentrations were nearly zero in the valley (i.e., the lowest-elevation site) and increased with elevation. Comparison of the O_3 exposures at the three sites (number of hours >0.08 ppm) showed that greater cumulative exposures were sustained at the higher elevations. Comparable data from an urban area (Bayonne) about 80 km southeast of High Point Mountain showed that the cumulative exposures were higher at all three of the mountain sites than in the urban area (Wolff et al., 1987). The investigators concluded from their concentration and meteorological data that elevated, mountainous sites in the eastern United States may be expected to be exposed to higher O_3 concentrations than valley sites throughout the year.

Winner et al. (1989) reported that, for three Shenandoah National Park sites (i.e., Big Meadows, Dickey Ridge, and Sawmill Run), the 24-h monthly mean O_3 concentrations tended to increase with elevation, but that the number of elevated hourly occurrences equal to or above selected thresholds did not. The authors reported that the highest elevation site (Big Meadows) experienced a smaller number of concentrations at or below the minimum detectable level than did the other two sites. The larger number of hourly average concentrations that occurred at or below the minimum detectable level at both Dickey Ridge and Sawmill Run resulted in lower 24-h averages at these sites.

Lefohn et al. (1990b), characterizing the O_3 exposures at several high-elevation sites, reported that, based on cumulative indices, the Whiteface Mountain summit site (WF1) experienced a slightly higher exposure than the lower elevation Whiteface Mountain (WF3) site. The site at the base of Whiteface Mountain (WF4) experienced the lowest exposure of the three O_3 sites. Among the MCCP Shenandoah National Park sites, the SH2 site experienced higher O_3 exposures than the high-elevation site (SH1). The "total dose" (correctly referred to as the sum of all hourly average concentrations) and sigmoidal (W126) indices were slightly higher at the SH2 than at the SH1 site. The data capture at the two sites for the 5-mo period was similar. However, the sum of the concentrations ≥0.07 ppm and the number of hourly concentrations ≥0.07 ppm were slightly higher at the SH1 than at the SH2 site. For the Whiteface Mountain sites, both the sum of the concentrations ≥0.07 ppm (SUM07) and the number of hourly concentrations ≥0.07 ppm were higher at the WF1 site than at the WF3 site.

When the Big Meadows, Dickey Ridge, and Sawmill Run, Shenandoah National Park, data for 1983 to 1987 were compared, a higher resolution of the differences among the regimes was observed when the cumulative indices were used. No specific trend could be identified that showed the highest elevation site, Big Meadows, had consistently experienced

higher O_3 exposures than the lower elevation sites. In 2 of the 5 years, the highest elevation site experienced lower exposures than the Dickey Ridge and Sawmill Run sites, based on the sum of all concentrations or sigmoidal indices. For 4 of the 5 years, the SUM07 index yielded the same result.

An important issue for assessing possible impacts of O_3 at high-elevation sites that requires further attention is the use of mixing ratios (e.g., parts per million) instead of absolute concentration (e.g., in units of micrograms per cubic meter) to describe O_3 concentration. In most cases, mixing ratios or mole fractions are used to describe O_3 concentrations. Lefohn et al. (1990b) have pointed out that the manner in which concentration is reported may be important when assessing the potential impacts of air pollution on high-elevation forests. Concentration varies as a function of altitude. Although the change in concentration is small when the elevational difference between sea level and the monitoring site is small, it becomes substantial at high-elevation sites. Given the same part-per-million value experienced at both a high- and low-elevation site, the absolute concentrations (i.e., micrograms per cubic meter) at the two elevations will be different. Because both O_3 and ambient air are gases, changes in pressure directly affect their volume. According to Boyle's law, if the temperature of a gas is held constant, the volume occupied by the gas varies inversely with the pressure (i.e., as pressure decreases, volume increases). This pressure effect must be considered when measuring absolute pollutant concentrations. At any given sampling location, normal atmospheric pressure variations have very little effect on air pollutant measurements. However, when mass/volume units of concentration are used and pollutant concentrations measured at significantly different altitudes are compared, pressure (and, hence, volume) adjustments are necessary. In practice, the summit site at Whiteface Mountain had a slightly higher O_3 exposure than the two low-elevation sites (Lefohn et al., 1991). However, at Shenandoah National Park sites, the higher elevation site experienced lower exposures than lower elevation sites in some years.

These exposure considerations are trivial at low-elevation sites. However, when one compares exposure-effects results obtained at high-elevation sites with those from low-elevation sites, the differences may become significant (Lefohn et al., 1990b). In particular, assuming that the sensitivity of the biological target is identical at both low and high elevations, some adjustment will be necessary when attempting to link experimental data obtained at low-elevation sites with air quality data monitored at the high-elevation stations.

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 O_3 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 O_3 concentrations experienced inside buildings. The ratio of the indoor/outdoor (I/O) O_3 concentrations is a parameter that has been widely used for studying the indoor and outdoor relationships, sources, and exposure patterns of O_3. However, the database on this subject is not large, and a wide range of I/O O_3 concentration relationships can be found in the literature. The only significant source of O_3 in indoor residential air is infiltration of outdoor O_3, with ventilation rates affecting the flow of air between indoor and outdoor (Zhang and Lioy, 1994).

Reported I/O values for O_3 are highly variable (U.S. Environmental Protection Agency, 1986) and range from <0.1 to 0.8 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 O_3 or photochemical oxidant. The results were highly variable. A relatively large number of factors can affect the difference in O_3 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 O_3 within buildings (U.S. Environmental Protection Agency, 1986). Although indoor concentrations of O_3 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 O_3. Experiments show that the fading of artists' pigments in the presence of O_3 is directly related to the product of concentration times duration of exposure. Druzik et al. (1990) reported that, in a survey of 11 museums, galleries, historical houses, and libraries in Southern California, facilities with a high air exchange with the outdoors and no pollutant removal system have indoor O_3 concentrations more than two-thirds those of outdoor concentrations. The author reported that museums with conventional air-conditioning systems showed indoor O_3 concentrations about 30 to 40% of those outside, whereas museums with no forced ventilation system, where slow air infiltration provides the only means of air exchange, have indoor O_3 levels typically 10 to 20% of those outdoors. Several other studies have been reported in the literature and Table 4-18 lists the I/O ratios reported from these efforts as well as those from earlier years.

Automobiles and other vehicles constitute another indoor environment in which people may spend appreciable amounts of time. As with buildings, the mode of ventilation and cooling helps determine the inside concentrations. The U.S. Environmental Protection Agency (1986) describes studies for the I/O ratios. In one study reported by Contant et al. (1985), the I/O ratios from 49 measurements inside vehicles were 0.44 for the mean, 0.33 for the median, and 0.56 for maximum concentrations measured. Chan et al. (1991) reported an I/O ratio of 0.20 for median in-vehicle concentrations (0.011 ppm) and time-matched fixed-site measurements (0.051 ppm).

At present, there are no long-term monitoring data on indoor air pollutant concentrations comparable to the concentration data available for outdoor locations. Thus, for estimates of the exposure of building or vehicle occupants to O_3 and other photochemical oxidants, it is necessary to rely on extrapolations of very limited I/O data.

4.8 Estimating Exposure to Ozone

4.8.1 Introduction

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

Table 4-18. Summary of Reported Indoor-Outdoor Ozone Ratios

Structure	Indoor-Outdoor Ratio	Reference
Hospital	0.67[a]	Thompson (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	Moschandreas et al. (1978)
Two offices	0.30	Moschandreas et al. (1978)
Residence		Moschandreas et al. (1981)
(gas stoves)	0.19	
(all electric)	0.20	
Office	0.29	Moschandreas et al. (1978)
School room	0.19 (max concentration)	Berk et al. (1980)
Residence	0.10-0.25	Berk et al. (1981)
Residences (1 each)		Stock et al. (1983)
(air-conditioned)	0.00-0.09	
(100% outside air; no air-conditioning)	1.00	
Residences (12) (air-conditioned)	0.21 (mean concentration) 0.12 (med. concentration) 0.59 (max concentration)	Contant et al. (1985)
Residences (41)	0.30	Lebowitz et al. (1984)
Residences (6)		Zhang and Lioy (1994)
(window open)	0.59 ± 0.16	
(window closed)	0.26 ± 0.12	
(air-conditioning)	0.28 ± 0.12	
Art gallery	0.50	Shaver et al. (1983)
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 concentration)	Davies et al. (1984)
Museums	<0.10	Shaver et al. (1983)

Table 4-18 (cont'd). Summary of Reported Indoor-Outdoor Ozone Ratios

Structure	Indoor-Outdoor Ratio	Reference
Museum	0.45	Nazaroff and Cass (1986)
Museums		Druzik et al. (1990)
(with high air exchange, but no air-conditioning)	0.69-0.84 (1 h) 0.50-0.87 (8 h)	
(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)	

[a]Measured as total oxidants.

potentially different from other locations, the volume may be considered a "microenvironment" (Duan, 1982). Microenvironments may be aggregated by location (i.e., indoor or outdoor) or activity performed at a location (i.e., residential, commercial) to form microenvironment types. Also, activity has two major dimensions: location and exertion. Various microenvironments can have different levels of ventilation that will significantly influence the delivered dose.

Air Quality Criteria for Carbon Monoxide (U.S. Environmental Protection Agency, 1991) discusses the difference between individual and population exposures. The document notes that Sexton and Ryan (1988) define the pollutant concentrations experienced by a specific individual during normal daily activities as "personal" or "individual" exposures. A personal exposure depends on the air pollutant concentrations that are present in the location through which the person moves, as well as on the time spent at each location. Because time-activity patterns can vary substantially from person to person, individual exposures exhibit wide variability (U.S. Environmental Protection Agency, 1991). Thus, although it is a relatively straightforward procedure to measure any one person's exposure, many such measurements may be needed to quantify exposures for a defined group. The daily activities of a person in time and space define the individual's activity pattern. Accurate estimates of air pollution exposure generally require that an exposure model account for the activity patterns of the population of interest.

From a public health perspective, it is important to determine the "population exposure", which is the aggregate exposure for a specified group of people (e.g., a community or an identified occupational cohort). Because exposures are likely to vary substantially between individuals, specification of the distribution of personal exposures within a

population, including the average value and the associated variance, is often the focus of exposure assessment studies.

In many cases, the upper tail of the distribution, which represents those individuals exposed to the highest concentrations, is frequently of special interest because the determination of the number of individuals who experience elevated pollutant levels can be critical for health risk assessments. This is especially true for pollutants for which the relationship between dose and response is highly nonlinear. Runeckles and Bates (1991) have pointed out the importance of peak concentrations in eliciting adverse human effects. As indicated in Section 4.1, results using controlled human exposures have shown the possible importance of concentration in relation to duration of exposure and inhalation rate. The implication of the importance of concentration can be translated into the conclusion that the simple definition of exposure (i.e., equal to concentration multiplied by time) may be too simplified.

Several human exposure models have been developed for most cases, because it is not possible to estimate population exposure solely from fixed-station data. Some of these models include information on human activity patterns (i.e., the microenvironments people visit and the time they spend there). These models also contain submodels depicting the sources and concentrations likely to be found in each microenvironment, including indoor, outdoor, and in-transit settings.

4.8.2 Fixed-Site Monitoring Information Used To Estimate Population and Vegetation Exposure

Based on the information provided in earlier sections in this chapter, fixed-site monitors alone cannot accurately depict population exposures for most cases, because indoor and in-transit concentrations of O_3 may be significantly different from ambient O_3 concentrations, and ambient outdoor concentrations of O_3 that people come in contact with may vary significantly from O_3 concentrations measured at fixed-site monitors. Fixed-site monitors measure concentrations of pollutants in ambient air. Ambient air as noted by the U.S. Environmental Protection Agency (1991) is defined in the *U.S. Code of Federal Regulations* (1991) as air that is "external to buildings, to which the general public has access." But the nature of modern urban lifestyles in many countries, including the United States, is that people spend an average of over 20 h per day indoors (Meyer, 1983). Reviews of studies summarized in Section 4.7 show that indoor O_3 concentration measurements vary significantly from simultaneous measurements in ambient air. The difference between indoor and outdoor air quality and the amount of time people spend indoors reinforce the conclusion that using ambient air quality measurements alone does not provide accurate estimates of population exposure in most cases.

It is assumed that exposure for vegetation is the same as the concentration information provided at fixed monitors in the field (see Sections 5.5 and 5.6). In some cases, because of foliar scavenging and height differences between the vegetation canopy and the pollutant monitor, the measured concentration is not equivalent to the vegetation exposure.

A subgroup, children attending summer camp, has been studied by several investigators to evaluate the influence of ambient air pollution on respiratory health and function. Because children are predominantly outdoors and relatively active while at camp, they provide a unique opportunity to examine the relationships between respiratory health and

function and concurrent air pollution levels. Children may be at potentially increased risk from air pollution by virtue of their lifestyle patterns, which often involve several hours of outdoor exercise, regardless of air quality, during daylight hours.

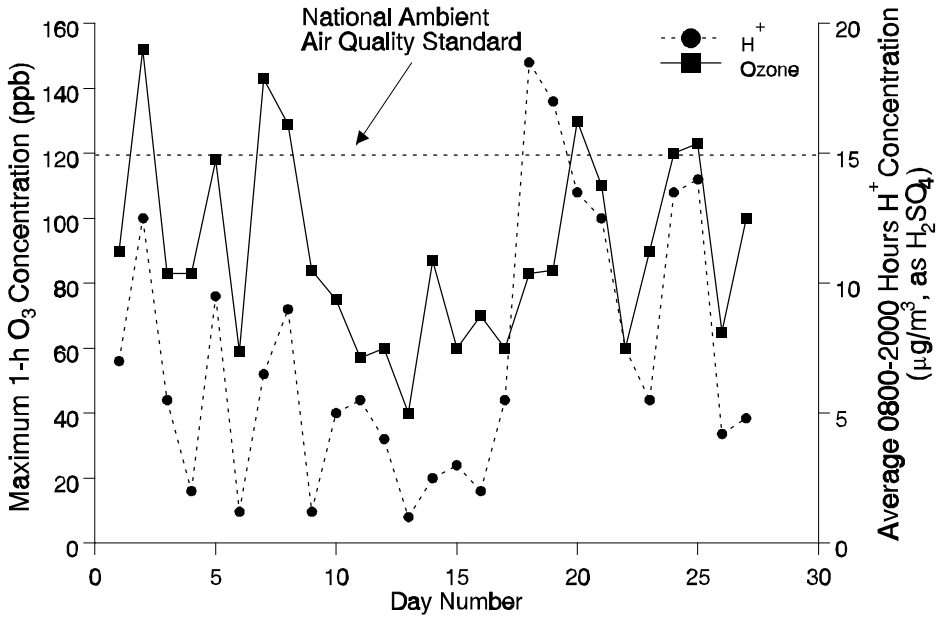
For campers, attempts have been made to estimate human exposure to O_3 using types of activity patterns (Mage et al., 1985; Paul et al., 1987). Mage et al. (1985) developed an objective approach to estimate the dose delivered to the lung of a 12-year-old camper by using pulmonary minute volume associated with a specific activity, the fractional penetration beyond the trachea, and infiltration of ozone indoors. Lioy and Dyba (1989) have applied the parameters used by Mage et al. (1985) to predict the delivered O_3 dose over a 4-day episodic period. The schedule of a hypothetical camper was matched to the actual O_3 concentrations, and the predicted doses were estimated.

Several studies involving children attending summer camp have been summarized in Chapter 7. In one study, Avol et al. (1990) reported that O_3 levels at a Southern California summer camp, located 190 km southeast of Los Angeles, CA, rose gradually throughout each day, displaying a "broad peak" between 1000 and 2000 hours each day. Daily maxima typically occurred in late afternoon (1500 to 1700 hours); subsequently, concentrations gradually declined to overnight O_3 levels of 0.025 to 0.050 ppm. Spektor et al. (1991) investigated the pulmonary function of 46 healthy children on at least 7 days for each child during a 4-week period at a northwestern New Jersey residential summer camp in 1988. The daily levels of 1-h peak O_3 and the 12-h average hygroden ion (H^+) concentrations are shown in Figure 4-27. On 5 of these days, the current NAAQS of 0.12 ppm was exceeded. The maximum hourly concentration attained during the study was 0.15 ppm. The year 1984 was a milder O_3 exposure year and Figure 4-28 summarizes the maximal 1-h O_3 concentrations at Fairview Lake during a 1984 study period (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, few 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 O_3 exposure in 23 children by Liu et al. (1993). The accuracy of the monitor was within 20% of the actual value. The authors collected indoor, outdoor, and personal O_3 concentration data as well as time-activity data in State College, PA. Results from the pilot study demonstrated that fixed-site ambient measurements may not adequately represent individual exposures. Outdoor O_3 concentrations showed substantial spatial variation between rural and residential regions. 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 R^2 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 O_3 exposure accurately. From these results, it is clear that additional data are needed to better quantify the O_3 exposures to which populations are exposed.

Figure 4-27. Maximum 1-h ozone (O^3) concentrations (in parts per billion) and average 0800 to 2000 hours strong acid concentrations (expressed as micrograms per



cubic meter of sulfuric acid [H_2SO_4]) for each day that pulmonary function data were collected at Fairview Lake camp in 1988. The correlation coefficient between O_3 and the hydrogen ion (H^+) was 0.56.

Source: Spektor et al. (1991).

4.8.4 Population Exposure Models

McCurdy (1994) has reviewed the current status of human exposure modeling. The author describes two distinct types of O_3 exposure models: (1) those that focus narrowly on predicting indoor O_3 levels and (2) those that focus on predicting O_3 exposures on a community-wide basis. The models that predict indoor O_3 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 O_3 exposure on a community-wide basis. These models and their distinguishing features are:

1. pNEM/O_3 based on the National Air Quality Standards Exposure Model (NEM) series of models (Paul et al., 1987; Johnson et al., 1990; McCurdy et al., 1991).
   - Uses mass-balance approach and seasonal considerations for I/O ratio estimation.
   - Variables affecting indoor exposure obtained by Monte Carlo sampling from empirical distributions of measured data.

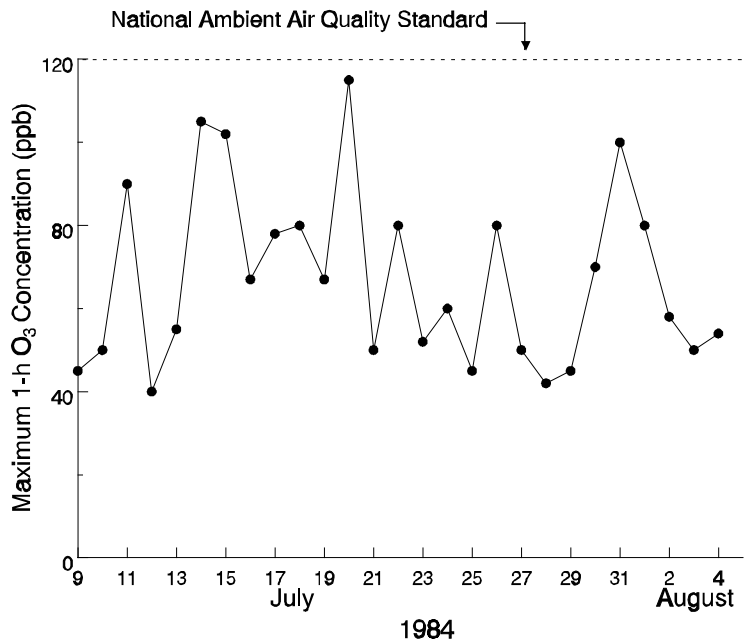


Figure 4-28. Maximal 1-h ozone concentrations at Fairview Lake during the study period.

Source: Spektor et al. (1988).

2. Systems Applications International (SAI)/NEM (Hayes et al., 1984; Hayes and Lundberg, 1985; Austin et al., 1986; Hayes et al., 1988; Hayes and Rosenbaum, 1988).
   - More districts and microenvironments and more detailed mass-balance model than pNEM/O_3.
   - Human activity data outdated and inflexible.
3. Regional Human Exposure Model (REHEX) (Lurmann and Colome, 1991; Winer et al., 1989; Lurmann et al., 1989; Lurmann et al., 1990).
   - More detailed geographic resolution than NEM.
   - Uses California-specific activity data and emphasizes in-transit and outdoor microenvironments.
4. Event probability exposure model (EPEM) (Johnson et al., 1992).
   - Estimates probability that a randomly selected person will experience a particular exposure regime.
   - Lacks multiday continuity.

McCurdy (1994) points out that all four models are related to the NEM. The NEM is an EPA exposure model developed in the 1980s (Biller et al., 1981). Outdoor air quality data are obtained from monitoring or modeling data. In most applications of NEM, fixed-site monitoring data are used. The hourly average values are transformed by a suitable relationship so that they better represent air quality outside of the various microenvironments of interest. McCurdy (1994) points out that the important point of the NEM spatial dimension is that people can be assigned to a monitor using U.S. census data. In addition,

community trips can be assigned among the districts, grid cells, or neighborhood types using census data. Thus, the NEM model simulates the movement of people through space for work-trip purposes. Interested readers are referred to McCurdy (1994) for further discussion of the pNEM model.

4.8.5 Concentration and Exposures Used in Research Experiments

It is important to adequately characterize the exposure patterns that result in vegetation and human health effects. Hourly average concentrations used in many of the high treatment experimental studies did not necessarily mimic those concentrations observed under ambient conditions. Although the ramifications of this observation on the effects observed are not clear, it was pointed out that the highest treatments used in many of the open-top chamber experiments were bimodal in the distribution of the hourly average concentrations. In other experiments designed to assess the effects of O_3 on vegetation, constant concentration (i.e., square wave) exposures were implemented. As has been discussed in earlier sections of this chapter, hourly average concentrations change by the hour and square wave exposure regimes do not normally occur under ambient conditions. In addition to the exposures used at the highest treatment levels, there is concern that the hourly average concentrations used in the control treatments may be lower than those experienced at isolated sites in the United States or in other parts of the world. Although the ramifications of using such exposure regimes are unclear, there is some concern that the use of atypically low control levels may result in an overestimation of vegetation yield losses when used as the baseline for evaluating the effects of treatments at higher concentrations (Lefohn and Foley, 1992).

For assessing the human health effects of O_3 exposure, a series of studies has explored prolonged 6.6-h O_3 exposures at low levels (i.e., 0.08 to 0.12 ppm) (Horstman et al., 1990). McDonnell et al. (1991), using similar hourly average concentration regimes, have confirmed the findings reported by Horstman et al. (1990). All the research investigations using 6.6-h durations have applied constant concentrations during the exposure period. If, as indicated in the introduction of this chapter, concentration is more important than duration and ventilation rate, different human health effects may occur as a result of different exposure regimes that have identical 6.6-h average concentrations. Because of this, it is important to explore the different types of exposure regimes that occur under ambient conditions during an 8-h episode.

Lefohn and Foley (1993) reported on an analysis of hourly average data for O_3 monitoring sites that never experienced an exceedance of an hourly average concentration ≥0.12 ppm and that experienced 8-h daily maximum average concentrations >0.08 ppm. For those monitoring sites that met the above two criteria, they identified the number of times the 8-h daily maximum average concentration exceeded 0.08 ppm during the monitoring year. For the period 1987 to 1989, there were 925 exposure regimes identified from 166 site-years of data that met the above criteria. The data were then organized into the following seven categories:

I. The occurrence of 8-h daily maximum averages >0.08 ppm and <0.09 ppm;
II. The occurrence of 8-h daily maximum averages >0.08 ppm but ≤0.082 ppm, which contained only hourly average concentrations >0.08 ppm but ≥0.082 ppm;
III. 8-h daily maximum averages >0.08 ppm, which contained hourly average concentrations <0.09 ppm;

IV. 8-h daily maximum averages >0.08 ppm and <0.09 ppm, which contained at least one hourly average concentration ≥0.09 ppm but <0.10 ppm;
V. 8-h daily maximum averages >0.08 ppm and <0.09 ppm, which contained at least one hourly average concentration ≥0.10 ppm;
VI. 8-h daily maximum averages <0.08 ppm, which contained at least one hourly average concentration ≥0.09 ppm but <0.10 ppm; and
VII. 8-h daily maximum averages <0.08 ppm, which contained at least one hourly average concentration ≥0.10 ppm.

Figure 4-29 summarizes the results of the analysis. The results indicated that there was a poor relationship between the value of the 8-h daily maximum average concentration and the frequency of occurrence of hourly average concentrations within specific ranges (e.g., between 0.09 and 0.10 ppm). In no case could the authors identify a monitoring site that experienced the square-wave type of exposure that was described in Category II (i.e., the occurrence of 8-h daily maximum averages >0.08 ppm but ≤0.082 ppm). Lefohn and Foley (1993) concluded that the square wave exposures used in the 6.6-h human health effects experiments were not found under ambient conditions. The authors identified 453 additional exposure regimes, where the 8-h daily maximum average was <0.08 ppm but experienced maximum hourly average concentrations ≥0.09 ppm. Thus, if hourly average concentrations ≥0.08 ppm are of concern for affecting human health, there will be instances where occurrences above this threshold are evident, but the 8-h average value is below 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 are discussed elsewhere in this document (Chapter 7, Section 7.2.6.3). Some effects on respiratory parameters have been reported in one study, but not in others. However, the PAN concentrations used in these studies have been well above the maximum ambient concentrations usually experienced many years ago within the Los Angeles Basin (U.S. Environmental Protection Agency, 1986) and, more importantly, above the maximum ambient concentrations in the more recent measurements considered in this section.

The PANs are of importance as reservoirs for NO_2 as NO_x is depleted relative to VOCs in plumes moving downwind into less polluted areas (Chapter 3, Section 3.2.4). In performance evaluation of ozone air quality models, measured concentrations of PANs are useful in model evaluation (Chapter 3, Section 3.6.4.2).

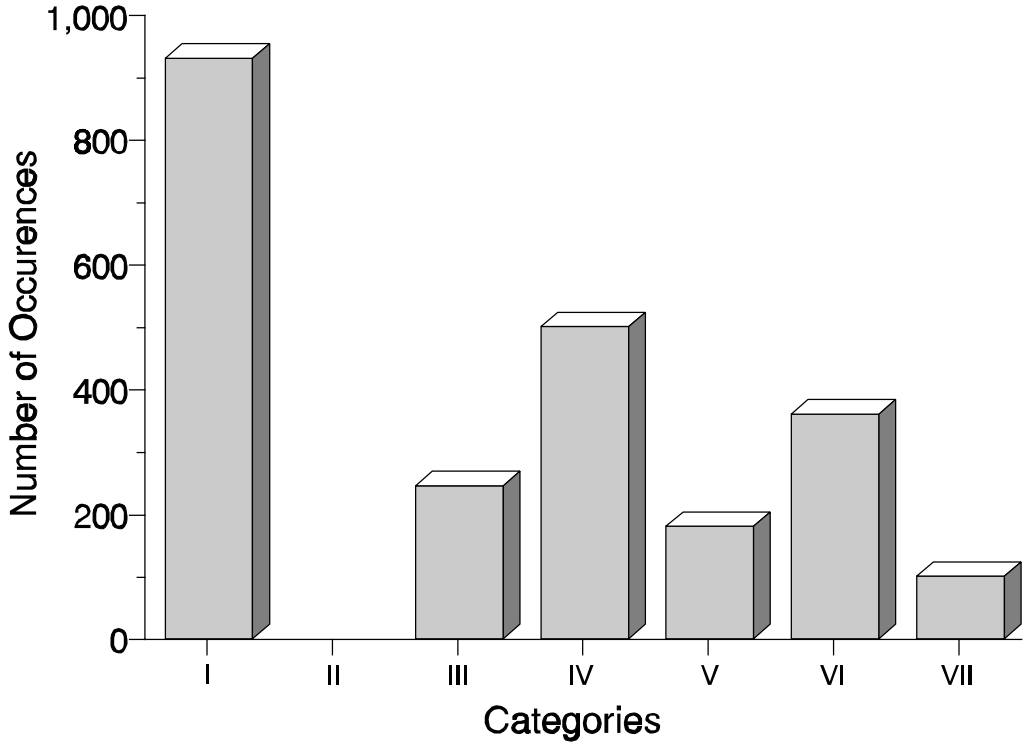


Figure 4-29. The number of occurrences for each of the seven categories described in text.

In the previous air quality criteria for O_3 and other photochemical oxidants (U.S. Environmental Protection Agency, 1986), extensive tabulations of PAN and peroxypropionyl nitrate (PPN, CH3CH2C(O)OONO2) concentrations were given based on measurements made between 1965 and 1981 from references up to 1983. In the present work, references from 1983 to the present are used for measurements of PANs in urban and rural locations. The urban area measurements are from the United States, Canada, France, Greece, and Brazil. The use of measurements from aboard serve to illustrate or support certain U.S. results as well as to demonstrate the widespread presence of PANs in the atmosphere. These PAN measurements usually were of limited duration, and the results should not be assumed to be comparable to those obtained at the O_3 monitoring sites discussed earlier in this chapter (see also Section 4.10).

4.9.2 Urban Area Peroxyacetyl Nitrate Concentrations

For urban sites, the prior criteria document for ozone and other photochemical oxidants contains a number of tables tabulating measurements of PAN, PPN, and PPN to PAN and PAN to O_3 ratios (Altshuller, 1983; U.S. Environmental Protection Agency, 1986). Based on comparisons of PAN measurements in Los Angeles in 1980 with those made in the 1960s, it was uncertain whether PAN concentrations had decreased. In the Los Angeles area, the average and maximum PAN concentrations reported ranged from 1.6 to 31 ppb and from 6 to 214 ppb, respectively. The wide variations, at least in part, were associated with the range of years, different seasons, and differing average times among studies. On average, the

PPN to PAN ratios among studies in Los Angeles ranged from 0.15 to 0.20, whereas the PAN to O_3 ratios among studies ranged from 0.04 to 0.20. In the earlier PAN measurement results, studies conducted in the South Coast Air Basin predominated.

The average PAN concentrations measured in other cities usually were lower than in the Los Angeles area, whereas the maximum PAN concentrations overlapped with the lower end of range in Los Angeles. The PPN and PAN ratios in other cities ranged from 0.1 to 0.4, whereas the PAN to O_3 ratios were in the 0.01 to 0.05 range.

Seasonally, PAN to O_3 ratios tended to be somewhat higher in the winter. The diurnal characteristics of O_3 and of PAN were similar, but not identical.

The urban area measurement results are tabulated in Table 4-19. The earlier maximum PAN concentrations reported usually were substantially higher than those given in Table 4-19. A possible exception occurs for the Claremont, CA, results. Measurements of PAN and PPN were made in 1989 and 1990 at sites downwind of Los Angeles: Perrin, 90 km to the east-southeast, and Palm Springs, 120 km to the east (Grosjean and Williams, 1992). The concentrations of PAN and PPN were high, and the concentration maxima occurred during the evening hours, which was consistent with downwind transport from the Los Angeles area rather than from local sources.

In Southern California, the maximum PAN concentrations appear to be more evenly distributed spatially during the fall than during the summer (Williams and Grosjean, 1990). At coastal and central locations, the PAN maxima during the fall were comparable to those observed at inland locations during the summer.

As observed previously, PAN concentrations in other U.S. cities and in cities in other countries tend to be substantially lower than in Los Angeles and its surrounding urban areas (Table 4-19). An exception occurs for the measurements from Paris (Tsalkani et al., 1991). Maximum PAN concentrations in the 20 to 35 ppb range were observed.

In measurements made in 1992 in Atlanta, GA, at the Georgia Institute of Technology campus site, not only were PAN and PPN measured, but very occasionally peroxymethacryloyl nitrate (MPAN, $CH_2{=}C(CH_3)\ C(O)OONO_2$) (a product of the atmospheric photooxidation of local biogenic sources of isoprene) was observed (Williams et al., 1993). Maximum diurnal concentrations of peroxyacyl nitrates and O_3 occur in late afternoon and early evening. The average MPAN concentration was 0.3 ppb, and the maximum value was 0.5 ppb and constituted about 15% of the concurrent PAN concentrations.

In a study in Rio de Janeiro performed to investigate the effects of the use of ethanol or ethanol-containing fuel on PAN concentrations, the maximum PAN concentration reached 5.4 ppb (Tanner et al., 1988). However, this maximum concentration is well below the maximum concentrations reported in and around Los Angeles, and it falls within the maximum PAN values reported for a number of other cities (Table 4-19).

4.9.3 Concentration of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Rural Areas

Prior measurements of nonurban PAN and PPN concentrations and PAN to O_3 ratios are available (Altshuller, 1983; U.S. Environmental Protection Agency, 1986). At nonurban sites that are not impacted by urban plumes, PAN and PPN concentrations are

Table 4-19. Summary of Measurements of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Urban Areas[a]

Site	Month/ Year	Number of Days Sampled	PAN Concentration (ppb) Average/Mean	Max	PPN Concentration (ppb) Average/Mean	Max	Reference
Long Beach, CA	6-12/1987	16	NA	16	NA	NA	Williams and Grosjean (1990)
Anaheim, CA	6-12/1987	14	NA	19	NA	NA	Williams and Grosjean (1990)
Los Angeles, CA	6-12/1987	16	NA	13	NA	NA	Williams and Grosjean (1990)
Burbank, CA	6-12/1987	16	NA	19	NA	NA	Williams and Grosjean (1990)
Azusa, CA	6-9/1987	11	NA	13	NA	NA	Williams and Grosjean (1990)
Claremont, CA	6-9/1987	10	NA	30	NA	NA	Williams and Grosjean (1990)
Perrin, CA	6/1989 to 6/1990	NA	1.6	9.1	NA	0.73	Grosjean and Williams (1992)
Palm Springs, CA	6/1989 to 6/1990	NA	1.6	7.6	NA	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	NA	Peake et al. (1988)
Calgary, Alberta, Canada	7/1981 to 2/1982	213	0.14	6.6	NA	NA	Peake and Sandhu (1983)
University of Calgary, Alberta, Canada	10/1980 to 8/1981	175	0.22	2.4	NA	NA	Peake and Sandhu (1983)
Simcoe, Ontario, Canada	6/1980 to 3/1981	191	1.3	5.6	NA	NA	Corkum et al. (1986)

Table 4-19 (cont'd). Summary of Measurements of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Urban Areas[a]

Site	Month/ Year	Number of Days Sampled	PAN Concentration (ppb) Average/Mean	Max	PPN Concentration (ppb) Average/Mean	Max	Reference
Rio de Janeiro							
Vila Isabel	7/1985	8	NA	5.4	NA	1.0	Tanner et al. (1988)
PUC/RJ	7/1985	4	NA	3.3	NA	0.6	Tanner et al. (1988)
Athens, Greece	2-11/1985	113	NA	3.7	NA	NA	Tsani-Bazaca et al. (1988)
Paris, France	11/1985 to 11/1986	NA	1.1	20.5	NA	NA	Tsalkani et al. (1991)

[a]See Appendix A for abbreviations and acronyms.

much lower than those in urban areas. Average PAN concentrations ranged between 0.1 and 1.0 ppb, whereas the PAN to O_3 ratios were at or below 1.

Concentrations of PAN, PPN, and other peroxyacyl nitrates have been reported (Table 4-20) at Tanbark Flat, CA, 35 km northeast of Los Angeles, during 1989, 1990, and 1991 and at Franklin Canyon, CA, 25 km west of Los Angeles, during 1991 (Grosjean and Williams, 1992; Grosjean et al., 1993). As indicated by the results tabulated in Table 4-20, the concentrations were high at these mountain sites, the PPN to PAN ratios were relatively high, and the concentration maxima occurred during the afternoon hours. These concentration levels of PAN and PPN are attributed to downwind transport from the Los Angeles urban area. The MPAN was occasionally detected with average concentrations of 1.2 ppb at Tanbark Flat and 1.0 ppb at Franklin Canyon in 1991.

At Tanbark Flat, the O_3 and PAN diurnal concentration patterns were similar to those in upwind urban areas. The PAN to O_3 ratios at the O_3 maximum were as follows: 1989, 0.05; 1990, 0.08; 1991, 0.05; all the ratios are within the same range as at sites in urban areas in and around Los Angeles.

Additional measurements of PAN and PPN or other peroxyacyl nitrates are available over a period of years at Niwot Ridge, CO, just west of the Denver-Boulder area; at Point Arena, CA; and at a forest site, Scotia, PA (Ridley et al., 1990). The concentrations reported at all of these sites are much lower than the mountain sites in California. The Niwot Ridge site concentrations, which show the effects of easterly upslope flow of air parcels from Denver-Boulder, are still low compared to the sites downwind of the urban Los Angeles area (Table 4-20).

The PAN concentrations at the Scotia rural site in the eastern United States tend to be somewhat higher than the Niwot Ridge or Point Arena sites (Table 4-20). This difference may relate to higher regional precursor concentration levels.

4.10 Concentration and Patterns of Hydrogen Peroxide in the Ambient Atmosphere

Efforts to measure H_2O_2 began in the 1970s, but the early reports of H_2O_2 concentrations above 10 ppb and even 100 ppb appear to be in error because of the artifact H_2O_2 generated within the presence of O_3 (Chapter 3, Section 3.5.1.3). Subsequent measurements of H_2O_2 in the 1980s resulted in maximum H_2O_2 concentrations at or below 5 ppb and mean concentrations at or below 1 ppb (Sakugawa et al., 1990).

Studies comparing more recent methods for measuring H_2O_2, which were conducted in North Carolina, indicated differences among measurement methods in synthetic mixtures of H_2O_2, including possible interferences, and in the ambient atmosphere of up to about ±25% (Kleindienst et al., 1988). However, results from the same study from mixtures irradiated in a smog chamber produced larger differences among methods, especially for the luminol technique compared to the fluorescence technique and with tunable-diode laser absorption spectroscopy. Another comparison study conducted in California resulted in differences between methods for measuring H_2O_2 that varyied by a factor or two (Lawson et al., 1988). In the measurements of H_2O_2 discussed below, the cryogenic fluorescence method or the scrubber-coil fluorescence method generally was used.

Table 4-20. Summary of Measurements of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Rural Areas[a]

Site	Month/ Year	Number of Days Sampled	PAN Concentration (ppb) Average/Mean	Max	PPN Concentration (ppb) Average/Mean	Max	Reference
Tanbark Flat, CA	8-10/1989	69	2.9	>16.1	0.75	5.1	Williams and Grosjean (1991)
	8,9/1990	34	4.8	22.0	0.76	4.3	Grosjean et al. (1993)
	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)
	6, 7/1984	23	≈0.25	NA	NA	NA	Fahey et al. (1986)
	8, 9/1984	21	≈0.25	NA	NA	NA	Fahey et al. (1986)
	6, 7/1987	46	0.81 ([b]) 0.21 ([c])	3.2	0.08 ([b]) 0.01 ([c])	0.45	Ridley et al. (1990)
Point Arena, CA	1/1984	14	0.12	1.1	0.005	0.07	Singh and Salas (1989)
	Spring 1985	NA	0.05	NA	NA	NA	Ridley (1991)
Scotia, PA	Summer 1986	NA	≈0.6	NA	NA	NA	Ridley (1991)
	6-8/1988	47	1.0	NA	NA	NA	Buhr et al. (1990)
Kananaskis Valley, Alberta, Canada	9/1979, 4/1982, 6-8/1982	NA	≈0.5	2.3	NA	NA	Peake et al. (1983)
Frijoles Mesa, NM	10/1987 to 1/1989	NA	0.26	1.9	NA	NA	Gaffney et al. (1993)

[a]See Appendix A for abbreviations and acronyms.
[b]Flow from Boulder-Denver area.
[c]Flow across the Rockies.

Based on interpretation of a compilation of H_2O_2 measurements made between 1984 and 1988 at a number of urban locations, at rural/remote locations, and on aircraft flights, it was concluded that the higher H_2O_2 concentrations were associated with the following measurement conditions: in afternoon hours, during summer months, at rural locations, and at lower latitudes (Sakugawa et al., 1990; Van Valin et al., 1987). The H_2O_2 concentrations increase from the surface to the top of the boundary layer (Daum et al., 1990). Available values for mean H_2O_2 concentrations at three U.S. locations were (1) at the summit of Whitetop Mountain, VA: summer, 0.80 ppb; winter, 0.15 ppb (Olszyna et al., 1988); (2) at the summit of Whiteface Mountain: 1986, 0.6 ppb; 1987; 0.8 ppb (Mohnen and Kadlecek, 1989); and (3) at Westwood, CA: summer, ≈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; 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 the 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 Bernardino 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 co-occurrence patterns, Lefohn et al. (1987b) grouped air quality data within a 24-h period starting at 0000 hours and ending at 2359 hours. 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 co-occurrences. When pollutant pairs occurred at or above a minimum concentration during the 24-h period, without occurring during the same hour, a "sequential-only" co-occurrence 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 co-occurrence pattern was defined as "complex-sequential".
A co-occurrence was not indicated if one pollutant exceeded the minimum concentration just before midnight and the other pollutant exceeded the minimum concentration just after midnight. As will be discussed below, studies of the joint occurrence of gaseous NO_2/O_3 and SO_2/O_3 reached two conclusions: (1) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, where an episode was defined by the threshold concentration used, and (2) the time between episodes is generally long (i.e., weeks, sometimes months) (Lefohn and Tingey, 1984; Lefohn et al., 1987b).

For exploring the co-occurrence of O_3 and other pollutants (e.g., acid precipitation, acidic cloudwater, and acidic sulfate aerosols), there are limited data available. In most cases, routine monitoring data are not available from which to draw general conclusions. However, published results are reviewed and summarized for the purpose of assessing an estimate of the possible importance of co-occurrence patterns of exposure.

4.11.2 Nitrogen Oxides

Ozone occurs frequently at concentrations ≥0.03 ppm at many rural and remote monitoring sites in the United States (Evans et al., 1983; Lefohn, 1984; Lefohn and Jones, 1986). Therefore, for many rural locations in the United States, the co-occurrence patterns observed by Lefohn and Tingey (1984) for O_3 and NO_2 were defined by the presence or absence of NO_2. As anticipated, Lefohn and Tingey (1984) reported that most of the sites analyzed experienced fewer than 10 co-occurrences (when both pollutants were present at an hourly average concentration ≥0.05 ppm). However, the authors did note that several urban monitoring sites in the South Coast Air Basin experienced more than 450 co-occurrences. The rural sites of Riverside, Fontana, and Rubidoux, CA, had more than 100 co-occurrences. Denver and San Jose, CA, also experienced more than 100 co-occurrences of O_3/NO_2. Lefohn and Tingey (1984) reported that for Rubidoux, because NO_2 concentration maxima tended to peak in the evenings or early morning, the co-occurrences were present at these times. For more moderate areas of the country, Lefohn et al. (1987b) reported that even with a threshold of 0.03 ppm O_3, the number of co-occurrences with NO_2 was small.

4.11.3 Sulfur Dioxide

Because elevated SO_2 concentrations are mostly associated with industrial activities (U.S. Environmental Protection Agency, 1992a), co-occurrence 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 co-occurrences of SO_2 and O_3. Only Rockport, IN, and Paradise No. 21 (KY) had more than 40 co-occurrences 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 there were numerous O_3 episodes above 0.05 ppm, and there was a high probability that when the SO_2 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 O_3 episodes at specific rural locations appeared to be associated with elevated SO_2 levels. The investigators defined the co-occurrence of O_3 and SO_2 to be when hourly mean concentrations were equal to or greater than 0.10 and 0.01 ppm, respectively. On reviewing the hourly mean O_3 and SO_2 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 County 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 co-occurrence of any form (i.e., simultaneous only, sequential, and complex co-occurrence). Thus, as reported by Lefohn et al. (1987b), the co-occurrence pattern of O_3 and SO_2 was infrequent.

The above discussion was based on the co-occurrence patterns associated with the presence or absence of hourly average concentrations of pollutant pairs. Taylor et al. (1992) have discussed the joint occurrence of O_3, nitrogen, and sulfur in forested areas using

cumulative exposures of O_3 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 O_3 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 co-occurrences of O_3 and SO_2 or O_3 and NO_2.

4.11.4 Acidic Sulfate Aerosols

Acid sulfates, which are usually composed of sulfuric acid (H_2SO_4), 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 µg/m^3 at a specific location or a number of locations simultaneously (Lioy, 1989). For many summertime studies, peaks of H_2SO_4 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 µm in diameter). Lioy (1989) reports that the acidic sulfate concentrations measured in the summertime can be found at 20 µg/m^3 for over an hour and can be found at high concentrations of 10 to 20 µg/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 µg/m^3 for periods longer 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 co-occur at some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is real. Our knowledge of the potential exposure of the co-occurrence of acidic sulfate aerosols and O_3 is limited because routine monitoring data for acidic aerosols are not available. Information on the co-occurrence patterns is limited to research studies and some of the results of these studies are 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 µg/m^3, reaching a 12-h maximum of 18.6 µg/m^3. Figure 4-27 shows the relationship between daily maximum O_3 and daily 12-h average H^+ concentrations. Thurston et al. (1992) reported occurrences in 1988 of maximum 24-h average concentrations of H^+ as high as 18.7 µg/m^3 (Buffalo, NY) 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, NY. 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 co-occurrences are experienced. Raizenne and Spengler (1989) described an episodic co-occurrence 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, (Figure 4-30). Thurston et al. (1994) conducted a study of ambient acidic aerosols in the Toronto, Ontario, metropolitan area in July and August of 1986, 1987, and 1988, and reported on the fine particle (aerodynamic equivalent diameter <2.5 µm) samples collected twice per day. The authors

reported that their results indicated that acidic aerosol episodes (i.e., $H^+ \geq 100$ nmol/m^3) occurred routinely during the summer months and that H^+ peaks were correlated with sulfate (SO_4) episodes. Figure 4-31 illustrates the relationship among SO_4, H^+, and O_3.

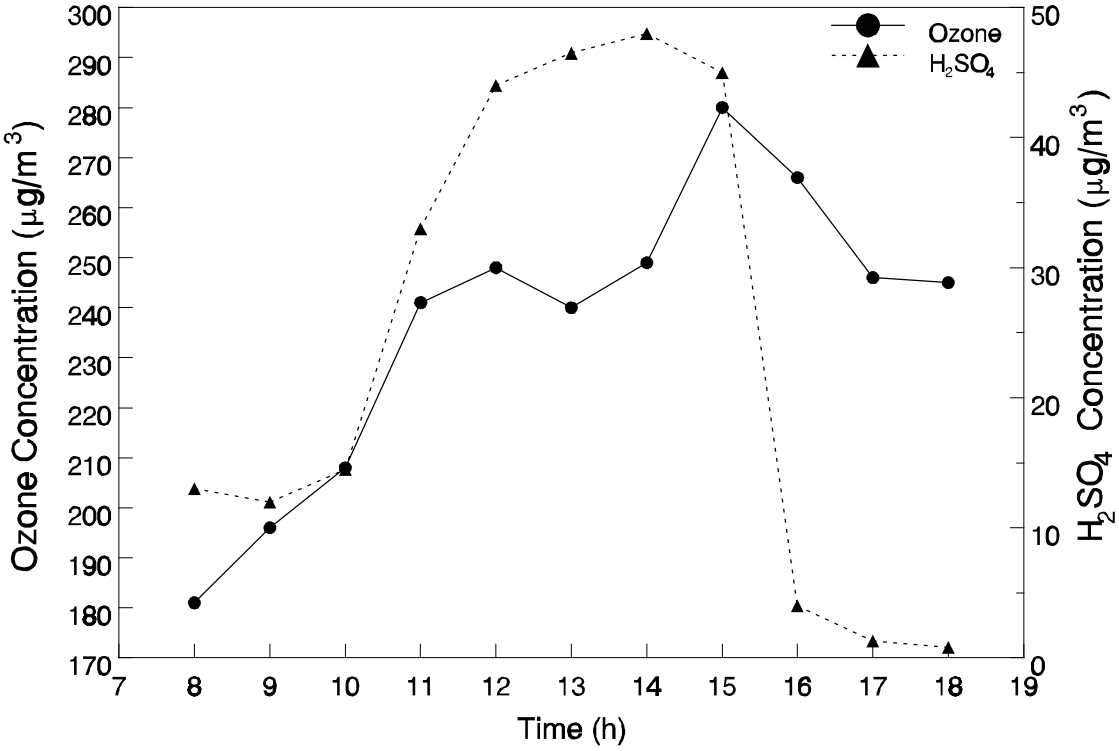


Figure 4-30. The co-occurrence pattern of ozone and sulfuric acid (H_2SO_4) for July 25, 1986, at a summer camp on the north shore of Lake Erie, Ontario, Canada.

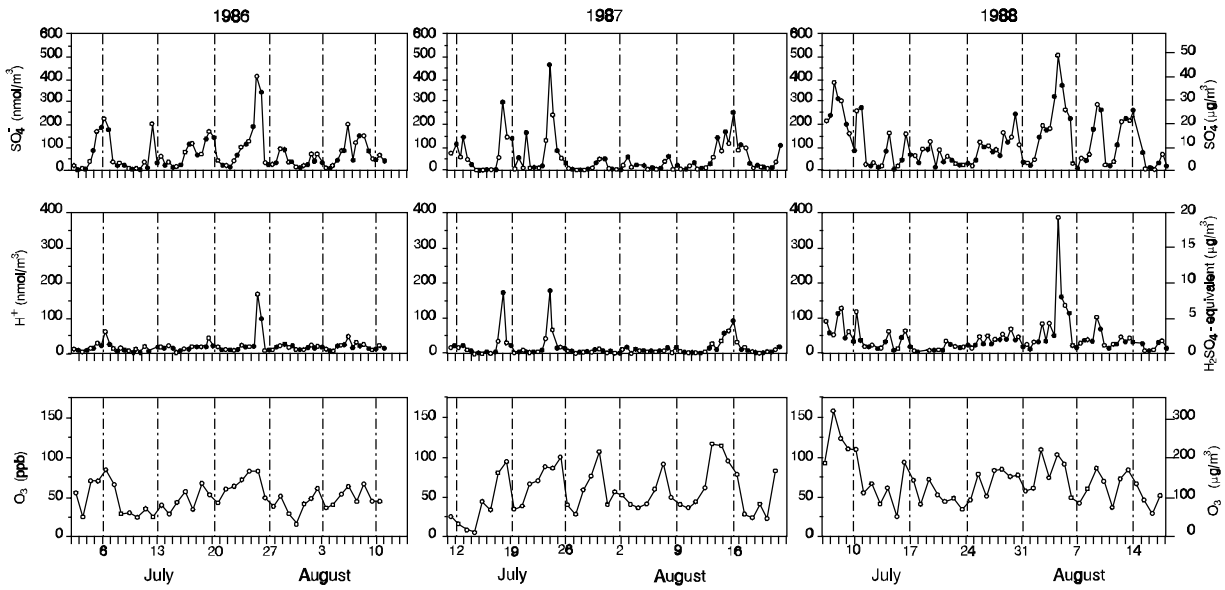
Source: Raizenne and Spengler (1989).

4.11.5 Acid Precipitation

Concern has been expressed about the possible effects on vegetation from co-occurring 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 co-occurrence patterns associated with the joint distribution of O_3 and acidic deposition (i.e., H^+). Lefohn and Benedict (1983) reviewed EPA's SAROAD monitoring data for 1977 through 1980 and, using National Atmospheric Deposition Program (NADP) and 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.

Figure 4-31. Sulfate (SO_4^-), hydrogen ion (H^+), and ozone (O_3) measured at Breadalbane Street (Site 3) in Toronto during July and August 1986, 1987, and 1988.

Source: Thurston et al. (1994).



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 O_3 concentrations were ≥0.1 ppm and 20% of the wetfall daily or weekly samples were below pH 4.0. Elevated levels of O_3 were defined as hourly mean concentrations equal to or greater than 0.1 ppm. Although for many cases, experimental research results of acidic deposition on agricultural crops show few effects at pH levels above 3.5 (National Acid Precipitation Assessment Program, 1987), it was decided to use a pH threshold of 4.0 to take into consideration the possibility of synergistic effects of O_3 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 O_3 and H^+ concentrations. The authors stated that they believed, based on the available data, the greatest potential for interaction between acid rain and O_3 concentrations 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., O_3 and acidic deposition) could be used because O_3 exposures are regional in nature. However, work by Lefohn et al. (1988a) has shown that hourly mean O_3 concentrations vary from location to location within a region, and that cumulative indices, such as the percent of hourly mean concentrations ≥0.07 ppm, do not form a uniform pattern over a region. Thus, extrapolating hourly mean O_3 concentrations from known locations to other areas within a region may provide only qualitative indications of actual O_3 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 O_3 collected at several comonitored locations. No attempt was made to include H^+ cloud deposition information. In some cases, for mountaintop locations (e.g., Clingman's Peak, Shenandoah, Whiteface Mountain, and Whitetop Mountain), the H^+ cloud water deposition is greater than the H^+ deposition in precipitation (Mohnen, 1989), and the co-occurrence 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 H^+ in precipitation, using data from sites that 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 H^+ deposition and total O_3 exposure were at least moderately high (i.e., annual H^+ deposition ≥0.5 kg ha^{-1} and an annual O_3 cumulative, sigmoidally weighted exposure (W126) value ≥50 ppm-h). With data compiled from all sites, it was found that relatively acidic precipitation (pH ≤ 4.31 on a weekly basis or pH ≤ 4.23 on a daily basis) occurred together with relatively high O_3 levels (i.e., W126 values ≥ 0.66 ppm-h for the same week or W126 values ≥ 0.18 ppm-h immediately before or after a rainfall event) approximately 20% of the time, and highly acidic precipitation (i.e, pH ≤ 4.10 on a weekly basis or pH ≤ 4.01 on a daily basis) occurred together with a high O_3 level (i.e., W126 values ≥ 1.46 ppm-h for the same week or W126 values ≥ 0.90 ppm-h immediately before or after a 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 co-occurrence of O_3 and acid precipitation, results have been reported on the co-occurrence 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 co-occurrences of O_3 and acidic cloudwater. The authors reported that both simultaneous and sequential co-occurrences were observed a few times each month above the cloud base. Episodes were classified by considering hourly O_3 average concentrations ≥0.07 ppm and cloudwater events with pH ≤ 3.2. The authors reported that simultaneous occurrences of O_3 and pH episodes occurred two to three times per month at two southern sites (Mitchell, NC, and Whitetop, VA) and the two northern sites (Whiteface Mountain, NY, and Moosilauke, NH) averaged one episode per month.
No co-occurrences were observed at the central Appalachian site (Shenandoah, VA), due to a much lower cloud frequency. Vong and Guttorp (1991) reported that the simultaneous occurrences were usually of short duration (mean = 1.5 h/episode) and were followed by an O_3-only episode. As would be expected, O_3-only episodes were longer than co-occurrences and pH episodes, averaging an 8-h duration.

4.12 Summary

Ozone is a pervasive compound that is detected at all monitoring locations throughout the world. To obtain a better understanding of the potential for ambient O_3 exposures affecting human health and vegetation, hourly average concentration information is summarized for urban, rural forested, and rural agricultural areas in the United States.

The distribution of O_3 or its precursors at a rural site near an urban source is affected by wind direction (i.e., whether the rural site is located up- or downwind from the source). It is difficult to apply land-use designations to the generalization of exposure regimes that may be experienced in urban versus rural areas, because the land use characterization of "rural" does not imply that a specific location is isolated from anthropogenic influences. Rather, the characterization implies only the current use of the land. Because it is possible for urban emissions, as well as O_3 produced from urban area emissions, to be transported to more rural downwind locations, elevated O_3 concentrations can occur at considerable distances from urban centers. Urban O_3 concentration values often are depressed because of titration by NO. Because of the absence of chemical scavenging, O_3 tends to persist longer in nonurban than in urban areas, and exposures may be higher in nonurban than in urban locations.

For vegetation, as indicated in Chapter 5 (Section 5.5), extensive research has focused on identifying exposure indices with a firm foundation on biological principles. Many of these exposure indices have been based on research results indicating that the magnitude of vegetation responses to air pollution is more an effect of the magnitude of the concentration than the length of the exposure. For O_3, the short-term (1- to 8-h), high concentration exposures (>0.1 ppm) have been identified by many researchers as being more important than long-term, low concentration exposures in producing visible injury to plants (see Chapter 5 for further discussion). Similarly, for human health considerations, results using controlled human exposures have shown the possible importance of concentration in relation to duration of exposure and inhalation rate.

In summarizing the hourly average concentrations in this chapter, specific attention is given to the relevance of the exposure indices used. For example, for human health considerations, concentration (or exposure) indices such as the daily maximum 1-h average concentrations, as well as the number of daily maximum 4- or 8-h average concentrations above a specified threshold, are used to characterize information in the population-oriented locations. For vegetation, several different types of exposure indices are used. Because much of the NCLAN exposure information is summarized in terms of 7-h average concentrations, this exposure index is used. However, because peak-weighted, cumulative indices (i.e., exposure parameters that sum the products of hourly average concentrations multiplied by time over an exposure period have shown considerable promise in relating exposure and vegetation response (see Chapter 5, Section 5.5), several exposure indices that use either a threshold or a sigmoidally weighted scheme are used in this chapter to provide insight concerning the O_3 exposures that are experienced at a select number of rural monitoring sites in the United States. The peak-weighted cumulative exposure indices such as SUM06, SUM08, and W126 are used.

Ozone hourly average concentrations have been recorded for many years by the State and local air pollution agencies who report their data to EPA. The 10-year (1983 to 1992) composite average trend for the second highest daily maximum hourly average concentration during the O_3 season for 509 trend sites and a subset of 196 NAMS sites,

shows that the 1992 composite average for the trend sites is 21% lower than the 1983 average and 20% lower for the subset of NAMS sites. The 1992 value is the lowest composite average of the past 10 years. The 1992 composite average is significantly less than all the previous 9 years, 1983 to 1991. The relatively high O_3 concentrations in 1983 and 1988 were attributable, in part, to hot, dry, stagnant conditions in some areas of the country that were especially conducive to O_3 formation.

From 1991 to 1992, the composite mean of the second highest daily maximum 1-h O_3 concentrations decreased 7% at the 672 sites and 6% at the subset of 222 NAMS sites. Also, from 1991 to 1992, the composite average of the number of estimated exceedances of the O_3 standard decreased by 23% at the 672 sites, and 19% at the 222 NAMS sites. Nationwide VOC emissions decreased 3% from 1991 to 1992 (U.S. Environmental Protection Agency, 1993). The composite average of the second daily maximum concentrations decreased in 8 of the 10 EPA regions from 1991 to 1992, and remained unchanged in Region VII. Except for Region VII, the 1992 regional composite means are lower than the corresponding 1990 levels. Although meteorological conditions in the east during 1993 were more conducive to O_3 formation than those in 1992, the composite mean level for 1993 was the second lowest composite average for the decade (1984 to 1993).

Information is provided in this chapter on methods used for investigating techniques for adjusting O_3 trends for meteorological influences. Historically, the long-term O_3 trends in the United States characterized by EPA have emphasized air quality statistics that are closely related to the NAAQS. Information is provided on the use of alternative indices. Besides EPA, additional investigators have assessed trends at several locations in the United States, and information is provided for both urban and rural areas.

Interest has been expressed in characterizing O_3 exposure regimes for sites experiencing daily maximum 8-h concentrations above specific thresholds (e.g., 0.08 or 0.10 ppm). Documented evidence has been published showing the occurrence, at some sites, of multihour periods within a day of O_3 at levels of potential health effects. Although most of these analyses were made using monitoring data collected from sites in or near nonattainment areas, one analysis showed that at five sites, two in New York state, two in rural California, and one in rural Oklahoma, an alternative O_3 standard of an 8-h average of 0.10 ppm would be exceeded even though the existing 1-h standard would not be. The study indicated the occurrence at these five sites, none of which was in or near a nonattainment area, of O_3 concentrations showing only moderate peaks but showing multihour levels above 0.10 ppm.

An important question is whether an improvement in O_3 levels would produce distributions of 1-h O_3 concentrations that result in a broader diurnal profile than those seen in high-oxidant urban areas where O_3 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. One research effort observed, using aerometric data at specific sites, how O_3 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 ($r = 0.51$). The investigators reported few changes in the shape of the average diurnal patterns as sites changed attainment status. The lack of a change

in shape may have explained why the investigators 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 O_3 exposure with an effect. For example, using O_3 ambient air quality data, the number of exceedances of 0.125 ppm and the number of occurrences of the daily maximum 8-h average concentrations ≥0.08 ppm have been compared with the result that a positive correlation (r = 0.79) existed between the second-highest 1-h daily maximum in a year and the expected number of days with an 8-h daily maximum average concentration >0.08 ppm O_3. However, there was not much predictive strength in using one O_3 exposure index to predict another. Similarly, the maximum 3-mo SUM06, second highest daily maximum hourly average concentration, and second highest daily maximum 8-h average concentration exposure indices were compared. For the rural agricultural and forest sites, the correlations among the indices were not strong.

One of the difficulties in attempting to use correlation analysis between indices for rationalizing the substitution of one exposure index for another for predicting an effect (e.g., SUM06 versus the second highest daily maximum hourly average concentration) is the introduction of the error associated with estimating levels of one index from those of another. Evidence has been presented in the literature for recommending that, if a different exposure index (e.g., second highest daily maximum hourly average concentration) is to be compared to, for example, the SUM06 for adequacy in predicting crop loss, then the focus should be on how well the two exposure indices predict crop loss using the effects model that is a function of the most relevant index and not on how well the indices predict one another. Less error would be introduced if either of the two indices were used directly in the development of an exposure-response model.

The EPA has indicated that a reasonable estimate, as an annual average, of O_3 background concentration near sea level in the United States today is from 0.020 to 0.035 ppm; this estimate included a 0.005 to 0.015 ppm contribution from the stratosphere. The EPA concluded that a reasonable estimate of natural O_3 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. Reviewing data from sites that appear to be isolated from anthropogenic sources, it has been reported that, in almost all cases, none of the sites experienced hourly average concentrations ≥0.08 ppm and that the maximum hourly average concentrations were in the range of 0.060 to 0.075 ppm. Using data from these sites, in the continental United States, the 7-mo (April to October) average of the 7-h daily average concentrations range from approximately 0.025 to 0.045 ppm. At an O_3 monitoring site at the Theodore Roosevelt National Park, 7-mo (April to October) averages of the 7-h daily average concentrations of 0.038, 0.039, and 0.039 ppm, respectively, were experienced in 1984, 1985, and 1986. These 7-h seasonal averages appear to be representative of the 8-h daily average O_3 concentrations that may occur at other fairly clean sites in the United States and other locations in the northern hemisphere.

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 levels or levels near minimum detectable amounts to an early afternoon peak. The diurnal pattern of concentrations can be ascribed to four simultaneous processes: (1) downward transport of O_3 from layers aloft,

(2) destruction of O_3 through contact with surfaces and through reaction with NO at ground level, (3) in situ photochemical production of O_3, and (4) horizontal transport of O_3 and its precursors.

Although it might appear that composite diurnal pattern diagrams could be used to quantify the differences in O_3 exposures among sites, caution has been expressed in 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; thus, they may not be adequate to distinguish O_3 exposure differences among sites. 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. For low-elevation sites, intraday variability is most significant due to the pronounced daily amplitude in O_3 concentration between the predawn minimum and midafternoon to early-evening maximum, whereas interday variation is more significant in the high-elevation sites.

Seasonal variations in O_3 concentrations in urban areas usually show the pattern of high O_3 in late spring or in summer and low levels in the winter. Because of temperature, relative humidity, and seasonal changes in 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 in which some of the highest O_3 concentrations of the last decade occurred, whereas 1989 was a cold and wet year in which some of the lowest concentrations occurred.

Several investigators have reported on the tendency for average O_3 concentrations to be higher in the second than in the third quarter of the year for many isolated rural sites. 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. However, for several clean rural sites, the highest exposures have occurred in the third quarter rather than in the second. For rural O_3 sites in the southeastern United States, the daily maximum 1-h average concentration was found to peak during the summer months. For sites located in rural areas, but not isolated from anthropogenic sources of pollution, the different patterns may be associated with anthropogenic emissions of NO_x and hydrocarbons.

Concentrations of O_3 vary with altitude and with latitude. There appears to be no generalizable conclusion concerning the relationship between O_3 exposure and elevation. The differences in exposure occur when one site is above the natural inversion and the other is not. An important issue for assessing possible impacts of O_3 at high-elevation sites that requires further attention is the use of mixing ratios (e.g., parts per million) instead of absolute concentration (e.g., in units of micrograms per cubic meter) to describe O_3 concentration. In most cases, mixing ratios, or mole fractions, are used to describe O_3 concentrations. The manner in which concentration is reported may be important when assessing the potential impacts of air pollution on high-elevation forests. Concentration varies as a function of altitude. Although the change in concentration is small when the elevational difference between sea level and the monitoring site is small, it becomes substantial at high-elevation sites. Given the same part-per-million value registering at both a high- and low-elevation site, the absolute concentrations (i.e., micrograms per cubic meter) at the two elevations will be different. Because both pollutants and ambient air are gases, changes in pressure directly affect their volume. This pressure effect must be considered when measuring absolute pollutant concentrations. Although these exposure considerations

are trivial at low-elevation sites, when one compares exposure-effects results obtained at high-elevation sites with those from low-elevation sites, the differences may become significant.

Most people in the United States spend a large proportion of their time indoors. Until the early 1970s, very little was known about the O_3 concentrations experienced inside buildings. Even to date, the database on this subject is not extensive, and a wide range of I/O O_3 concentration relationships can be found in the literature. Reported I/O values for O_3 are highly variable. A relatively large number of factors can affect the difference in O_3 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 O_3 within buildings. The I/O O_3 concentration ratios generally fall in the range of 0.1 to 0.7, and indoor concentrations of O_3 will almost invariably be less than those outdoors.

It is important that accurate estimates of both human and vegetation exposure to O_3 be available for assessing the risks posed by the pollutant. Examples are provided on how both fixed-site monitoring information and human exposure models are used to estimate risks associated with O_3 exposure.

In many cases, the upper tail of the distribution, which represents those individuals exposed to the highest concentrations, often generates special interest because the determination of the number of individuals who experience elevated pollutant levels can be critical for health risk assessments. This is especially true for pollutants for which the relationship between dose and response is highly nonlinear.

Because it is not possible to estimate population exposure, in most cases, solely from fixed-station data, several human exposure models have been developed. Some of these models include information on human activity patterns (i.e., the microenvironments people visit and the times they spend there). These models also contain submodels depicting the sources and concentrations likely to be found in each microenvironment, including indoor, outdoor, and in-transit settings.

A subgroup that has been studied by several investigators to assess the influence of ambient air pollution on their respiratory health and function is children attending summer camp. Because children are predominantly outdoors and relatively active while at camp, they provide a unique opportunity to assess the relationships between respiratory health and function and concurrent air pollution levels. Examples are provided on the type of exposure patterns that children experience.

A personal exposure profile can be identified by using a personal exposure monitor. Few data are available for individuals using personal exposure monitors. Results from a pilot study demonstrated that fixed-site ambient measurements may not adequately represent individual exposures. Outdoor O_3 concentrations showed substantial spatial variation between rural and residential regions. The study showed that the use of fixed-site measurements could result in an error as high as 127%. In addition, the study showed that models based on time-weighted I/O concentrations explained only 40% of the variability in personal exposures. The investigators concluded that contributions from diverse indoor and outdoor microenvironments could estimate personal O_3 exposure accurately.

The field of human exposure modeling is relatively young, with the first rigorous exposure modeling analyses appearing in the mid-1970s and the theoretical constructs regarding human exposure to environmental pollution being published in the early 1980s. Two distinct types of O_3 exposure models exist: (1) those that focus narrowly on predicting

indoor O_3 levels and (2) those that focus on predicting O_3 exposures on a community-wide basis. The following four distinct models address the prediction of O_3 exposures on a community-wide basis: (1) pNEM/O_3, (2) SAI/NEM, (3) REHEX, and (4) EPEM. All four O_3 exposure models are derived from the NEM (NAAQS exposure model), which was first developed in the early 1980s. Most applications of NEM use fixed-site monitoring data, U.S. census data, and human-activity data. The calculations result in an estimate of the O_3 concentration experienced by an individual in each microenvironment that the person inhabits.

The hourly average concentrations used in many of the high-treatment experimental vegetation and human health effects studies did not necessarily simulate those concentrations observed under ambient conditions. Although the ramifications of this observation on the effects observed are not clear, it has been pointed out that the highest treatments used in many of the vegetation open-top chamber experiments were bimodal in the distribution of the hourly average concentrations. In other experiments designed to assess the effects of O_3 on vegetation, constant concentration (i.e., square wave) exposures were implemented. As discussed in earlier sections of this Chapter, square wave exposure regimes do not normally occur under ambient conditions. Similar square wave exposures have been used in human health effects studies. In addition to the exposures used at the highest treatment levels for vegetation experiments, there is concern that the hourly average concentrations used in the charcoal-filtered control treatments may be lower than those experienced at isolated sites in the United States and in other parts of the world. Although the ramifications of using such exposure regimes is unclear, there is some concern that the use of atypically low control levels may result in an overestimation of vegetation yield losses when used as the baseline for evaluating the effects of treatments at higher concentrations.

Published data on the concentrations of photochemical oxidants other than O_3 in ambient air are neither comprehensive nor abundant. A review of the data shows that PAN and PPN are the most abundant of the non-O_3 oxidants in ambient air in the United States, other than the inorganic nitrogenous oxidants such as NO_2 and possibly nitric acid. At least one study has reported that a higher homologue of the series, peroxybenzoyl nitrate (PBzN), like PAN, is a lachrymator. No unambiguous identification of PBzN in the ambient air of the United States has been made.

Given the information available on PAN, the concentrations of PAN that are of most concern are those to which vegetation could potentially be exposed, especially during daylight hours in agricultural areas. These are followed in importance by concentrations both indoors and outdoors, in urban and nonurban areas, to which human populations potentially could be exposed. Most of the available data on concentrations of PAN and PPN in ambient air are from urban areas. The levels to be found in nonurban areas will be highly dependent on the transport of PAN and PPN or their precursors from urban areas, because the concentrations of the NO_x precursors to these compounds are considerably lower in nonurban than in urban areas.

There have been several attempts to characterize air pollutant mixtures. Pollutant combinations can occur at or above a threshold concentration either together or temporally separated from one another. Studies of the joint occurrence of gaseous NO_2/O_3 and SO_2/O_3 have concluded that the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, and that the time between episodes is generally long (i.e, weeks, sometimes months). Using hourly averaged data collected at rural sites for vegetation considerations, the periods of co-occurrence represent a small portion of the potential plant growing period. For human

ambient exposure considerations, the simultaneous co-occurrence of NO_2/O_3 was infrequent in most cases. However, for several sites located in the South Coast Air Basin, more than 450 simultaneous co-occurrences of each pollutant, at hourly average concentrations ≥0.05 ppm, were present. Although the focus of co-occurrence research has been on patterns associated with the presence or absence of hourly average concentrations of pollutant pairs, some researchers have discussed the joint occurrence of O_3, nitrogen, and sulfur in forested areas, combining cumulative exposures of O_3 with data on dry deposition of sulfur and nitrogen. One study reported that several forest landscapes with the highest dry deposition loadings of sulfur and nitrogen tended to experience the highest average O_3 concentrations and the largest cumulative exposure. Although the investigators concluded that the joint occurrences of multiple pollutants in forest landscapes were important, nothing was mentioned about hourly co-occurrences of O_3 and SO_2 or O_3 and NO_2.

Knowledge of the potential exposure of the co-occurrence of acidic sulfate aerosols and O_3 is limited because routine monitoring data for acidic aerosols are not available. Information on the co-occurrence patterns is limited to research studies; some of the results are provided in this chapter. Acid sulfates, which are composed of H_2SO_4, 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 μg/m^3 at a specific location or a number of locations simultaneously. For many summertime studies, peaks of H_2SO_4 or H^+ appear to be associated with the presence of a slow-moving high pressure system. Acid sulfates are found primarily in the fine particle size range (<2.5 μm in diameter). The acidic sulfate concentrations measured in the summertime can be found at 20 μg/m^3 for over an hour and at high concentrations of 10 to 20 μg/m^3 for 6 to 24 h at one or more sites. Acidic sulfate aerosol concentrations can occur at concentrations in the summertime above 10 μg/m^3 for periods longer than 5 h. 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 co-occur at some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is real and requires further characterization.

Concern has been expressed about the possible effects on vegetation from co-occurring exposures of O_3 and acid precipitation. One study explored the relationship between O_3 and H^+ in precipitation, using data from sites that monitored both O_3 and wet deposition simultaneously and within one minute latitude and longitude of each other. The investigators reported that individual sites experienced years in which both H^+ deposition and total O_3 exposure were at least moderately high (i.e., annual H^+ deposition ≥0.5 kg ha^{-1} and an annual O_3 cumulative sigmoidally weighted exposure (W126) value ≥50 ppm-h). Based on data compiled from all sites, relatively acidic precipitation (pH ≤ 4.31 on a weekly basis or pH ≤ 4.23 on a daily basis) occurred together with relatively high O_3 levels (i.e., W126 values ≥ 0.66 ppm-h for the same week or W126 values ≥ 0.18 ppm-h immediately before or after a rainfall event) approximately 20% of the time, and highly acidic precipitation (i.e, pH ≤ 4.10 on a weekly basis or pH ≤ 4.01 on a daily basis) occurred together with a high O_3 level (i.e., W126 values ≥ 1.46 ppm-h for the same week or W126 values ≥0.90 ppm-h immediately before or after a 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 H^+ and O_3 were located in the eastern portion of the United States, often in mountainous areas.

The co-occurrence of O_3 and acidic cloudwater in high-elevation forests has been characterized. The frequent O_3-only and pH-only, single-pollutant episodes, as well as the simultaneous and sequential co-occurrences of O_3 and acidic cloudwater, have been reported. Both simultaneous and sequential co-occurrences were observed a few times each month above the cloud base.

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