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HWAY AIR QUALITY IMPACT APPRAISALS

Vol. I. Introduction to Air Quality Analysis

June 1978

Final Report

Prepared for

FEDERAL HIGHWAY ADMINISTRATION
Offices of Research & Development
Washington, D.C. 20590

FOREWORD

This report is the first of a two volume series entitled, "Highway Air Quality Impact Appraisals:" Volume I, "Introduction to Air Quality Analyses;" and Volume II, "Guidance for Highway Planners and Engineers." These two reports are intended to provide transportation planners and engineers with guidance on how to perform air quality analyses.

Volume I presents basic information useful for analyzing local or regional air quality impacts. This report is useful as a general reference work, particularly on the subjects of emissions, atmospheric processes, and air quality models.

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Director, Office of Research
Federal Highway Administration

NOTICE

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16. Abstract

This report is the first of a two volume series titled, "Highway Air Quality Impact Appraisals-Volume I, Introduction to Air Quality Analyses, and Volume II, Guidance for Highway Planners and Engineers." These two reports are intended to provide transportation planners and engineers with guidance on how to perform air quality analyses.

Volume I presents basic information useful for analyzing local or regional air quality impacts. Subjects discussed include basic characteristics, sources, removal processes, and air quality standards for five pollutants--hydrocarbons, nitrogen oxides, sulfur oxides, particulates, and photochemical oxidants; emissions, control devices, and legislation on vehicular emissions; nonvehicular anthropogenic and natural sources of those five pollutants; construction of emissions inventories; relative contributions of vehicular emissions to air quality at regional, urban, and roadway spatial scales; physical and chemical processes that affect pollutant concentrations; an assessment of types of air quality models, including algebraic (Gaussian), trajectory, and grid numerical models; and the design and use of air quality monitoring programs. The treatment of these issues is designed spcifically for the highway planner or engineer who is required to perform air quality evaluations of transportation or land use plans. A glossary is included. Volume I may be useful as a general reference work, particularly on the subjects of emissions, atmospheric processes, and air quality models.

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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

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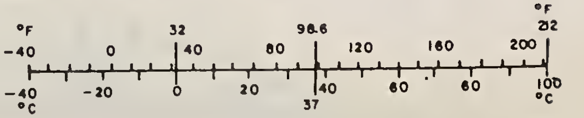
*1 in ≡ 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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The authors thank the Washington staff of the Federal Highway Administration for many valuable comments regarding the needs of transportation planners and engineers for information on air quality analysis and the appropriateness of the treatment of these issues herein. The authors also wish to acknowledge the many valuable comments and suggestions for improving this report made by Mr. Andrew Ranzieri of the State of California Air Resources Board. Finally, the contribution of Mr. Mark Meldgin, the editor of this volume, is gratefully acknowledged.

I INTRODUCTION

Emissions from motor vehicles are largely responsible for certain types of air pollution in many urban areas, and in some rural areas as well. Projects or plans such as new transit facilities, shopping centers, and zoning ordinances, which affect land use and transportation patterns, may cause significant changes in air quality. In recognition of this situation, various regulations have been instituted requiring analysis of the air quality impacts of land use or transportation plans. Such an analysis includes both projection of the vehicular and nonvehicular emissions associated with a plan and prediction of the air quality impact of those emissions. The predictions are then used to determine compliance with air quality regulations.

Analyzing air quality poses some difficulty: Although a great deal is known about air pollution, little of it has been presented in the context of transportation planning. To provide guidance for transportation planners and engineers on how to perform air quality analyses, the Federal Highway Administration funded the preparation of two reports. Volume I (this volume) presents basic information concerning pollutants, emissions, atmospheric processes, measurement methods, and predictive techniques. Volume II draws upon the contents of Volume I in describing how air quality considerations should be included in various transportation planning situations.

Topics are discussed in this volume in the order in which they arise in a typical air quality analysis, as shown in Figure 1. (The Roman numerals in Figure 1 correspond to chapter numbers.) The contents of each chapter are briefly described below.

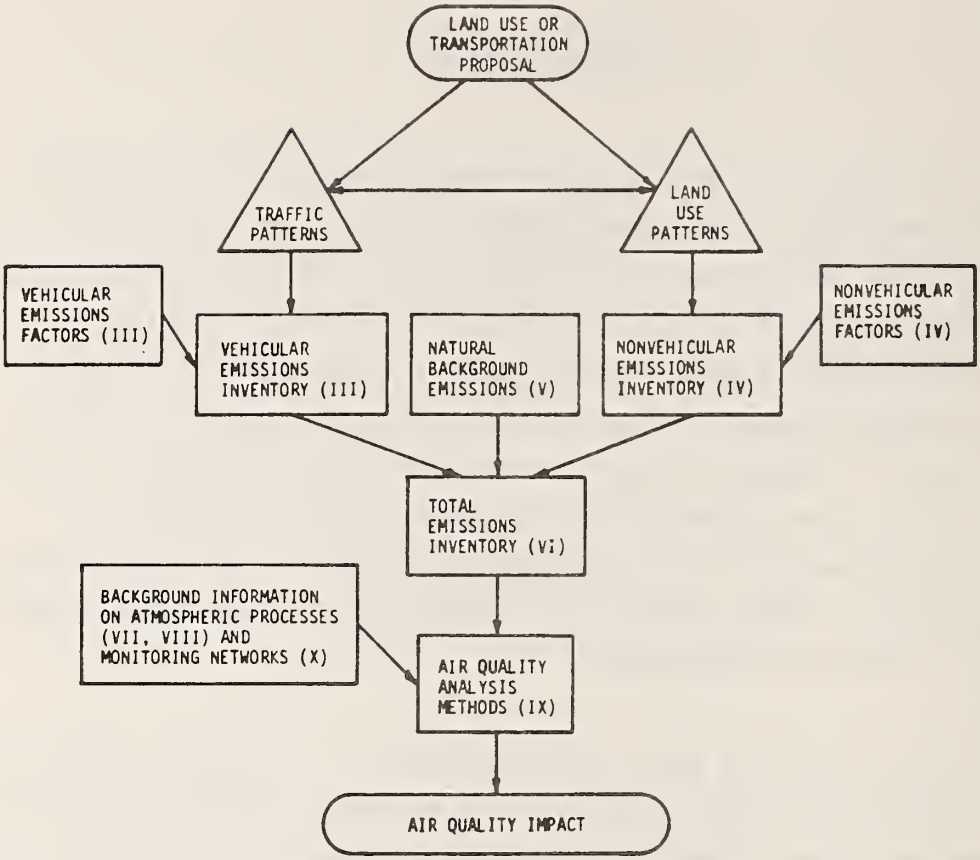

FIGURE 1. FLOW CHART OF THE AIR QUALITY ANALYSIS OF A TRANSPORTATION PLAN. Roman numerals indicate chapters in this report.

Chapter II provides a basic introduction to air pollutants. Each of the pollutants involved in vehicular air pollution is described in terms of its physical and chemical characteristics, sources and removal processes, health effects, and applicable air quality standards. The chapter includes a description of various emissions sources, distinguishing between vehicular and nonvehicular sources, and natural and anthropogenic sources. It also identifies the major industries and activities producing the emissions and the space and time scales at which the various emissions are important. Chapter II provides an overview of air pollution and serves to acquaint the reader with some information and concepts described in more detail in later chapters.

Chapter III explains the role of motor vehicles in air pollution. The chapter explains why motor vehicles emit pollutants, how emissions are controlled, what legal requirements are applicable to vehicular emissions, and how total vehicular emissions from a highway corridor or larger area can be predicted. It includes guidance for revising emissions rates and inventories as more information becomes available, but the information contained in this chapter is the state of the art as of this writing.

Chapter IV covers nonvehicular anthropogenic emissions, that is, emissions from neither vehicular nor natural sources. The types of sources, their spatial and temporal variations, and applicable emission standards and control methods are described. Sources of data and methods for constructing regional inventories of nonvehicular anthropogenic emissions are also discussed. This category of sources is important because of the interactions between vehicular and other emissions. An air quality analysis of a transportation plan must include all types of sources.

Chapter V treats the third major category of emissions, namely emissions from natural sources such as volcanoes, forests, swamps, and deserts. Natural emissions of pollutants that are also emitted by motor vehicles are discussed in detail. Data on emissions rates are summarized, but the chapter concludes that the available information is not sufficient for constructing a regional inventory of emissions from natural sources. However, the material in Chapter V provides background for a comparison of the effects of the three categories of emissions, which is contained in Chapter VI.

The purpose of Chapter VI is to put vehicular sources in perspective with other sources of emissions. This task is carried out by comparing the emissions rates of vehicular and other anthropogenic sources and by comparing air quality in unpolluted areas with that in urban areas. Comparisons are made at both the regional level and the corridor level to indicate the effects of vehicles both near roadways and on regional air quality.

Chapter VII discusses the processes that can affect air pollutants after they are emitted into the atmosphere. These processes include transport by winds, chemical reactions, and removal processes. This material is basic to an understanding of how the various processes interact to produce the observed ambient concentrations of air pollutants.

Chapter VIII describes the relative importance of various physical and chemical processes at each of three transportation environments: the microscale, which is primarily concerned with effects in the immediate vicinity of a roadway; the mesoscale, which includes most urban and other regional analyses; and the synoptic or macroscale, which is primarily concerned with interregional effects. This information is a key input to the selection of the processes to be treated in an air quality model. In fact, the potential performance of an air quality model is often measured by its priorities in the treatment of the processes important at the scale it was designed to treat.

The first eight chapters provide information essential for understanding Chapter IX, which introduces a number of air quality prediction techniques and identifies those likely to be of value to transportation planners. The techniques are divided into several classes, including physical models, statistical-empirical models, and deterministic-mechanistic mathematical models. The concepts, data requirements, and operational features of each class are described in detail and an estimate of the expected accuracy of each class is given. This chapter is crucial to understanding the guidance and procedures for air quality impact evaluations contained in Volume II [Reference 1].

Chapter X concludes the main text with a discussion of the collection and analysis of air quality data. The design of an air sampling program for both meteorological and air quality data is described, including siting, monitoring equipment, selection of measurement techniques, and statistical analysis of results. A section on the graphical presentation of monitoring data is also included Finally, the use of such data in evaluating model performance is described. The Appendix lists a number of air quality models and references in which they are described. A glossary and an index are also included in this volume.

In Volume II (FHWA-RD-78-100), the legislative basis for air quality regulations is discussed and the use of the technical tools treated in this volume is related to various transportation planning situations. More specifically, situations are divided into regional and subregional plans, and subregional plans are further divided into corridors, specific small localities, and larger portions, or subareas, of regions. The type of emissions inventory, the monitoring data required, and the models necessary for analyzing the air quality impact of a transportation plan all depend on the nature of the plan. Volume II describes analyses methods for each of these cases individually.

In summary, the information contained in this volume is intended for use by transportation planners and engineers in developing an understanding of the technical issues that are part of an air quality impact evaluation. Volume II draws on this body of information in presenting guidance and procedures for implementing an appropriate air quality analysis method in the evaluation of a transportation plan.

II OVERVIEW OF AIR POLLUTANTS

This chapter introduces the main air pollutants of concern in highway planning and engineering. No prior familiarity with air pollution analysis on the part of the reader is assumed. Various pollutants are described along with their sources, the physical and chemical processes that produce them, the problems they cause, the air quality standards applicable to them, and the temporal and spatial scales of their emissions. Chapters III, IV, and V discuss in greater detail the contributions of emissions from vehicles, other anthropogenic sources, and natural sources to the atmospheric concentrations of these pollutants. This chapter is intended to give the transportation planner or engineer a perspective on the pollutants involved rather than to provide a comprehensive reference. The material presented in this chapter is fundamental to the understanding of the causes of air pollution, its effects, and its control.

A. CARBON MONOXIDE

Carbon monoxide (CO) is a colorless, odorless, tasteless gas produced primarily by incomplete combustion of fuel in motor vehicles, which currently account for about 75 percent of the CO in most urban areas. Combustion processes other than motor vehicle operation produce CO in relatively minor quantities. CO is also released from natural sources such as the photodissociation of carbon dioxide (CO_2), forest fires, and the oxidation of methane. At an urban scale, CO is relatively inert, that is, it undergoes little chemical change. The primary processes through which it is removed from the atmosphere are absorption by soil and slow chemical oxidation to CO_2.

CO is of interest as an air pollutant because of its ability to combine with hemoglobin in blood to form carboxyhemoglobin (COHb), which prevents the normal transfer of oxygen from the lungs to the rest of the body [2]. At modest concentrations, impairment of vision and time estimation ability occurs, and at high concentrations, CO causes death.

The National Ambient Air Quality Standards for CO are 35 ppm (40 mg/m^3) for a one-hour average and 9 ppm (10 mg/m^3) for an eight-hour average (see Table 1). As for most federal air quality standards, they are not to be exceeded more than once per year. In fact, they are frequently exceeded; concentrations as high as 80 ppm (one-hour average) have been measured, though annual geometric mean values are seldom greater than 10 ppm. Fortunately, CO emissions controls have reduced CO concentrations in many areas over the last few years and further reductions may be expected [3]. It should be noted that, to provide a margin of safety, all air quality standards are set at levels significantly below the expected threshold level for health effects. Typically, the margin is a factor of roughly 1.5.

B. HYDROCARBONS

The hydrocarbons (HC) that affect air quality are, for the most part, colorless compounds of carbon and hydrogen and, in some cases, oxygen that exist in the atmosphere primarily as vapor. The most important of these hydrocarbons include paraffins, aromatics, olefins, and aldehydes. They are emitted from incomplete combustion, petroleum refining, the use of chemical solvents, and food processing. Typically, 50 to 65 percent of the hydrocarbons in an urban area come from vehicles, but in rural areas natural processes, such as the decay of organic material and the release of hydrocarbons from trees, are the major sources of HC. In fact, natural HC emissions are responsible for the names of the Great Smoky Mountains and the Blue Ridge Mountains. Hydrocarbons are removed from the atmosphere primarily through chemical conversion to CO_2, H_2O, and other compounds [4].

Hydrocarbons are not usually considered a problem in themselves, but rather as one of the precursors of photochemical smog. Chemically reactive hydrocarbons react in the presence of sunlight and oxides of nitrogen to form photochemical oxidants, the major component of which is ozone. These compounds are discussed in Section II.F. Although the

TABLE 1. AMBIENT AIR QUALITY STANDARDS

Pollutant	Averaging Time	California Standards*		Federal Standards†		
		Concentration§	Method∇	Primary†Δ	Secondary†**	Method†
Carbon monoxide	12 hours	10 ppm (11 mg/m^3)	Nondispersive infrared spectroscopy	--	--	
	8 hours	--		10 mg/m^3 (9 ppm)	Same as primary standards	Nondispersive infrared spectroscopy
	1 hour	40 ppm (46 mg/m^3)		40 mg/m^3 (35 ppm)		
Hydrocarbons (corrected for methane)	3 hours (6-9 a.m.)	--	--	160 µg/m^3 (0.24 ppm)	Same as primary standard	Gas chromatography using flame ionization detection
Suspended particulate matter	Annual geometric mean	60 µg/m^3	High-volume sampling	75 µg/m^3	60 µg/m^3	High-volume sampling
	24 hours	100 µg/m^3		260 µg/m^3	150 µg/m^3	
Lead (particulate)	30-day average	1.5 µg/m^3	High-volume sampling, dithizone method	--	--	--
Visibility-reducing particles	1 observation	In sufficient amount to reduce the prevailing visibility§§ to 10 miles when the relative humidity is less than 70%		--	--	--
Nitrogen dioxide	Annual average	--		100 µg/m^3 (0.05 ppm)	Same as primary standard	Colorimetric method using NaOH
	1 hour	0.25 ppm (470 µg/m^3)	Saltzman method	--	--	
Sulfur dioxide	Annual average	--		80 µg/m^3 (0.03 ppm)	60 µg/m^3 (0.02 ppm)	Pararosaniline method
	24 hours	0.04 ppm (105 µg/m^3)	Conductimetric method	365 µg/m^3 (0.14 ppm)	260 µg/m^3 (0.10 ppm)	
	3 hours	--		--	1300 µg/m^3 (0.5 ppm)	
	1 hour	0.5 ppm (1310 µg/m^3)		--	--	
Photochemical oxidants (corrected for NO$_2$)	1 hour	0.10 ppm (200 µg/m^3)	Neutral buffered potassium iodide	160 µg/m^3 ∇∇ (0.08 ppm)	Same as primary standard	Chemiluminescence
Hydrogen sulfide	1 hour	0.0[illegible] ppm (4[illegible] µg/m^3)	Cadmium hydroxide stractan method	--	--	--

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* California standards are not to be equalled or exceeded at all (unlike some federal standards†).

† Federal standards for periods shorter than one year are not to be exceeded more than once per year.

§ Concentration expressed first in units in which it was promulgated. Equivalent units given in parentheses are based upon a reference temperature of 25°C and a reference pressure of 760 mm of mercury.

∇ Any method that can be shown to the satisfaction of the California Air Resources Board to give equivalent results at or near the concentration specified in the air quality standard may be used.

Δ Federal primary standards: the levels of air quality necessary, with an adequate margin of safety, to protect the public health. Each state must attain the primary standards no later than three years after that state's implementation plan is approved by the EPA.

** Federal secondary standards: the levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant. Each state must attain the secondary standards within a "reasonable time" after its implementation plan is approved by the EPA.

†† Reference method as described by the EPA. An "equivalent method" of measurement may be used but must have a "consistent relationship to the reference method" to be approved by the EPA.

§§ Prevailing visibility is defined as the greatest visibility that is attained or surpassed around at least half of the horizon circle, but not necessarily in continuous sectors.

∇∇ Corrected for SO$_2$ as well as NO$_2$.

Source: Ref. 5.

direct effects of hydrocarbons of human and plant health are less important than the effects of oxidants, several hydrocarbons have irritating odors (such as those released during coffee roasting) and some are health hazards (such as benzene and aldehydes).

Some HC species are more reactive than others. For example, aldehydes and olefins in urban air generally increase the rate of production of photochemical oxidants more than similar amounts of aromatics and paraffins. As a result, reducing the reactivity of HC emissions in an area will retard the formation of photochemical oxidants even if the quantity of hydrocarbons emitted does not change. Since different types of sources usually emit the various types of hydrocarbons in different proportions, some types of sources have a more significant effect on oxidant concentrations than others.

The National Ambient Air Quality Standard for hydrocarbons dictates that the average HC concentration from 6 a.m. to 9 a.m., corrected for methane, is not to exceed 0.24 ppm (160 $\mu g/m^3$) more than once per year. The standard applies to that time of day (morning commute hours) because HC emitted during that period usually results in greater formation of photochemical oxidants than similar amounts of HC emitted earlier or later in the day. Methane is excluded because it is much less reactive than other hydrocarbons. There is no standard set to prevent direct effects of hydrocarbons.

Ambient hydrocarbon concentrations as high as 6 ppm (6 a.m. to 9 a.m. average) have been measured in Los Angeles. Typical geometric mean concentrations in urban areas are 0.3 to 0.7 ppm (one-hour average). In many cities, notably Los Angeles, Denver, and San Diego, oxidant standards are often violated, and reducing 6 a.m. to 9 a.m. hydrocarbon concentrations is the usual approach to reducing smog levels, as discussed later in this report. Fortunately, in recent years controls have been instituted on many hydrocarbon sources, resulting in a downward trend in HC concentrations that is expected to continue [3].

C. PARTICULATES

Particulates include all solid particles and liquid droplets in the atmosphere--a tremendous number of compounds. Some of the more important particulates are windblown dust and soil, smoke, fly ash, pollen, and aerosols formed from photochemical reactions. Eventually, particulates reach the ground by settling out, by serving as nuclei for condensation in a cloud (this process is called rainout), or by being "washed out" by rain.

It is difficult to characterize particulate emissions because of the wide variety of species and sources. A number of industries are sources of large amounts of emissions, as are agricultural burning, windblown dust and sea salt, backyard burning, and others. In most cities, automotive sources account for about 5 to 10 percent of total anthropogenic particulate emissions. Most often, fuel combustion accounts for the largest share, and various industrial processes constitute a close second, though in some cities this situation is reversed. Clearly, these emissions depend on the kinds of industry present and the agricultural, climatological, and vehicular conditions in the area.

Two particulates of interest to highway planners and engineers are lead and asbestos, both of which can be emitted by motor vehicles. Both are toxic: the former affects the respiratory and nervous systems, and the latter causes asbesteosis, a form of lung cancer. Fortunately, lead emissions can be controlled with low-lead fuels. Although asbestos is used in brake and clutch linings, motor vehicles emit very little asbestos [6,7]

The effects of particulates depend on their types and sizes. Inhaled particles larger than 1 micron are filtered by the body's natural processes, but smaller particles reach the lungs. Some species are directly toxic, such as lead, asbestos, sulfuric acid mist, hydrogen fluoride, and certain oil mists, which result in a variety of respiratory ailments [8]. Particulate matter combined with high concentrations of sulfur dioxide is believed by many investigators to have significant effects on the respiratory tract [8,9].

Particulate matter in size ranges comparable to the wavelength of light (0.1 to 10 microns) is a major component in visibility reduction (along with humidity) [10], and in high concentrations it affects the total amount of ultraviolet radiation reaching the earth's surface. Although it has been demonstrated that urban areas sometimes receive about 35 percent less ultraviolet radiation than surrounding rural areas, the health-related implications of this effect are not clear [11].

Air quality standards for particulate matter are set to protect human and plant health. The federal primary standards are 75 $\mu g/m^3$ for the annual geometric mean and 260 $\mu g/m^3$ for the 24-hour average not to be exceeded more than once per year. The corresponding secondary standards are 60 $\mu g/m^3$ and 150 $\mu g/m^3$, respectively. The primary and secondary California standards are 60 $\mu g/m^3$ and 100 $\mu g/m^3$, respectively. These standards are frequently exceeded in many areas. In addition, California has a standard for lead of 1.5 $\mu g/m^3$ for a 30-day average, which is also exceeded in many areas.

There is no federal visibility standard at present, but California has set a standard dictating that no observation of visibility should be under 10 miles when the relative humidity is less than 70 percent. This standard is frequently exceeded in California cities.

D. OXIDES OF NITROGEN

This category includes two gaseous pollutants, nitric oxide (NO), which is colorless, and nitrogen dioxide (NO_2), which is reddish-brown and has a pungent odor. NO_2 may be responsible for part of the reddish-brown color of photochemical smog. Together NO and NO_2 are referred to as NO_x. [Other oxides of nitrogen, such as NO_3, N_2O_4, and N_2O_5, are not of primary interest to transportation planners.]

Most NO_x in urban areas is emitted as NO, which is formed from the reaction of nitrogen and oxygen in high temperature combustion. A study of nine urban areas shows that an average of about 65 percent of NO_x emissions come from motor vehicles, with the remainder largely from power plants, petroleum refineries, and chemical plants, especially nitric acid manufacture. However, this ratio will change as older vehicles are replaced with newer ones with NO_x control equipment. NO_x is also emitted by natural sources, mainly bacterial action in soil, but naturally occurring NO_x concentrations are low (see Chapter V for further discussion). NO_x is removed from the atmosphere largely through conversion to nitrate particles, which ultimately reach the ground through the same processes as other particulates.

NO_x plays a significant and complex role in the formation of photochemical smog by reacting in the presence of sunlight and hydrocarbons to form photochemical oxidants, primarily ozone (O_3). Oxidant concentrations do not increase in proportion to NO_x concentrations; in fact, increasing NO_x decreases oxidant under certain conditions. Oxidants are discussed in greater detail in Sections II.F and VII.C.

NO_x has a substantial effect on atmospheric visibility due to the formation of brown haze and nitrate aerosol [12]. The amount of visibility reduction in a polluted atmosphere is, however, also a function of humidity and the concentration of particulate matter [8]; so a given level of NO_x is more noticeable in the presence of sufficient amounts of the other two influences.

NO_2 has been shown to cause changes in lung tissue in animals, producing an effect similar to emphysema. NO, in contrast, does not appear to produce a health hazard. Similarly, NO_2 exposure can reduce growth in sensitive plants, whereas NO shows no comparable effect [12].

The National Ambient Air Quality Standard dictates that the annual arithmetic mean NO_2 concentration should be no greater than 0.05 ppm (100 $\mu g/m^3$). This standard is seldom exceeded, though exceedances have occurred in major cities, including Los Angeles, San Francisco, and Chicago. The California one-hour NO_2 standard of 0.25 ppm (470 $\mu g/m^3$) is exceeded frequently [13]. A federal short term (e.g., three-hour-average) NO_2 standard may be established in the near future.

E. SULFUR OXIDES

Sulfur oxides (SO_x) include sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfuric acid (H_2SO_4), and sulfate salts; the first two are gases, and the last two are particulates. Most SO_x is emitted as SO_2, a colorless gas with an irritating odor. The other species are formed primarily through the chemical reactions of SO_2 in the atmosphere.

SO_x is emitted primarily from industrial sources that either burn fuel containing sulfur or use sulfur-containing compounds in chemical operations and from residential and commercial heating where oil containing sulfur is burned. Such sources may be responsible for 90 percent of SO_2 emissions in a typical urban area [14]. When natural gas cannot be used, air pollution control agencies have prescribed the use of low-sulfur fuel wherever possible. Unfortunately, these "clean" fuels are in short supply, and it is likely that SO_2 emissions in some areas will increase in the next few years. Automobiles account for less than 5 percent because of the low sulfur levels in gasoline. There are also a few natural sources of SO_2, principally volcanoes and fires. SO_x is removed from the air by conversion to sulfate particles, which ultimately reach the ground through the same processes as other particulates.

Although the health effects of SO_x are still a subject of controversy, it is believed by many that widespread respiratory illness in sensitive individuals may result from conditions of simultaneously elevated concentrations of SO_2 and particulate matter [9], as in the London air pollution episode of 1952. The opposing view is that other variables may account for the effects ascribed to SO_x during smog episodes and that controlled studies show no more than minor effects at ambient levels. SO_2 can cause damaging effects on both plants and materials, the latter probably by atmospheric oxidation in the presence of humidity and particulates to form sulfuric acid droplets, which are corrosive to metals, building materials, and cloth.

Sulfur dioxide is subject to two types of air quality standards. Primary standards are set to protect human health, and secondary standards are designed to protect vegetation. National primary standards for SO_2 are 80 $\mu g/m^3$ (0.03 ppm) annual arithmetic mean and 365 $\mu g/m^3$ (0.14 ppm) 24-hour average, to be exceeded no more than once per year. The corresponding secondary standards are 60 $\mu g/m^3$ (0.02 ppm) and 260 $\mu g/m^3$ (0.10 ppm), respectively. In addition, there is a secondary three-hour standard of 1300 $\mu g/m^3$ (0.5 ppm). California has a 24-hour standard also, 105 $\mu g/m^3$ (0.04 ppm), which is far more stringent than the national standard.

All of these standards are frequently exceeded in cities where substantial quantities of fuel oil are burned for residential heating [13]. Ambient air quality is particularly sensitive to such sources because they are widespread and because residential emissions occur close to the ground, as contrasted to utilities with high smokestacks. In cities that are located in regions where the climate is mild, SO_2 concentrations are much lower; therefore, SO_2 is a far more significant problem in the northern states. SO_2 control is the subject of ongoing research; it may be expected that emissions will be further reduced in future years.

F. PHOTOCHEMICAL OXIDANTS

The pollutants discussed above are primary pollutants, meaning that they are emitted directly into the atmosphere. In contrast, photochemical oxidants are not emitted, but are secondary pollutants, formed principally through the action of sunlight on HC and NO_x. Certain natural processes, such as the occasional injection of ozone from the stratosphere, can cause high ground-level oxidant concentrations. These oxidants are reactive gaseous compounds that are partly responsible for many of the effects associated with photochemical smog: visibility reduction, damage to vegetation, eye irritation, cracking of rubber, and, in some people, breathing problems.

Ozone formation is a very complex process, as can be seen from the description in Section VII.C, but its main features are as follows. The process begins with the photolysis of NO_2 by ultraviolet light to produce NO and an oxygen atom. The oxygen atom then reacts with O_2 to produce O_3. In the absence of hydrocarbons, NO can react with O_3 to regenerate NO_2 and O_2, leading to a steady state between NO_2, NO, and O_3 in which the O_3 concentration is low. When hydrocarbons are present, however, they are oxidized in a sequence of reactions that increases the NO_2/NO ratio, thus increasing the steady-state ozone concentration. The formation of photochemical oxidants depends on not only the NO_2/NO ratio, but also the concentrations and types of HC and NO_x emitted, the HC/NO_x concentration ratio, the solar intensity, and the meteorological conditions. Given this information, it should not be surprising that predicting oxidant concentrations is very difficult. The difficulty is increased by oxidant removal processes (primarily reaction with surfaces) and by the time required for the photochemical reactions. (The maximum HC and NO_x concentrations usually occur during morning rush hour, but the maximum O_3 concentration almost invariably occurs in the afternoon.) These difficulties give rise to the need for oxidant prediction methods such as isopleth diagrams and air quality models, which are described in Chapter IX.

The primary and secondary federal standards for photochemical oxidants are both 160 $\mu g/m^3$ (0.08 ppm) for a one-hour average. California has a one-hour-average standard of 200 $\mu g/m^3$ (0.10 ppm). All three standards are exceeded frequently during the summer in many locations where there are plenty of sunlight, stagnant air, and NO_x and HC sources. Concentrations as high as 1400 $\mu g/m^3$ (0.7 ppm) have been recorded in the Los Angeles area, although geometric mean values are usually between 40 $\mu g/m^3$ (0.02 ppm) and 60 $\mu g/m^3$ (0.03 ppm).

The general structure of oxidant problems is that emissions of HC and NO_x in the morning react in the presence of sunlight over the next few hours to produce a peak oxidant concentration in the early afternoon. As these reactions occur the air mass is being transported by the wind. Consequently, the peak oxidant concentrations tend to occur downwind of the areas where the emissions were released. Therefore, unlike nonreactive pollutants such as CO, photochemical oxidants cannot be said to be caused by a specific source, nor do peak concentrations invariably occur in the vicinity of emissions sources. Thus photochemical oxidants are an area-wide pollution problem.

G. OTHER POLLUTANTS

The previous sections discuss photochemical oxidants and all the primary pollutants for which national standards exist except hydrogen sulfide (H_2S). However, an increasing number of other pollutants are either known to have or suspected of having serious effects, and controls for these pollutants are being formulated or contemplated. Transportation planners need to consider mainly pollutants directly related to motor vehicles, and so no further discussion of other pollutants is included in this chapter.

H. TYPES OF POLLUTANT SOURCES

Pollutants are emitted from a variety of sources, which can be characterized in different ways depending on one's analytical needs:

> <u>Anthropogenic versus natural</u>. Anthropogenic sources are introduced by human activity. The remainder are considered natural sources.

> <u>Point versus area</u>. Large, isolated emitters are considered to be point sources, for example, smokestacks and volcanoes. Area sources are the aggregate of many small

sources, such as vehicular traffic, residential heating, small commercial operations, and resuspended soil from arid land.

> Stationary versus mobile. Automobiles, trains, boats, airplanes, and other sources whose location varies with time are considered mobile sources. The remainder, such as factories, homes, farms, forests, and power plants, are termed stationary.

> Vehicular versus other anthropogenic. Vehicular sources include all highway arterial street and minor street traffic. "Other anthropogenic" sources include all of the remaining man-made sources.

> Emission types. A variety of operations produce pollutant emissions. The examples of each category given below are adapted from the EPA format for national emissions reports [14]:

- Fuel combustion
  - External and internal combustion engines
  - Residential fuel use
  - Power generation
  - Industrial fuel use
  - Commercial fuel use
- Industrial processes
  - Chemical manufacturing
  - Food agriculture
  - Primary and secondary metals
  - Mineral products
  - Petroleum refining
- Solid waste disposal
  - Incineration
  - Open burning
- Transportation--land vehicles

- Gasoline
  - Light vehicles
  - Heavy vehicles
  - Off-highway vehicles
- Diesel
  - Heavy vehicles
  - Off-highway vehicles
  - Rail vehicles
  - Aircraft
  - Vessels
  - Gas-handling vehicles.

The classifications presented above are important for analyzing air quality problems and for determining rational control strategies. All anthropogenic sources are amenable to emissions control, but point sources are more easily controlled because a specific technology can be developed and maintained for each source. Similarly, motor vehicle emissions are subject to regulation as a group, though maintenance and inspection are more difficult than for point sources. Other area sources tend to be more diverse and therefore more difficult to identify and control. By examining the emissions and the related control options for each category, one can determine the relative efficiency of various strategies for reducing emissions.

I. SPATIAL VARIATIONS IN EMISSIONS

For most air pollutants, natural emissions far exceed anthropogenic emissions on a global basis. As shown in Chapter V, SO_2 is the only common pollutant for which anthropogenic emissions are more than a minor portion of the total. Although there appears to be no air pollution problem (except for SO_2) on a global scale, the situation is quite different when smaller areas are considered. In particular areas, anthropogenic emissions far exceed natural emissions. In addition, geographical areas vary widely in their ability to "cleanse" themselves through the flushing action of winds or natural removal processes. Air pollution studies of localized high concentrations of contaminants require very specific data on the locations of emissions.

Few sources are important on a global scale, and most of these are natural. Volcanoes are major sources of particulates, for example, as are deserts. Biological processes in forests are a major source of hydrocarbons, and bacterial action in soil is a major source of NO_x. Other examples are presented in Chapter V. Man-made sources have had little influence on the global atmosphere thus far, though it has been reported that nuclear explosions in the atmosphere in the early 1960s released quantities of NO sufficient to affect the ozonosphere. Similar consequences have been predicted for an SST fleet and for fluorocarbons released from aerosol spray cans [15]. Thus far, none of these emissions has been proved to be damaging.

Thus far no nationwide effects of air pollutant emissions have been reported, but several regional scale problems have been noted. Oxidants are known to be a regional problem in the northeastern United States, where emissions in one urban area influence concentrations hundreds of kilometers downwind [16]. It has been reported that plumes of SO_2 from large sources may travel hundreds of kilometers [17]. Smog from the Los Angeles basin has damaged trees in the San Bernardino National Forest [18] roughly 80 to 160 kilometers away, and it has been reported that the acidity of soil in the northeastern part of the country is increasing as a result of the deposition of acid droplets [19].

Concentrations of the various pollutants differ from one state to another depending on climate, population, raw materials and industries, and land use and development. These variations are reflected in the regional emissions totals complied by the EPA [14] for the 242 air quality control regions (AQCRs) into which the United States have been divided for air quality analysis purposes. An example of a regional emissions inventory for an AQCR is given in Section IV.D.

An even smaller spatial scale is of interest to the highway planner or engineer faced with the problem of locating a facility to provide minimum air quality degradation in the corridor and in the region as a whole. Determining air quality impacts within a corridor requires extremely detailed knowledge of the magnitudes and locations of nearby sources; thus, corridor emissions inventories often have a spatial resolution as fine as a few meters. Regional studies, however, usually consider air quality impacts within grid cells several kilometers on a side, though an emissions inventory based on a 1 km grid has been developed [20].

J. TEMPORAL VARIATIONS IN EMISSIONS

The responses of plants and animals to an air pollutant are affected by both the magnitude and duration of the pollutant concentration. Pollutants may be harmful in both high concentrations over short periods of time and long term low-level exposures. This situation is reflected in the wording of air quality standards: both concentration and averaging time are specified. It has also motivated a great deal of study of the temporal variations in ambient concentrations and emissions.

Variations of emissions with time are of interest on several scales:

> Longer than a year. For evaluations of the effectiveness of existing controls and for estimations of future needs, it is useful to study trends over many years at a single location.

> Annual. The longest period that is used as an averaging time for an air quality standard is one year. Emissions factors are occasionally estimated on an annual basis, often because information pertaining to shorter intervals is proprietary or because seasonal fluctuations are unimportant.

> Seasonal. Variations in climate cause air pollution emissions from a wide range of sources to vary seasonally.

Power generation, industrial operations, vehicular traffic, and space heating are all subject to significant seasonal changes. Monthly variations are relatively minor within a given season.

> <u>Weekly</u>. Weekly variations are based primarily on the distinction between workdays and nonworkdays. Some industries and government operations reduce or eliminate production on weekends and holidays. Vacation traffic is often of local importance.

> <u>Diurnal</u>. Emissions from many industries, utilities, and municipal operations vary according to the time of day. Vehicular emissions reach a peak during commute hours and are lowest at night. Relatively few operations continue on a 24-hour basis (refineries are one example of an exception).

The major temporal variations in emissions can be explained simply in terms of variations in temperature and working hours.

K. SUMMARY

This chapter provides an overview of what pollutants emitted by motor vehicles are important, their physical properties, what problems they cause, and where and when those problems are significant. The following chapters present greater detail on the emissions of those pollutants from vehicles, other anthropogenic sources, and natural sources. In addition, they present material specifically relevant to the analytical needs of transportation planners and engineers, including techniques for determining emissions from a section of highway or an entire region, methods for projecting future emissions, sources of relevant data, and other topics.

III VEHICULAR EMISSIONS

One basic air pollution-related task of the highway planner or engineer is the estimation of vehicular emissions. Estimates must be prepared for passenger cars, trucks, and motorcycles, for both old and new vehicles, vehicles operating at different speeds, temperatures, and altitudes, and so on. The individual emissions estimates must then be combined with traffic data to determine total emissions on a roadway or network of roads. Emissions inventories of this type are essential parts of air quality analyses. The material in this chapter is designed to familiarize the highway planner with the mechanics of estimating emissions in typical planning situations and how highway design decisions affect emissions rates.

A. TYPES OF VEHICULAR EMISSIONS

When the automobile was first sold in large quantities, it was advertised as a cure for the urban pollution problems that existed then, the most serious of which were animal excrement and dust on city streets. Years later, as the number of vehicles on the road grew, smog occurred in some areas as a result of HC and NO_x emissions, largely from motor vehicles. From this discovery in the early 1950s came the first serious study of vehicular emissions and their control.

Vehicular emissions are produced mainly from three sources: the exhaust, the crankcase, and fuel evaporation. Exhaust emissions are the largest, accounting for about 65 percent of the hydrocarbons from vehicles with no emissions controls and nearly all of the emissions of other pollutants. Exhaust emissions are largely composed of unburnt and partially burnt fuel (a typical mix of exhaust hydrocarbons is shown in Table 2), carbon monoxide formed as a result of incomplete combustion, and NO and NO_2 produced by the reaction of nitrogen and oxygen at high temperatures. Crankcase emissions, called "blow-by," result from the leakage of gases around the pistons during the compression and power strokes. In vehicles without emissions controls, pollutants composed of about 85 percent hydrocarbons and 15 percent exhaust gas are released into the atmosphere through a draft tube. Evaporative emissions issue directly from the fuel tank and carburetor. When the tank is refilled, the mixture of air and fuel vapors in the "empty" part of the tank escapes into the atmosphere. Evaporation of fuel from the carburetor occurs largely when a hot engine is allowed to stand (called a "hot soak"): Engine heat is absorbed into the carburetor, thereby vaporizing fuel, which escapes into the atmosphere.

TABLE 2. HYDROCARBON EMISSIONS FROM MOTOR VEHICLES IN THE LOS ANGELES BASIN BY WEIGHT FRACTION

Species	Weight Fraction
Paraffins (excluding methane)	54%
Ethylene	4%
Olefins (excluding ethylene)	5%
Aromatics	21%
Unreactive hydrocarbons	16%
Aldehydes*	5%

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* Aldehyde emissions are assumed (because they would not have been detected by the measurement method used), and so the sum of the weight fractions is greater than 1.

Source: Ref. 21.

In addition to the major pollutants CO, NO_x, and HC, vehicles emit lesser amounts of sulfur oxides and particulates, including very small amounts of lead, bromine, and chlorine [22]. Vehicles equipped with catalytic converters have been reported to emit sparks that may cause fires. Also, vehicles emit asbestos and foresterite from the wearing of brake and clutch linings. Furthermore, traffic causes wear of both roadways and tires, which produces resuspended particulate matter, such as asphalt and tire dust.

B. EMISSIONS CONTROL

The first legislation in the United States to control automotive emissions was passed in 1963 in California; since then, emissions controls have become increasingly stringent, as shown in Table 3. The 1963 law required that 1964 and later model cars sold in California be equipped with positive crankcase ventilation (PCV) systems, which return blow-by to the engine intake manifold. The PCV system reduces crankcase emissions to virtually zero without adversely affecting performance, thereby decreasing overall hydrocarbon emissions from a vehicle without other emissions controls by about 20 percent. Similar federal regulations became effective in 1968 for passenger cars and in 1970 for heavy duty vehicles. At that time, the federal government assumed responsibility for setting all motor vehicle emissions standards. California, however, was granted a waiver to establish emissions standards more stringent than the federal regulations.

To control evaporative losses from the fuel tank, which account for about 18 percent of hydrocarbon emissions from an automobile without emissions controls, the federal government required that all automobiles starting with the 1971 model year have either a vapor recovery system that uses the crankcase to store the hydrocarbon vapors or an absorption-regeneration system that uses a canister of activated carbon to store the vapors until the engine is restarted. These systems are designed to reduce evaporative emissions to the federal standard of 2 grams per test, which represents a substantial reduction from uncontrolled levels.

Exhaust emissions, which are the largest of the three main types of vehicular emissions, are also the most difficult to control. The first

TABLE 3. FEDERAL AND CALIFORNIA VEHICLE EMISSIONS STANDARDS

(a) CO, HC, and NO_x Emissions from Passenger Cars and Light Duty Trucks

Year	Standard	Cold Start Test[*]	Carbon Monoxide	Hydrocarbons	Oxides of Nitrogen
Prior to controls		Seven-mode	3.4%	850 ppm	1000 ppm
		Seven-mode	(80 g/mi)	(11 g/mi)	(4 g/mi)
1966-1967	California	Seven-mode	1.5%	275 ppm	No standard
1968-1969	California and federal	Seven-mode			
		50-100 CID	2.3%	410 ppm	No standard
		101-140 CIO	2.0%	350 ppm	No standard
		Over-140 CID	1.5%	275 ppm	No standard
1970	California and federal	Seven-mode	23 g/mi	2.2 g/mi	No standard
1971	California	Seven-mode	23 g/mi	2.2 g/mi	4 g/mi
	Federal	Seven-mode	23 g/mi	2.2 g/mi	--
1972	California	Seven-mode or	23 g/mi	1.5 g/mi	3 g/mi
		CVS-I	39 g/mi	3.2 g/mi	3.2 g/mi[**]
	Federal	CVS-I	39 g/mi	3.4 g/mi	--
1973	California	CVS-I	39 g/mi	3.2 g/mi	3 g/mi
	Federal	CVS-I	39 g/mi	3.4 g/mi	3 g/mi
1974	California	CVS-I	39 g/mi	3.2 g/mi	2 g/mi
	Federal	CVS-I	39 g/mi	3.4 g/mi	3 g/mi
1975	California[†]	CVS-II	9 g/mi	0.9 g/mi	2.0 g/mi
	Federal[†]	CVS-II	15 g/mi	1.5 g/mi	3.1 g/mi
	California[§]	CVS-II	20 g/mi	2.0 g/mi	2.0 g/mi
	Federal[§]	CVS-II	20 g/mi	2.0 g/mi	3.1 g/mi
1976	California[†]	CVS-II	9 g/mi	0.9 g/mi	2.0 g/mi
	Federal[†]	CVS-II	15 g/mi	1.5 g/mi	3.1 g/mi
	California[§]	CVS-II	17 g/mi	0.9 g/mi	2.0 g/mi
	Federal[§]	CVS-II	20 g/mi	2.0 g/mi	3.1 g/mi
1977	California[†]	CVS-II	9 g/mi	0.41 g/mi	1.5 g/mi
	Federal[†]	CVS-II	15 g/mi	1.5 g/mi	2.0 g/mi
	California[§]	CVS-II	17 g/mi	0.9 g/mi	2.0 g/mi
	Federal[§]	CVS-II	20 g/mi	2.0 g/mi	3.1 g/mi
1978	California[†]	CVS-II	9 g/mi	0.41 g/mi	1.5 g/mi
	Federal[†]	CVS-II	15 g/mi	1.5 g/mi	2.0 g/mi
	California[§]	CVS-II	15 g/mi	0.9 g/mi	2.0 g/mi
	Federal[§]	CVS-II	20 g/mi	2.0 g/mi	3.1 g/mi

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[*] These driving cycle tests are described in Section D.

[†] Passenger cars.

[§] Light duty trucks.

[**] Seven-mode with hot start.

TABLE 3 (Concluded)

(b) CO, HC, and NO_x Emissions from Heavy Duty Vehicles over 6000 Pounds

Year	California Standard	Carbon Monoxide	Hydrocarbons	HC + NO_x
1969-1971*	Gasoline	1.5%	275 ppm	--
1972	Gasoline	1.0%	180 ppm	--
1973-1974	Gasoline and diesel	40 g/BHP-hr	--	16 g/BHP-hr
1975-1976	Gasoline and diesel	30 g/BHP-hr	--	10 g/BHP-hr
1977	Gasoline and diesel	25 g/BHP-hr	--	5 g/BHP-hr

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g/BHP-hr = grams per brake horsepower-hour.

* Federal standards remained at this level through 1973. The federal government adopted standards for heavy duty gasoline and diesel vehicles for 1974 and subsequent model years that are identical to California's 1973-1974 standards.

(c) California Smoke Standards for Heavy Duty Vehicles

Vehicle Model Year	Maximum-Smoke Standard
Before 1971	Ringelman 1 or 20% opacity for up to 10 seconds
1971 and later	Ringelman 2 or 10% opacity for up to 10 seconds

(d) Crankcase Emissions

Vehicle Model Year	Vehicle Type	California Standard	Federal Standard
1964 and later	All	Virtually zero	--
1968	Light duty	--	Virtually zero
1970	Heavy duty	--	Virtually zero

(e) Evaporative Emissions of Hydrocarbons

Effective Year	Vehicle Type	Federal Standard (g/test)
1970	Light duty	6
1972	Light duty	2
1973	Heavy duty gasoline-powered	2

Source: Ref. 23.

exhaust emissions standards were established in California for 1966 model cars; federal standards began with 1968 models. Both sets of standards included progressively more stringent controls on future models. Manufacturers responded with a variety of engineering solutions, including:

- Engine operating adjustments, such as changes in the air-to-fuel ratio, compression ratio, timing, and operating temperature.
- Air injection systems that pump air into exhaust gases.
- Exhaust reactors to convert hydrocarbon exhaust emissions into CO_2 and water.
- Exhaust recycling that returns exhaust to the intake manifold to lower peak cylinder temperatures and, hence, NO_x emissions.
- Catalytic converters, some of which can reduce NO_x to N_2 and others which can oxidize HC and CO to CO_2 and H_2O.
- Real-time monitoring of exhaust gases and automatic adjustments of operating parameters based on exhaust gas composition.
- New engine designs, such as the stratified charge engine, which uses a precombustion chamber with a rich fuel-to-air ratio to ignite a leaner mixture in the main portion of the cylinder.

Some of these solutions adversely affected performance and fuel economy, resulting in consumer dissatisfaction and resistance to the standards from the manufacturers. It appears, however, that the long term prospects for vehicles with low emissions and adequate performance are excellent.

Retrofitting, the installation of emissions control devices on older automobiles, is also practiced in some states but is not mandated by federal law. It is useful because a significant number of older vehicles are still on the road (though vehicles older than about 10 years are relatively scarce). Unfortunately, some of the retrofit devices have debilitating effects on fuel economy and performance.

Increasingly stringent vehicular emissions standards have led to the use of catalytic converters. Two types of converters are in use: One catalyzes the reduction of NO to N_2 by the overall reaction $2NO + 2CO \rightarrow N_2 + 2CO_2$; the other oxidizes CO and HC to CO_2 and H_2O. They can be used in series, with the NO catalyst first, to reduce NO_x, CO, and HC emissions. The efficiency of catalysts in reducing emissions deteriorates with use, as shown in Table 4.

TABLE 4. INITIAL EMISSIONS RATES AND DETERIORATION RATES USED TO CALCULATE THE EMISSIONS FACTORS FOR LIGHT DUTY VEHICLES

Emission Control Category	Model Years	Initial Emissions Rate (g/mi)	Deterioration Rate (increase in emissions in g/mi per 10,000 miles)
		(a) Hydrocarbons	
Pre-control	Pre-68	5.67	0.47
Pre-catalyst	68-74	2.80	0.64
Catalyst	75-78	1.38	0.28
		(b) Carbon Monoxide	
Pre-control	Pre-68	56.43	7.59
Pre-catalyst	68-74	36.40	6.79
Catalyst	75-78	23.70	3.14
		(c) Nitrogen Oxides	
Pre-control	Pre-68	3.40	0.0
Pre-catalyst no NO_x control	68-72	4.70	0.0
Pre-catalyst NO_x control	73-74	3.40	0.0
Catalyst	75-76	2.47	0.18
Catalyst	77-78	2.38	0.17

Source: Ref. 23.

Emissions controls on heavy duty vehicles also began with the 1963 California state law requiring that all vehicles manufactured for sale in California be equipped with PCV devices. Beginning in 1969, federal legislation established increasingly stringent exhaust emissions standards for gasoline-powered heavy duty vehicles. Exhaust emissions standards for diesel vehicles were first required by California in 1973 and by the federal government a year later. Evaporative emissions standards for heavy duty vehicles were also first set in 1973.

The discussion has thus far centered on emissions of three pollutants--HC, CO, and NO_x--because the largest air pollution problems due to motor vehicles are caused by these species and their interactions. No standards have been set for emissions of other pollutants from motor vehicles, except for the regulation limiting smoke emissions from heavy duty vehicles (see Table 3) and the requirement that new cars run on unleaded fuel.

C. THE DEPENDENCE OF EMISSIONS ON OPERATING PARAMETERS

To understand the methods used to calculate the emissions from a given vehicle under particular driving conditions, one must first know how and why emissions depend on the operating conditions. For example, engine temperature, atmospheric pressure, cruising speed, acceleration and deceleration rates, and fuel composition all have significant and sometimes opposite effects on the emissions of the various pollutants.

The following variables relating to engine and vehicle design and operation affect exhaust emissions:

> Design
  - Range of air-to-fuel ratios
  - Compression ratio
  - Ignition timing
  - Combustion chamber geometry
  - Ratio of vehicle weight to engine power.

> Operation
  - Engine speed
  - Ambient temperature
  - Altitude
  - Engine temperature
  - Type of fuel
  - Choke action
  - Acceleration or deceleration.

The operating variables listed above can be expressed in terms of the vehicle speed, the season and location in which the vehicle is operating, and the temperature (hot or cold) of the engine. Also, fuel type is important primarily in terms of lead content.

CO is formed during incomplete combustion, which results from either a rich (high) fuel/air ratio or a ratio so lean (low) that the fuel does not ignite properly. Hydrocarbons in exhaust are unburnt or partially burnt fuel. Therefore, both CO and HC emissions are higher during idling, acceleration, and deceleration, when the fuel/air mixture tends to be rich, than during cruising at a constant speed.

Oxides of nitrogen are formed by high temperature combustion, as noted earlier, and therefore are lowest at idle and deceleration and highest at acceleration. NO_x emissions for cruising automobiles depend on engine temperature and, hence, vehicle speed. Lead emissions depend largely on the lead content of the fuel; however, lead emissions also vary with driving patterns. It is believed that lead collects on the cylinder walls at low speeds and flakes off during high speed operation [22]. Less is known about other particulates, but it has been observed that particulate emissions are greater when the engine temperature is low [24].

One of the basic problems in controlling exhaust emissions is now clear: Engine design and operating changes that decrease CO and HC emissions tend to increase NO_x and lead emissions, and vice versa.

The temperature and pressure of ambient air also affect emissions. Figure 2 shows how CO, NO_x, and HC emissions during the CVS-II test cycle (described later) vary with ambient temperature. These variations reflect the additional time required for the engine to reach normal operating temperature when the ambient air is cold. Since atmospheric pressure decreases with altitude, higher emissions of HC and CO and lower emissions of NO_x occur at high altitudes because of reduced air flow through engines.

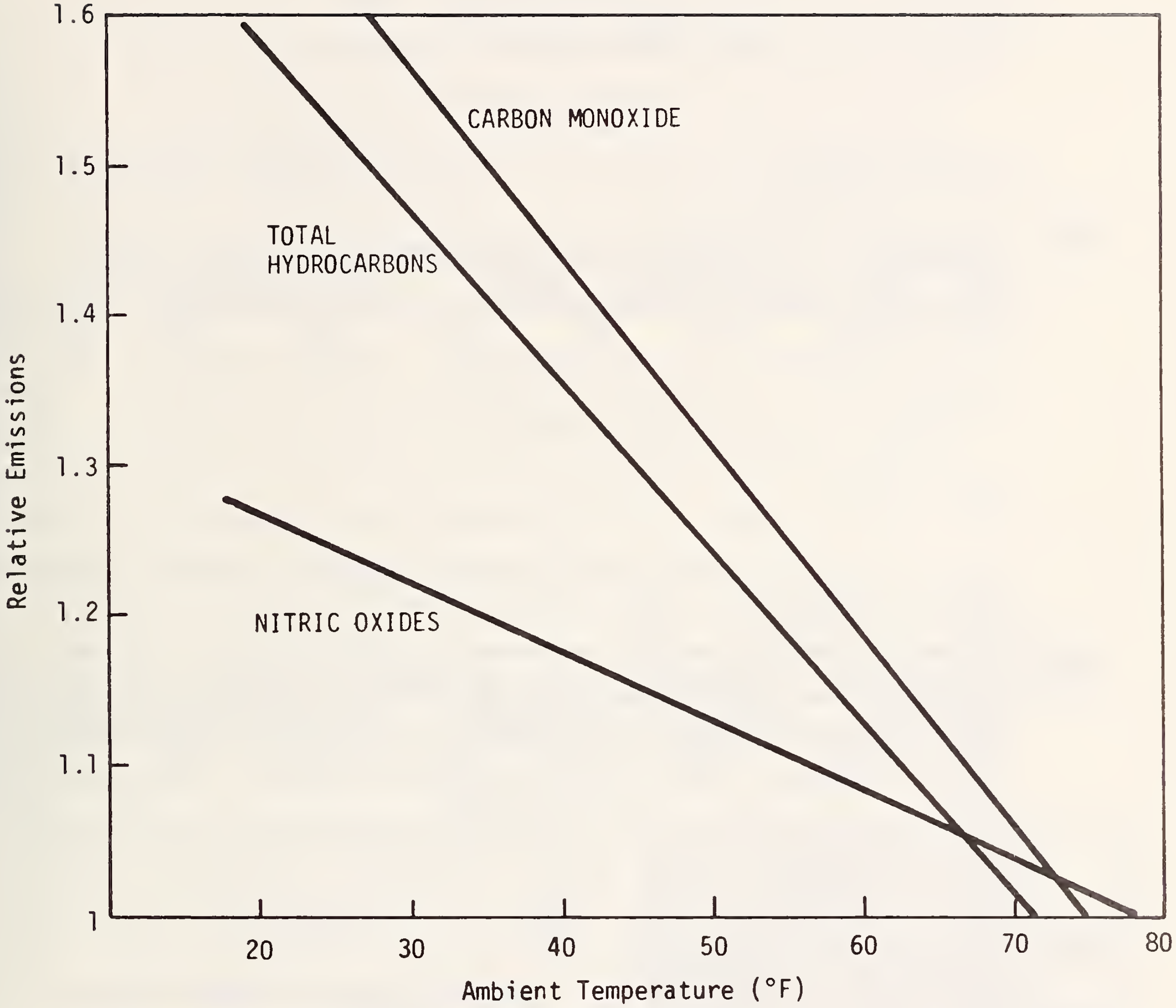
D. VEHICULAR EMISSIONS FACTORS

1. Gasoline-Powered Light Duty Vehicles

a. CO, Hydrocarbons, and NO_x

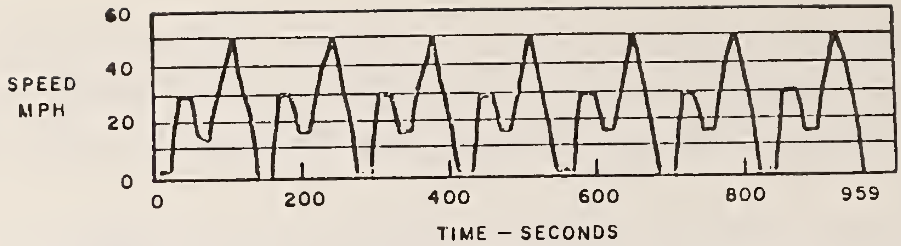
Owing to the variations in emissions caused by operating conditions, one must determine a method for testing the emissions rates of a vehicle to ensure compliance with emissions standards. Ideally, the method chosen would include each of the possible modes of operation (idle, cruise, acceleration, deceleration, hot and cold start) in proportions representative of actual driving. This philosophy has been adopted by the EPA in a series of progressively improved test methods based on standardized driving cycles.

All of the methods proposed thus far are based on the concept of simulating an average commute trip between a suburb and a city. This trip is represented by a driving cycle, which is assumed to represent the driving habits of the general population. Although the driving cycle is useful as a basis for certification tests, typical operating conditions can vary widely from one region to another. The earliest method (known as the seven-mode cycle, or California driving cycle) identified seven modes of operation, including various levels of acceleration, deceleration, and cruise, to represent a typical commuter trip involving freeway driving [as shown in Figure 2(a)]. In this method and the other methods described below, engines are run on a stationary test apparatus and the emissions are collected in large bags for subsequent analysis. In 1972 the CVS-I (constant

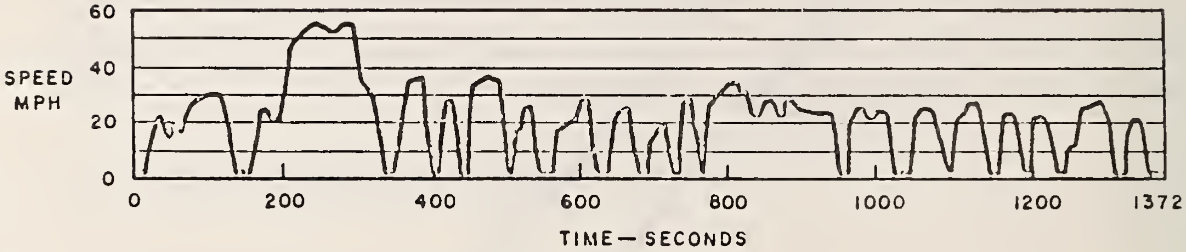


Source: Ref. 25.

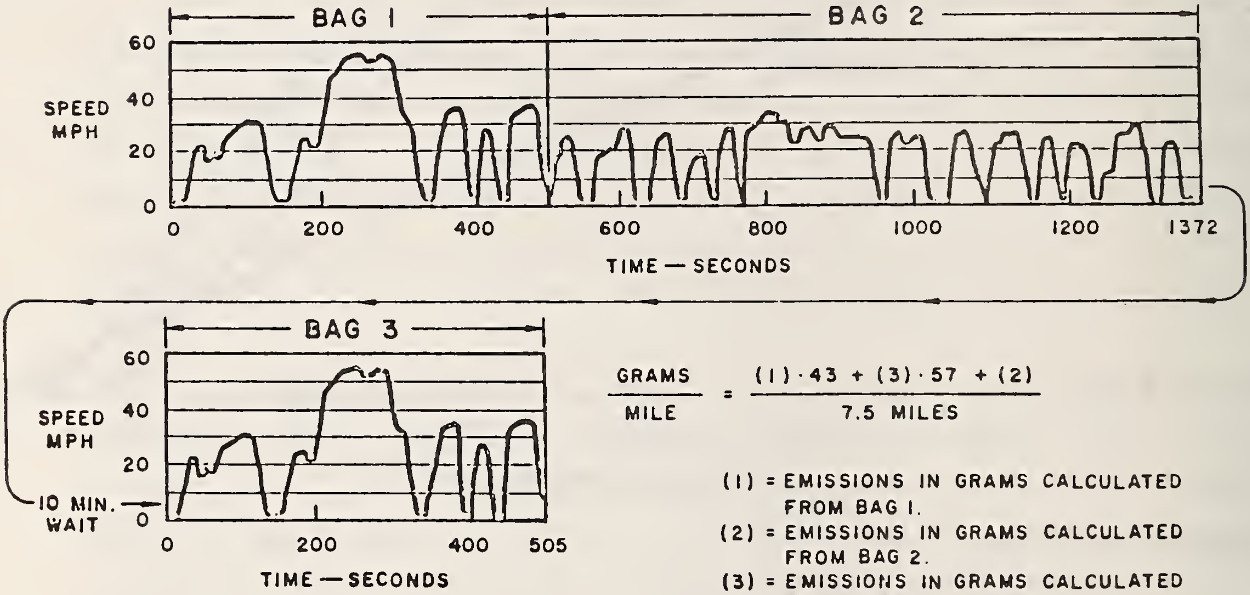
FIGURE 2. LIGHT DUTY VEHICLE TEMPERATURE CORRECTION FACTORS FOR CVS-II EMISSION FACTORS



(a) Seven-mode Cycle



(b) CVS-I Cycle



$$\frac{\text{GRAMS}}{\text{MILE}} = \frac{(1)\cdot 43 + (3)\cdot 57 + (2)}{7.5 \text{ MILES}}$$

(1) = EMISSIONS IN GRAMS CALCULATED FROM BAG 1.
(2) = EMISSIONS IN GRAMS CALCULATED FROM BAG 2.
(3) = EMISSIONS IN GRAMS CALCULATED FROM BAG 3

(c) CVS-II Cycle

Source: Ref. 5.

FIGURE 3. THE SEVEN-MODE, CVS-I, AND CVS-II DRIVING CYCLES

volume sampling) cycle, believed to be more representative of a typical commute trip, was adopted; its speed/time profile is shown in Figure 3(b). In 1975, a 10-minute waiting period after completion of the CVS-I cycle and an additional 505 seconds of driving identical to the first 505 seconds were added to the CVS-I cycle; this, referred to as the CVS-II cycle, is shown in Figure 3(c). Three bags are used in the CVS-II: one to collect the first 505 seconds to determine emissions during the "cold transient" period; a second during the remaining 23 minutes of the CVS-I portion called the "stabilized" period; and a third after the 10-minute wait, called the "hot transient" period.

A random sample of each new car model is tested in this fashion at 4000-mile intervals for a total of 50,000 miles to determine whether new cars meet emissions standards. Each year the results are widely publicized. In addition, each year the EPA tests vehicles in use in several cities to determine emissions of vehicles subject to actual use and maintenance [26]. These results demonstrate that actual emissions rates often vary considerably from those measured in the new car tests of the same model because of deterioration and poor maintenance.

Because of the importance of the type of driving mode in determining emissions, considerable research has been performed with the goal of quantifying emissions for various driving modes. This work has resulted in the development by EPA of the Modal Emissions Model, a computer program to estimate light duty vehicle emissions for any arbitrary driving cycle provided as input [6]. This model is termed "modal" because it considers separately four modes of vehicle operation--namely, acceleration, deceleration, cruise, and idle. It accurately reproduces the results of the EPA driving cycle tests. Table 5, developed using this model, indicates the emissions from an average vehicle (based on the 1971 national vehicle mix) at sea level and also at 1 mile above sea level for various modes of operation. The column labeled "California" presents emissions rates in grams per mile appropriate for Los Angeles; these are slightly lower because of California's more stringent emissions control requirements.

TABLE 5. VEHICULAR EMISSIONS FACTORS FOR THE 1971 NATIONAL VEHICLE MIX FROM THE MODAL EMISSIONS MODEL

(in grams; cruise emissions in grams per mile)

	California			Low Altitude			High Altitude		
Mode	HC	CO	NO_x	HC	CO	NO_x	HC	CO	NO_x
Acceleration from 0-32* (6 seconds, 173 feet)	21.10	260.99	28.95	22.32	294.35	27.95	28.08	816.43	6.99
Acceleration from 32-60 (12 seconds, 959 feet)	6.44	97.48	12.55	6.90	111.10	12.44	9.34	320.27	4.30
Acceleration from 0-20 (6 seconds, 114 feet)	14.22	186.24	13.18	14.68	199.61	13.26	14.81	341.74	6.12
Acceleration from 20-35 (10 seconds, 473 feet)	5.79	62.95	8.61	6.14	71.05	8.53	7.66	192.14	3.18
Deceleration from 50-0 (10 seconds, 370 feet)	7.16	95.79	1.57	8.20	108.37	1.54	9.37	210.13	0.72
Idle (g/min)	1.21	16.08	0.25	1.31	16.93	0.26	1.41	18.41	0.194
Cruise at 60	2.57	25.01	6.31	2.80	27.27	6.40	3.85	68.40	4.52
Cruise at 55†	2.55	24.80	5.66	2.75	27.11	5.75	3.75	64.75	4.08
Cruise at 50†	2.53	24.59	5.02	2.71	26.95	5.09	3.66	61.11	3.63
Cruise at 45	2.51	24.39	4.37	2.66	26.79	4.44	3.56	57.46	3.19
Cruise at 40†	2.63	25.95	3.75	2.76	28.51	3.82	3.62	55.86	2.77
Cruise at 35†	2.74	27.53	3.14	2.85	30.23	3.19	3.69	54.26	2.35
Cruise at 30	2.86	29.10	2.52	2.95	31.95	2.57	3.75	52.66	1.93
Cruise at 25†	3.51	37.82	2.02	3.63	41.20	2.06	4.44	59.24	1.59
Cruise at 20†	4.17	46.54	1.52	5.65	50.44	1.55	5.12	65.83	1.26
Cruise at 15	4.82	55.26	1.02	4.99	59.69	1.04	5.81	72.41	0.92

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[*] Units of miles per hour.

[†] Emissions interpolated from the Modal Emissions Model.

Conversion factors: 1 gram per mile = 0.62 grams per kilometer;
1 mile per hour = 1.6 kilometers per hour.

The results of the emissions tests and computer estimates, such as the one described above, are used to calculate representative emissions rates of CO, NO_x, and HC in grams per mile for vehicles of various ages and types. These representative rates, called "emissions factors," are often used to compile regional vehicular emissions inventories.

Because of the absence of emissions standards for other pollutants, relatively little work has been done to determine emissions rates for lead, sulfates, asbestos, and trace elements from light duty vehicles. Table 6 presents light duty vehicle emissions rates that have been reported in the literature. Table 7 presents emissions factors for some of these contaminants for heavy duty vehicles as reported by the EPA. These pollutants are discussed further in the following subsections.

b. Lead and Lead Compounds

Lead emissions are caused by the addition of tetraethyl lead to gasoline to raise its octane rating. The lead content of gasoline varies depending on the type of fuel and the octane rating, as shown in Table 8. Since adjustments for local climatology are often needed, fuel composition varies from region to region. It would be useful to determine the lead contents and quantities sold of premium and regular fuel in any given region to compile an emissions inventory for lead. However, such data are not readily available.

About 75 percent of lead in fuel escapes into the atmosphere, and the remainder is retained in the crankcase oil, oil filter, and exhaust system. Of the portion emitted, about 93 percent is lead-containing aerosol; the remainder is organic vapor. It has been estimated that 43 percent of the

TABLE 6. FREEWAY PARTICULATE PRODUCTION RATES FOR LIGHT DUTY VEHICLES

(milligrams per mile)

Species	Gas	Motor Oil	Brake Linings	Exhaust Train	Tires	Road Bed	Total
Na	--	--	--	--	--	7 (1.4)	7 (1.4)
Mg	--	--	--	--	--	4 (0.8)	4 (0.8)
Al	--	--	1.2	--	--	23 (4.6)	24 (5.8)
Si	--	--	0.1	--	--	60 (12.0)	60 (12.1)
P	0.2	--	N	--	--	N	0.2 (0.2)
S	15	--	N	--	--	N	30 (15)
Cl	10	--	N	--	--	N	10 (10)
K	--	N	N	--	N	4.3 (0.8)	4.3 (0.8)
Ca	--	N	N	--	N	34.5 (7.0)	34.5 (7.0)
Fe	--	N	0.01	20 (10)	0.02	8.61 (1.8)	28.6 (11.9)
Cu	--	N	N	--	N	N	
Zn	--	0.20	N	--	8 (1.6)	N	8.2 (1.8)
Br	22	N	N	--	N	N	22 (22)
Pb	60	N	N	--	N	N	60 (60)

-- = not available.

N = known and negligible.

Note: Numbers in parentheses were generated by using a refinement of the technique described in Ref. 22.

Source: Ref. 22.

TABLE 7. PARTICULATE AND SULFUR OXIDE EMISSIONS FACTORS FOR HEAVY DUTY GASOLINE-POWERED VEHICLES

(grams per kilometer)

Pollutant	Emissions
Particulate	
Exhaust	1.45
Tire wear	0.32T*
Sulfur oxides (SO_x as SO_2)	0.58

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*T = number of tires divided by four.

Source: Ref. 25.

TABLE 8. LEAD CONTENT OF GASOLINE IN SOUTHERN CALIFORNIA IN 1969

(grams per liter)

Season	Regular Grade	Premium Grade
Winter 1968-1969	0.47	0.67
Summer 1969	0.54	0.77
Average	0.50	0.72

Source: Ref. 24.

lead-containing aerosol is of a size less than 9 μm in diameter, the maximum size capable of remaining suspended in the atmosphere for a significant length of time [22]. Therefore, about 30 percent of the total lead content of fuel is emitted as suspendable aerosol (about 55 μg per mile based on 2.5 grams of lead per gallon and 13.6 miles per gallon fuel economy) and 5 percent as organic vapor (about 9 μg per mile). These results agree fairly well with experimental observations [22].

c. Asbestos

Asbestos is used in brake and clutch linings and is sometimes added to concrete at the ends of freeway off-ramps to reduce wear. Asbestos fibers are carcinogenic, as evidenced by the occurrence of asbesteosis in those who work with the fiber. Prior to this discovery, which was delayed by the approximately 25-year period between exposure and the appearance of symptoms, the use of asbestos was uncontrolled. For example, it was sprayed on construction sites as a fire retardant, and it was allowed to circulate freely in certain industrial operations, particularly automobile brake repair shops. Both of these sources are now subject to control.

Naturally, the question arose as to whether significant amounts of asbestos are emitted into the atmosphere from wear on brake and clutch linings. Several studies have been performed strongly indicating that over 99 percent of the asbestos is converted by the heat of friction in normal brake and clutch operation to a relatively benign compound called foresterite [7, 27]. During emergency fast stops, however, the lining is essentially torn violently apart, preventing the ordinary friction conversion process and resulting in asbestos emissions.

Asbestos levels were monitored in Los Angeles in both an on-freeway and off-freeway location, the latter near several busy streets [7]. The results indicate no appreciable difference in ambient concentrations between the two locations: levels varied between 10 fibers per liter and well below 1 fiber per liter (the detection limit of the instrument). This finding compares favorably with the Occupational Safety and Health

Administration standard of 2000 fibers per liter averaged over eight hours for occupational exposure. Thus, the evidence does not indicate a serious asbestos hazard due to automotive operation.

d. Sulfur Compounds

Sulfur is contained to a varying degree in all sources of crude oil from which gasoline and diesel fuel are produced. The actual sulfur content of fuel may vary from about 0.004 to about 0.05 percent by weight. The EPA has used 0.032 percent as a representative figure for gasoline. The sulfur content of diesel fuel is higher, however, averaging about 0.20 percent. Table 9 shows the typical sulfur content of gasoline sold in Southern California in 1974.

Sulfur can be emitted from vehicles in three main forms: gaseous oxides, sulfate particulates (such as lead sulfate), and sulfuric acid aerosols.

TABLE 9. SULFUR CONTENT OF GASOLINE IN SOUTHERN CALIFORNIA IN 1974

Gasoline Grade	Sulfur Content (weight percent)	Percentage of 1974 total California sales for that grade
Premium	0.039%	43.5%
Nonpremium		
Regular	0.061	56.5
Unleaded	0.026	(Assumed small in 1974)

Source: Ref. 24.

Table 10 presents EPA emissions factors for sulfur oxides from various vehicle types. These factors are based on the assumption that all the sulfur in the fuel is emitted as SO_2. These factors may be high because some of the sulfur is emitted as sulfate or sulfuric acid aerosol and some is retained in the exhaust system. About 15 to 20 percent of the sulfur in gasoline is emitted as particulates, but insufficient data are available to determine the chemical identity of the sulfur-containing particulates. It appears likely, however, that the emissions may contain sulfates of metal ions, such as lead [22].

Significant quantities of sulfuric acid aerosol are emitted primarily from vehicles equipped with catalytic converters for HC and CO emissions control and from diesel vehicles, for which sulfuric acid aerosol constitutes between 0.5 and 3 percent of total sulfur emissions. The sulfuric acid aerosol emissions from vehicles equipped with catalysts have been found to depend on the sulfur content of the fuel, the type of catalyst, the fuel economy of the vehicle, the deterioration of the catalyst, and the amount of excess air supplied to the catalyst. At low driving speeds, the sulfur tends to form sulfates on the surface of the catalyst, whereas at high speeds the higher catalyst temperatures cause the sulfur to be emitted as sulfuric acid. Table 11 shows emissions factors for various percentages of sulfur content in fuel under urban and highway driving conditions. In all cases, the highway emissions are higher.

e. Other Pollutants

Emissions rates of other species presented earlier in Table 5 should not be considered as conclusive, owing to the limited amount of data, yet they do provide an indication of the emissions of certain species that are not often estimated. The estimates of particulate emissions due to the road bed and tires agree well with the EPA figures for tire wear, and the lead emissions agree fairly well with estimates based on the lead content of gasoline and the proportion emitted.

TABLE 10. EPA EMISSIONS FACTORS FOR SELECTED POLLUTANTS FROM HIGHWAY VEHICLES

(grams per mile)

	Vehicle Class and Emissions Factor Rating[*]						
	Light Duty Gasoline Vehicle (EFR = C)	Light Duty Gasoline Truck (EFR = C)	Heavy Duty Gasoline Vehicle (EFR = B)	Light Duty Diesel Vehicle (EFR = B)	Heavy Duty Diesel Vehicle (EFR = B)	Motorcycles	
Pollutant						Two-stroke	Four-stroke
Particulates				0.73		0.33	0.046
Exhaust	0.34	0.34	0.91		1.3[*]		
Tire wear	0.20	0.20	0.20T[†]		0.20T[†]		
Sulfur oxides (as SO_2)	0.13[§][**]	0.18[§][**]	0.36[§][**]	0.54[§]	2.8[§][**]	0.038[**]	0.022[**]
Aldehydes (as HCHO)	--	--	--	--	0.3	0.11	0.047
Organic Acids	--	--	--	--	0.3	--	--

EFR = emissions factor rating: "A" corresponds to relatively accurate estimates, and "D" to relatively uncertain estimates.

[*] Particulates from diesel exhaust occur in two major forms: black smoke and white smoke. White smoke is obtained when the fuel droplets are kept cool in an environment containing abundant oxygen (cold starts). Black smoke is emitted when the fuel droplets are subjected to high temperatures in an environment lacking oxygen (road conditions). For heavy duty diesel vehicles, the sulfuric acid emissions are estimated to be from 0.5 to 3.0 percent of sulfur oxide emissions on the basis of engineering judgment.

[†] T is an adjustment factor obtained by dividing the number of tires per truck by four.

[§] Average fuel economy assumptions are as follows: 13.6 miles per gallon for light duty gasoline vehicles, 10.0 for light duty gasoline trucks, 6.0 for heavy duty gasoline vehicles, and 4.6 for heavy duty diesel vehicles.

[**] Fuel property assumptions are as follows: gasoline fuel is 0.032 percent sulfur by weight and 6.1 pounds per gallon density for light duty gasoline vehicles and trucks and for heavy duty gasoline vehicles. Gasoline fuel is 0.043 and 0.022 percent sulfur by weight for two-stroke motorcycles and for premium fuel for four-stroke cycles, respectively.

Source: Ref. 25.

TABLE 11. SULFURIC ACID EMISSIONS FACTORS FOR 1975 LIGHT DUTY VEHICLES

(grams per kilometer)

Fuel Sulfur Content	Urban Cycle	Highway Test
0.050%	0.016	0.050
0.051	0.016	0.051
0.026	0.008	0.026

Ref. 24.

2. Other Vehicles

This section deals with emissions from vehicles other than gasoline-powered light duty vehicles, including:

- > Light duty diesel-powered vehicles
- > Light duty gasoline-powered trucks and buses
- > Heavy duty gasoline-powered vehicles
- > Heavy duty diesel-powered vehicles.

Light duty diesel-powered vehicles are manufactured by several companies but are used relatively little in this country. Diesel engines emit considerably smaller quantities of CO and HC and somewhat less NO_x than gasoline engines without emissions controls [25], one reason for their increasing popularity. The applicable standards and test procedures are the same as those for gasoline-powered light duty vehicles. Table 12 shows emissions factors based on tests of several Mercedes 220D automobiles. The results compare favorably with other light duty vehicles. Light duty gasoline-powered trucks and buses, defined as those weighing under 8500 pounds, are subject to standards slightly higher than those

TABLE 12. EMISSIONS FACTORS FOR PRE-1973 LIGHT DUTY DIESEL-POWERED VEHICLES

Pollutant	Grams per Mile
Carbon monoxide*	1.7
Exhaust hydrocarbons	0.46
Nitrogen oxides* (NO_x as NO_2)	1.6
Particulates	0.73
Sulfur oxides†	0.54

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*Estimates are the arithmetic mean of tests of vehicles.

†Assuming the use of a diesel fuel containing 0.20 percent sulfur.

Source: Ref. 25.

of passenger cars (see Table 3). For the most part, trucks and buses in this category use the same engine models as some passenger cars; so the difference in emissions is due to higher vehicle weight.

Heavy duty gasoline- and diesel-powered vehicles are subject to the same standards (see Table 3). The rates are expressed in grams per brake horsepower-hour to account for wide variations in vehicle weight. There is a smoke standard based on the Ringelman system, which is used to identify particular shades of gray, and an evaporative emissions standard of 2 grams per test. As for light duty vehicles, crankcase emissions from heavy duty vehicles are nil. Diesel-powered vehicles tend to emit more SO_2 than gasoline-powered vehicles because diesel fuel contains more sulfur than gasoline does. Emissions from heavy duty vehicles are not tested using the driving cycles (CVS-I or CVS-II) for light duty vehicles. Instead, a representative sample is driven along a 7.24-mile stretch in San Antonio, Texas, which includes freeway, arterial, and local/collector highway segments. A sampler is carried on board to collect part of the exhaust, which is later analyzed. The vehicles are tested after being warmed up, and the average speed is about 18 mph, depending on traffic conditions.

Motorcycles are relatively heavy emitters for their modest engine size, particularly the two-cycle variety. However, because they constitute only a small fraction of total vehicles, no control has been required to date.

E. CONSTRUCTION OF VEHICULAR EMISSIONS INVENTORIES

An emissions inventory is basically used in one of two ways: to help determine what emissions controls will be most effective or to evaluate the effectivenss of a control program. An inventory enables identification of the sources contributing to air quality problems and their relative magnitudes. It can help identify underlying trends that are not apparent from pollutant concentration data because of the year-to-year variability in meteorology. An inventory is necessary for calculating the level of emissions control required to achieve air quality goals. This calculation also requires a quantification of the relationship between emissions and pollutant concentrations. This section deals with inventories for vehicular emissions; Section IV-D covers inventories for non-vehicular anthropogenic emissions. Relationships between emissions and pollutant concentrations are treated in Chapter IX.

Two spatial scales in emissions inventories are of interest to the highway planner: the corridor (a specific facility), and the region (usually a single urban area). A corridor inventory is usually compiled to determine the effects of a roadway on receptors within a few kilometers. In some cases, every corridor in a region is considered individually to estimate a regional emissions inventory. Annual regional totals are useful in identifying trends. More detailed information, however, is useful in analyzing the effect of changes in the spatial or temporal distribution of emissions caused by, say, the construction of new links on the highway network or additional mass transit. Regional totals can be stratified spatially using grids (sometimes as fine as 1 km) or temporally (the usual interval is one hour). Grid-based air quality models, which are particularly appropriate for such analysis, require spatially and temporally stratified emissions.

Emissions inventories are subject to many sources of uncertainty; lack of data, inexact procedures for calculating emissions, spatial and temporal variations in emissions, lack of validation, and data reduction and transfer problems. The true accuracy of emissions inventories is not known. As an educated guess, uncertainties range from as low as 30 to 50 percent for a corridor inventory to as much as a factor of two for a regional inventory.

1. Corridor Inventories

The procedure for calculating total light duty vehicle emissions from a corridor entails characterizing the emissions rates of the "average" vehicle in the region and then using those rates and traffic data to compute corridor totals. The characteristics of the average vehicle are based on the regional vehicle age distribution (from vehicle registration data), average vehicle mileage speed variation and traffic volume hour by hour in both directions and the mix of light duty and heavy duty vehicles for a specific corridor can provide the traffic data required for developing emissions estimates. Gradients in the road may also be noted.

To calculate corridor emission, one determines an emissions rate for contaminants from an average vehicle representative of the given corridor. Then, total emissions from light duty vehicles can be calculated for each hour by multiplying the emissions rates by the appropriate traffic volume (for both directions of flow). Heavy duty vehicles emissions are most accurately calculated separately for gasoline and diesel vehicles based on the emissions factors in the latest supplement (No. 5 as of this writing) of Ref. 25. California emissions factors, which are sometimes different, are available from Ref. 28. This reference also includes information similar in type to Ref. 25, but in some cases it is more detailed and is thus a useful supplement to the EPA document.

The effects of special roadway characteristics primarily influence operating mode and are therefore accounted for implicitly in Table 5. One exception is a steep grade, for which emissions are likely to differ in proportion to the quantity of fuel used.

The previous paragraphs describe a readily available procedure, approved by the EPA, for calculating emissions of NO_x, HC, and CO from a single roadway. In practice, it may be difficult to collect all the required data or to perform the specified calculations. Frequently, simpler techniques are used, the most popular of which is calculation of average daily light duty vehicle miles traveled, and then multiplication of this figure by a region-wide estimate of average emissions per mile under typical driving conditions (such as those in the federal test procedure) for the "average" vehicle in the region.

This technique differs from the more detailed method principally in that speed and vehicle mix are not considered individually for the corridor; therefore, if the corridor is not typical of average conditions, substantial errors may result. The heavy duty portion of the vehicle miles traveled can be estimated similarly by multiplying the total heavy duty vehicle miles traveled by an estimate of average emissions per mile, such as those given in Ref. 25.

No standard procedures for determining emissions of other pollutants have yet been promulgated by the EPA except for heavy duty vehicles (see Table 3). To determine emissions of asbestos, sulfates, other particulates, or trace elements, one must first find reports of individual experiments, such as those described earlier, and then estimate emissions factors from their results. Several such factors were discussed earlier (see Table 6).

EPA has a continuing program for the development of increasingly accurate emissions factors. Consequently, there has been a substantial effort to quantify the effects of accelerations and decelerations on the emissions rates. Emissions factors that account for speed changes are referred to as modal emissions factors. Applying the modal factors requires detailed knowledge of traffic flow, which may require traffic monitoring programs.

A method of producing modal emissions factors that may be readily used by highway planners was developed in the course of this study. The method will be described in considerable detail in an upcoming FHWA publication. The driving cycles described in the upcoming publication were used as input to the Modal Emissions Model, an EPA computer program for estimating emissions for specific driving cycles. The model's calculations are based on speed-dependent emissions data collected and analyzed by EPA staff; they consider periods of acceleration, deceleration, cruise, and idle individually. The emissions from each of those four modes were calculated and added to provide a total for the driving cycle. The results of these calculations, shown in Table 13 for five facility types and five levels of service (29), support the following conclusions:

- Level of service strongly influences the emission of CO and HC. In all cases, as the level of service improves (from E to A), emissions per vehicle decrease. Emissions of HC and CO vary by factors of about three and four, respectively, from the lowest case to the highest.
- Improvements in level of service influence NO_x emissions inconsistently, causing emissions to increase in some cases and decrease in others. Interestingly, the variation from the lowest case to the highest is within a factor of two.

TABLE 13. LIGHT DUTY VEHICLE EMISSIONS FACTORS BY ROADWAY TYPE AND LEVEL OF SERVICE FOR 1977 49-STATE AVERAGE VEHICLE MIX*

(in grams per mile except as noted)

Facility Type	Level of Service	CO	Reactive Hydrocarbons	NO_x	Mileage (miles per gallon)
Central business district	A	40.953	3.443	2.671	19.329
	B	50.683	4.057	2.563	17.508
	C	65.744	4.989	2.482	15.298
	D	90.110	6.471	2.031	12.787
	E	135.083	9.267	1.769	9.733
Major arterial	A	37.852	3.271	3.706	19.053
	B	50.596	4.061	4.068	16.758
	C	63.403	4.863	4.378	14.929
	D	70.771	5.389	3.959	14.111
	E	90.065	6.628	3.980	12.218
Collector	A	52.861	4.202	3.139	16.924
	B	58.202	4.540	2.773	16.178
	C	66.827	5.057	2.518	15.136
	D	89.997	6.472	2.006	12.817
	E	135.398	9.313	1.763	9.732
Urban freeway	A	24.079	2.519	4.906	20.078
	B	28.306	2.629	4.478	20.166
	C	34.932	2.954	4.246	19.540
	D	77.368	5.206	4.989	14.640
	E	88.857	6.482	5.396	13.072
Rural highway	A	25.497	2.534	4.422	20.550
	B	31.309	2.761	4.180	20.130
	C	41.616	3.416	4.222	18.611
	D	77.182	5.745	4.831	14.187
	E	90.702	7.017	5.409	12.535

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* California vehicles are excluded.

Note: 1 gram per mile = 0.62 grams per kilometer;
1 mile per gallon = 1.6 kilometers per gallon

> Central business district and collector streets tend to produce the largest emissions of CO and HC per vehicle mile traveled.

> Urban freeways and rural highways tend to produce the smallest emissions of CO and HC per vehicle mile traveled.

2. Regional Inventories

The EPA requires that a vehicular emissions inventory be developed each year for every air quality control region (AQCR), most of which correspond to single urban areas. The results are published annually by the EPA in a volume entitled "Nationwide Emissions Survey." This section addresses the construction of such a vehicular emissions inventory for any region.

The fundamental principle is simple: Regional* vehicular emissions are the sum of the emissions from every corridor in the region. The best emissions inventories are compiled in this fashion. Unfortunately, it is usually too difficult to collect detailed information for every section of every street and highway; thus, some accuracy is typically sacrificed. Alternatively, a regional emissions inventory can be based on estimated regional total vehicle miles traveled and regional average emissions factors. Occasionally, an emissions inventory is based on regional gasoline sales data and an average grams per gallon emissions factor.

The selection of a method for constructing an emissions inventory depends on the availability of data and analytical resources and the problem to which it will be applied. For example, analysis of annual emissions trends requires less detailed information than evaluation of specific control strategies, which often requires fine resolution of emissions for input to air quality models or other analytical procedures. Four methods for compiling regional inventories are described below.

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* See Volume II for a detailed discussion of the definition of "region."

a. Manual Link-by-Link Summation

In this method, emissions from each section of freeway and arterial street are estimated using traffic volume data, and emissions from traffic on minor streets are roughly approximated. The data used include the following:

- Daily total vehicle miles traveled for each highway and arterial street. These data are often available on maps from local agencies.
- Fraction of the daily total vehicle miles traveled occurring during each hour. This information is usually not available for every street, but it can be estimated from traffic counts made at selected locations.
- Peak and off-peak route speeds. These are estimated directly from data or by determining the level of service possible for a given road according to the calculated flow rate and known capacity [29]. Since this is a difficult procedure, it should be carried out by someone familiar with local traffic.
- Light and heavy duty vehicle mix. Data may be available from local agencies; if not, they can be roughly estimated from zoning, facility type, or regional average information.
- Traffic volume on minor streets. This refers to traffic other than that on highways and major arterials. It can be estimated by a regional transportation model (see below) or by assuming that it is proportional to the traffic volumes on the nearby major thoroughfares.

For each of the streets explicitly identified, the above information can be used to construct corridor emissions totals that include the effects of hourly speed and volume and vehicle mix and that use regional emissions factors estimated from Table 13.

The minor street totals are estimated from the vehicle miles traveled in each hour and from the average emissions factors.

Since exhaust emissions are significantly higher before the engine has reached a normal operating temperature, it is necessary to consider the effects of cold starts, which are often included in the emissions factors. However, errors in the temporal distribution of emissions are likely to result because the effects of cold starts are greatest in the early morning on arterial and minor streets. This problem can be mitigated by applying separate emissions factors for hot-running and cold-running vehicles and then assuming that a certain fraction of the vehicle miles traveled in each hour are cold running. If the spatial distribution of trip origins is known, the cold starts can be allocated accordingly, thus reducing spatial errors.

Evaporative emissions occur largely when a hot engine is shut off; the effect is enhanced by elevated daytime temperatures. If the spatial distribution of trip destinations is known, these emissions can be allocated accordingly; otherwise, spatial errors may result. The temporal distribution of evaporative emissions can be treated similarly to that of cold starts, or it can be allocated evenly over the daylight hours. The corridor-by-corridor plus minor street emissions figures can then be aggregated into a regional total or can be assigned to a grid. This type of inventory has been constructed for the Los Angeles area [30]. That inventory is one of the most accurate and complete regional emissions inventories ever compiled; a tremendous amount of manual effort was required in reading the maps of vehicle miles traveled, in estimating diurnal variations and average route speeds, and in entering the information into the computer files.

b. Automated Link-by-Link Summation

Fortunately, in some cases it is possible to avoid much of the manual processing by using the output of a regional transportation planning model, if one exists for the area of interest, to drive a program that automatically calculates emissions for each highway segment for each hour. It is, of course, desirable to use an updated calibration of the transportation model if possible. This approach was adopted in a study of the San Francisco Bay area [20]. The Metropolitan Transportation Commission (MTC) in that area maintains a file containing travel demand by origin and destination on a relatively fine grid and a digitized version of the highway-arterial street network. A computer program was available to "load" this travel demand on the network, producing estimates of daily vehicle miles traveled and peak and off-peak speeds on every link in the network. The program also estimated traffic that did not cross the boundary of a grid cell; this was taken to represent minor street traffic. For the study in Ref. 20, a diurnal variation was adopted based on hourly traffic count data, and a vehicle mix was assumed. The predicted traffic flow rates compared favorably with traffic counts. All this information was used as input to a computer program containing emissions factors to estimate the hour-by-hour emissions of motor vehicles on a one-km grid throughout the region.

This procedure sacrifices some accuracy in using a simulation program to calculate vehicle miles traveled rather than using actual traffic counts. Also, the daily traffic figures are generally averaged over a year and therefore exclude seasonal differences, which because of climate or vacation attraction significantly influence emissions factors in some areas. However, an important advantage is gained: The computer programs are able to simulate the effects of changes in travel demand, the highway network, or emissions factors. Also, since the method requires specification of the origins and destinations of all trips, it is possible to allocate cold starts and hot soaks to the appropriate grid squares. Therefore, it is much easier to evaluate the air quality impact of a set of alternative transportation plans using automated link-by-link summation.

c. Gasoline Sales

If only seasonal or annual total emissions estimates are required for a region, it is possible to base an inventory on regional gasoline sales, provided that regional average emissions rates in grams per gallon of gasoline can be estimated (grams of emissions per mile x miles per gallon of gasoline = grams of emissions per gallon of gasoline). In fact, estimates produced in this manner probably will agree with totals obtained using more complex methods within 20 to 30 percent, despite the crudeness of the approach and the complete exclusion of external trips. Of course, there is no spatial or temporal stratification. Since all highway departments have access to link-node data, using gasoline sales data to estimate emissions is seldom the preferred approach.

d. Specialized Inventories

One specialized case of particular interest is the New York City motor vehicle emissions inventory. Because of the large proportion of heavy duty vehicles in that city, it was considered necessary to gather detailed information on vehicle type and operation [31]. In the development of that inventory, 7 weight classes, 7 vehicle types, 11 body types, 11 user categories, and 2 fuel types were considered, and several studies were performed to produce tables indicating the vehicle miles traveled for the various classes and links of the highway and arterial street network. In another study, individual emissions factors were estimated for eight classes of vehicles, including personal cars, three kinds of taxis, and gasoline and diesel trucks and buses, allowing the vehicle miles traveled of the various types to be associated with the appropriate emissions factors [32]. The level of detail provided in that study formed the basis for an extremely detailed emissions inventory.

F. FUTURE ESTIMATION OF EMISSIONS

EPA's AP-42 Supplement 5 [25] provides emissions factors designed to be used for future years. These factors are based on current projections of control requirements, deterioration factors for vehicular emissions control devices, and vehicle age distribution. Furthermore, EPA revises AP-42 to reflect new information on emissions factors. Therefore, this reference may be relied upon to provide continually updated emissions factors for both current and future years.

G. SUMMARY

This chapter familiarizes the transportation analyst with the basic components of the problem of motor vehicle emissions. In particular, the discussion identifies and explains vehicular emissions, describes emission control standards, summarizes the variables that affect emissions, and outlines some approaches used to compile emissions inventories. The following chapters deal with other anthropogenic emissions and natural emissions.

IV NONVEHICULAR ANTHROPOGENIC EMISSIONS

Highway planners and engineers frequently need to determine the effects on compliance with air quality standards of various changes in traffic facilities. Because concentrations of some pollutants may be affected by nonvehicular and natural emissions as well as vehicular emissions, some knowledge of all three is necessary to assess air quality effects. This chapter discusses nonvehicular anthropogenic emissions, particularly of pollutants also emitted by vehicles. Chapter V discusses natural sources and natural background concentrations. The discussion in this chapter begins with the types of nonvehicular sources of air pollution and proceeds with the spatial and temporal variations of those emissions and the standards and control methods applied to them.

A. SOURCES

Table 14 lists the main sources of nonvehicular anthropogenic emissions, and Table 15 shows the approximate contributions of the various source categories to total emissions in the United States in 1973. As shown in Table 15, both vehicular and nonvehicular sources contribute heavily to total CO, HC, and NO_x emissions, but nonvehicular sources are primarily responsible for particulate and SO_2 emissions. Those pollutants emitted by nonvehicular sources that are not emitted by motor vehicles (for example, fluorides, ammonia, hydrogen sulfide, heavy metals other than lead, and mercaptans) are not treated in detail here. For those pollutants emitted by both types of sources, differences in the ways in which the emissions occur (for example, through stacks as opposed to automobile exhaust) affect their contributions to surface air quality degradation.

TABLE 14. MAJOR SOURCES OF NONVEHICULAR ANTHROPOGENIC EMISSIONS

Activity	Point Sources	Area Sources
Fuel combustion	Power generation, industrial operations	Space heating
Industrial processes	Chemical manufacturing, food processing, mineral products, petroleum refineries, wood processing	Coal mining, strip mining, lumbering
Solid waste disposal	Municipal incineration, open burning	Residential burning, on-site incineration
Transportation		Aircraft operations
Miscellaneous	Surface coating, organic solvent use	Dirt roads

TABLE 15. APPROXIMATE CONTRIBUTIONS OF VARIOUS SOURCE CATEGORIES TO TOTAL ANTHROPOGENIC EMISSIONS IN THE UNITED STATES IN 1973

(percentage of total emissions)

Source Category	Particulates	Sulfur Oxides	Nitrogen Oxides	Hydrocarbons	Carbon Monoxide
Fuel combustion	42	78	51	2	2
Area	9	7	8	1	1
Point	33	71	43	1	1
Industrial (point)	44	20	4	25	14
Solid waste disposal	4	0	1	4	3
Area	3	0	1	3	2
Point	1	0	0	1	1
Highway vehicles	6	2	42	48	69
Other transportation	1	0	2	12	7
Miscellaneous area sources	3	0	1	9	5

Source: Derived from Ref. 14.

It is difficult to characterize nonvehicular emissions because of the wide range of sources of the various pollutants, the uneven distribution throughout the nation of the various industries producing these emissions, and the variations in population density and climate from place to place. A few observations about major emitters are possible, however, particularly those sources that are present in many areas, such as fossil fuel power plants, oil refineries, residential heating, and to a lesser extent waste disposal, metals processing, and aircraft operations.

Power generation is a major source of air pollution throughout the United States. The particular pollutants emitted depend primarily on the type of fuel burned. Plants fired with natural gas tend to emit relatively small quantities of HC and NO_x and negligible amounts of particulates. Oil- and coal-fired plants emit far more of all three pollutants. None of the plants emit CO, and all emit comparable percentages of the sulfur in the fuel. Although natural gas contains negligible amounts of sulfur, the sulfur content of oil may vary from a fraction of a percent to about 2 percent, and the sulfur content of coal varies from a fraction of a percent to about 5 percent. In the future, low-sulfur fuels will probably become increasingly expensive as supplies dwindle. However, desulfurization of fuel is a topic of current research and may eventually mitigate this problem.

Petroleum refining is also a principal source of pollution in many areas. For example, nonvehicular sources account for 82 percent of HC emissions in Houston, compared with 23 percent in Denver, and the difference is due primarily to petroleum industry operations. Unlike power plant emissions, which are usually emitted from a small number of high stacks, refinery emissions occur from an array of sources and numerous stacks. These emissions include HC due to leaks, CO and NO_x from combustion, and particulates and sulfur oxides from a variety of operations. Ordinarily, oil refining is a closed process except for the pressure relief system and vents, so that emissions under optimum conditions are relatively low. Furthermore, pollution control systems may be economically attractive because they recover materials previously emitted into the atmosphere. Detailed information concerning the rates of refinery emissions is available in Ref. 25.

Solid waste disposal is often accomplished through burning and thus is a significant source of particulates, HC, and CO on a national level. Commercial and municipal incineration are controllable at the stack, but open-site burning is not. In some areas, open burning is either outlawed completely or allowed only on days that provide adequate atmospheric ventilation.

Metal processing is one of several industries that contribute significantly to air pollution problems in some areas. For example, the EPA inventory for Birmingham, Alabama, shows that as of 1973 56 percent of CO emissions were from nonvehicular sources, compared with the national average of 24 percent. The difference is due largely to emissions from the metal processing industry. Similar situations occur in areas with other industries too numerous and diverse in character to present here. Descriptions of various types of industrial sources are available in Ref. 33, and detailed emissions factors are given in Ref. 25.

Aircraft operations are significant pollution sources in many urban areas and in some rural areas as well. Airports are usually considered as point sources, whereas flight paths are considered as elevated corridors. Emissions from turbines and jets are similar and include unburnt fuel (HC), CO, and NO_x. Control methods are available and have been extensively applied to aircraft engines, thus reducing emissions levels.

Residential space heating and other widespread combustion processes are important area sources of pollution, particularly in cold climates. This category is represented in Table 15 (presented earlier) by the fuel combustion area source entry. Although these sources emit particulates, SO_x, and NO_x, their emissions account for no more than 10 percent of the national totals. Currently, there are no federal laws directly covering emissions from residential or small commercial combustion sources. Emissions factors for residential and commercial heating are given in Ref. 25.

B. SPATIAL VARIATIONS

Pollutant emissions of all types vary tremendously from one place to another both regionally and locally. Often a single source dominates its immediate area, for example, an airport, a refinery, or a mining and processing operation. On a larger scale, certain types of industries, such as petroleum refineries, locate in specific parts of the country and may strongly influence air quality in those areas. Other sources, such as residential and commercial fuel use and waste disposal, tend to vary with population and climate.

As part of this study, annual statewide emissions per capita and per square mile were examined. The following patterns were evident:

- The highest and lowest statewide emissions per square mile differ by more than a factor of 100.
- Higher than average per capita emissions can usually be attributed to specialized local industrial activity. For example, the petroleum industry and slash burning are responsible for high particulate emissions in Montana; Louisiana has high HC and CO emissions due to chemical manufacturing; high NO_x emissions in Michigan result from the heavy use of industrial fuels; and high NO_x emissions in Pennsylvania come from the petroleum industry.
- With the exceptions noted above, total emissions correlate fairly well with population, as might be expected.

Wide variations in emissions also occur on a smaller scale because of large point sources, some of which tend to be located near transportation. For example, refineries tend to be located along waterfronts, and food processing industries are often located near rail lines or highways. In contrast, domestic heating and small commercial operations tend to be distributed according to population. Emissions from railroads and aircraft operations aloft occur along specific corridors. Thus, nonvehicular emissions have point, area, and corridor-based components, whereas motor vehicle emissions occur in a large number of corridors, some of which are treated individually and others grouped as area sources.

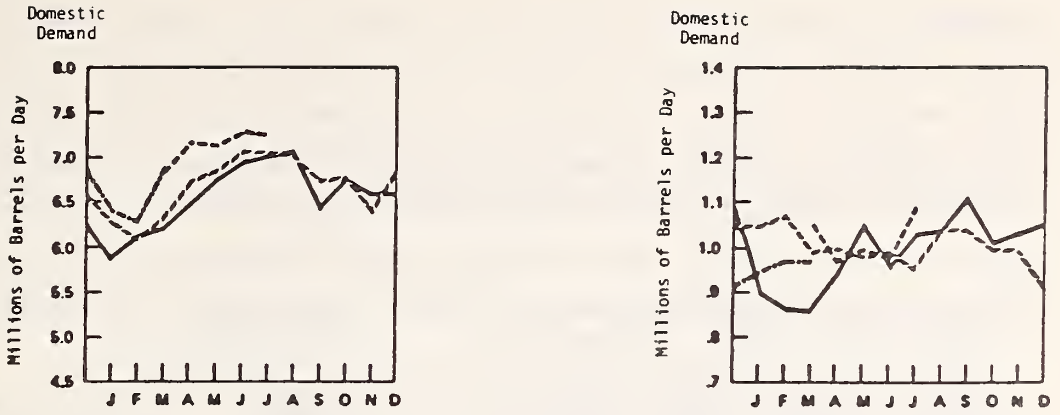
C. TEMPORAL VARIATIONS

Emissions of nonvehicular anthropogenic sources vary both seasonally and diurnally according to the type of operation. Much of the seasonal variations in emissions can be identified by tracing the consumption patterns of various types of fuels. Figure 4 shows several such patterns, demonstrating that fuel usage peaks in the winter months and is lowest during the summer. Electricity generation has peaks in both summer and winter due to heating and cooling needs. Industrial operations, however, tend to be relatively invariant throughout the year.

Diurnal variations are significant for power plants, which usually operate in accordance with hourly demand, and industrial operations, which shut down during part of the day. In contrast, 24-hour operations, such as oil refineries and some power plants that operate at capacity constantly, do not exhibit diurnal variations. Area distributed emissions, primarily space heating, probably have significant diurnal variations, but no conclusive data are available.

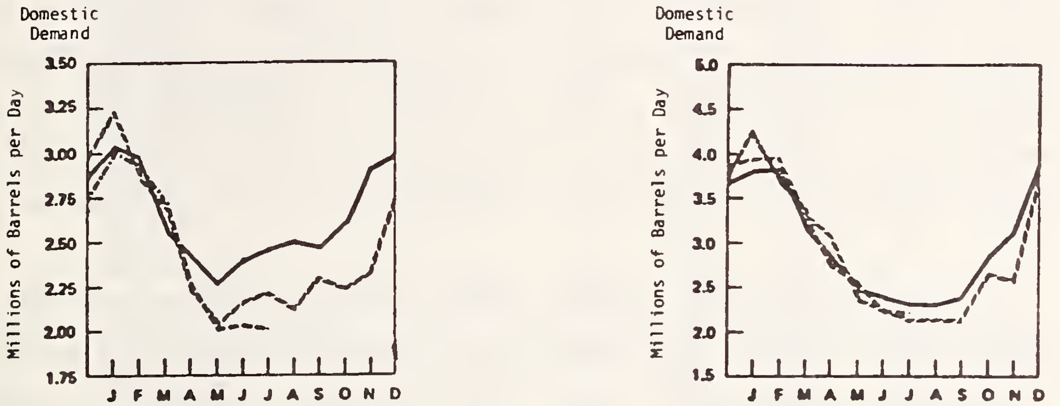
D. NONVEHICULAR EMISSIONS INVENTORIES

Inventories of nonvehicular anthropogenic emissions are constructed for the same purposes as vehicular emissions inventories, which are discussed in Section III.C. Nonvehicular emissions inventories for anthropogenic sources can be compiled in different ways, depending on the



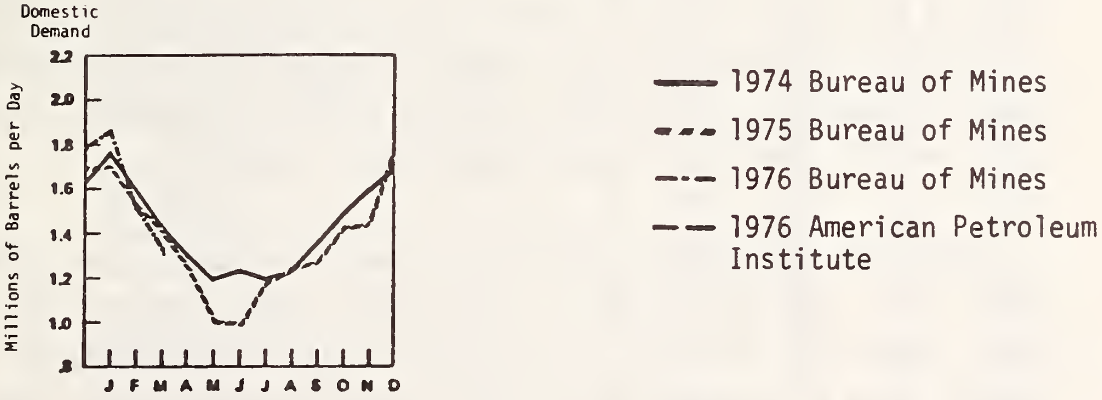
(a) Motor Gasoline

(b) Jet Fuel



(c) Residual Fuel Oil

(d) Distillate Fuel Oil



(e) Natural Gas Liquids

Source: Ref. 34.

FIGURE 4. CONSUMPTION OF PETROLEUM PRODUCTS IN THE UNITED STATES BY MONTH OF YEAR

pollutants and sources involved and the resolution in space and time. Often an emissions inventory compiled for an urban area consists of annual emissions totals categorized only by broad classes of sources. These totals are useful in evaluating trends, and they can accurately indicate the contribution of various sources to air quality problems if the spatial and temporal distributions of the sources are such that the sources contribute approximately uniformly to air quality degradation.

When the objective is prediction of the effect on local air quality due to a proposed change in emissions, a more detailed emissions inventory is necessary. In this case, the temporal distribution of emissions distinguishes between different seasons and between workdays and holidays. The spatial distribution is useful in analyzing the effects of specific emissions on air quality in specific locations. This type of inventory is appropriate for estimating the air quality impact of a new oil refinery or an increase in population in part of an urban area.

Inventories similar to that shown in Table 16 are maintained for most parts of the United States by the individual states and by local air pollution agencies (if any). More detailed information is kept in many areas, and some cities (e.g., Los Angeles, San Francisco, and St. Louis) have been the subjects of federally funded studies that have included the compilation of extremely detailed emissions inventories. In addition, the EPA maintains a detailed centralized national emissions file for point sources called the NEDS (National Emissions Data System) [14], which is compiled from data supplied by local agencies.

Emissions inventories distinguish between point, corridor (often called line), and area sources. The locations and emissions rates of point sources can be accurately described in most cases. Corridor sources, such as railroads and aircraft, have reasonably well-known locations, and their emissions rates can be estimated according to operations. Area sources are agglomerates of small sources for which

TABLE 16. SAMPLE STATE-COMPILED ANNUAL EMISSIONS INVENTORY FOR AIR QUALITY CONTROL REGION 036, METROPOLITAN DENVER

Emission categories	Pollutant, tons per year				
	Particulates	Sulfur oxides	Nitrogen oxides	Hydro-carbons	Carbon monoxide
GRAND TOTAL	45,497	25,144	98,984	119,366	600,606
-AREA	20,836	10,596	76,027	112,233	581,019
-POINT	24,661	14,548	22,957	7,133	19,587
FUEL COMBUSTION-AREA	13,253	6,746	11,589	779	1,962
-POINT	10,468	12,362	21,972	268	817
External Combustion-area	13,253	6,746	11,589	779	1,962
-point	10,468	12,362	21,972	268	817
Residential Fuel-area	411	146	2,519	332	895
Anthracite Coal	0	0	0	0	0
Bituminous Coal	54	61	8	54	242
Distillate Oil	15	64	18	4	7
Residual Oil	0	0	0	0	0
Natural Gas	310	19	2,480	248	620
Wood	33	2	13	26	26
Electric Generation-point	8,721	11,462	18,192	191	591
Anthracite Coal	0	0	0	0	0
Bituminous Coal	8,644	9,920	7,228	136	350
Lignite	0	0	0	0	0
Residual Oil	2	42	28	1	1
Distillate Oil	22	1,375	1,067	20	30
Natural Gas	53	124	9,870	34	209
Process Gas	0	0	0	0	0
Coke	0	0	0	0	0
Solid Waste/Coal	0	0	0	0	0
Other	0	0	0	0	0
Industrial Fuel-area	12,206	5,286	5,857	244	613
-point	1,370	714	3,182	42	143
Anthracite Coal-area	0	0	0	0	0
-point	0	0	0	0	0
Bituminous Coal-area	11,731	3,429	2,256	150	301
-point	1,264	437	570	17	44
Lignite-point	0	0	0	0	0
Residual Oil-area	222	1,536	580	29	39
-point	31	208	85	4	6
Distillate Oil-area	108	312	434	22	29
-point	25	66	101	5	7
Natural Gas-area	144	9	2,587	43	244
-point	50	3	2,426	15	87
Process Gas-area	0	0	0	0	0
-point	0	0	0	0	0
Coke-point	0	0	0	0	0
Wood-area	0	0	0	0	0
-point	0	0	0	0	0
Liquid Petroleum Gas-point	0	0	0	0	0
Bagasse-point	0	0	0	0	0
Other-point	0	0	0	0	0
Commercial-Institutional Fuel-area	637	1,314	3,213	203	454
-point	378	187	598	35	83
Anthracite Coal-area	0	0	0	0	0
-point	0	0	0	0	0
Bituminous Coal-area	164	108	43	9	34
-point	317	76	30	2	4
Lignite-point	0	0	0	0	0
Residual Oil-area	83	576	217	11	14
-point	14	57	38	2	3
Distillate Oil-area	215	620	861	43	57
-point	9	51	36	2	2
Natural Gas-area	174	10	2,091	139	348
-point	37	2	495	30	74
Wood-area	0	0	0	0	0
-point	0	0	0	0	0
Liquid Petroleum Gas-point	0	0	0	0	0
Miscellaneous-point	0	0	0	0	0
Internal Combustion-point	0	0	0	0	0
Electric Generation	0	0	0	0	0
Distillate Oil	0	0	0	0	0
Natural Gas	0	0	0	0	0
Diesel Fuel	0	0	0	0	0
Industrial Fuel	0	0	0	0	0
Distillate Oil	0	0	0	0	0
Natural Gas	0	0	0	0	0
Gasoline	0	0	0	0	0
Diesel Fuel	0	0	0	0	0

TABLE 16 (Concluded)

Emission categories	Pollutant, tons per year				
	Particulates	Sulfur oxides	Nitrogen oxides	Hydro-carbons	Carbon monoxide
Other	0	0	0	0	0
Commercial-Institutional	0	0	0	0	0
Diesel Fuel	0	0	0	0	0
Other	0	0	0	0	0
Engine-Testing	0	0	0	0	0
Aircraft	0	0	0	0	0
Other	0	0	0	0	0
Miscellaneous	0	0	0	0	0
INDUSTRIAL PROCESS-POINT	13,815	2,150	904	6,747	17,689
Chemical Manufacturing	0	0	34	222	7
Food/Agriculture	248	0	0	0	0
Primary Metal	1	50	0	0	0
Secondary Metals	0	65	0	0	0
Mineral Products	13,409	0	0	60	47
Petroleum Industry	132	2,035	834	934	17,635
Wood Products	10	0	0	6	0
Evaporation	10	0	0	5,446	0
Metal Fabrication	0	0	0	0	0
Leather Products	0	0	0	0	0
Textile Manufacturing	0	0	0	0	0
Inprocess Fuel	4	0	36	2	0
Other/Not Classified	0	0	0	78	0
SOLID WASTE DISPOSAL-AREA	464	42	107	940	2,724
-POINT	378	36	81	118	1,081
Government-point	0	0	0	0	0
Municipal Incineration	0	0	0	0	0
Open Burning	0	0	0	0	0
Other	0	0	0	0	0
Residential-area	320	11	53	783	2,310
On Site Incineration	195	3	6	548	1,643
Open Burning	126	8	47	236	667
Commercial-Institutional-area	131	29	49	144	381
-point	377	21	63	100	1,021
On Site Incineration-area	82	26	31	51	117
-point	99	21	25	25	84
Open Burning-area	50	3	19	93	264
-point	319	0	38	75	938
Apartment-point	0	0	0	0	0
Other-point	0	0	0	0	0
Industrial-area	12	3	4	13	33
-point	0	15	18	18	60
On Site Incineration-area	8	3	3	5	11
-point	0	15	18	18	60
Open Burning-area	4	0	1	8	21
-point	0	0	0	0	0
Auto Body Incineration-point	0	0	0	0	0
Other-point	0	0	0	0	0
Miscellaneous-point	0	0	0	0	0
TRANSPORTATION-AREA	7,119	3,808	64,331	101,765	576,333
Land Vehicles	6,723	3,632	63,053	92,537	570,820
Gasoline	5,338	1,487	45,426	89,404	562,421
Light Vehicles	4,503	1,167	36,803	63,942	409,599
Heavy Vehicles	812	308	8,356	24,711	144,321
Off Highway	23	12	266	750	8,502
Diesel Fuel	1,385	2,145	17,627	3,133	8,399
Heavy Vehicles	552	772	6,705	969	4,855
Off Highway	381	341	4,223	462	1,190
Rail	453	1,032	6,699	1,702	2,354
Aircraft	395	174	1,275	2,301	5,090
Military	259	49	124	602	646
Civil	58	12	52	257	1,467
Commercial	78	113	1,098	1,443	2,977
Vessels	0	1	4	133	423
Bituminous Coal	0	0	0	0	0
Diesel Fuel	0	0	0	0	0
Residual Oil	0	0	0	0	0
Gasoline	0	1	4	133	423
Gas Handling Evaporation Loss	0	0	0	6,794	0
MISCELLANEOUS-AREA	0	0	0	8,749	0
Forest Fires	0	0	0	0	0
Structural Fires	0	0	0	0	0
Slash Burning	0	0	0	0	0
Frost Control	0	0	0	0	0
Solvent Evaporation Loss	0	0	0	8,749	0

Source: Ref. 14.

specific locations and quantities are not known; for the purpose of an emissions inventory, it is usually assumed that these sources are distributed according to population.

1. Point Source Inventories

Point source emissions inventories estimate the emissions of each source individually using one of the following methods:

- Stack test results or other emissions measurements.
- Materials balance using engineering knowledge and expertise concerning the nature of the process (e.g., calculating SO_2 emissions from a power plant on the basis of the volume and sulfur content of the incoming fuel).
- Emissions factors.

Emissions factors are available from the EPA's "Compilation of Air Pollutant Emission Factors" [25], which is continually updated with published supplements. This document covers an impressive list of processes that produce pollutant emissions. The list includes utility and industrial operations, mobile sources of all kinds, waste disposal processes, and agricultural operations. For each item, a ratio of emissions to throughput of each of the relevant pollutants is included. For example, motor vehicle emissions are given in grams per mile, aircraft emissions in kilograms per hour in various operating modes, and coal combustion emissions in kilograms per metric ton of coal burned. Therefore, in the absence of emissions measurements or materials balance calculations, the emissions from most point sources can be estimated using the procedures outlined by the EPA in Refs. 25 and 35.

2. Area Source Inventories

For an inventory of nonvehicular emissions, the following area source categories are considered:

> Stationary source fuel consumption
> Solid waste disposal
> Evaporative losses
> Vessels
> Off-highway fuel use.

Emissions from fuel combustion are usually estimated on the basis of the quantity and type of fuel sold to each source category (e.g., residential heating; commercial and institutional heating, which includes stores, schools, public buildings, and hospitals; and industrial fuel use by manufacturers too small to be classified as point sources). Often local fuel dealers can supply the necessary data on fuel sales, and Ref. 25 contains the appropriate emissions factors to estimate air pollutants from these sources. If local dealers do not supply fuel usage data, assumptions are made on the basis of census data and statewide totals. Details on the methods approved by the EPA are available in Ref. 35.

Most solid waste disposal occurs in land fill or large municipal incinerators; however, small incinerators and backyard burning may be significant sources of pollutants. For some areas, surveys of waste disposal practices may be useful in determining the quantity of solid waste in the area. Alternatively, a nationwide average can be used [35]. In either case, the total can be apportioned spatially according to population using the appropriate emissions factors taken from Ref. 25.

Evaporative losses from gasoline storage or solvent use operations can be estimated as a portion of regional sales distributed according to population. If the solvent sales data are unavailable, emissions from evaporation can be calculated by assuming that they are proportional to population and using the emissions factors found in Ref. 25.

Emissions from vessels are based on estimates of fuel consumption and vessel operations data. Similarly, emissions from the operation of off-highway vehicles (e.g., tractors, lawnmowers, snowmobiles, construction equipment) can be estimated by applying an annual average per-unit fuel consumption rate for each type of equipment. The appropriate data on the number and type of off-highway vehicles are available from survey publications: "Census of Agriculture" [36] and "County Business Patterns" [37]. In addition, off-highway fuel usage data are available from the Bureau of Mines. Such emissions are apportioned according to land use patterns.

In summary, the basic principle for estimating emissions for all these categories is the same: first determine the amount of fuel (or solvent) used by each type of emitter and then apply the appropriate emissions factor. Data on fuel usage are available from a variety of sources depending on the operation; emissions factors have been estimated and published by the EPA for most categories. The emissions are apportioned according to land use or population distribution.

3. Corridor Source Inventories (Nonvehicular)

This category includes railroad and aircraft operations, both of which are considered separately because the location of the corridor in which these emissions occur is well known, though the exact quantities and locations of the emissions may not be.

Emissions factors are available for various aircraft in different modes of operations [25], and detailed data on flight operations are usually available. Therefore, estimating total emissions is relatively straightforward. For a spatially stratified inventory, it is necessary to determine the emissions along each flight path, for which data are available at major airports. Because aircraft emissions occur aloft, they have a different effect on ground-level concentrations than that of ground-level sources. This difference is explored further in later chapters.

Railroad emissions estimates are based on the type and number of trains operating in each corridor in the area. This information is often difficult to obtain, but data on fuel use by state are usually available and can be apportioned to smaller regions on the basis of the number of miles of track within the region. For further spatial stratification, some corridor-by-corridor operations data must be used. Although railroad yard operations may cause significant emissions, estimation of their quantity is difficult. The current EPA guidelines call for ". . . doubling the measured track mileage in counties where it is known there are significant yard operations" [35]. Unfortunately, this method does not allow proper spatial estimation. Railroad emissions are thus surprisingly difficult to estimate, but they do not appear to contribute a major share of emissions in most areas.

E. EMISSIONS STANDARDS

The 1970 Clean Air Act required the states to design implementation plans consisting of comprehensive strategies for controlling air quality so that it meets the national standards. The Act also mandates the promulgation of emissions standards for newly constructed facilities of many types. These so-called New Source Performance Standards are presented in Table 17. Emissions control efforts since then have been driven by these two requirements.

The requirements for the state implementation plans do not specify the particular types of control to be used, but rather offer a set of control options. For stationary sources, the two main options are the use of cleaner-burning fuel or the addition of control devices to reduce the emissions factors. Each state has developed its own strategy, resulting in different sets of emissions standards from state to state. The New Source Performance Standards, however, are set by the federal government and apply to the nation as a whole. They provide

TABLE 17. FEDERAL NEW SOURCE PERFORMANCE STANDARDS FOR STATIONARY SOURCES OF AIR POLLUTANTS

Source Type	Operating Unit to Which Standards Apply	Pollutant	Maximum Emissions† (per unit of throughput) or Maximum Opacity (percent)	Unit of Throughput Used as a Measure	Comments
Fossil fuel fired steam generators ≥263 x 10^6 kcal/hr heat input or ≥250 x 10^6 Btu/hr heat input	Any affected facility*	Particulates	0.18 g 0.10 lb	10^6 cal total heat input 10^6 Btu total heat input	
		Opacity§	20%		
		Sulfur dioxide	1.4 g 0.8 lb	10^6 cal total heat input 10^6 Btu total heat input	For liquid fossil fuel.
			2.2 g 1.2 lb	10^6 cal total heat input 10^6 Btu total heat input	For solid fossil fuel.
			$\frac{y(1.4) + z(2.2)}{y + z}$	10^6 cal total heat input	y = fraction of total heat input from liquid fuel. z = fraction of total heat input from solid fuel.
		Nitrogen oxides (expressed as NO_2)	0.36 g 0.20 lb	10^6 cal total heat input 10^6 Btu total heat input	For gaseous fossil fuel.
			0.54 g 0.30 lb	10^6 cal total heat input 10^6 Btu total heat input	For liquid fossil fuel.
			1.26 g 0.70 lb	10^6 cal total heat input 10^6 Btu total heat input	For solid fossil fuel.
			$\frac{x(0.36) + y(0.54) + z(1.26)}{x + y + z}$	10^6 cal total heat input	x = fraction of total heat from gaseous fuel. y = fraction of total heat from liquid fuel. z = fraction of total heat from solid fuel. NO_x standards do not apply if liquid or solid fuel containing more than 2.5% by weight of sulfur is used for any fraction of the total heat input.

TABLE 17 (Continued)

Source Type	Operating Unit to Which Standards Apply	Pollutant	Maximum Emissions† (per unit of throughput) or Maximum Opacity (percent)	Unit of Throughput Used as a Measure	Comments
Petroleum refineries	Fluid catalytic cracking unit catalyst regenerator, fluid catalytic cracking unit, or incinerator waste heat boiler	Particulates	1 kg	1000 kg of coke burn-off in catalyst regenerator	If additional liquid or solid fuels are used in the incinerator waste heat boiler, additional particulate emissions are allowable in the following amounts: 0.18 g per 10^6 cal of total heat input and 0.10 lb per 10^6 Btu of total heat input.
			1 lb	1000 lb of coke burn-off in catalyst regenerator	
		Opacity§	30%	--	Not to be exceeded for more than three minutes in any hour.
	Fluid catalytic cracking unit catalyst regenerator	Carbon monoxide	0.050% by volume	--	
	Fuel gas combustion device	Sulfur dioxide	0.23 g/dscm**	--	Maximum allowable concentration in fuel gas. If SO_2 emissions control devices are used, they must be at least as effective as if this condition had been met.
			0.10 g/dscf††	--	
Nitric acid production	Any affected facility*	Nitrogen oxides (expressed as NO_2)	1.5 kg	Per metric ton of 100% nitric acid produced	
			3.0 lb	Per ton of 100% nitric acid produced	
		Opacity	10%		

TABLE 17 (Continued)

Source Type	Operating Unit to Which Standards Apply	Pollutant	Maximum Emissions[+] (per unit of throughput) or Maximum Opacity (percent)	Unit of Throughput Used as a Measure	Comments
Sulfuric acid production	Any affected facility[*]	Sulfur dioxide	2 kg	Per metric ton of 100% sulfuric acid produced	
			4 lb	Per ton of 100% sulfuric acid produced	
		Sulfuric acid mist	0.075 kg	Per metric ton of 100% sulfuric acid produced	
			0.15 lb	Per ton of 100% sulfuric acid produced	
		Opacity[§]	10%		
Incinerators	Any affected facility	Particulates	0.18 g/dscm[**] 0.08 g/dscf[††]		Maximum allowable concentrations in emitted gases (corrected for 12% CO_2).
Portland cement plants	Kiln	Particulates	0.15 kg	Per metric ton of feed to kiln (dry weight)	
			0.30 lb	Per ton of feed to kiln (dry weight)	
		Opacity	10%		
	Any affected facility	Opacity	10%		

TABLE 17 (Concluded)

Source Type	Operating Unit to Which Standards Apply	Pollutant	Maximum Emissions[†] (per unit of throughput) or Maximum Opacity (percent)	Unit of Throughput Used as a Measure	Comments
Lead smelters	Blast (cupola) or reverberatory furnace	Particulates	50 mg/dscm[**] 0.022 g/dscf[††]		Maximum allowable concentrations of particulates in ejected gases.
		Opacity[§]	20%		
	Pot furnace	Opacity	10%		
Brass and bronze input production plants	Reverberatory furnace	Particulates	50 mg/dscm 0.022 g/dscf		Maximum allowable concentrations of particulates in ejected gases.
		Opacity	20%		
	Blast (cupola) or electric furnace	Opacity	10%		
Iron and steel plants	Any affected facility[*]	Particulates	50 mg/dscm 0.022 g/dscf		Maximum allowable concentrations in ejected gases.
Sewage treatment plants	Sewage sludge incinerator	Particulates	0.65 g	Per kilogram of dry sludge input	
			1.30 lb	Per ton of dry sludge input	
		Opacity	20%		

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[*] The term "affected facility" refers to any plant or unit that falls within a specified category.

[†] Allowable emissions are specified either as the allowable concentrations of pollutants in emitted gases or as allowable emissions for the specified measure of the throughput of the plant.

[§] Opacity refers to the fraction by which emissions reduce the transmission of light. In all the above cases where a violation of the opacity standards occurs solely because of the presence of chemically uncombined water, such violations are exempted.

[**] Dry standard cubic meter.

[††] Dry standard cubic foot.

Source: Ref. 38

for stringent, controlled emissions levels; these regulations are expected to expedite the development of control technologies compatible with these goals.

F. CONTROL METHODS

Pollutant emissions from most sources can be reduced by

- > Process changes. Changing the air-to-fuel ratio in a boiler to reduce NO_x emissions is one example.
- > Fuel changes. The use of low-sulfur coal or fuel oil to reduce SO_x emissions is a common example.
- > Add-on devices. The addition of a floating roof to a tank that stores petroleum products reduces HC emissions by reducing vaporization within the tank.

Changing to low-sulfur fuels has been the major means of SO_2 control to date. Conversion to nuclear or solar energy can be viewed as a change in both fuel and process. Other proposals for reducing emissions have included using methanol made from coal as a fuel because it is a relatively clean-burning source of energy.

Add-on devices are widely used to reduce emissions from processes producing substantial quantities of particulates. Filters of various forms (e.g., screens, layers of paper, sand) are selected for use on the basis of the size and kind of particulates to be removed, the nature of the gaseous effluent, and the cost and efficiency of the filters. Another add-on device for removing particulates is the electrostatic precipitator, which charges the particulates and then collects them on an electrically grounded surface. Scrubbers can also be used to remove particulates; they first wet the effluent to capture the particulates within small bubbles and then remove them on a collecting surface.

Gaseous pollutants can be removed with a scrubber using a liquid in which the pollutant is highly soluble. SO_2, NO_x, some hydrocarbons, and several other pollutants can be removed using this technique. Adsorption of gaseous pollutants on a solid surface is effective for removing light hydrocarbons, SO_2, water vapor, and other pollutants, depending upon the composition of the surface used. A third technique uses cooling to cause a gaseous pollutant to condense out of the effluent; this technique is often applied for hydrocarbon control. Another device effective for removing most hydrocarbon emissions is the burning of combustible gases to produce CO_2 and water.

The information presented here on control devices merely outlines some of the basic technologies of an expanding field. The EPA monitors developments in control technology for most industries and can supply up-to-date information.

G. SUMMARY

This chapter presents an outline of the types of nonvehicular sources that contribute to air pollution problems. The following issues have been treated:

> What kinds of sources are significant.
> What data are available to calculate emissions totals.
> What procedures are usually followed in calculating emissions totals.
> What emissions standards apply.

This information is used in Chapter VI in assessing the relative contributions of vehicular, nonvehicular, and natural emissions to air quality degradation.

V NATURAL EMISSIONS

The third major category of emissions are those caused by naturally occurring processes. The scent of a pine forest, for example, is caused by hydrocarbon emissions from the trees, emissions that can interact with anthropogenic or natural NO_x to produce ozone. In many areas natural sources account for a significant portion of pollutant concentrations, and so they must be considered in air quality analysis and planning. Unfortunately, relatively little is known about emissions rates of natural sources. Because some types of natural emissions from vegetation increase with temperature and solar radiation, and perhaps also with humidity, and because natural sources tend to emit slowly over large areas, their emissions rates are difficult, if not impossible, to measure. Thus the effects of natural sources are usually considered as part of background pollutant concentrations, which are defined loosely as the concentrations in air that is unaffected by local emissions. These quantities, usually measured upwind of the region of interest to the analysis, include pollutants from both natural and distant (and diffused) anthropogenic emissions.

The highway planner may be satisfied with the understanding that background concentrations must be accounted for in air quality analyses, without distinguishing between natural and distant anthropogenic sources. However, since naturally occurring concentrations are significant in many situations, the material in this chapter is provided to give some understanding of natural emissions and the difficulties encountered in their quantification. It also provides an indication of what species are likely to be found in various environments, e.g., near oceans, forests, deserts, swamps, and so forth.

A large number of particulate and gaseous pollutants are produced by natural processes. Particles of various compositions arise from windblown dust, forest fires, volcanoes, and sea spray. Gases produced by natural processes include the five gaseous pollutants of main interest in this report, namely CO, reactive hydrocarbons (HC), NO_x, SO_2, and ozone, as well as hydrogen sulfide, ammonia, and methane. The latter three pollutants are of interest because they can be converted into or promote the formation of the former five.

Table 18 presents estimated yearly global emissions rates for these pollutants, indicating their relative emissions from anthropogenic and natural sources. Note that for most pollutants natural emissions exceed anthropogenic emissions on a global basis; however, any attempt to compare these data with the concentration at any given location is meaningless without considering the spatial, seasonal, and diurnal variations of emissions. In fact, for some pollutants, the natural sources (such as volcanoes and forests in the case of SO_2 and reactive hydrocarbons, respectively) may be so far removed from major anthropogenic sources that the concentrations of those pollutants in various places are attributable almost entirely to either natural or anthropogenic sources

Natural emissions of some pollutants exhibit diurnal or seasonal variations. For example, bacterial action, which releases NO_x and other pollutants, is greatly reduced during winter in cold areas. Emissions of reactive hydrocarbons occur predominantly from the foliage of trees, and the rate of emission depends on both the light intensity and the temperature, which vary substantially both diurnally and seasonally. Furthermore, natural emissions may differ significantly from year to year because of yearly variations in total rainfall, cloud cover, and temperature.

The brief discussion above illustrates the complexity of evaluating the relative contributions of natural and anthropogenic emissions to pollutant concentrations at any given time and location. For most pollutants, insufficient data or knowledge of the source exist for even crude quantification of the spatial and temporal variations of natural emissions. Enough is known about the sources of some pollutants, however,

TABLE 18. WORLDWIDE EMISSIONS OF SELECTED POLLUTANTS

	Major Sources		Estimated Emissions (kg)				
Pollutant	Anthropogenic	Natural	Anthropogenic	Natural	Estimated Residence Time	Solubility in Water*	Major Removal Mechanisms
Carbon monoxide	Auto exhaust, combustion processes	Oxidation of methane, photodissociation of CO_2, forest fires, oceans	360×10^9	3000×10^9	<0.5 years	0.00284	Soil absorption, chemical oxidation
Reactive hydrocarbons	Auto exhaust, combustion of oil	Biological processes in forests	27×10^9	175×10^9	--	--	Photochemical oxidation
Nonreactive hydrocarbons	Auto exhaust, combustion of oil	Biological processes in swamps	70×10^9	300×10^9	16 years (CH_4)	6.45×10^{-4} (CH_4)	Biological action
Nitric oxide	Combustion	Bacterial action in soil, photodissociation of N_2O and NO_2	53×10^9	768×10^9	5 days	0.00618	Oxidation to NO_2
Nitrogen dioxide	Combustion	Bacterial action in soil, oxidation of NO				--	Photochemical reactions; oxidation to nitrate; scavenging
Ammonia	Coal burning, fertilizer, waste treatment	Biological decay	4×10^9	170×10^9	7 days	62.9	Reaction with SO_2; oxidation to nitrate; scavenging
Sulfur dioxide	Combustion of coal and oil	Volcanoes, forest fires	65×10^9	2×10^7	4 days	11.3	Oxidation to sulfate before or after absorption by oarticulates; soil/surface water absorption
Hydrogen sulfide	Chemical processes, sewage treatment	Volcanoes, biological decay	3×10^9	100×10^9	2 days	0.385	Oxidation to SO_2
Ozone	No direct emissions, but produced from anthropogenic HC and NO_x emissions	Tropospheric reactions and transport from the stratosphere	--	--	--	--	Photochemical reactions, absorption by land surfaces (soil and vegetation) and surface water

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* In grams per 100 grams of H_2O at 20°C.

Sources: Refs. 39 and 40.

to permit qualitative statements about their emission variations. Using such information, one can speculate on the possible contribution of natural emissions to measured concentrations. The following sections discuss the natural sources of selected pollutants.

A. CARBON MONOXIDE

Recent discoveries of CO sources indicate that natural sources yield about ten times more CO than all anthropogenic sources in the northern hemisphere. For example, as much as 220 x 10^9 kg of CO per year may be released from the ocean [41,42]. Other, less important sources include volcanoes, marshes, forest fires, electrical storms, photodissociation of CO_2, and oxidation of natural emissions of reactive hydrocarbons. The most important source of CO may be the oxidation of methane, accounting for perhaps 900 x 10^9 kg of CO per year [43]. Since methane sources are widely distributed, CO is probably produced relatively uniformly throughout the world. The slow oxidation of methane allows time for wide dispersion of the CO produced. On a temporal basis, one would expect the production of CO from this source to peak during the summer months because the photochemical reactions that lead to the oxidation of methane are sunlight-dependent. Other sources of CO, with the exception of emissions from the ocean, are expected to be intermittent, and some sources are restricted to specific areas. Although anthropogenic emissions increase annually, the global mean CO concentration has not changed, indicating the presence of strong natural sinks as well as sources.

B. HYDROCARBONS

Plant species are known to release appreciable quantities of volatile hydrocarbons into the atmosphere. For example, atmospheric concentrations of organic substances such as isoprene and pinenes have been shown to vary diurnally and to correlate with the mass of foliage in forest and field regions [44]. Hydrocarbon samples taken at two rural sites in Virginia during the spring and early summer of 1974 indicated that nonmethane hydrocarbon levels exceeded 0.24 ppmC (6 to 9 a.m. average)--the national guideline--during most of the sampling period [45,46]. They also indicated that the natural emissions are higher in the spring than in the summer or winter months. The rate of natural hydrocarbon emissions is dependent not only on the plant species, but also on environmental factors that vary geographically, seasonally, and diurnally.

C. PARTICULATES

A suspension of solid or liquid particulate matter in the atmosphere is called an aerosol. Typical constituents of atmospheric aerosols include silicates, salts such as $NaCl$, $MgCl_2$, $MgSO_2$, Na_2SO_4, $NaNO_3$, $(NH_4)_2SO_4$, NH_4Cl, and NH_4NO_3, acids such as H_2SO_4 and organic acids, metal oxides, organic combustion products, biological material, volcanic material, and extraterrestrial material. Their sources include volcanoes, the ocean, soil and rock, grass, brush, and forest fires, pollen, and meteoric material. Using data obtained from the National Air Surveillance Network, one can estimate the contributions of these natural sources to aerosol concentrations. Table 19 shows the distribution of selected cities by population and average particle concentration for the period from 1951 to 1967. Table 20 shows the corresponding particulate concentration distribution for selected nonurban monitoring sites. As these data indicate, average suspended particulate mass concentrations range from about 10 $\mu g/m^3$ in remote nonurban areas to about 60 $\mu g/m^3$ near urban locations. In urban areas, averages range from 60 to 220 $\mu g/m^3$, depending on the size of the city and its industrial activity. In heavily polluted areas, concentrations up to 2000 $\mu g/m^3$ have been recorded [8]. Hence, if the natural sources that affect the concentrations at remote locations emit comparable amounts of pollutants at the urban locations in the sample, then the contribution of natural particulates to the aerosol concentration measured at the urban locations is relatively small.

TABLE 19. DISTRIBUTION OF SELECTED CITIES BY POPULATION CLASS AND PARTICLE CONCENTRATION, 1957 TO 1967

[Avg. particle concentration $\mu g/m^3$]

Population class	<40	40 to 59	60 to 79	80 to 99	100 to 119	120 to 139	140 to 159	160 to 179	180 to 199	>200	Total cities in table	Total cities in U.S.A.
>3 million	----	----	----	----	----	----	1	----	1	----	2	2
1–3 million	----	----	----	----	----	----	2	1	----	----	3	3
0.7–1 million	----	----	1	----	2	----	4	----	----	----	7	7
400–700,000	----	----	----	4	5	6	1	1	1	----	18	19
100–400,000	----	3	7	30	24	17	12	3	2	1	99	100
50–100,000	----	2	20	28	16	12	6	5	1	3	93	180
25–50,000	----	5	24	12	12	10	2	1	2	3	71	--------
10–25,000	----	7	18	19	9	5	2	3	1	----	64	[a] 5,453
<10,000	1	5	7	15	11	2	1	2	----	----	44	--------
Total urban	1	22	77	108	79	52	31	16	8	7	401	--------

[a] Incorporated and unincorporated areas with population over 2,500.

Source: Ref. 8.

TABLE 20. DISTRIBUTION OF SELECTED NONURBAN MONITORING SITES BY CATEGORY OF URBAN PROXIMITY, 1957 TO 1967

Category	Average particle concentrations, $\mu g/m^3$				Total
	<20	20–39	40–59	60–79	
Near urban [a]	-----	1	3	1	5
Intermediate [b]	-----	5	6	-----	11
Remote [c]	4	5	-----	-----	9
Total nonurban	4	11	9	1	25

[a] Near urban—although located in unsettled areas, pollutant levels at these stations clearly indicate influence from nearby urban areas. All of these stations are located near the northeast coast "population corridor."

[b] Intermediate—distant from large urban centers, some agricultural activity, pollutant levels suggest that some influence from human activity is possible.

[c] Remote—minimum of human activity, negligible agriculture, sites are frequently in state or national forest preserve or park areas.

Source: Ref. 8.

The rates at which suspended particulates are emitted by natural sources vary both spatially and temporally, with the possible exception of particulates from meteors. The time dependence of emissions from large intermittent emitters such as volcanoes and wild fires is highly irregular. However, when such emissions do occur, they can significantly affect particulate concentrations hundreds or thousands of miles from the source. Emissions of salt particles from the ocean, which are obviously more regular, have been measured in significant quantities even at large distances inland. Typically, the total mass of salt particles 4 km inland is 15 percent of that at the coast, and the concentration 30 km inland is about 8 percent of that at the coast [47].

Particles also enter the atmosphere as a result of wind erosion of soil and rocks. Dust generated in this way can be transported over very long distances. For example, an estimated 10 million tons of red dust from Africa were deposited in England in 1903, and more recently, dust from the African deserts has been collected along the coast of Barbados [48]. Locally, pollen can contribute very high concentrations of aerosols to the environment during the growing season, depending on local wind, rainfall, and, to some extent, man's activities.

The California Aerosol Characterization Experiment (ACHEX) was conducted in 1974 partly to determine the contributions of sea salt and soil dust to the total aerosol. Estimates of aerosol mass concentration at five locations are listed in Table 21. The results for Fresno indicate that in a 24-hour period soil dust can contribute substantially to the total aerosol mass. However, a significant fraction of soil dust may be associated with anthropogenic activities, such as agriculture, and is thus not strictly a natural pollutant.

D. NITROGEN-CONTAINING GASES

Oxides of nitrogen--particularly nitric oxide and nitrogen dioxide--are important air pollutants partially because they interact with

TABLE 21. 24-HOUR SOURCE ANALYSIS BASED ON CHEMICAL ELEMENT BALANCE FOR SELECTED CALIFORNIA SITES

(micrograms per cubic meter)

Source	Pasadena 9-20-72	Pomona 10-24-72	Riverside 9-20-72	Fresno 9-1-72	San Jose 10-20-72
Sea salt	0.7 ± 0.06	5.7 ± 0.6	1.3 ± 0.1	0 ± 0.4	19.4 ± 0.5
Soil dust	19.8 ± 0.1	15.1 ± 0.5	28.5 ± 0.9	51.1 ± 2.8	29.6 ± 1.1
Total mass	86.7	161.5	114.6	108.5	133.5
Km from ocean	41	36	53	174	43

Source: Ref. 10.

hydrocarbons to produce photochemical oxidants. Although the most abundant oxide of nitrogen in the lower atmosphere is nitrous oxide (N_2O), it does not contribute significantly to the formation of tropospheric ozone, so it is not discussed below.

Relatively little is known about natural sources of NO and NO_2, but there is considerable evidence that they are released from soil. Measurements of NO and NO_2 concentrations in widely separated rural areas of the country have shown that there is a natural background level ranging from a few thousandths of a part per million to about 0.01 ppm [49]. Simultaneous measurements of NO_2 concentrations at 30 and 120 feet above the earth have revealed that the former are always greater than the latter [50], suggesting that the earth is a source of NO_2. Unfortunately, production rates of NO and NO_2 by soils are difficult to measure or estimate, and good data are lacking. It has been estimated that biological sources of NO and NO_2 contribute 23.4×10^{10} kg (as nitrogen) per year compared with 1.6×10^{10} kg per year from anthropogenic sources [51].

Although there is little agreement on the magnitude of NO and NO_2 emissions from natural sources, measurements of these gases in rural atmospheres indicate such low concentrations that if natural emissions are significant, then strong sinks must also exist. For example, measurements prior to 1970 in many parts of the world indicate background NO_2 concentrations generally below 0.005 ppm [52-54]. In 1972, the mean one-hour-average NO_2 concentration measured at a rural Maryland site was 0.007 ppm and the NO concentration was generally below the limit of detectability of the instrument [55].

Ammonia (NH_3) is important for its role in the formation of aerosols and its possible role in producing oxides of nitrogen. Some researchers contend that soil releases little NO and NO_2 compared with that produced by oxidation of atmospheric ammonia, which they think produces 7×10^{10} kg of NO_x (as nitrogen) per year [56]. Most atmospheric ammonia results from the bacterial decomposition of organic material on the earth's surface. Although the ocean may contribute some NH_3 to the atmosphere, there has been no accurate measurement of it to date. It has been estimated that all of these biological sources together release about 10^{10} to 10^{12} kg of ammonia each year [51,57].

The spatial variations of emissions of NO_x and NH_3 are expected to follow closely the distribution of vegetation. Temporal variations are primarily seasonal fluctuations in the rate of emission of ammonia related to the changing water content of the soil. Also, all emissions of nitrogen-containing gases are temperature-dependent because they are related to bacterial decomposition of organic material, a process that is accelerated by hot weather.

E. SULFUR-CONTAINING GASES

The two primary sulfur-containing gases present in the atmosphere are hydrogen sulfide (H_2S) and sulfur dioxide (SO_2). Hydrogen sulfide reacts to form SO_2, which is considered to be detrimental to human health. SO_2 is also a precursor of sulfates, which can combine with moisture in the air to form sulfuric acid droplets, which in turn affect both plant and animal life.

The primary source of H_2S is decaying vegetation in swamps, bogs, and other land areas; it has also been suggested that the oceans may be a source of sulfides [58]. Little else is known about H_2S production; estimates of concentrations are the results of balancing sulfur budgets. However, the conditions under which hydrogen sulfide is produced can be specified since it is the product of the anaerobic decay of material by bacteria. Thus, the rate of production depends on temperature but not sunlight, and the rate of emissions of H_2S by decay processes should have a strong seasonal variation but only a weak diurnal variation. The spatial variation of hydrogen sulfide emissions should closely follow the distribution of vegetation.

Some researchers have concluded that the only significant natural source of SO_2 is volcanic activity [39]. Emissions of SO_2 from volcanoes have been estimated to be 10 to 100 times lower than anthropogenic emissions [59,60]. Thus, it appears that natural emissions of SO_2 are important only in the vicinity of volcanic sources.

F. OZONE

Ozone is not emitted from anthropogenic or natural sources; rather, it is formed in the atmosphere. Known ozone formation processes include: 1) photolysis of oxygen molecules in the stratosphere, 2) photochemical oxidation of methane, and 3) photochemical reactions involving hydrocarbons and nitrogen oxides in the lower atmosphere (i.e., the troposphere). The first two processes are natural sources of ozone. The last process, which is largely responsible for urban ozone concentrations, can be considered a natural or anthropogenic source or a mixture, depending on the sources of the HC and NO_x.

Ozone formed in the stratosphere can reach the ground by so-called stratospheric intrusions. Approximately 20 to 40 intrusions occur annually over the United States. Ozone injected into the troposphere during stratospheric intrusions can reach the ground either with or without the aid of precipitation. When precipitation is not involved, it appears that stratospheric ozone contributes one-hour-average ground-level concentrations no larger than 0.05 ppm. Where precipitation-induced downdrafts transport ozone to the ground, one-hour-average concentrations in excess of 0.20 ppm can occur, but the frequency of these occurrences is not known. Based on an analysis of regions of the United States where stratospheric intrusions are expected to occur, Figure 5 shows areas of the country where stratospheric ozone is expected to affect surface concentrations.

Thus, the NAAQS for photochemical oxidants (0.08 ppm) can be violated in the absence of anthropogenic sources in many locations. Since the formation of smog requires sunlight and large stratospheric injections occur in conjunction with precipitation, the events are relatively simple to distinguish. However, the applicable EPA regulations do not currently account for such events.

The photochemical oxidation of methane to produce ozone is very slow, so only nonmethane hydrocarbons are normally considered in analyzing urban ozone problems. Natural sources emit far more methane than other hydrocarbons, and some ozone is formed from this methane, air, NO_x, and sunlight [15,61,62]. It has been estimated that ozone concentrations in the troposphere resulting from methane oxidation are on the order of 0.01 ppm [15].

The third ozone formation process mentioned above involves photochemical reactions of hydrocarbons and nitrogen oxides. A recent study illustrates the difference in the ozone-forming potential by this process of purely rural air and rural air contaminated by aged urban pollutants [49]. Rural air was collected in transparent bags at Wooster,

Source of Map: Ref. 63.

FIGURE 5. ESTIMATED NORTHERN LIMIT OF REGION MOST LIKELY TO BE AFFECTED BY STRATOSPHERIC OZONE DURING SPRINGTIME INTRUSIONS. The heavy dashed line indicates the northern limit; hatched areas denote regions in which radioactive fallout associated with stratospheric intrusions has been detected.

Ohio, and Spring Valley, Idaho, and irradiated with natural sunlight. In the Midwest and on the East Coast, many rural areas are near urban centers. Hence, samples taken in Ohio are likely to contain some aged, or partially reacted, pollutants from urban areas.

The results of that study [49] indicated that the nonmethane hydrocarbon concentration at the Idaho site (considered not to be influenced by urban emissions) was 50 percent higher than in Ohio, and the NO concentration at the Idaho site was three times higher than at the Ohio site. Irradiation of the samples for six hours produced higher ozone concentrations at the Ohio site despite a slightly lower mean radiation flux. The study concluded that ozone concentrations in the range of 0.02 to 0.06 ppm could be attributed to natural emissions, whereas ozone in excess of 0.08 ppm was probably associated with urban precursors. A qualitative correlation was found between the ozone produced in captured air samples and their initial NO_x concentrations.

The same study also investigated the effect of adding NO_x to the rural air samples [49]. Oxides of nitrogen were added to both Ohio and Idaho samples to give approximately equal hydrocarbon-to-NO_x ratios of about 6. The ozone concentration in the Ohio air sample with added NO_x after five hours of irradiation was about 0.035 ppm, or one-half the ozone concentration in a similar sample without added NO_x. In contrast, the ozone produced in the Idaho air sample increased from 0.02 ppm to 0.075 ppm with added NO_x. Clearly, the hydrocarbons in the Ohio air sample differ from those in the Idaho sample. The Ohio air sample could thus be considered to contain already reacted hydrocarbons since the addition of NO_x did not activate further ozone formation. The degree of reaction may indeed be a contributing factor, but another may be different relative reactivities of hydrocarbons emitted from the natural sources in the two areas.

G. SUMMARY

It is clear that the quantification of natural emissions is an exceedingly difficult task, and relatively little progress has been made to date. Therefore, a regional natural emissions inventory is not considered a practical option in air quality analysis. Although a corridor-based natural emissions inventory might be possible, it would be of uncertain accuracy and little practical value. Consequently, comparison of the relative magnitudes of natural and anthropogenic emissions must be based on ambient concentration measurements rather than on emissions estimates. Specifically, when performing an air quality analysis one uses upwind concentration measurements to characterize clean air, that is, air not affected by local anthropogenic emissions. The techniques for performing this type of analysis are discussed in Chapter VI.

VI AIR QUALITY IN VARIOUS ENVIRONMENTS

In this chapter the focus of this report shifts from pollutant emissions to pollutant concentrations. The previous three chapters described emissions of CO, HC, particulates, NO_x, and SO_x from vehicular, other anthropogenic, and natural sources; this one describes in detail typical emissions and ambient concentrations of those pollutants and photochemical oxidants in selected urban areas. Transportation planners can use this material to develop an understanding of typical air quality and the contribution of motor vehicles to air pollution. This chapter also provides valuable background for the discussions in Chapters VII and VIII of the atmospheric processes that transform emissions into observed air quality. It begins with a discussion of available air quality data pertinent to the spatial and temporal scales of interest to transportation planners. Following that, air quality in rural and urban areas and roadway corridors is reviewed.

A. AVAILABLE AIR QUALITY DATA

1. Sources of Data

To obtain the available air quality data for a specific urban area, one must contact authorities such as the local EPA office, the local air pollution control board (if one exists), or the public health department. The earliest comprehensive collection of air quality data for many U.S. cities is presented in the air quality criteria documents published by the U.S. Department of Health, Education and Welfare [2,8,12,64,65,66]. Statistical summaries of air quality data are also routinely printed by the EPA, statewide enforcement bodies such as the California Air Resources Board (CARB), and local authorities such as the South Coast Air Quality Management District (SCAQMD) (formerly the Los Angeles Air Pollution

Control District or LAAPCD). The statistical analyses presented in these reports may be sufficient for planning purposes in many cases. Under the regulations for development of state implementation plans, all states are required to collect air quality data from all state-operated and locally operated monitoring stations and submit these data to the EPA each quarter. These data then become part of the National Aerometric Data Bank (NADB). The EPA analyzes these data and publishes annual national air quality and emissions trends reports [67], which contain useful summaries of air quality in many regions of the United States, including most major cities. Finally, special intensive monitoring efforts have been carried out in some locations. These studies often last several months and some of them include data obtained with airborne monitoring equipment pertaining to air quality and meteorology hundreds of meters aloft. Examples include the Regional Air Pollution Study (RAPS) in St. Louis and the Los Angeles Reactive Pollutant Program (LARPP). Such intensive studies provide a richer body of data than is normally available.

2. Monitoring Networks

Ambient pollutant concentrations are monitored routinely at many locations across the United States. Some monitoring stations are part of a nationwide network, such as the Continuous Air Monitoring Program (CAMP) or the National Air Surveillance Network (NASN); a statewide network, such as the Statewide Cooperative Air Monitoring Network (SCAN) in California; or a local network, such as the stations in the Southern California air basin. In many urban areas, stations are operated and maintained by local air pollution control boards, such as the SCAQMD. In other cases, stations are operated by either the local EPA office or another enforcement body.

Ambient air quality monitoring stations can be located according to population, pollutant sources, or background concentrations. Population-oriented stations are in urban localities, which usually places them sufficiently far from major individual pollutant sources (such as power plants) to indicate average concentrations over a small region (about one square kilometer). The majority of monitoring sites in the measurement networks are of this type. Tables 22 and 23 show the distribution of particulate and SO_2 monitoring stations across the United States.

The measurement techniques and sampling intervals used depend on the type of pollutant and the monitoring network. Measurements can be made continuously or intermittently, and sampling intervals can range from 5 minutes to 24 hours. Under most circumstances, pollutant concentrations are not reported for averaging intervals of less than one hour. In some cases, different techniques for measuring concentrations of a particular pollutant can cause significant differences in the values obtained. For example, the NO_2 concentrations measured at CAMP and NASN monitoring sites were found to differ consistently by a factor of three for six different cities and for each of three full years of monitoring data [64]. It is therefore important to note the measurement techniques used at different monitoring stations.

3. Forms in Which Data Are Presented

Air quality data from measurement networks can be presented in many different forms for interpretation. Figures depicting diurnal or seasonal variations in concentrations, graphs and tables indicating the frequency distributions of measured concentrations, and isopleth maps showing the spatial variation of pollutant concentrations are just a few of the forms used. (These forms are illustrated in Section X.E.)

The air quality of an urban or suburban region is often discussed in terms of the frequency of violation of state or federal ambient air quality standards. Thus, these standards provide a rough measure of the ambient concentrations of some pollutants. Federal and California air quality standards are presented in Table 1 in Chapter II. Standards are specified for several different time-averaging intervals, and the measurement technique to be used is specified in each case. California standards are often more stringent than federal standards, especially in the case of SO_2. Frequently, more than one standard is specified for a pollutant, corresponding

TABLE 22. SURVEILLANCE CATEGORIES FOR PARTICULATE MONITORING SITES IN 1973

Surveillance type	Geographical area Northeast	South	North Central	Midwest	West	Nation
Population-oriented	333	95	179	243	75	925
Source-oriented	9	1	10	1	3	24
Background	8	3	7	11	6	35
Total	350	99	196	255	84	984

Source: Ref. 68.

TABLE 23. SURVEILLANCE CATEGORIES FOR SULFUR DIOXIDE MONITORING SITES IN 1973

(number of sites)

Surveillance type	Geographical area Northeast	South	North Central	Midwest	West	Nation
Population-oriented	65	18	62	33	21	199
Source-oriented	1	1	2	0	0	4
Background	4	2	2	2	0	10
Total	70	21	66	35	21	213

Source: Ref. 68.

relatively low concentrations of lead and hydrogen sulfide (H_2S) are tolerable in the atmosphere, whereas relatively high concentrations of carbon monoxide and sulfur dioxide are allowed.

In addition to the frequency of violation of air quality standards, certain statistical quantities are also of interest in characterizing air quality. It has been found that the ambient concentrations of many pollutants roughly fit a lognormal distribution [2,8,12,64,65,66]. For the lognormal distribution, the geometric mean is a measure of the central tendency, and the standard geometric deviation is a measure of the dispersion of the data. These quantities are analogous to the mean and the standard deviation of the "normal" distribution, that is, the familiar bell-shaped curve. Air pollution data are frequently summarized as lognormal distributions.

B. AIR QUALITY IN RURAL ENVIRONMENTS

Air quality in rural areas is discussed before air quality in urban areas because it indicates typical background pollutant concentrations and the spatial extent of the influence of anthropogenic emissions. High background concentrations are of particular importance to transportation planners and engineers because they can significantly reduce the allowable anthropogenic emissions consistent with air quality goals.

It is often difficult to ascertain the relative contributions of anthropogenic and natural emissions to the air quality at some rural site. In areas far from anthropogenic sources, one would expect pollutant concentrations to be influenced primarily by natural emissions. However, pollutants can be transported over considerable distances. In one study, an urban plume was still distinguishable 100 km downwind of a city [69]. Another study, based on measurements of ozone and Freon-11 in England, concluded that under suitable meteorological conditions ozone and its precursors can be transported for distances of 100 to 1000 km [70]. Hence, an area must be far from anthropogenic sources before its ambient pollutant concentrations can be considered to be due solely to natural emissions.

The approximate ranges of concentrations of various pollutants in both remote areas and rural areas near cities are given in Table 24. The "natural background concentrations" in this table were estimated from measurements in remote areas, far from anthropogenic sources and major natural sources. "Rural" concentrations were measured in rural areas within 50 km of cities. The rural CO, NO_x, SO_2, and ozone concentration ranges in Table 24 were estimated based on a series of field studies at rural stations around Columbus, Cincinnati, and Dayton, Ohio. The stations were less than 50 km from an urban area--some were less than 10 km away. Nonmethane hydrocarbons are not frequently measured. For this table, measurements in rural Missouri about 30 km from the nearest town were used to estimate the rural concentrations of nonmethane hydrocarbons. The ammonia concentration figures were based on an estimate of the continental average for this gas. Sulfate and particulate concentrations were based on measurements at nine rural stations.

Considerable local deviations from the concentrations in Table 24 can occur because of large natural sources. For example, nonmethane hydrocarbons that are apparently of natural origin have been measured at 0.6 ppm near the Dismal Swamp in Virginia [45, 46] and in the forests of Idaho [49]. Concentrations of particulates from windblown dust can exceed 1000 $\mu g/m^3$. Hence, although the natural background concentrations in Table 24 may broadly represent concentrations in the absence of anthropogenic emissions, higher concentrations may occur in particular areas because of large natural emissions.

Note that rural concentrations of particulates and ozone can exceed existing air quality standards. In the case of particulates, it is virtually impossible to achieve the standards through the imposition of emission controls when the cause is natural windblown dust. Natural background ozone concentrations can approach the federal standard, thus severely limiting allowable anthropogenic emissions. In areas such as the eastern United States, the multitude of cities can lead to a regional ozone problem. In these situations, there is a need to develop local transportation plans and emissions control strategies in the context of a regional strategy for achieving air quality goals.

TABLE 24. APPROXIMATE NATURAL BACKGROUND AND RURAL CONCENTRATIONS OF VARIOUS POLLUTANTS

	Natural Background Concentrations			Rural Concentrations		
Pollutant	μg/m^3	ppm	Reference	μg/m^3	ppm	Reference
CO	10 - 300	0.01 - 0.26	71, 72	229 - 802	0.2 - 0.7	73
Hydrocarbons						
Methane	1000	1.4	39	>1000	>1.4	74
Nonmethane	<1	<0.002 ppmC	39	27 - 103	~0.05 - 0.18 ppmC	74
Particulates	~20		4	30 - 80*		75
Oxides of Nitrogen						
NO	0.25 - 2.5	0.0002 - 0.002	39	<61	<0.05	76
				<12	<0.01	73
NO_2	1.9 - 2.6	0.0009 - 0.0013	39	10 - 20	0.005 - 0.01	73
				<94	<0.05	76
Ammonia		0.0053	49	4 - 20	0.006 - 0.03	75
Sulfur oxides						
SO_2	1 - 4	0.00035 - 0.0014	39	<183	<0.07	76
SO_4	<5		77	2 - 7*		75
	~2		4			
Ozone		0.02 - 0.06 from stratosphere	78	0 - 400	0.- 0.2	73
		0.01 - 0.06 from natural	78			

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* Arithmetic mean concentration.

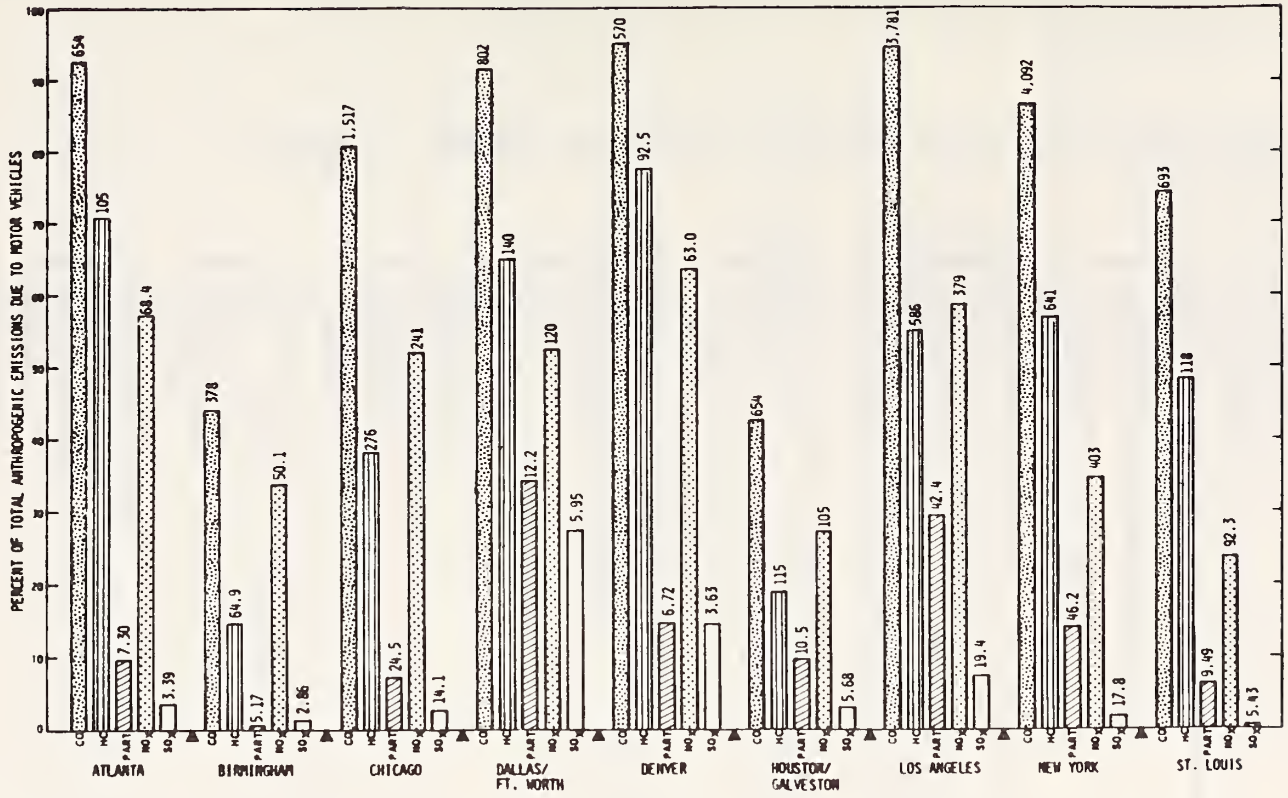
C. AIR QUALITY IN URBAN AREAS

This section discusses emissions and air quality in nine urban areas. These areas were selected to represent a variety of climates, industrial mixes, and typical lifestyles. Figure 6 shows the percentages of total anthropogenic emissions due to motor vehicles in the nine urban areas. The number at the top of each bar is the total emissions (in thousands of tons per year) of that pollutant from motor vehicles in that urban area. The striking feature of this graph is the marked variation in emissions patterns between different areas. Emissions in some cities, such as Atlanta, Denver, and Los Angeles, appear to be dominated by motor vehicles, whereas emissions in other cities, notably Birmingham and Houston/Galveston, are more strongly influenced by nonvehicular sources.

Figure 7 shows the mean, highest, and second-highest concentrations and number of violations of air quality standards for five pollutants in the same nine urban areas in 1974. This figure provides some indication of the air quality problems in the various areas. For example, note that the federal standards for oxidant and NO_2 were exceeded in all nine of the urban areas. In contrast, only Chicago, New York, and St. Louis reported violations of the federal 24-hour SO_2 standard. Figure 6 and 7 will be referred to frequently in the following sections, which discuss emissions and observed concentrations of CO, hydrocarbons, NO_x, SO_x, particulates, and oxidants in the those nine urban areas.

1. Air Quality Data for Carbon Monoxide

In most cities, the main fraction of carbon monoxide is emitted by automobiles. The mean percentage of CO emissions from motor vehicles for the nine urban areas in Figure 6 is 78 percent, and the range varies from 95 percent in Denver to 43 percent in Houston/Galveston. Denver has no strong nonvehicular sources of CO, but Houston has large petroleum refineries and chemical industries, which have high CO emissions. Similarly, in



Note: The total emissions from motor vehicles in each area are listed at the top of the appropriate bar in units of thousands of tons per year.

Source: Ref. 14.

FIGURE 6. PERCENTAGES OF TOTAL ANTHROPOGENIC EMISSIONS OF FIVE POLLUTANTS DUE TO MOTOR VEHICLES IN NINE URBAN AREAS IN 1974

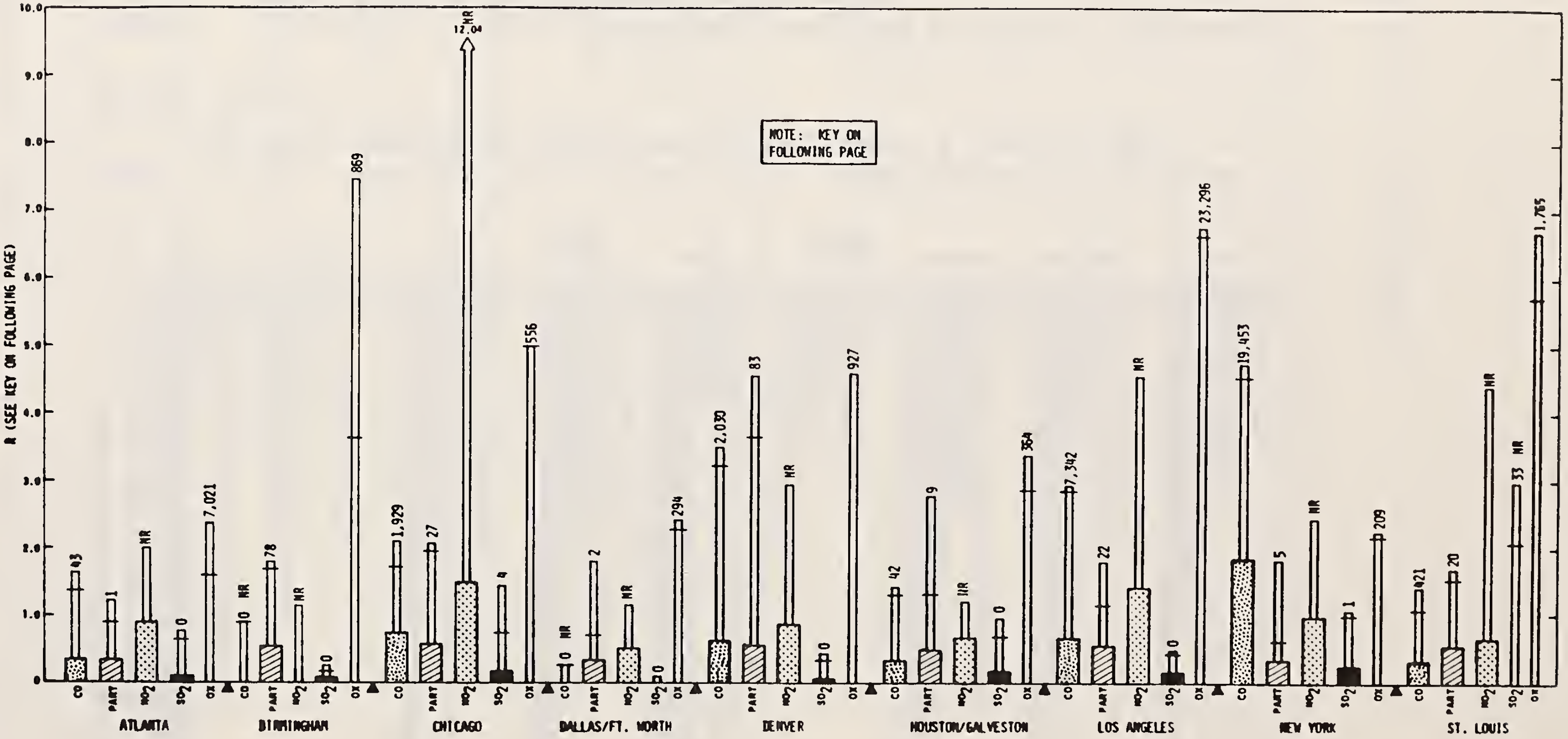
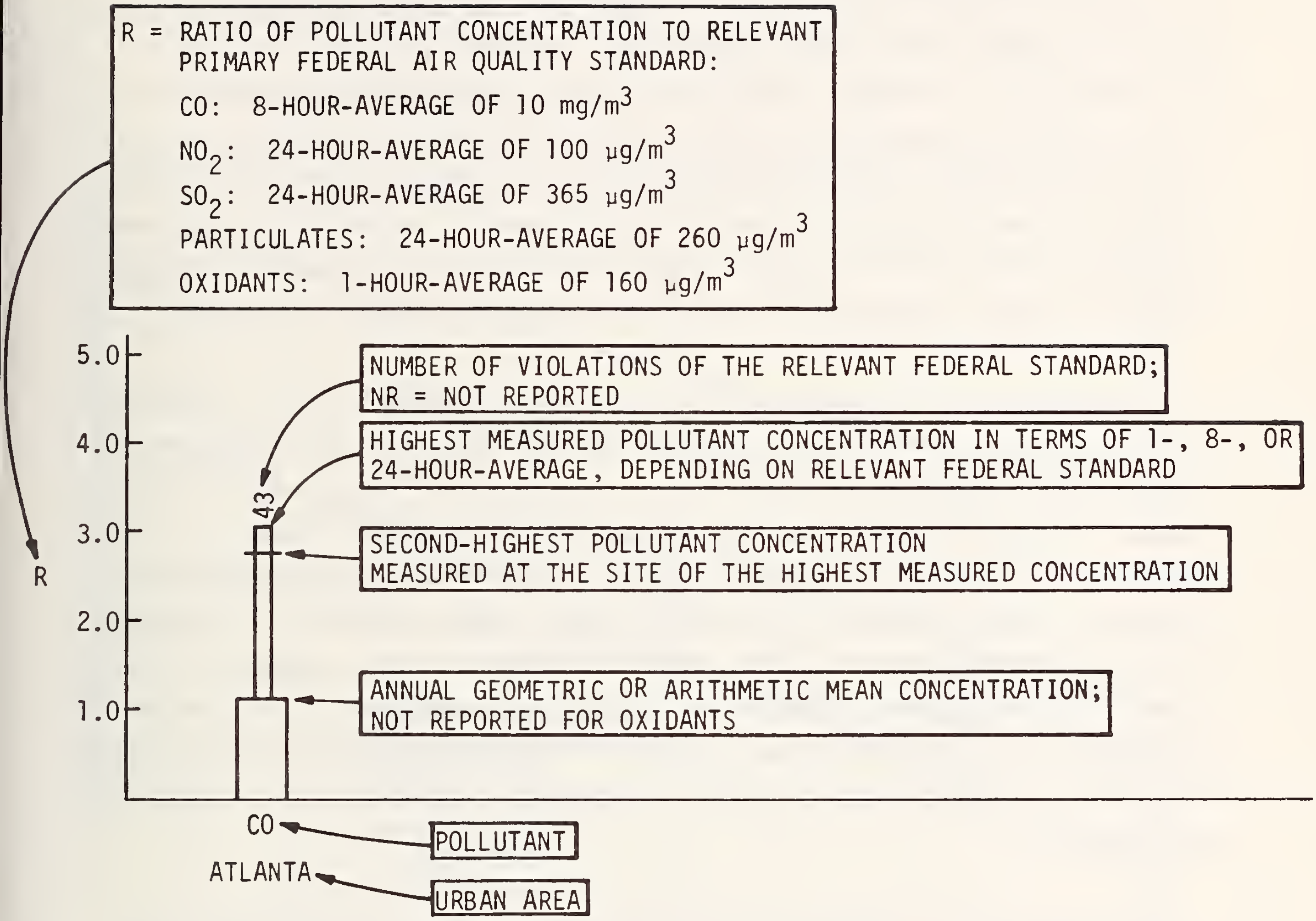


FIGURE 7. SUMMARY OF AIR QUALITY IN NINE URBAN AREAS DURING 1974



Source: Ref. 79.

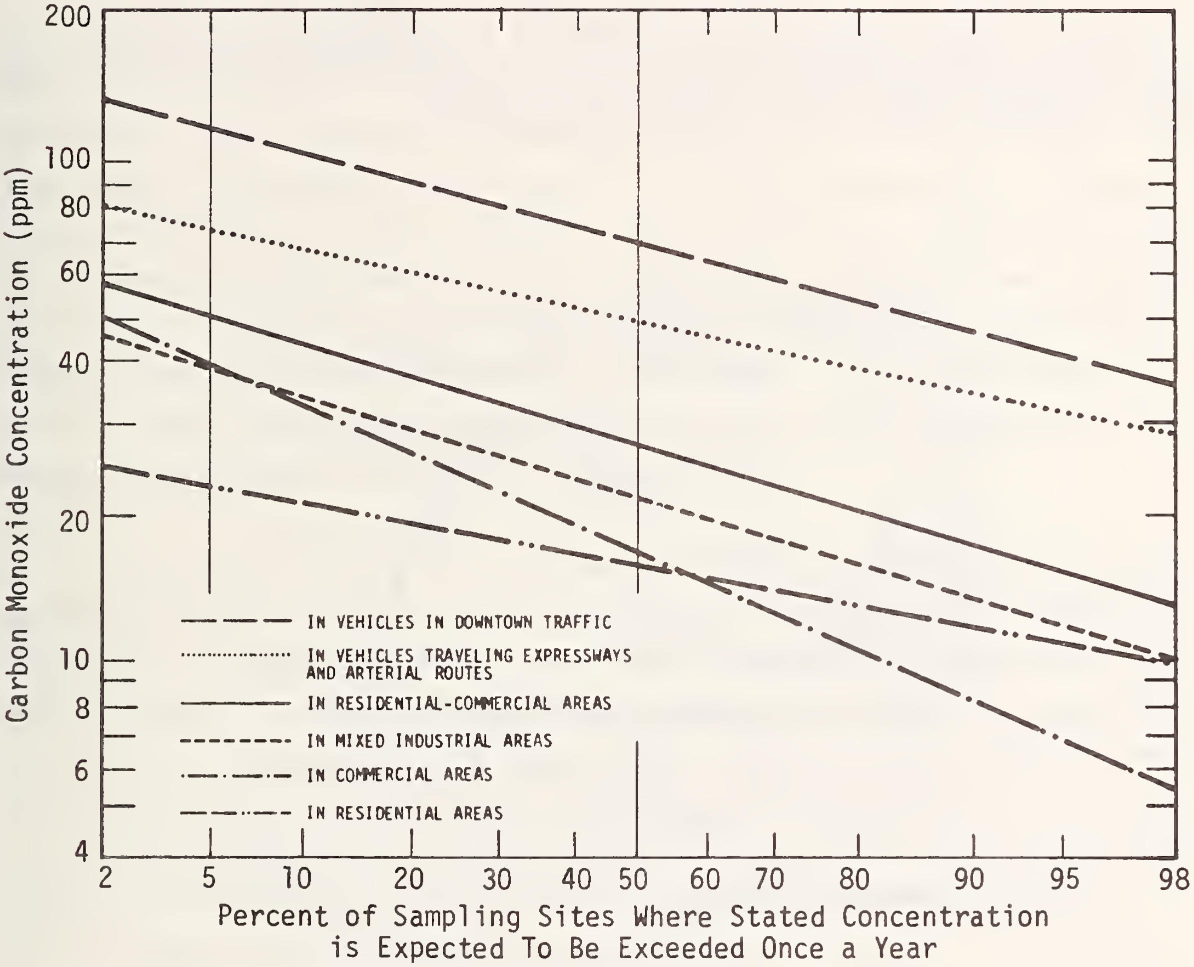
FIGURE 7. (Concluded)

Birmingham vehicles account for only 44 percent of the total CO emissions because the large metal processing industry contributes more to the total CO burden.

As shown in Table 1 in Chapter II, two federal standards are specified for carbon monoxide; 10 mg/m^3 for an eight-hour-average and 40 mg/m^3 for a one-hour standard, not to be exceeded more than once per year. At the low CO concentrations normally experienced in urban atmospheres, approximately 4 to 12 hours are required for carboxyhemoglobin levels in the human body to reach equilibrium with the average ambient CO concentration [2]. Hence, in terms of health impact, the eight-hour-average CO concentrations are more meaningful than one-hour-averages, and violations of the eight-hour standard can have greater significance than violations of the one-hour standard.

Exceedances of the one-hour and eight-hour CO standards occur frequently in most cities, primarily near heavily traveled roads. In fact, the number of exceedances measured in a given urban area is primarily a function of the number of monitoring stations located near heavily traveled roadways. For example, in 1974, nearly 20,000 exceedances of the eight-hour standard were recorded in New York City. Of the other urban areas included in Figure 6, all but Birmingham and Dallas/Ft. Worth exhibited a sizable number of violations of the eight-hour standard and at least one violation of the one-hour standard. The highest one-hour average recorded was 80 mg/m^3 in Denver, and the highest geometric mean of eight-hour averages recorded was 18.6 mg/m^3 in New York City.

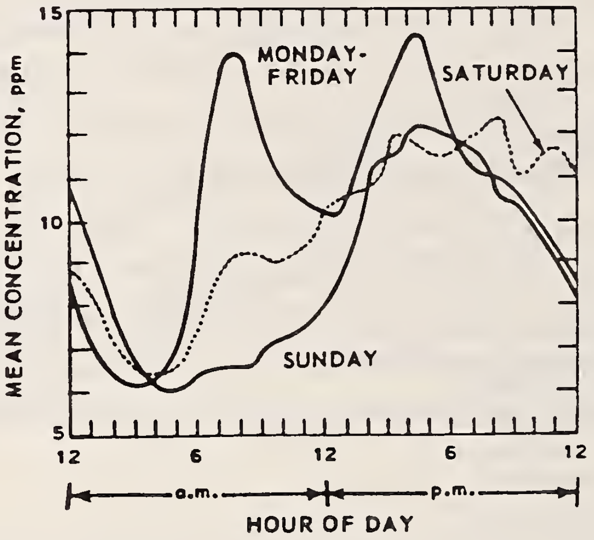
Since high CO concentrations occur primarily around heavily traveled downtown streets, and most central business districts are heavily traveled, the reason for the wide variation in maximum concentrations among cities is not obvious. Such variations may be attributed to the exact location of monitoring equipment with respect to the roadway and the effects of altitude and temperature on emissions rates. Variations in geometric mean concentrations may be due to these effects and to the duration of the traffic peak. Figure 8 shows data from several cities indicating expected CO concentrations at various locations. The data clearly show that relatively high concentrations can be expected in downtown areas and in areas with significant expressway traffic and that relatively low concentrations can be expected in residential areas. These concentrations appear to differ by as much as a factor of four or five. Note the frequency with which the one-hour federal CO standard (35 ppm) is exceeded.



Source: Ref. 2.

FIGURE 8. APPROXIMATE VARIATION OF MAXIMUM ANNUAL EIGHT-HOUR-AVERAGE CONCENTRATIONS OF CARBON MONOXIDE EXPECTED AT VARIOUS TYPES OF SITES

The most typical diurnal variations in CO concentrations are illustrated in Figure 9. The morning and evening peaks on weekdays correspond to rush-hour traffic. On weekend days a single peak occurs in the evening, corresponding perhaps to recreational activities. The double peak pattern in CO concentraitons on weekdays might be altered under some circumstances. For example, the typical diurnal variation in CO conentrations in Los Angeles does not include a strong second peak, mainly because of higher wind speeds and inversion heights in the afternoon, which produce greater dispersion of pollutants. In some congested central business districts, such as Manhattan, traffic remains near saturation level all day, leading to high CO concentrations throughout the day rather than a double peak pattern.



Source: Ref. 2.

FIGURE 9. DIURNAL VARIATION OF CARBON MONOXIDE CONCENTRATIONS ON WEEKDAYS, SATURDAYS, AND SUNDAYS IN CHICAGO, 1962-1964

Seasonal variations in CO concentrations occur mainly as a result of variations in meteorological parameters. An analysis of CAMP data for the years 1964 through 1967 shows that on the average, the highest CO concentrations tend to occur in the fall, followed by summer, spring, and winter [2]. In some locations, however, the highest concentrations occur in winter followed by fall, spring, and summer [68,79]. Since there is no clear general trend, the seasonal variation of CO concentrations should be assessed for each site individually.

The year-to-year trends in CO concentrations allow projection of the expected CO air quality. In the period from 1970 to 1975, the majority of monitoring sites in the nation showed a decrease in CO concentrations, but the eight-hour-average standard was still violated frequently. The one-hour standard was not often violated, though there was no trend of decreasing one-hour-average concentrations. It should be noted that year-to-year variations in meteorological parameters play a significant role in determining trends in pollutant concentrations. Hence, evaluation of the effectiveness of emissions control strategies on the basis of observed concentrations must be carried out with caution.

In summary, ambient concentrations of CO in most major urban areas are quite high. The observed one-hour averages are normally about a factor of two below the federal one-hour standard (40 mg/m^3), though occasional violations occur. The observed eight-hour averages are frequently comparable to, and in many cases are in excess of, the eight-hour-average CO standard of 10 mg/m^3. Observed maximum one-hour-average CO concentrations show a trend of decreases in many parts of the country, but not all. However, the frequency of violation of the eight-hour federal standard has dropped greatly over the past few years in many cities.

2. Air Quality Data for Hydrocarbons

Hydrocarbons (HC) are not in themselves considered to be severely damaging to human health and welfare, especially at the concentrations normally prevalent in urban atmospheres. Photochemical reactions involving hydrocarbons and oxides of nitrogen, however, result in the formation of oxidants, ozone, and peroxyacyl nitrates, all of which are harmful. The concentrations of hydrocarbons in the atmosphere are hence of interest indirectly. Data on ambient HC concentrations are not widely available, but detailed data on HC emissions are available from the emissions inventories for each air quality control region published by the EPA and from other sources.

The importance of motor vehicles with regard to atmospheric HC concentrations can be placed in perspective by referring to Figure 5. Motor vehicles contribute as little as 15 to 20 percent of the total anthropogenic HC emissions in areas such as Birmingham and Houston/Galveston where industrial activities (e.g., petroleum refining) cause the majority of HC emissions. In contrast, motor vehicles emit as much as 70 to 80 percent of anthropogenic HC emissions in Atlanta and Denver because of the absence of major industrial HC sources. On the average, vehicles contribute about 50 percent of urban anthropogenic HC emissions. Natural emissions of HC may be significant if there are large quantities of vegetation upwind of the urban area of interest. This situation may lead to significant background HC concentrations in the air upwind of the urban area.

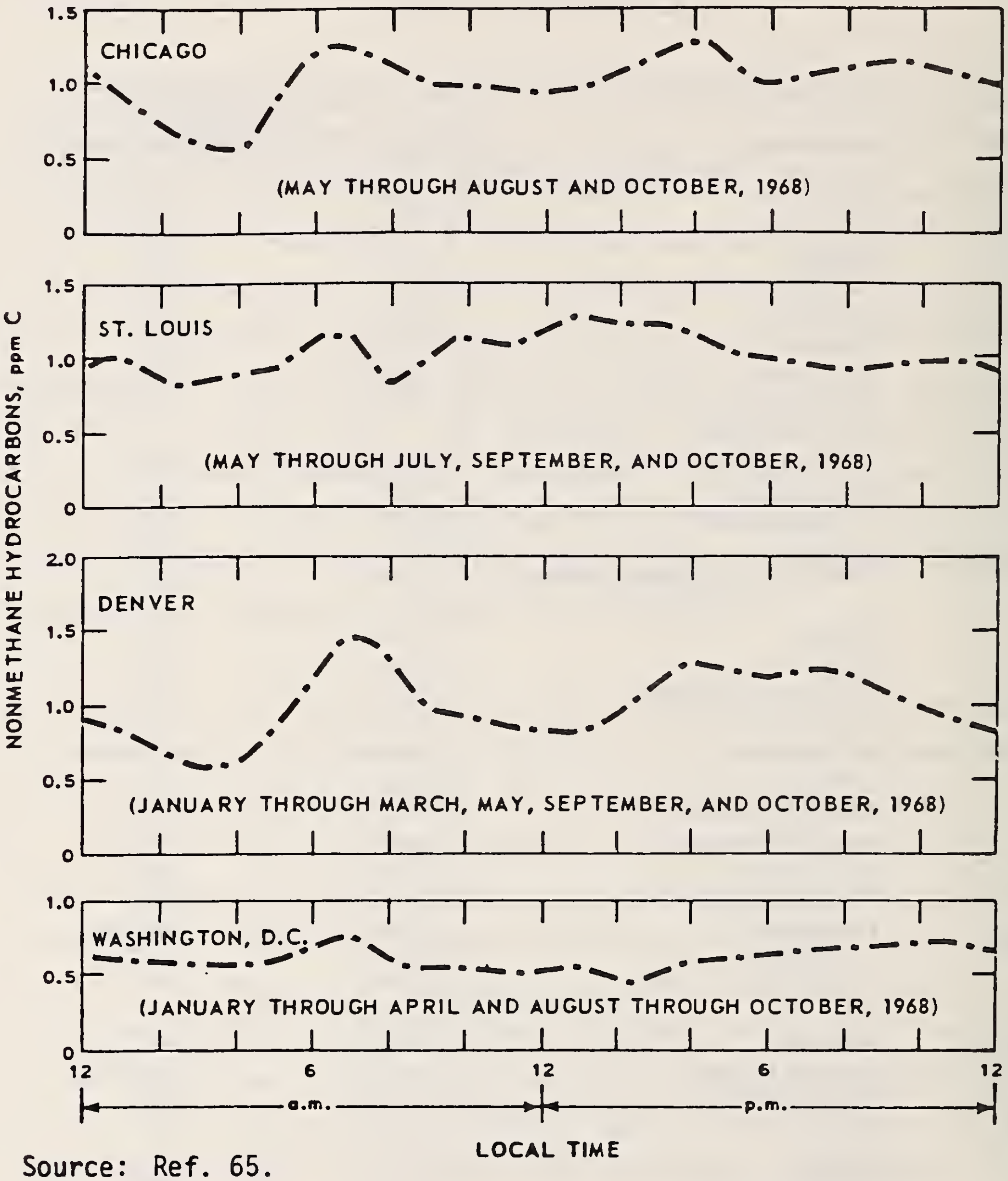
Hydrocarbons in urban atmospheres consist of a wide variety of species, as suggested by the average composition for Los Angeles shown in Table 25. Most ambient hydrocarbons fall into one of five classes: methane, total alkanes (excluding methane), alkenes, acetylene, and aromatics. Methane is overwhelmingly the dominant constituent; it is about 85 percent of the hydrocarbons (in parts per million). Only hydrocarbons that participate in photochemical oxidant formation, called "reactive hydrocarbons," are of interest, however, and methane, acetylene, and benzene are not reactive. Oxygenated hydrocarbons, such as aldehydes and ketones, are important constituents of smog but are difficult to measure. Detailed analyses of air samples for HC composition are not routinely carried out. Instead, only methane and total nonmethane hydrocarbon (NMHC) concentrations are usually reported.

TABLE 25. AVERAGE HYDROCARBON COMPOSITION OF 218 AMBIENT AIR SAMPLES IN LOS ANGELES IN 1965

Compound	Concentration	
	ppm	ppm (as carbon)
Methane	3.22	3.22
Ethane	0.098	0.20
Propane	0.049	0.15
Isobutane	0.013	0.05
n-Butane	0.064	0.26
Isopentane	0.043	0.21
n-Pentane	0.035	0.18
2,2-Dimethylbutane	0.0012	0.01
2-Methylpentane		
2,3-Dimethylbutane	0.014	0.08
Cyclopentane	0.004	0.02
3-Methylpentane	0.008	0.05
n-Hexane	0.012	0.07
Total alkanes (excluding methane)	0.3412	1.28
Ethylene	0.060	0.12
Propene	0.018	0.05
1-Butane + Isobutylene	0.007	0.03
trans-2–Butene	0.0014	0.01
cis-2–Butene	0.0012	Negligible
1-Pentene	0.002	0.01
2-Methyl-1-Butene	0.002	0.01
trans-2-Pentene	0.003	0.02
cis-2-Pentene	0.0013	0.01
2-Methyl-2-Butene	0.004	0.02
Propadiene	0.0001	Negligible
1,3-Butadiene	0.002	0.01
Total alkenes	0.1020	0.29
Acetylene	0.039	0.08
Methylacetylene	0.0014	Negligible
Total acetylene	0.0404	0.08
Benzene	0.032	0.19
Toluene	0.053	0.37
Total aromatics	0.0850	0.56
Total	3.7886	5.43

Source: Ref. 65.

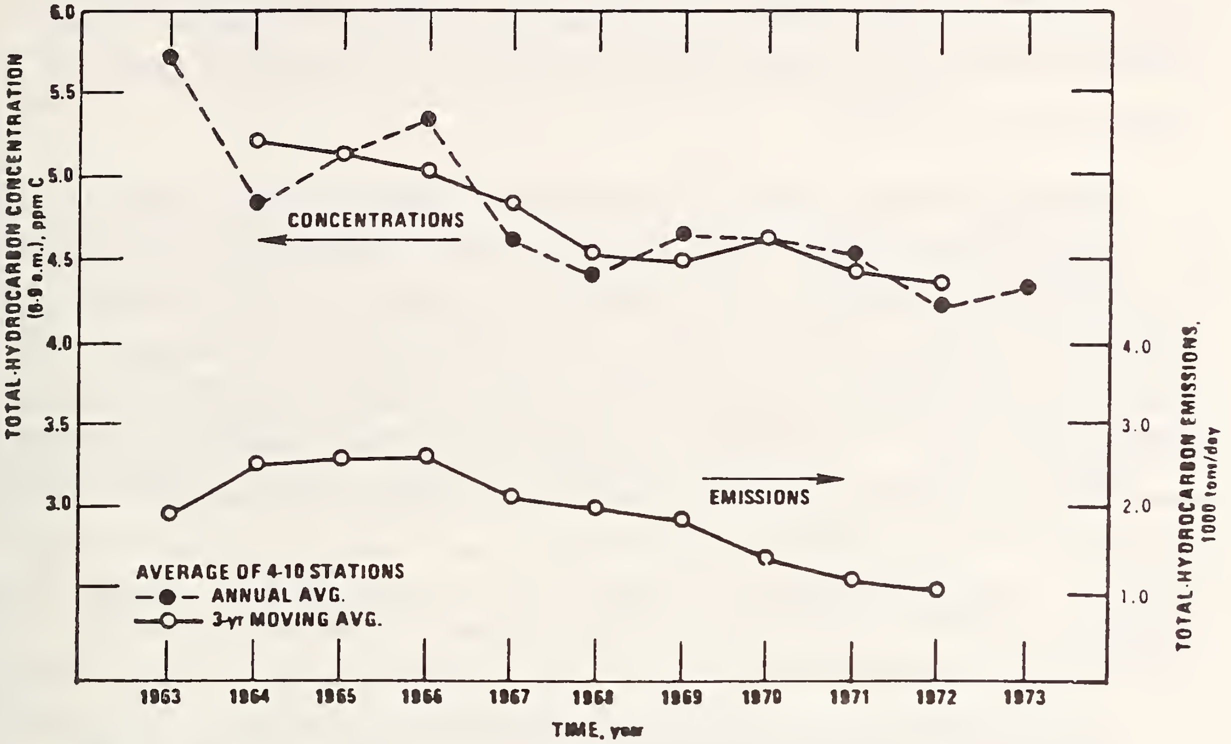
Typical diurnal variations in nonmethane hydrocarbon concentrations for several cities are presented in Figure 10. The concentrations are generally on the order of 1 ppm. In some cases, the data show peak concentrations corresponding to morning and evening rush-hour traffic. In other cases, these peaks are not well defined, perhaps because of the many other sources of hydrocarbons.



Source: Ref. 65.

FIGURE 10. NONMETHANE HYDROCARBON CONCENTRATIONS AVERAGED BY HOUR OF DAY OVER SEVERAL MONTHS FOR VARIOUS CITIES

Urban HC concentrations have shown a gradual decrease, probably due largely to the reduction in HC emissions brought about by emissions control measures. The trend in HC emissions and ambient HC concentrations in Los Angeles is shown in Figure 11.



Source: Ref. 68.

FIGURE 11. AMBIENT HYDROCARBON CONCENTRATIONS AND EMISSIONS IN THE SOUTH COAST AIR BASIN (LOS ANGELES), JULY THROUGH SEPTEMBER, 1963-1973

3. Air Quality Data for Nitrogen Oxides

Anthropogenic NO_x emissions are primarily due to fuel combustion in vehicles and industrial and utility operations. Electricity generation is the largest single source of NO_x on a national basis, but vehicles are a significant source in many urban areas. The relationships between vehicular and other anthropogenic NO_x emissions in urban areas depend largely on regional driving habits, electricity generation, and industrial operations. It seems reasonable to expect a low proportion of NO_x emissions due to motor vehicles in heavily industrialized areas and a high proportion in areas that are not heavily industrialized. For the nine cities listed in Figure 6, the percentage contribution of motor vehicles to total NO_x emissions in 1974 varied from about 24 percent in St. Louis to about 64 percent in Denver. Natural processes also produce significant quantities of NO_x, but these sources are normally so widely distributed and emit at such a low rate that they probably do not have a significant impact on urban-scale air quality.

Anthropogenic NO_x emissions consist of a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2). The majority of the NO_x emissions that arise from combustion processes consist of about 95 percent NO and 5 percent NO_2. The relative percentages of NO and NO_2 change after emission because of chemical reactions in the atmosphere, eventually leading to an equilibrium between NO and NO_2. NO can thus be viewed as a primary (emitted) pollutant, whereas NO_2 is largely a secondary pollutant (formed in the atmosphere). Ambient air quality standards have not been specified for NO, but for NO_2 there are a one-hour California standard and an annual federal standard (see Table 1).

The federal air quality standard for NO_2, 100 $\mu g/m^3$ for the annual average, is exceeded in several cities. Although Chicago and Los Angeles are the only cities shown in Figure 7 that violate the standard, three others come close. Most of the cities listed in that figure have annual averages of roughly comparable magnitude, but the highest single 24-hour-average concentration varies greatly from city to city. This variation may be caused by the effects of monitoring site location, local meteorology, and large emitters. In addition, errors in the collection and reporting of data are possible. California has its own standard, 470 $\mu g/m^3$ NO_2 for a one-hour average. This standard is exceeded in several areas in California, including Los Angeles and San Francisco, often for two or even three consecutive hours.

Although automobiles emit roughly 40 to 50 percent of total NO_x emissions in most large cities, the spatial variations in NO_2 concentrations are not as directly related to motor vehicle operation as are CO concentrations. The reasons for this are that NO_2 is a secondary pollutant, formed over a period of hours as NO gradually oxidizes, and that nonvehicular sources emit a greater proportion of the total CO than of the total NO_x. Thus maximum NO_2 concentrations frequently occur some distance downwind of regions where vehicular NO_x emissions are high.

To some extent, NO concentrations exhibit the same diurnal pattern as do CO concentrations. The morning and evening peaks corresponding to peak traffic are not as well defined for NO as for CO, since large quantities of NO_x are also emitted from other sources. Diurnal variations of NO_2 are even less reflective of traffic patterns. There are no sharp peaks corresponding to morning and evening rush-hour traffic, though there does appear to be some tendency for higher concentrations during those hours.

NO concentrations show marked seasonal variations, but NO_2 concentrations do not. The NO trends are due to variations in meteorology and variations in NO_x emissions, which tend to be higher in the winter when additional sources of NO_x, such as space heaters, become active. The smaller amount of overall atmospheric mixing in the late fall and winter months and the lower reaction rates (due to lower temperatures and less sunlight) lead to higher NO concentrations during that time of year. For NO_2, the varying reaction rates, meteorological parameters, and emissions rates are complications that point toward no clear trend in seasonal variations. Some cities (such as Chicago) show a tendency for higher NO_2 concentrations in the summer, but others (such as Denver and Los Angeles) tend towards higher concentrations in the winter.

Standards on automotive NO_x emissions were imposed in 1971 in California, followed by federal standards in 1973. CO and hydrocarbon standards were, however, applied much earlier--1966-1967 in California and 1968-1969 for the rest of the nation. Since NO_x emissions controls followed HC and CO emissions controls, early attempts to control CO and HC emissions were made at the expense of increased NO_x emissions. NO_x emissions from automobiles began to decline only after the imposition of NO_x controls. These trends in emissions were reflected in ambient NO_2 concentrations, which gradually increased from 1965 through 1972 and then decreased through 1974.

It must be kept in mind that trends in NO_2 concentrations are affected by variations in both emissions and meteorology. Rather large and abrupt changes in annual average NO_2 concentrations from one year to the next probably reflect changes in meteorology and an underlying steady trend in emissions. Furthermore, data indicate that the meteorological conditions leading to the highest short-term NO_2 concentrations do not necessarily occur in the same year as those leading to the worst annual average concentrations.

4. Air Quality Data for Sulfur Dioxide

Motor vehicles burning gasoline or diesel fuel emit sulfur dioxide (SO_2), sulfates ($SO_4^=$), and sulfuric acid (H_2SO_4) formed from the small quantities of sulfur present in those fuels. Since diesel fuel contains much more sulfur, sulfur oxide emissions from diesel-powered vehicles are larger than from gasoline-powered vehicles. The total sulfur dioxide and sulfur oxides emissions from motor vehicles normally constitute only a small fraction of total anthropogenic emissions of those compounds. Of the nine cities listed in Figure 6, only two, Dallas/Ft. Worth and Denver, had vehicular emissions greater than 10 percent of the total anthropogenic SO_2 emissions; in Denver, the fraction was 15 percent, and in Dallas/Ft. Worth, 28 percent. These cities have few significant SO_2 sources and large motor vehicle use, indicating that in the near absence of other sources of SO_2 motor vehicles may contribute a significant fraction of total SO_2 emissions.

As shown in Table 1, two primary and three secondary federal standards are specified for sulfur dioxide--an annual arithmetic average, a 24-hour average, and a 3-hour average secondary standard. The 24-hour primary standard was met in 1974 in six of the nine cities included in Figure 7. Since there does not appear to be a consistent pattern of violations from one city to the next, violations are probably the result of specific localized sources rather than regional trends.

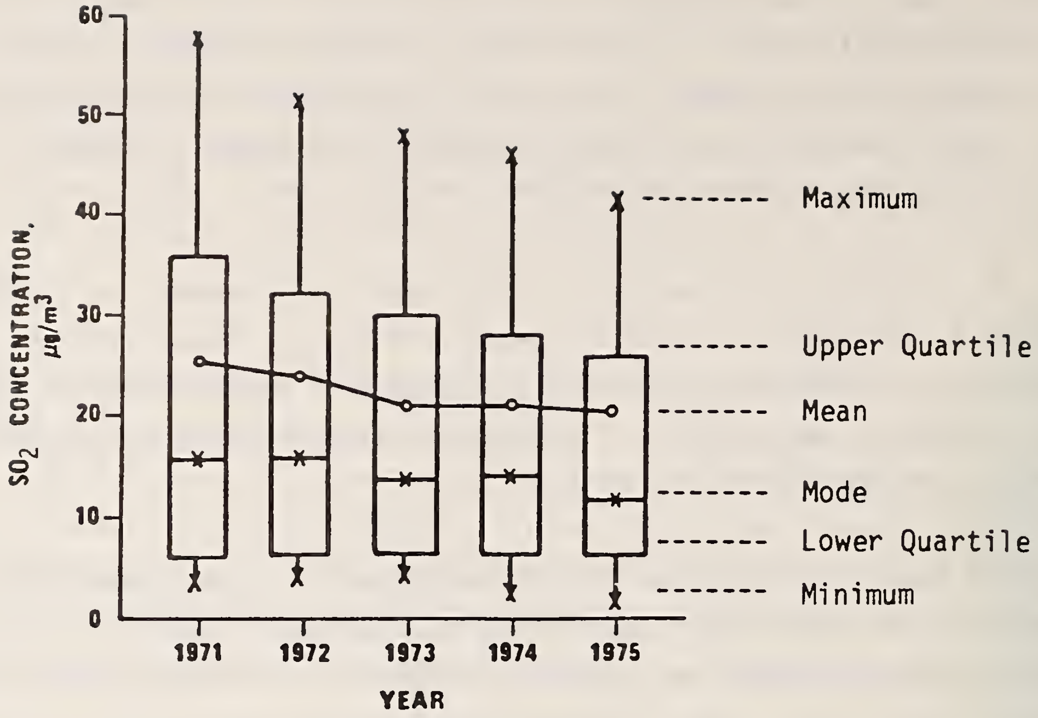
SO_2 concentrations generally show diurnal and seasonal variations related to variations in meteorology and emissions. Concentrations generally peak in the early morning hours because of low atmospheric dispersion. Cities in which fuel oil is used for space heating have substantially higher SO_2 concentrations in winter.

The spatial distribution of SO_2 measurements in many urban areas indicates that the highest SO_2 concentrations occur very close to the regions with the highest population density. However, in some cases, large point sources of SO_2 (e.g., power plants and refineries) are located in sparsely populated areas, resulting in high local concentrations.

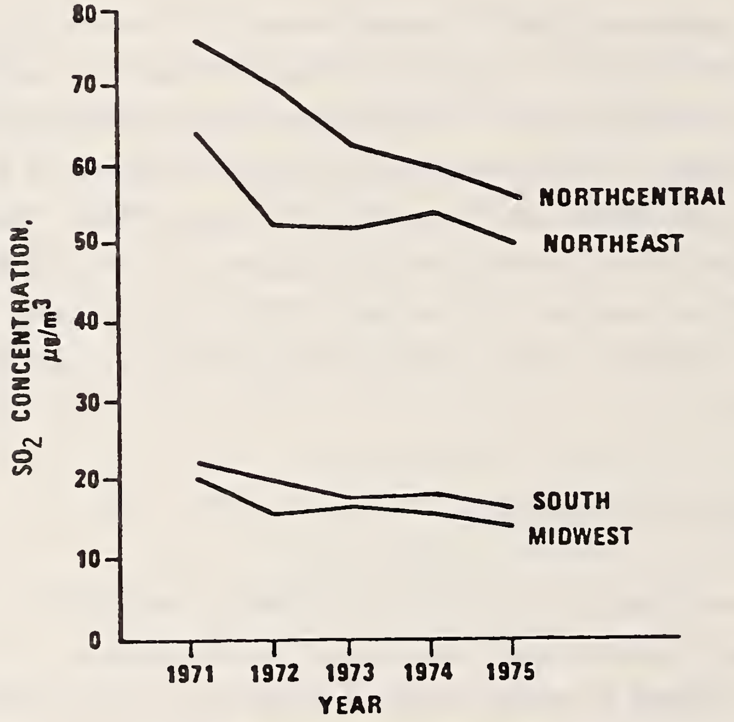
Nationwide, SO_2 concentrations at urban and rural sites have decreased somewhat over the past few years. There is evidence, however, that a leveling off has occurred in recent years. This trend in SO_2 concentrations is illustrated in Figure 12(a). The trends in SO_2 concentrations in geographical regions of the United States are presented in Figure 12(b). Clearly, the greatest improvement in SO_2 concentrations occurred in the north central United States, probably as a result of the use of low-sulfur fuels. In cities there has been a general trend toward decreasing SO_2 concentrations with some exceptions.

5. Air Quality Data for Particulates

Motor vehicles are directly responsible for only a fraction of the total anthropogenic particulate emissions in most urban regions. For the nine urban areas listed in Figure 6, motor vehicles generally contributed less



(a) Annual Averages



(b) Nintieth Percentiles

Source: Ref. 80.

FIGURE 12. SULFUR DIOXIDE TRENDS, 1971-1975

than 15 percent of anthropogenic particulate emissions in 1974, but as much as 30 percent in two cities (Los Angeles and Dallas/Ft. Worth). Unfortunately, motor vehicles are primarily responsible for emissions of lead, due to the lead in some gasolines, and increasing amounts of sulfuric acid and sulfate particulates, due to the use of catalytic converters in late-model cars.

Atmospheric particulates span a broad range both in size and in chemical composition. Particles in the size range from 0.1 to 1 μm have the greatest impact on visibility, and particles in the size range from 0.1 to 10 μm are most important to atmospheric chemical reactions. Routine air pollution measurements are made of particles in the size range from 0.1 to 10 μm as "suspended particulate matter" and of particles larger than 10 μm as "dustfall," since the latter class of particles has a much greater tendency to settle rapidly out of the atmosphere.

Atmospheric particulates can also be classified according to their sources [13]:

- > Natural continental aerosol
  - Windblown dust particles averaging 0.5 μm in diameter.
  - Particles smaller than 0.4 μm resulting from photochemical reactions and hydrocarbon emissions from vegetation.
  - Small particles involving gases such as SO_2, H_2S, NH_3, and O_3.
  - Particles from volcanic eruptions.
- > Natural marine aerosol, resulting from the evaporation of sea spray. It consists essentially of sea salt (NaCl) and occurs in particle sizes greater than 0.5 μm.
- > Man-made aerosols
  - Solid particles (smoke) formed in combustion processes.
  - Particles smaller than 0.5 μm in diameter formed from photochemical reactions.

It has been found that particles smaller than 0.1 μm decrease in concentration with elevation above ground level, indicating that they are terrestrial in origin. However, particles in the 0.1 to 1 μm size range reach a maximum concentration at an elevation of about 18 km.

The size distribution of aerosols is generally such that almost all the particles are less than 0.1 μm in diameter, but particles in the 0.1 to 1.0 μm range provide most of the surface area for interactions. Finally, on a volume or mass basis, a double maximum distribution is exhibited. The smaller particles, between 0.1 and 1 μm in diameter, are almost exclusively formed by the condensation of vapors, whereas the larger particles consist of dust, fly ash, and mechanically generated aerosol [13]. As for composition, sulfates often constitute the largest fraction of the particulates, followed by benzene-soluble organics, nitrates, and ammonium compounds. Considerable amounts of some metals, notably iron, lead, and zinc, are also present.

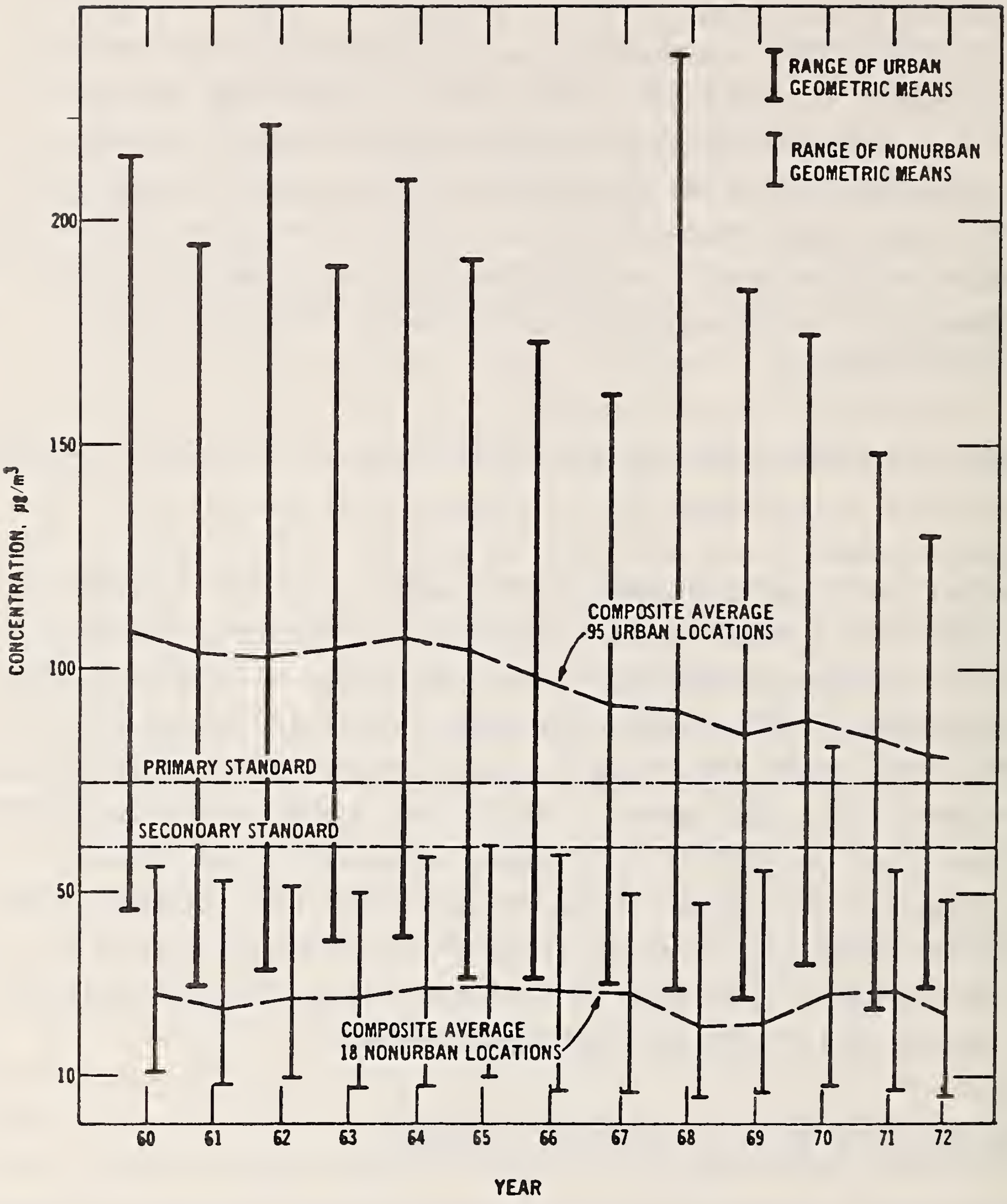
Two federal standards are specified for total suspended particulates--an annual geometric mean of 75 $\mu g/m^3$ and a 24-hour-average concentration of 260 $\mu g/m^3$ (see Table 1). (Note that the geometric mean is usually somewhat lower than the arithmetic mean for air quality data.) Both of these standards are exceeded in many urban areas. Birmingham and Denver, for example, recorded 78 and 83 exceedances, respectively, during 1974. The highest value shown in Figure 7 for particulates is 1180 $\mu g/m^3$ in Denver--more than four times the federal standard. The lowest maximum 24-hour-average shown in that figure is 217 $\mu g/m^3$ for New York City, which is below the federal standard. The annual geometric means vary between 84 and 153 $\mu g/m^3$. Curiously, St. Louis, which exhibited the highest annual geometric mean in 1974, had a relatively modest maximum 24-hour-average value. Although detailed analysis is needed to determine the cause of this phenomenon, a combination of steady emissions rates and stable meteorology may have produced these results. The data show that stations that recorded significant violations of the federal annual standard also observed a significant number of violations of the federal 24-hour standard.

Urban particulate concentrations have been steadily dropping since the early 1960s, presumably as a result of recently applied particulate emissions controls. This decrease in urban particulate concentrations is illustrated in Figure 13, which shows that whereas the maximum annual average particulate concentration was as high as 210 $\mu g/m^3$ in 1960, it dropped to about 130 $\mu g/m^3$ in 1972. Furthermore, the composite average for 95 urban locations dropped from about 110 $\mu g/m^3$ to about 80 $\mu g/m^3$ over the same period. The average for nonurban stations, which is strongly indicative of natural background levels, has remained relatively constant at about 25 to 30 $\mu g/m^3$. This suggests that the decrease in particulate concentrations at urban locations is primarily a result of more effective control of anthropogenic particulate emissions rather than a change in background particulate concentrations.

Urban particulate concentrations exhibit diurnal and seasonal variations that are generally predictable [8]. High particulate concentrations frequently occur between 6 a.m. and 8 a.m. as a result of low atmospheric dispersion (low wind speeds and mixing depths) and a concomitant increase in the emissions from various sources of particulates, including automobile traffic. In cities where the majority of particulates is formed from photochemical reactions, the maximum concentration in the size range from 0.1 to 1 μm occurs near 12 a.m. The highest concentration of particulates somewhat smaller than 0.1 μm occurs earlier. There is no clear trend for particulates larger than 1 μm. For most cities, weekend concentrations are lower than weekday concentrations because of reduced activity of particulate sources. Finally, most cities with cold winters experience higher particulate concentrations in winter as a result of increased fuel use for space heating, street sanding, and other winter-related activities.

6. Air Quality Data for Photochemical Oxidants

Photochemical oxidants, principally ozone (O_3) and peroxyacetyl nitrate (PAN), are formed in the atmosphere through photochemical reactions involving



Source: Ref. 68.

FIGURE 13. ANNUAL GEOMETRIC MEAN CONCENTRATIONS OF TOTAL SUSPENDED PARTICULATES AT URBAN AND RURAL STATIONS OF THE NATIONAL AIR SAMPLING NETWORK

oxides of nitrogen, hydrocarbons, atmospheric oxygen, and other constituents of the atmosphere. (These reactions are described in Section VII.C.) The typical daily cycle of pollutant concentrations is illustrated in Figure 14. Oxidant concentrations are normally relatively low at night (0.01 ppm or less). Starting in the early morning hours, automobile traffic and other sources of emissions lead to a gradual increase in the concentrations of the primary pollutants--NO, CO, and hydrocarbons. Photochemical oxidation leads to a rapid disappearance of NO and a concomitant buildup in NO_2 and O_3. NO_2 concentrations peak at midmorning and then begin to decrease as a result of dilution processes in the atmosphere. The slower reactions leading to O_3 formation continue, creating a peak O_3 concentration around midday, roughly at the time of maximum insolation. As the intensity of insolation decreases later in the day, O_3 is removed by reaction with fresh NO emissions and gradually drops to low nighttime concentrations. The concentrations of CO, NO_2, and oxidants decrease during the evening, many emissions sources cease activity, and some pollutants are transported from the region by the wind.

The federal air quality standard for oxidants is exceeded frequently in many areas. Because of the nature of the processes leading to oxidant formation, areas with large morning emissions of HC and NO_x on hot, sunny days tend to have the highest oxidant concentrations. Los Angeles is a common example, though other areas have recorded similarly high maximum concentrations. However, the highest one percent of the one-hour-average concentrations recorded in Los Angeles exceed 725 $\mu g/m^3$, a value more than twice the highest one percent of any of the other eight cities listed in Figure 7.

Diurnal and seasonal variations in oxidant concentrations are best illustrated by examination of their trends for monthly mean and maximum concentrations, which are presented in Figures 15 and 16. Ozone and oxidant concentrations peak at midday, which corresponds with the periods of high insolation and low atmospheric ventilation. Furthermore, the seasonal variations are much more noticeable in plots of monthly maximum concentrations than in monthly means. The reason for this is that the monthly means include the low concentrations of O_3 measured during the nighttime and twilight hours, which tend to mask the other variations.

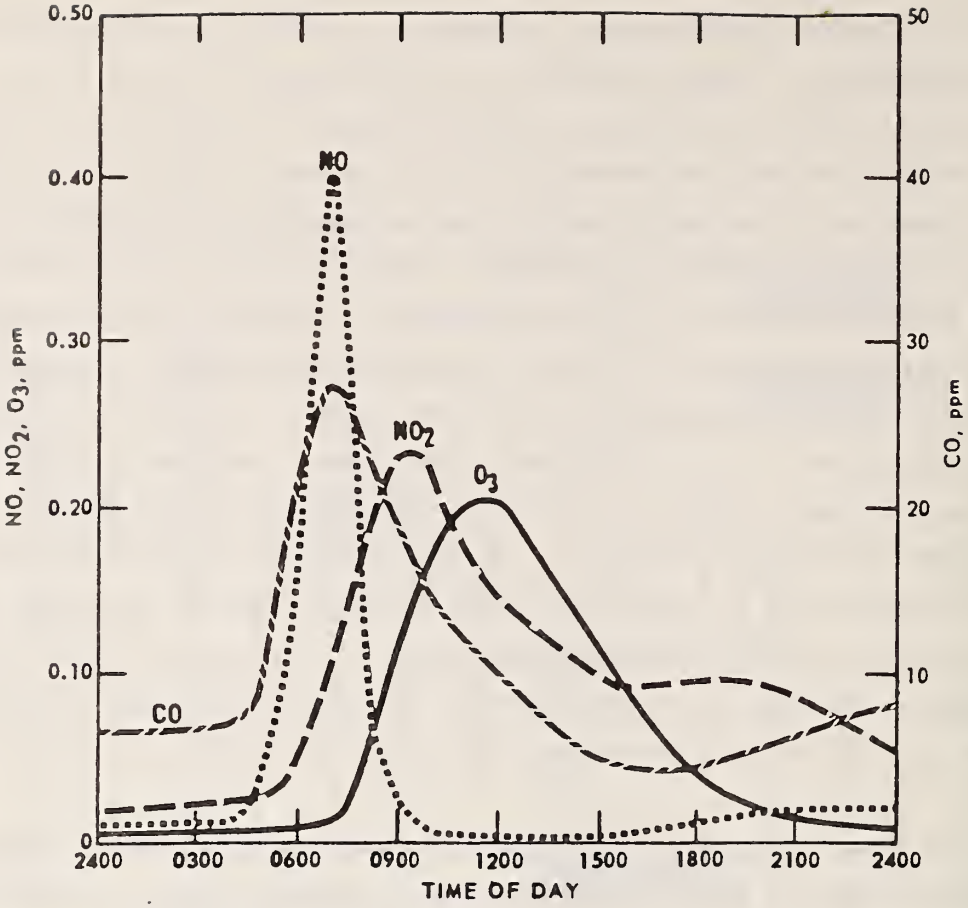


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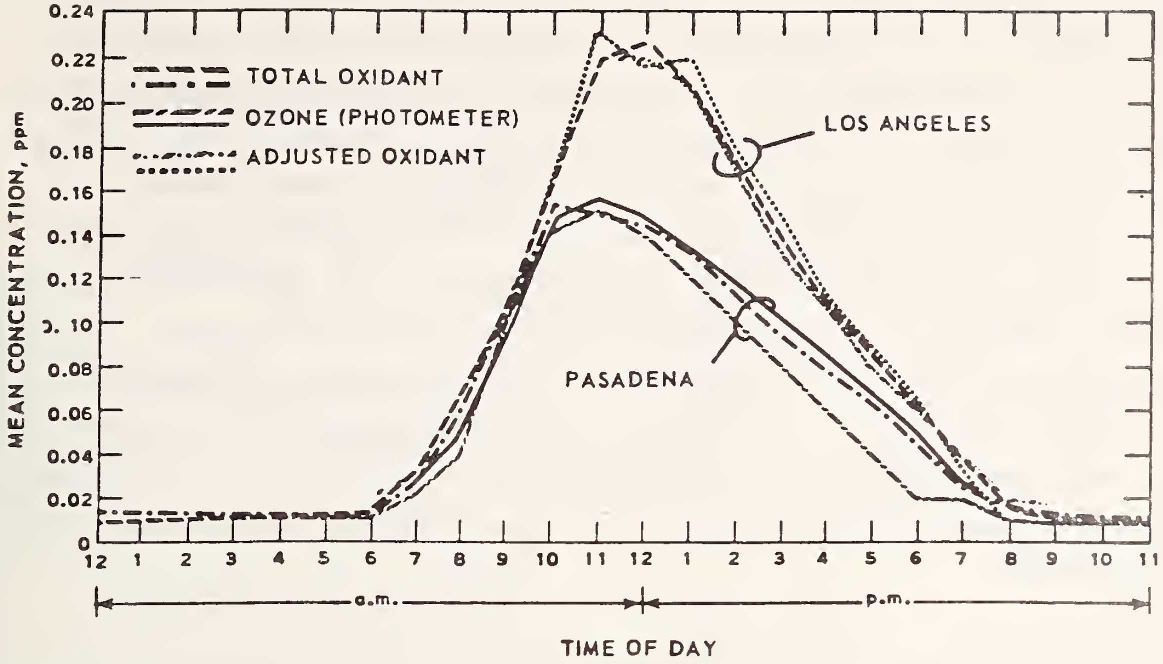
FIGURE 14. AVERAGE ONE-HOUR-AVERAGE CONCENTRATIONS OF SELECTED POLLUTANTS AT MONITORING SITES IN LOS ANGELES, CALIFORNIA ON 19 JULY 1965

The transport of pollutants by wind frequently causes the pollutant cloud from one subregion of an urban area to drift over a downwind subregion, causing a significant impact on the air quality there. Such effects are especially noticeable with secondary pollutants such as ozone: They are continuously being formed by chemical interactions within the pollutant cloud, which counteracts the diluting effects of atmospheric dispersion. Such transport effects are frequently observable in Los Angeles. A southwesterly sea breeze frequently carries the pollutants from downtown and western Los Angeles toward the north and northeast. These pollutants are then trapped along the northern boundaries of the area by the encircling



Source: Ref. 12.

FIGURE 15. HOURLY VARIATIONS OF MEAN ONE-HOUR-AVERAGE CONCENTRATIONS OF OZONE, OXIDANT, AND OXIDANT ADJUSTED FOR NO_2 AND SO_2 RESPONSE IN LOS ANGELES AND PASADENA, JULY 1964

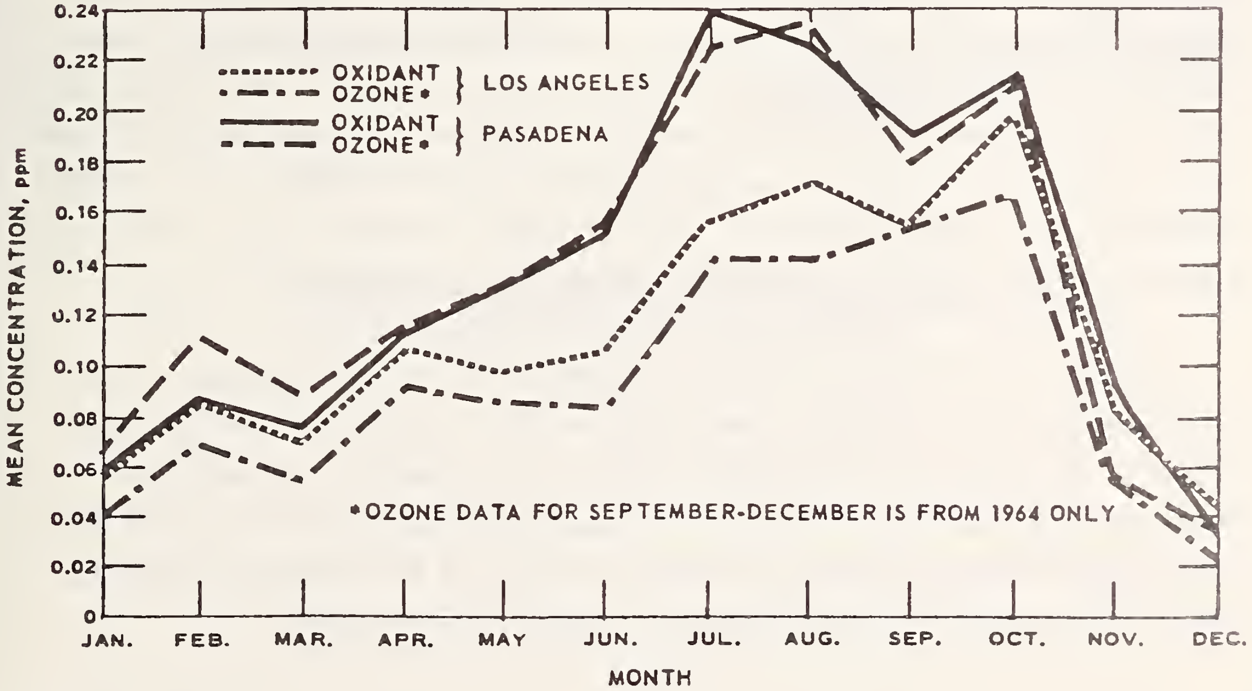


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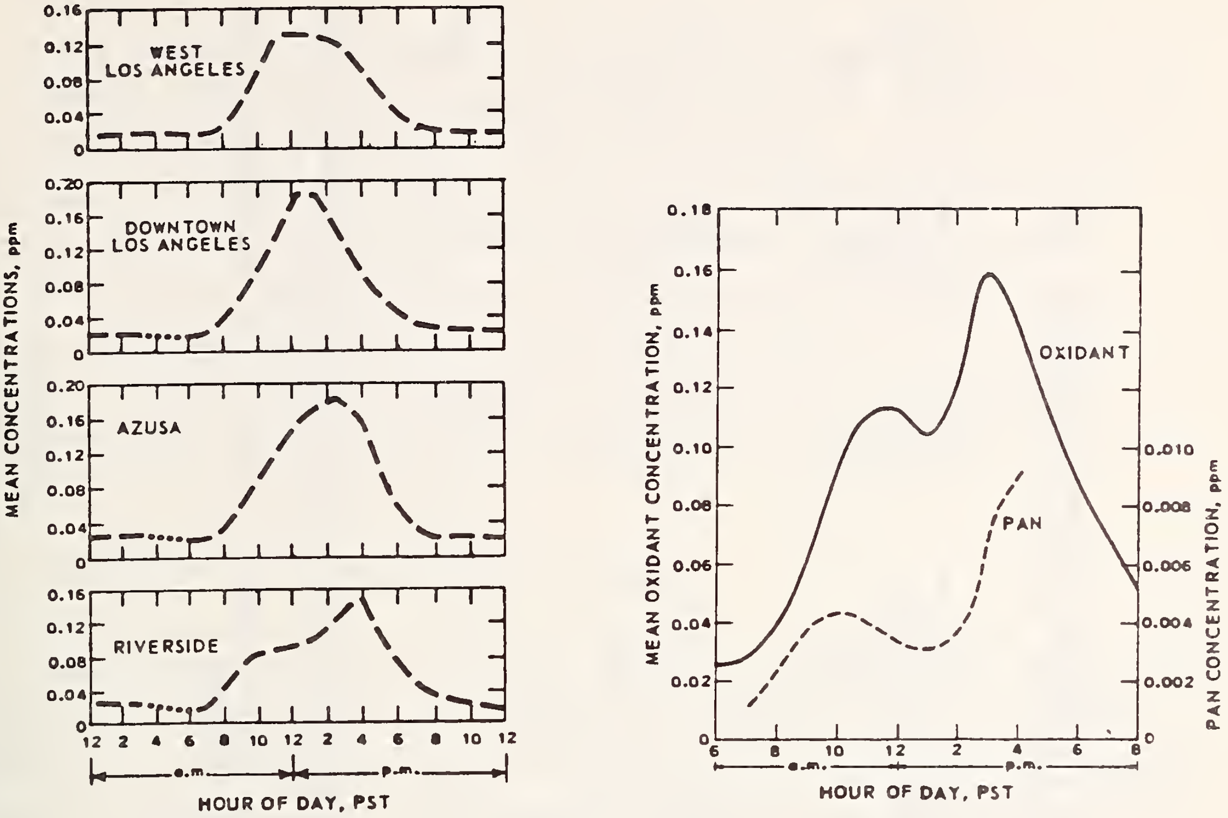
FIGURE 16. MONTHLY VARIATIONS OF MEAN DAILY MAXIMUM ONE-HOUR-AVERAGE OZONE AND OXIDANT CONCENTRATIONS IN LOS ANGELES AND PASADENA, 1964-1965

mountains. Hence, the highest oxidant concentrations occur at the base of these mountains, along the northern perimeter of the region. For example, Figure 17(a) presents the diurnal variations in ozone concentrations at four monitoring stations, the westernmost being West Los Angeles, with the others at 10 to 20 mile intervals to the east. Note that the peak oxidant concentration occurs at a progressively later hour in the afternoon from one station to the next moving eastward. The occurrence of the peak concentration probably corresponds to the eastward drift of the pollutant cloud. At the station lying farthest to the east (Riverside), two peaks occasionally occur. It is possible that the first peak corresponds to production of oxidant from local emissions and the second to the pollutant cloud drifting in from upwind areas. This double peak pattern is more clearly evident in the data given in Figure 17(b).

Atmospheric concentrations of oxidants have been monitored for a relatively long time in the Los Angeles basin. This data base has been examined by the EPA to determine long term trends in atmospheric concentrations of photochemical oxidants [67]. The number of days on which violations of the federal one-hour oxidant standard occurred and the average duration of high concentrations on those days are presented in Table 26. This table shows clearly that there has been a general trend toward reduced oxidant concentrations throughout the Los Angeles basin over the years. The average number of days exceeding the federal one-hour standard decreased steadily, and the average duration of such episodes also decreased somewhat. Records of ambient oxidant concentrations at several other locations in California also indicate, in most cases, a trend of decreasing concentrations.

Ambient oxidant data outside the State of California are generally available only for the years since 1973 or 1974. Such short periods are normally insufficient to determine trends in air quality. An analysis of third quarter data at 21 sites in 10 states revealed a decreasing tendency for oxidant/ozone violations in eastern cities and an increase in Denver, but no firm conclusions about regional trends could be drawn.



(a) Oxidant Concentrations at Selected California Sites, October 1965

(b) Oxidant and PAN Concentrations at the Air Pollution Research Center, Riverside, California, September 1966

Source: Ref. 12.

FIGURE 17. DIURNAL VARIATION OF MEAN ONE-HOUR-AVERAGE OXIDANT AND PAN CONCENTRATIONS IN CALIFORNIA

TABLE 26. VIOLATIONS OF THE FEDERAL STANDARD FOR OXIDANT FROM 1965 TO 1975 IN THE LOS ANGELES AIR BASIN

Index	1965 and 1966	1967 and 1968	1969 and 1970	1971 and 1972	1973 and 1974
Average number of days per year with oxidant concentrations over 160 μg/m^3 (8 pphm)	176	162	144	109	105
Average daily duration,* hr	5.1	4.8	4.6	3.8	4.3
Average number of days per year with oxidant concentrations over 320 μg/m^3 (16 pphm)	70	59	45	26	26
Average daily duration,† hr	3.1	3.1	2.8	2.1	2.9

---

* The average daily duration is the average number of hours per day the oxidant concentration exceeded the federal standard.

† The average daily duration is the average number of hours per day the oxidant concentration exceeded twice the federal standard.

Source: Ref. 67.

7. Summary

The preceding sections show that vehicles are the major sources of CO and significant sources of HC and NO_x in many urban areas. In contrast, they are minor contributors to SO_x and particulate emissions. Atlanta, Chicago, Los Angeles, New York City, and St. Louis are all examples of this pattern. In areas with high vehicle use and relatively little industrialization, such as Dallas/Ft. Worth and Denver, vehicles contribute somewhat more of the SO_x and particulate emissions. Specific industrial activities, such as the steel industry in Birmingham and the petroleum industry in Houston/ Galveston, cause relative vehicular emissions of certain pollutants to differ markedly from average values.

D. AIR QUALITY IN THE PROXIMITY OF A ROADWAY

Vehicular emissions affect primary pollutant concentrations most in the immediate vicinity of a roadway. Atmospheric processes generally disperse pollutants more and more as they are carried downwind from a roadway. Unless a pollutant undergoes very rapid chemical transformation, its secondary products will form somewhere downwind of the source. This section discusses air quality on roadways and within about 500 feet downwind. According to one study, at that distance CO concentrations generally tend to approach the background concentrations upwind of the roadway [8]. Other primary pollutants should exhibit similar behavior.

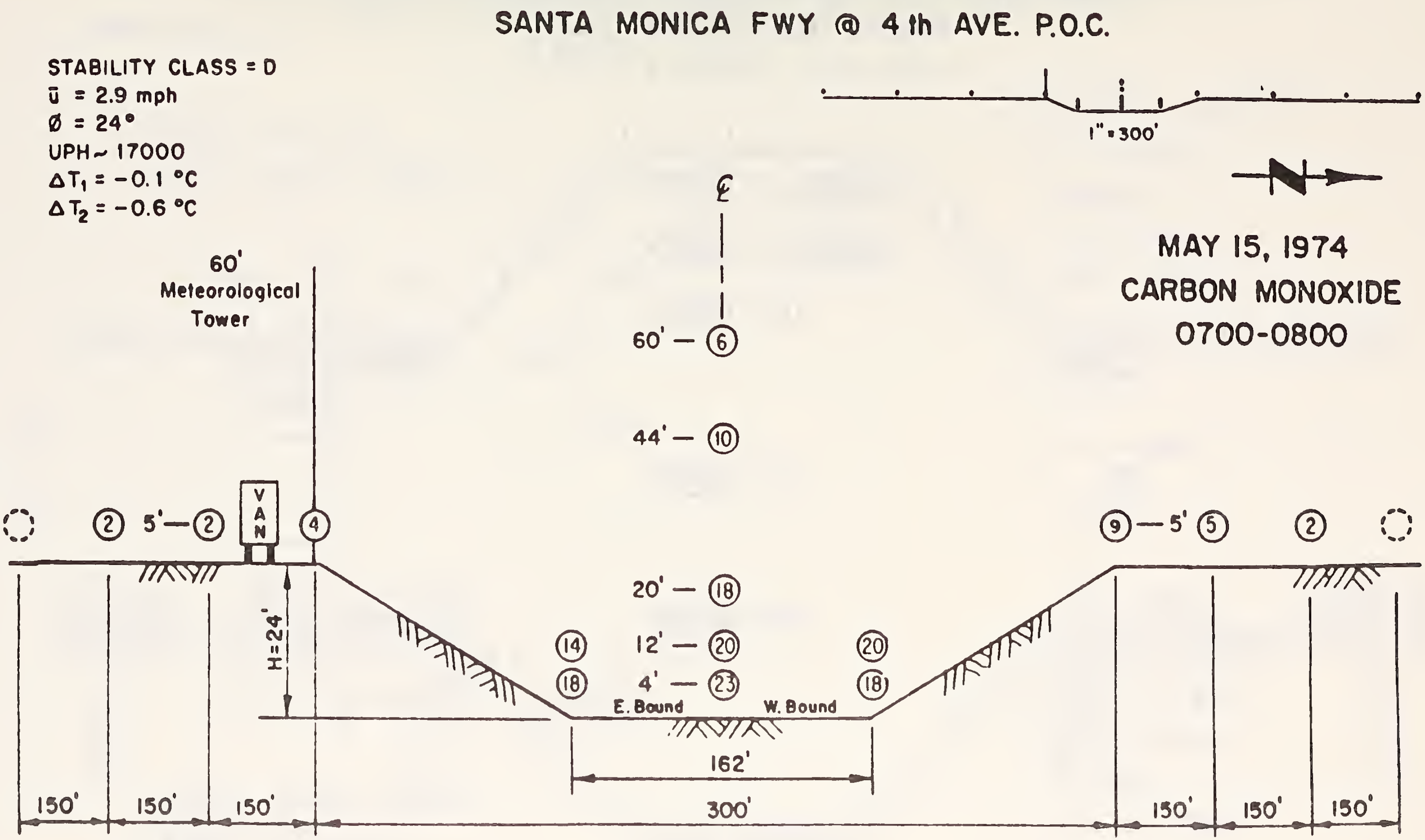
Pollutant concentrations within vehicles on roadways are of some interest because they indicate the exposure of drivers to air pollutants. Few data are available on in-vehicle concentrations. In one recent study, CO concentrations greater than 25 ppm were measured for 30 minutes in an automobile following a truck up a long, steep grade [81]. (Recall that the federal CO standard is 35 ppm for one hour.) A brief study of in-vehicle concentrations suggests that they are unlikely to exceed air quality standards except in unusual cases, and in those cases the concentrations at the downwind edge of the roadway might be greater than in the vehicles. Thus, no air quality standards apply specifically to in-vehicle concentrations, nor are any anticipated, and in-vehicle concentrations are not discussed further in this report.

Figures 18 through 21 illustrate the concentrations and spatial distributions of various pollutants in and around a depressed roadway in Los Angeles [82]. In these figures, ϕ is the angle between the roadway and the wind direction. (When $\phi = 90$ the wind is blowing directly across the roadway.) Note that:

> The concentrations of primary pollutants (CO, HC, particulates, lead, and NO) are highest near the roadway.
> The concentrations generally decrease with height above the roadway.
> The concentrations immediately downwind of the roadway are higher than those immediately upwind.

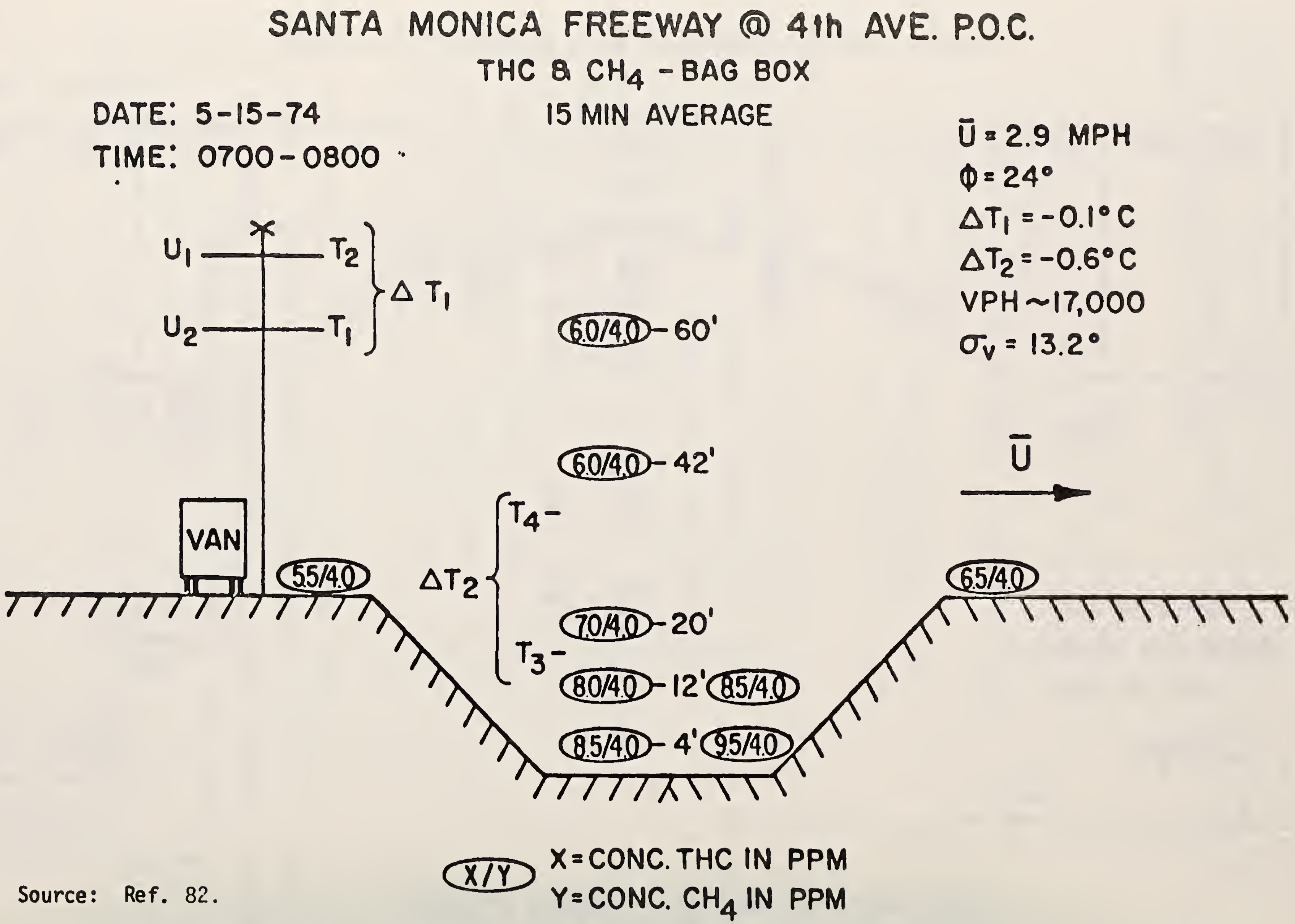
Each of these observations is consistent with the simple conceptual picture of a roadway illustrated in Figure 22. In this figure, the mechanical mixing cell is a region of intense turbulent mixing induced by the passage of motor vehicles. As pollutants are transported downwind from this cell, they are continually diluted (presuming the absence of other emissions) until the background concentration is approached. For example, the ambient CO concentration upwind of the roadway in Figure 18 appears to be 2 ppm. The CO concentration drops to that level again at about 369 (69 + 150 + 150 = 369) feet downwind from the edge of the roadway. Figure 23 illustrates a situation where the federal one-hour air quality standard for CO of 35 ppm is violated in many locations around a fill section [83]. Similarly, Figure 24 presents a situation where the federal eight-hour CO standard of 9 ppm is violated.

Unfortunately, there is a paucity of data pertaining to the spatial distributions of the other pollutants emitted by motor vehicles. Although it is not possible to make general statements regarding possible violations of air quality standards on the basis of the limited results presented in Figure 19 through 21, several observations can be made. Figure 19 shows that the concentration of methane (CH_4) is essentially invariant, indicating that most of the vehicular hydrocarbon emissions are nonmethane hydrocarbons.



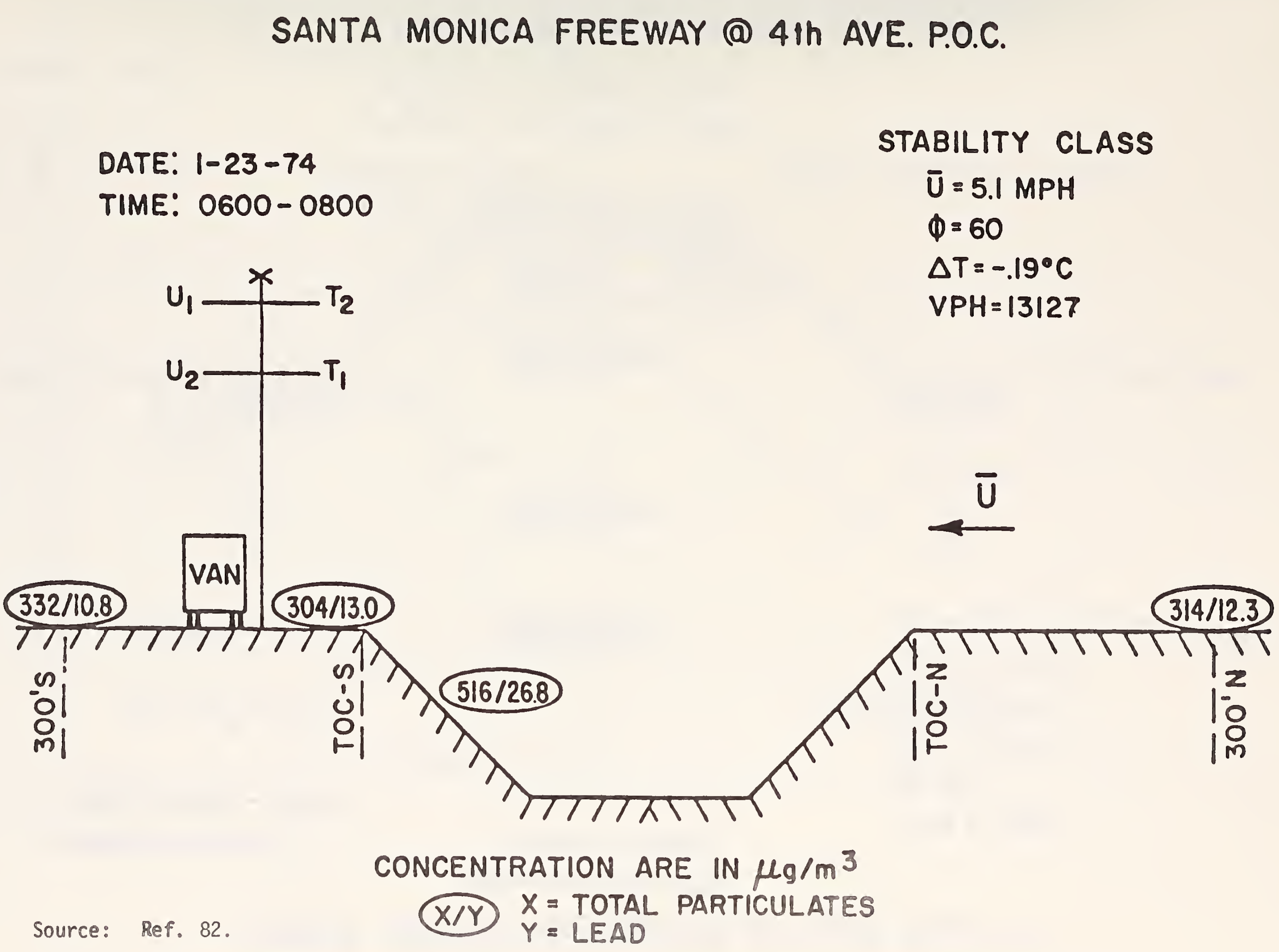
Source: Ref. 82.

FIGURE 18. DISTRIBUTION OF CO IN A DEPRESSED ROADWAY SECTION



Source: Ref. 82.

FIGURE 19. DISTRIBUTION OF TOTAL HYDROCARBONS AND METHANE IN A DEPRESSED ROADWAY SECTION



Source: Ref. 82.

FIGURE 20. DISTRIBUTION OF TOTAL PARTICULATES AND LEAD IN A DEPRESSED ROADWAY SECTION

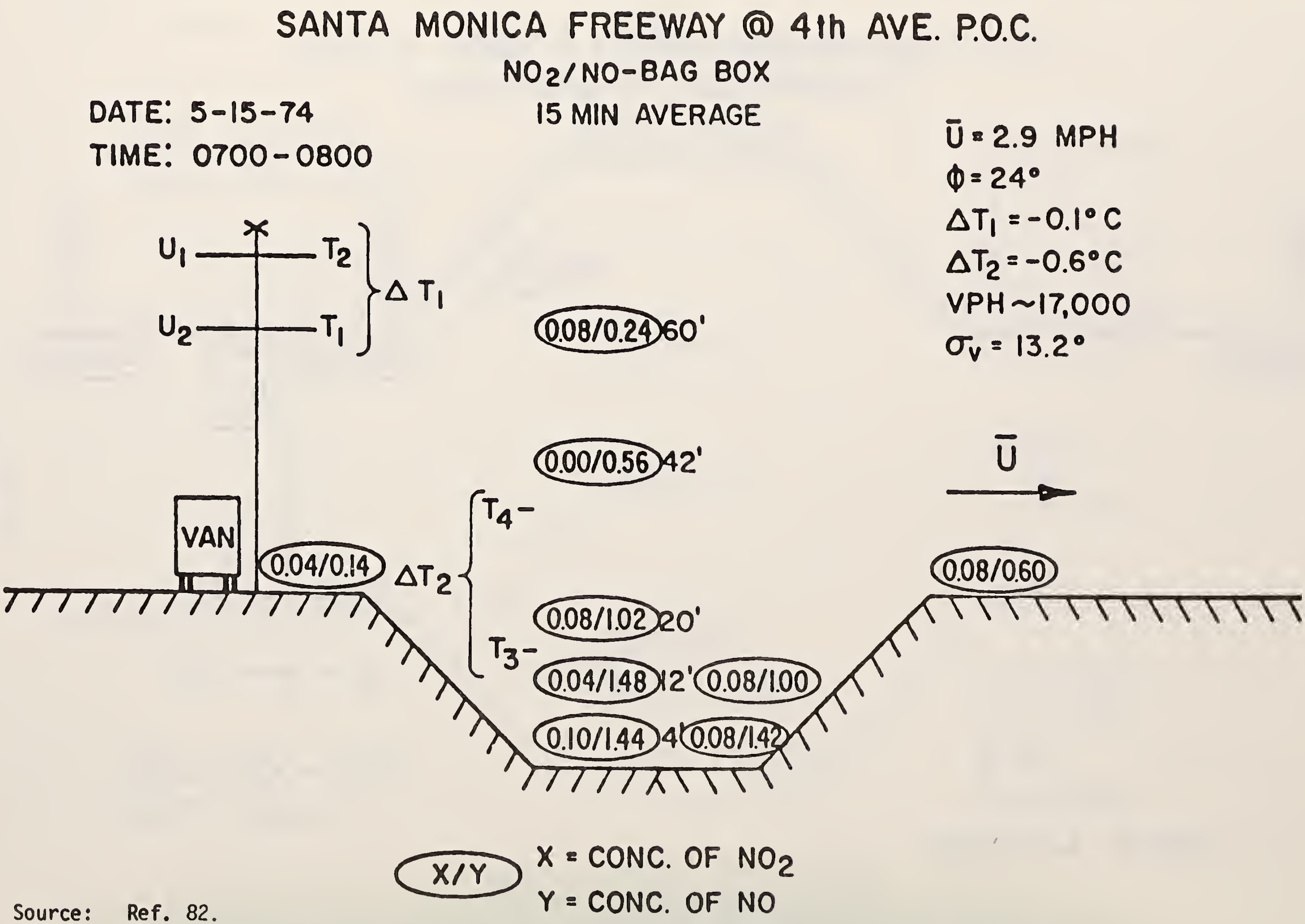


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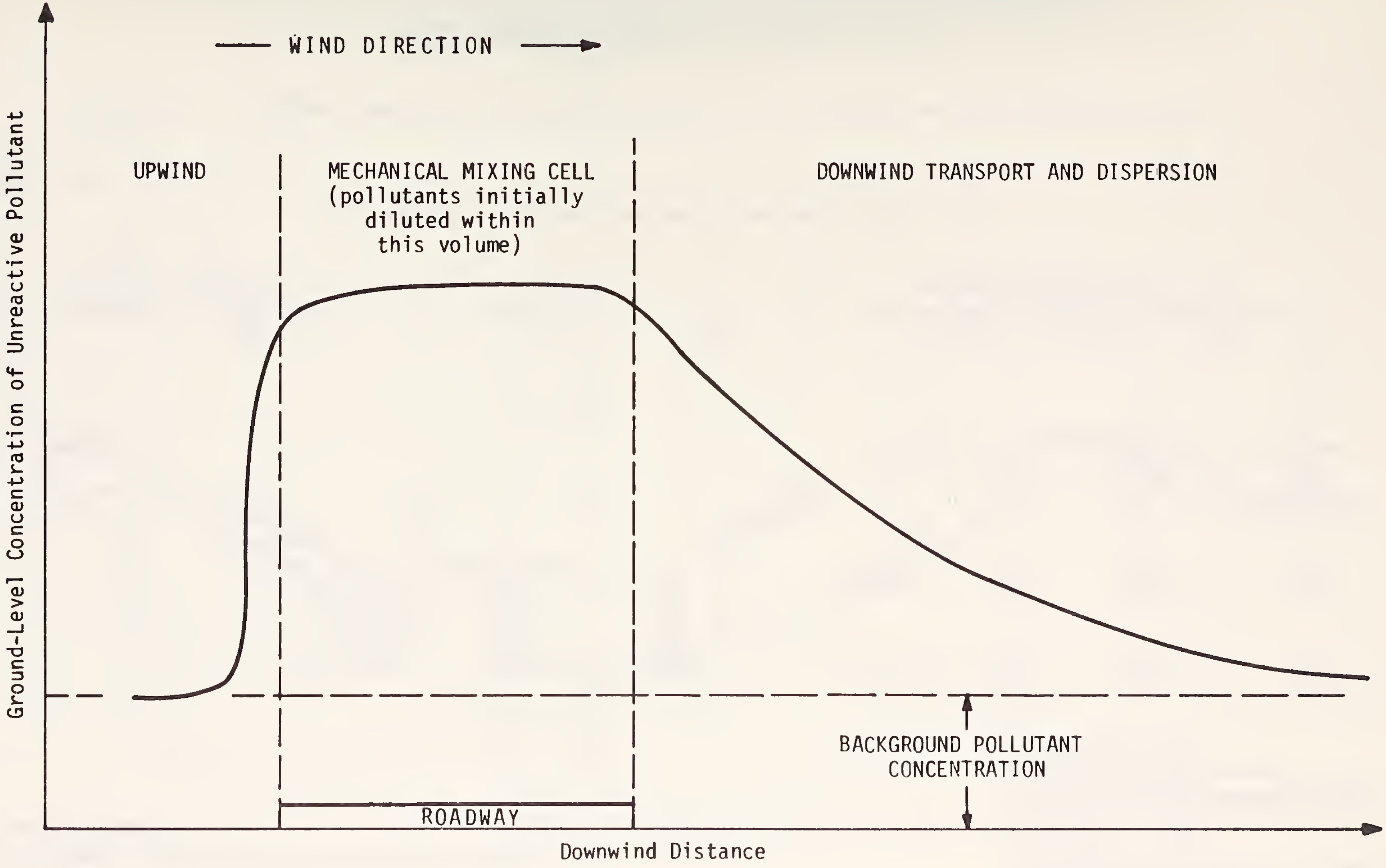
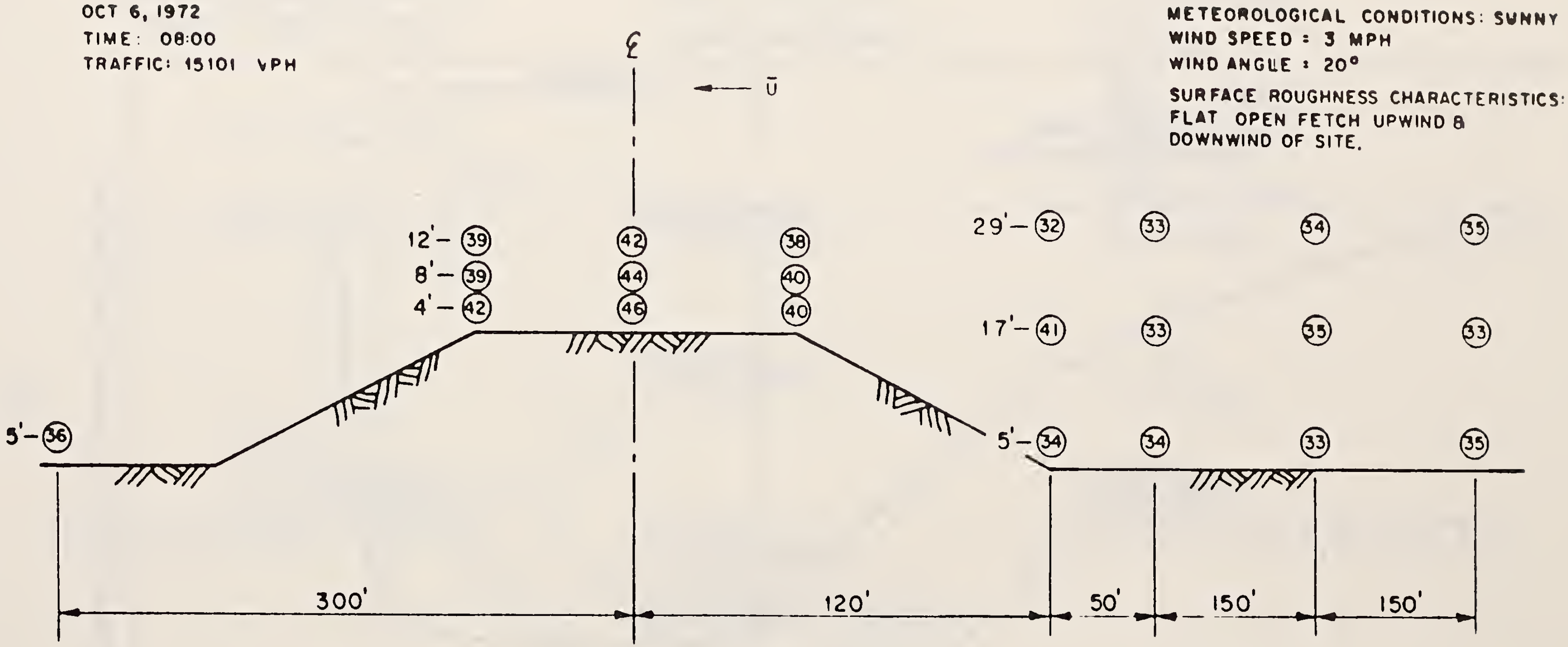
FIGURE 21. DISTRIBUTION OF NO AND NO_2 IN A DEPRESSED ROADWAY SECTION



Source: Adapted from Ref. 83.

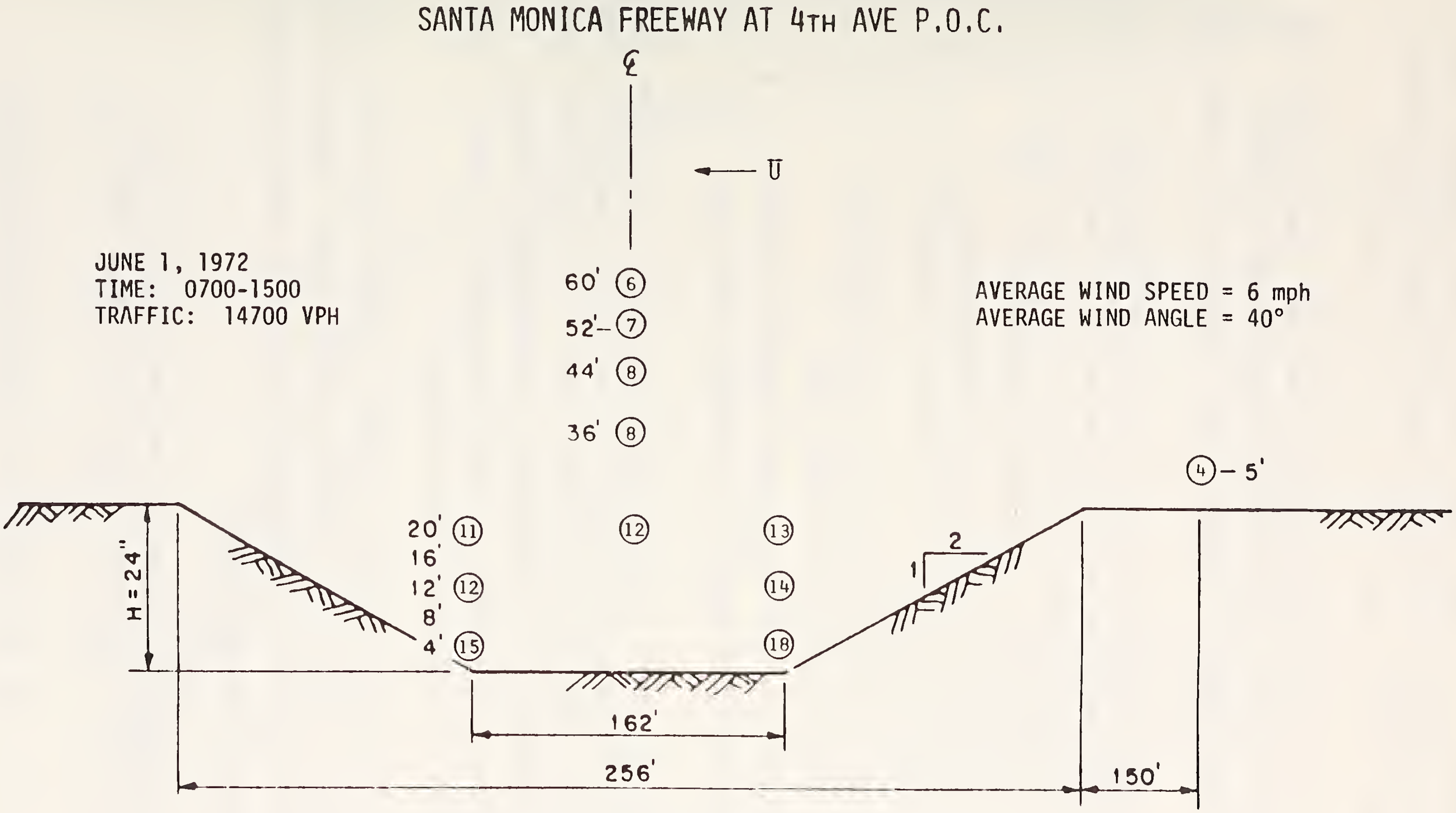
FIGURE 22. CONCEPTUAL MODEL OF AIR QUALITY IN THE VICINITY OF A ROADWAY



① Denotes one-hour-average CO concentration in ppm.

Source: Ref. 83.

FIGURE 23. A HIGHWAY CORRIDOR EXHIBITING VIOLATIONS OF THE FEDERAL ONE-HOUR STANDARD FOR CO



① Denotes eight-hour-average CO concentration in ppm.

Source: Derived from data presented in Ref. 83.

FIGURE 24. A HIGHWAY CORRIDOR EXHIBITING VIOLATIONS OF THE FEDERAL EIGHT-HOUR STANDARD FOR CO

Figure 20 illustrates that lead constitutes less than 10 percent of the total particulate burden. And finally, Figure 21 clearly indicates that most of the NO_x emitted by motor vehicles is in the form of NO.

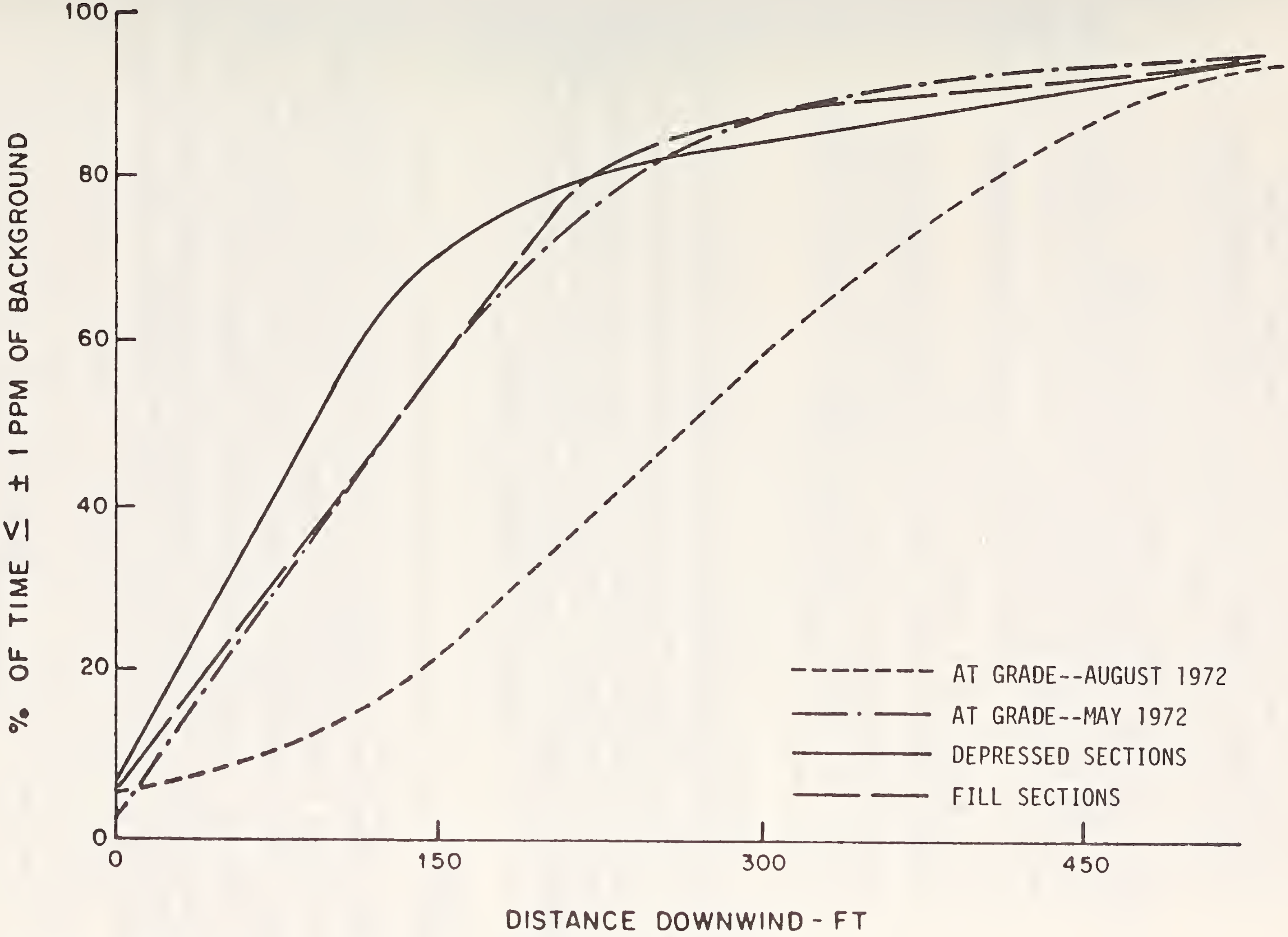
In one study, numerous CO measurements were made around roadways in the Los Angeles area [82]. Three highway geometries were studied: depressed, at-grade, and fill sections. Some findings of this study are:

> The highest CO concentrations, 10 to 25 ppm greater than background, were observed at the median of the roadway.
> CO concentrations 150 feet downwind of the roadway tended to be 1 to 4 ppm above background concentrations.
> Turbulent mixing was generally sufficiently strong to remove vertical concentration gradients immediately downwind of the roadway.
> Background CO concentrations were reached 200 to 300 feet downwind of roadways in urban areas.
> Background CO concentrations were reached at distances exceeding 400 feet downwind of roadways in open areas.

Figure 25 summarizes some findings of that study [83]. The at-grade findings for August 1972 differ significantly from those for April 1972, probably because of meteorological conditions. Note that these findings are based on a single study of air pollution around roadways in Southern California: Other roadways under different meteorological conditions may exhibit somewhat different quantitative behavior.

Temporal variations in primary pollutant concentrations around a roadway are induced by variations in emissions and dispersion. Important factors influencing both the spatial and temporal variations of primary pollutant concentrations near roadways include:

> Emissions--Concentrations of a relatively inert pollutant such as CO are proportional to the emissions of that



Source: Ref. 83.

FIGURE 25. ATTAINMENT OF BACKBROUND CO CONCENTRATIONS DOWNWIND OF FILL, AT-GRADE, AND DEPRESSED HIGHWAY SECTIONS

pollutant from the nearby roadway, assuming all other factors are equal.

> Turbulent mixing--Pollutant concentrations near roadways are reduced when turbulent mixing is enhanced. Limited mixing conditions tend to occur more frequently during the night and during the winter (see Section VII.B). Structures near roadways generally enhance turbulent mixing.

> Wind speed--Pollutant concentrations near roadways decrease when the wind speed increases. Calm or light winds favor pollutant buildup around a roadway.

> Wind direction--Pollutant concentrations are higher immediately downwind of a roadway than upwind.

> Roadway design--Elevated roadways may allow emissions to be more dispersed before reaching the ground than similar emissions from at-grade or depressed roadways. Depressed roadways tend to restrict pollutant dispersion.

The conditions most conducive to significant pollutant buildup in a highway corridor are high emissions (rush-hour traffic), calm or very light winds, and a stably stratified atmosphere. This discussion points out the great influence on air pollutant concentrations of the wind speed and atmospheric stability. These characteristics of the atmosphere, and many others, are discussed in the next two chapters.

E. SUMMARY

This chapter has described air quality in various settings including urban and rural areas and highway corridors. The contributors of motor vehicles, other anthropogenic, and natural sources have been described. The general types of air quality problems found in various parts of the nation were also described. Finally, this chapter introduces several factors that influence the development of high pollutant concentrations. These factors are discussed further in Chapters VII and VIII.

VII ATMOSPHERIC PHYSICAL AND CHEMICAL PROCESSES

Thus far this report has discussed emissions and ambient concentrations but passed over the links between them, the many atmospheric processes that affect air pollutants. A knowledge of these processes is useful to transportation planners for two reasons:

> It helps them to qualitatively relate pollutant emissions to pollutant concentrations.
> It forms a basis for understanding air quality models and planning air quality monitoring programs.

This chapter is a general introduction to atmospheric processes of importance in air pollution. It begins with a brief discussion of various processes and how they are related, and goes on to discuss in some detail the movement of pollutants, their chemical reactions, and the processes that remove them from the atmosphere. Chapter VIII expands on this introduction by discussing the processes that are important at three spatial scales of interest in transportation planning.

The atmospheric processes that affect air pollutants can be separated into two types, physical and chemical. Many physical processes are associated with pollutant transport, that is, the movement of pollutants from one point in the atmosphere to another through the action of the wind. Chemical processes refer to the transformations that a reactive pollutant can undergo through interaction with sunlight, air, or other pollutants. For example, hydrocarbons, nitrogen oxides, and sunlight produce ozone through a complicated chemical process. Not all atmospheric processes are solely physical or chemical. The removal of pollutants from the atmosphere, for example, often occurs through a combination of physical and chemical processes in which the pollutant is first transported to the surface and then undergoes chemical transformation.

Many of the physical and chemical processes discussed in this chapter are introduced in Figure 26. This figure shows the processes occurring in a control volume, that is, a fixed, stationary volume of any size, which is at the earth's surface. As shown in Figure 26, air, perhaps containing pollutants, enters and leaves the control volume primarily by two modes of atmospheric transport: advection (the average wind) and turbulent diffusion. The vertical movement of air, which can mix pollutants within a larger volume, is sometimes inhibited by a temperature inversion (not shown). Pollutants may be emitted directly into the control volume, and they may be formed and consumed by chemical reactions within it. Pollutants may also be transported into the volume or removed from it by gravitational settling, precipitation scavenging, and other mechanisms. Finally, since the volume is at the earth's surface, pollutants may be removed by surface uptake mechanisms such as absorption by plants, soil, structures, or water. Thus, even in qualitative terms, concentrations of air pollutants are affected by many complicated processes.

The concentrations of air pollutants are also affected by some factors ignored in Figure 26. For example, the rates of almost all chemical reactions depend on temperature. The rates of a few important reactions depend on the intensities of sunlight in particular wavelength bands. In addition, the processes shown in Figure 26 affect one another. To cite just two examples, the vegetation in the control volume affects both the absorption of pollutants and the atmospheric transport through that volume. Again, emissions into that volume, if warmer than the ambient air, increase pollutant concentrations but also promote vertical atmospheric transport because warm air rises.

Physical and chemical influences on air quality are discussed below in four categories: atmospheric transport, temperature inversions, chemical reactions, and removal phenomena. The next chapter discusses the relative importance of each process at different spatial scales.

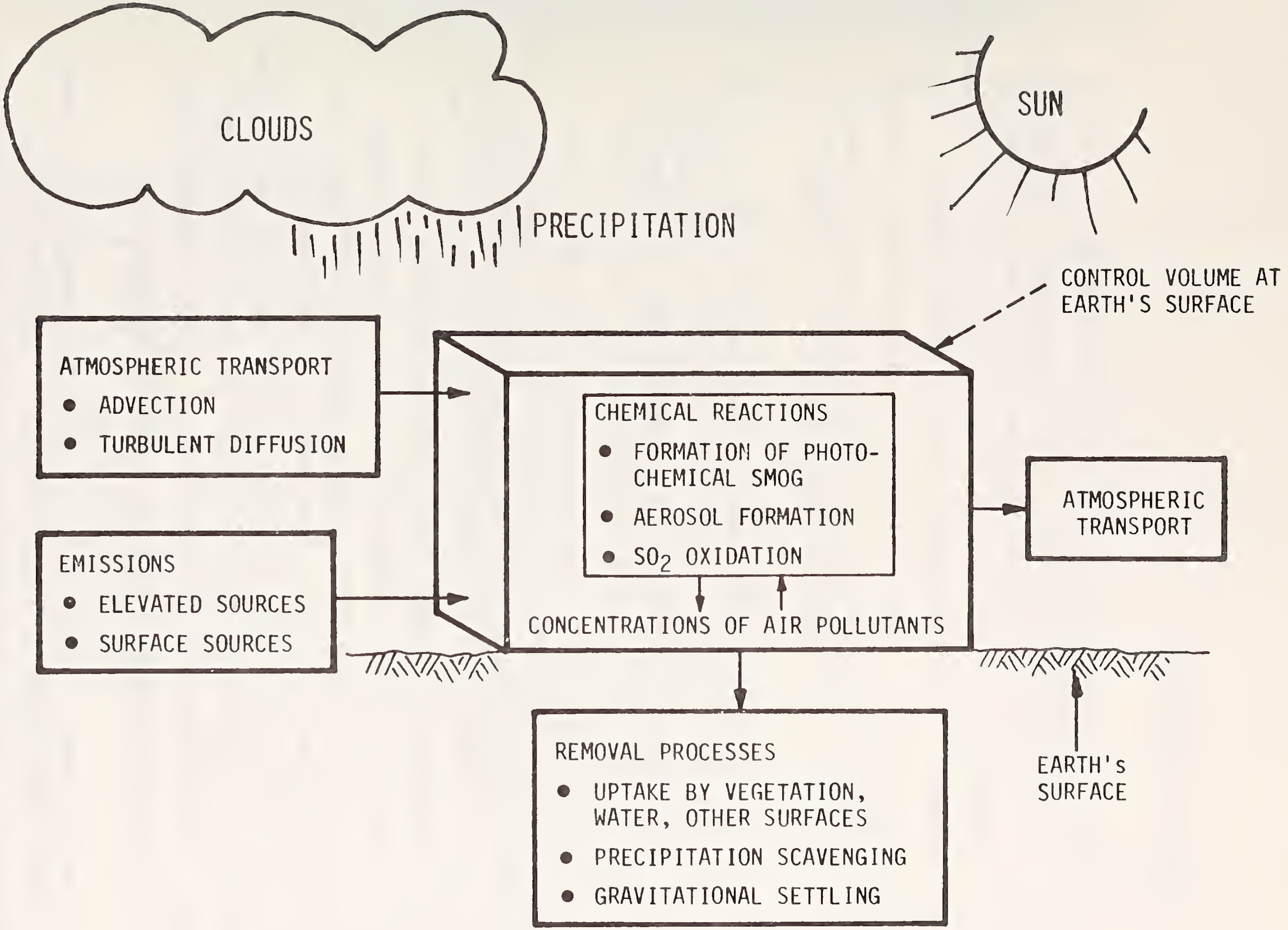


FIGURE 26. SOME PROCESSES THAT AFFECT CONCENTRATIONS OF AIR POLLUTANTS

A. ATMOSPHERIC TRANSPORT

Atmospheric transport refers to the transfer of material from one location in the atmosphere to another. For the most part, the following discussion in confined to transport phenomena within the lower portion of the troposphere, which itself consists of the lowest 10 to 15 kilometers of the atmosphere. Later discussions in this chapter concerning the fate of air pollutants on the synoptic (regional) scale touch upon transport phenomena associated with the upper troposphere and the stratosphere, which is roughly 15 to 50 kilometers above the earth's surface.

In discussing transport phenomena in the troposphere, it is useful to consider three layers. As depicted in Figure 27, the <u>surface layer</u> is the first 50 to 100 meters of the atmosphere. It is in this layer that the influence of terrain, buildings, and localized heat sources on meteorology and air quality is most pronounced. In the <u>planetary boundary layer</u>, which includes the first 300 to 500 meters above ground, the influence of surface features on atmospheric motion decreases from a maximum at the ground to essentially zero at the top. Note that the planetary boundary layer includes the surface layer. Finally, above the planetary boundary layer, the influence on atmospheric motion of surface effects, such as surface friction and local temperature differences, ceases. Atmospheric motions above this layer, in the so-called <u>geostrophic layer</u>, consist of large scale thermal circulations, as modified by Coriolis effects arising from the earth's rotation. Except as noted, the discussions of transport phenomena that follow pertain to processes within the planetary boundary layer.

In descriptions of atmospheric transport, two processes are commonly discussed: advection and turbulent diffusion. These processes are distinguished by the fluctuations in wind speed and direction appropriate to each. Suppose, for example, one obtained an instantaneous wind speed record, such as the one depicted in Figure 28, from a weather station.

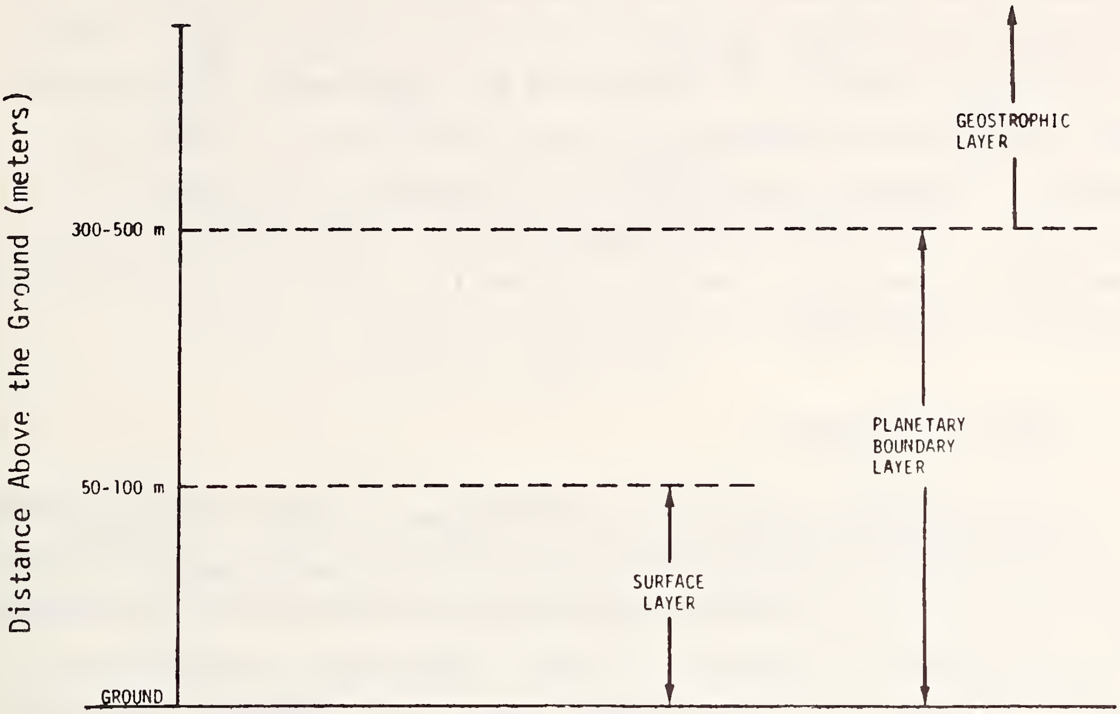


FIGURE 27. REGIONS OF THE TROPOSPHERE CLASSIFIED ACCORDING TO THE INFLUENCE OF THE EARTH'S SURFACE

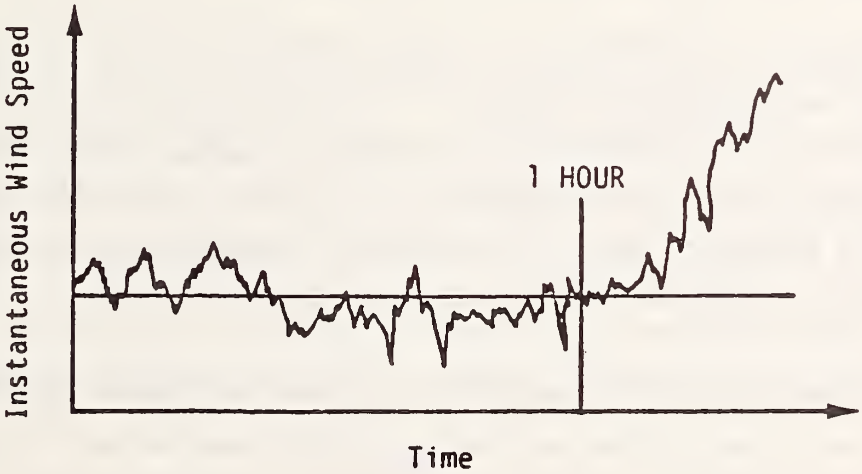


FIGURE 28. TYPICAL RECORD OF WIND SPEED AT A POINT IN A TURBULENT ATMOSPHERIC FLOW

At any instant, the instantaneous wind speed can be expressed as the sum of the mean wind speed and a wind speed fluctuation about the mean. Because of the randomness of instantaneous wind velocities, however, it is impossible to measure or predict the fluctuations precisely. One of the principal advantages of decomposing the instantaneous wind speed into mean and fluctuating components is that deterministic and stochastic methods of analysis, respectively, can be applied to the study of each component. The physical significance of the mean and fluctuating wind components is that they give rise to advective transport and turbulent diffusion, respectively.

1. Advective Transport

Briefly stated, advection is the transport of material through the action of a mean or average wind velocity. As a simple example, consider the release of a hypothetical "neutrally buoyant" particle at some point in the atmosphere. ("Neutrally buoyant" means that no buoyancy forces act on the particle.) If photographs were taken at constant time intervals of the particle's position as it moved downwind, a composite picture of the particle's trajectory could be made, perhaps one like that shown in Figure 29. Between any two positions A and B along the particle's trajectory, the average wind velocity that is advecting the particle can be determined simply by dividing the particle's displacement by the time period during which the displacement occurred.

It should be clear that the average wind velocity is influenced by the length of the averaging period. As the averaging period increases, variations in wind velocities tend to become smoothed; conversely, for shorter and shorter periods the variations in wind velocities tend to become more irregular, and for a very short averaging period the mean wind velocity approaches the instantaneous wind velocity.

Advection occurs on a variety of temporal and spatial scales. For example, large particulates emitted by vehicles may be carried by the bulk motion of the wind only a few tens of meters. On a much larger scale,

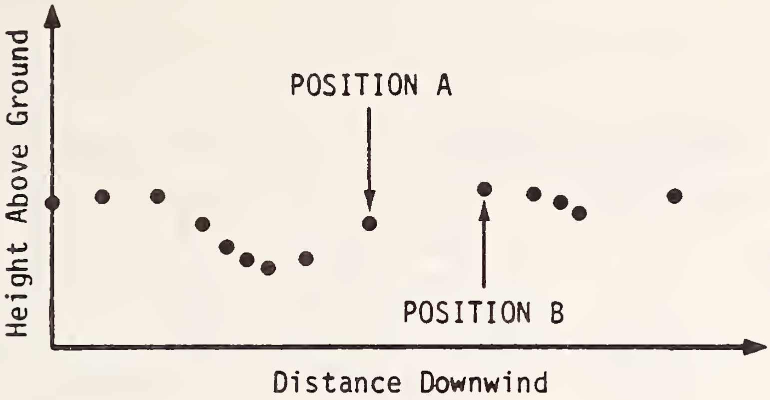


FIGURE 29. TIME LAPSE TRAJECTORY OF A PARTICLE ADVECTED BY THE WIND

gaseous pollutants emitted in urban areas may be advected thousands of kilometers. Consequently, advective transport should be discussed within the context of specified temporal and spatial scales.

2. Turbulent Diffusion

Turbulent diffusion refers to the observed spreading or dilution of particles in the atmosphere as a consequence of random, irregular fluctuations in the wind. Suppose that at some point in the turbulent atmosphere a cluster of neutrally buoyant particles was released. The motion of the particles might be similar to that depicted in Figure 30, which shows two important transport processes. First, the center of mass of the cluster of particles is advected downwind. Second, with respect to the cluster's center of mass, individual particles are spread farther apart. The latter effect is called turbulent diffusion by analogy with the diffusion of molecules in still air. However, the analogy is not exact; in turbulent diffusion whole parcels (or eddies) of material undergo erratic displacement, whereas in molecular diffusion only individual molecules diffuse. Because considerably more material is contained in turbulent eddies and because they are transported over far greater distances in the flow than

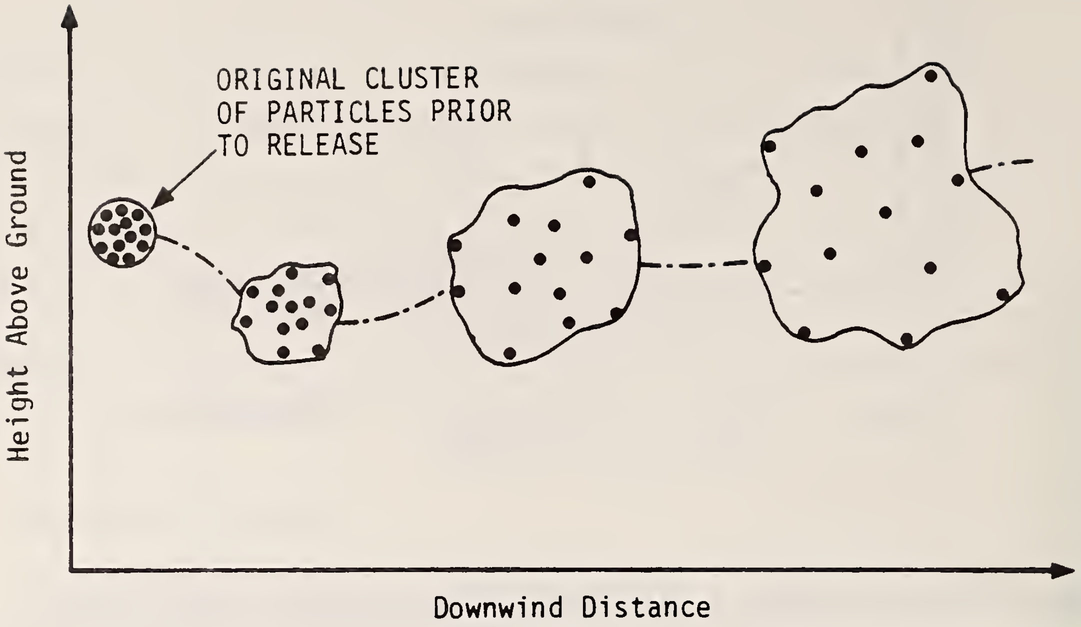


FIGURE 30. TURBULENT DIFFUSION OF A CLUSTER OF NEUTRALLY BUOYANT PARTICLES IN THE ATMOSPHERE

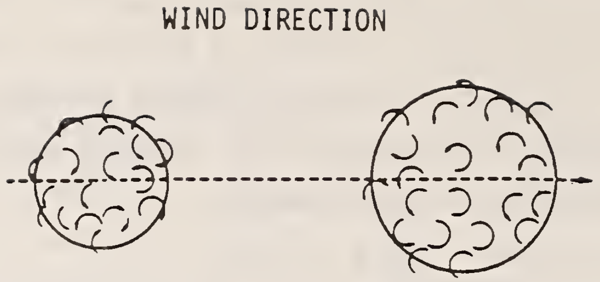
individual molecules diffuse, molecular diffusion in the atmosphere is generally insignificant compared with turbulent diffusion.

A wide range of eddy sizes exist in the atmosphere. For example, turbulent eddies generated by the passage of an automobile may have spatial scales on the order of the size of the vehicle. In contrast, eddies generated by airflow over a mountain ridge may have characteristic sizes on the order of the height of the ridge. The size of the turbulent eddies is very important to the rate of pollutant dilution. For example, consider a power plant emitting puffs of effluents into a turbulent atmosphere. If the ambient turbulence is characterized by eddies whose spatial scale is small compared with each puff's dimension, then turbulent mixing of the puffs and the atmosphere may be relatively slow. Conversely, if characteristic eddy sizes are large compared with the size of the puffs, then each puff is likely to be carried as a whole from one location to another, again with relatively little mixing. If typical eddy sizes are of the same order as the puff size, atmospheric turbulence can be extremely effective in mixing the puffs, leading to rapid dilution. As with advective transport, it is important to consider the relevant temporal and spatial scales when discussing turbulent diffusion. Figure 31 depicts the qualitative relationship between eddy size, initial cluster size, and rate of dilution. In the next chapter further attention is given to the role that turbulent diffusion plays in diluting air pollutants.

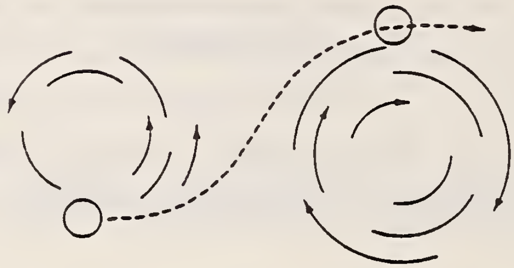
3. Dispersion Phenomena

So far, atmospheric transport has been discussed in terms of the transfer of material due to the bulk motion of the wind (advection) and mixing by random fluctuations in the wind velocity (turbulent diffusion). The term "dispersion" is often used to refer to certain combinations of advection and turbulent diffusion. Some simple examples of dispersion are given below.

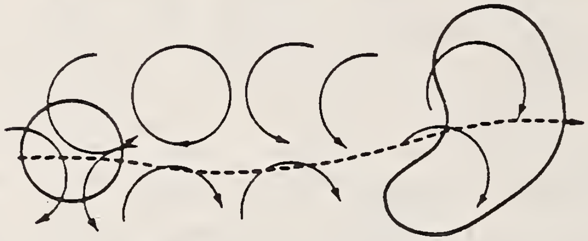
The wind direction, wind speed, or both often exhibit wind shear, that is, they change with height above the ground. Consider a turbulent flow in which a wind speed shear is present (i.e., a turbulent shear flow). Because the flow is turbulent, random irregular motion will occur, giving rise to turbulent diffusion. However, because of the wind shear, the average wind velocities and velocity fluctuations can be expected to be greater in some regions of the flow than in others. In the example in Figure 32, the combination of atmospheric turbulence and wind shear leads to more rapid spreading of particles in regions far away from the ground than close to the ground. This process is sometimes referred to as shear dispersion.



(a) A Large Cluster in a Uniform Field of Small Eddies



(b) A Small Cluster in a Uniform Field of Large Eddies



(c) A Cluster in a Field of Eddies of the Same Size as the Cluster

Source: Ref. 84.

FIGURE 31. IDEALIZED DIFFUSION PATTERNS

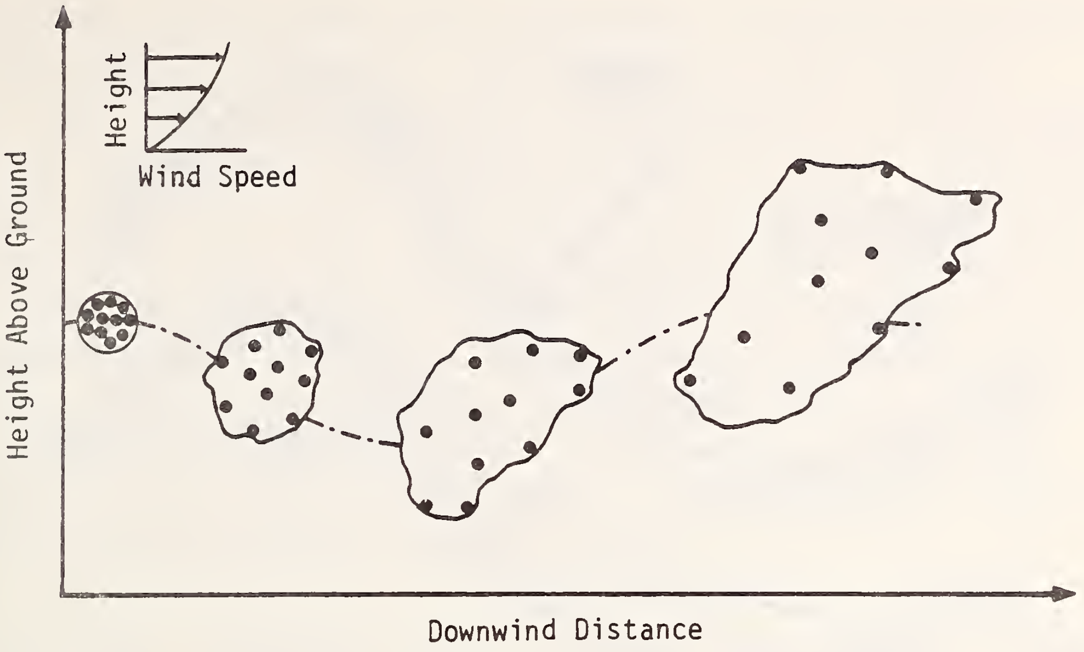


FIGURE 32. ATMOSPHERIC DISPERSION OF A CLUSTER OF PARTICLES IN A TURBULENT SHEAR FLOW

Velocity shears of the type shown in Figure 32 often arise from the retardation of the lower level wind by surface friction. Wind shear can arise in other ways, however. Figure 33 shows an example in which cool nighttime air flows downslope (a so-called drainage flow). In the figure, the drainage flows are undercutting an upper level wind in the opposite direction. A parcel of air located near the interface of the two flows would be subject to shearing in addition to any turbulent mixing that might exist. Thus, any pollutants in that parcel would be spread considerably faster than if the spread was governed by turbulent diffusion alone.

Dispersion is particularly important in regions where wind shear is pronounced and atmospheric turbulence is intense. Both of these conditions occur in urban areas and over rugged terrain because surface irregularities cause velocity shears in all directions and enchance the production of turbulence. The influence of surface features and atmospheric turbulence on the dispersion of pollutants is discussed in greater detail later in this chapter.

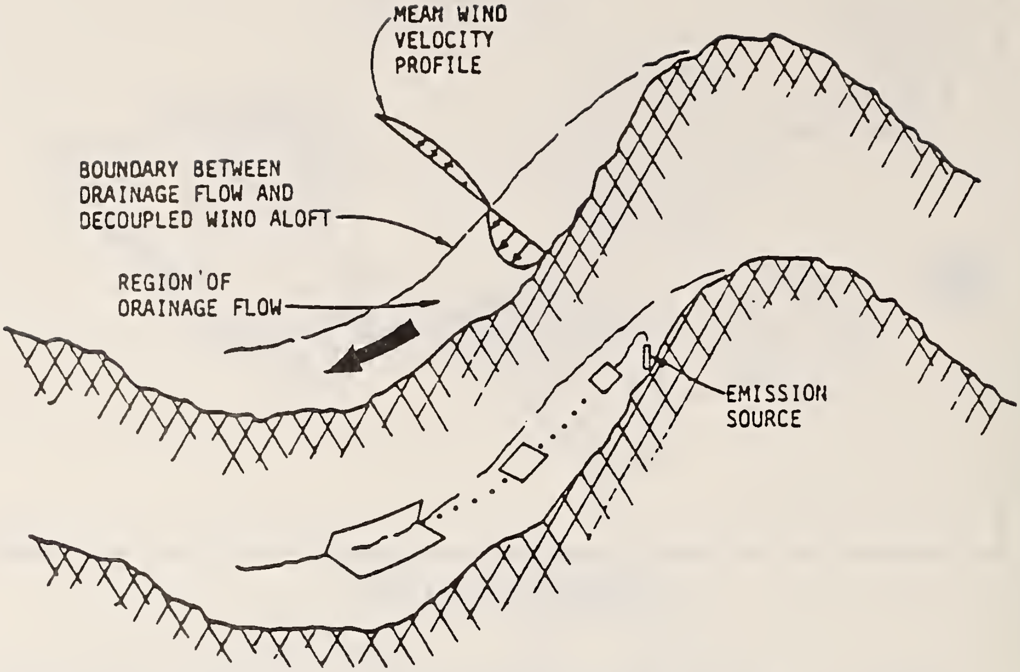


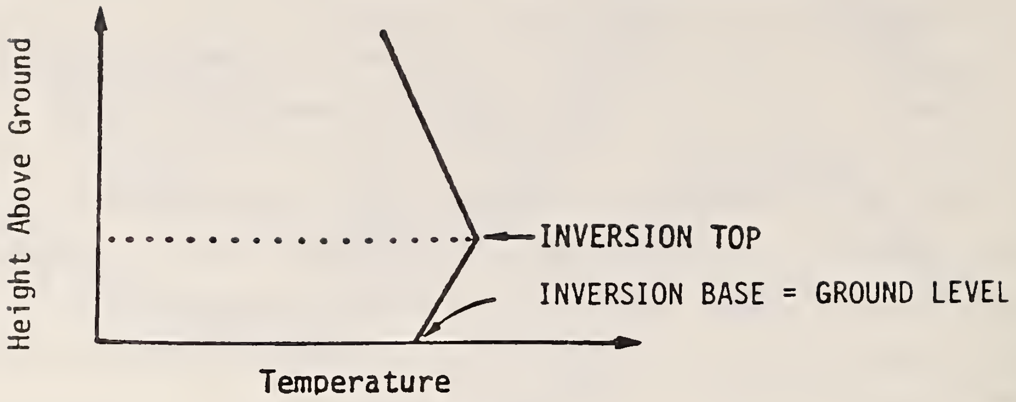
FIGURE 33. EXAMPLE OF AN AIR PARCEL DEFORMED BY A COMPLEX SHEAR FLOW INVOLVING DRAINAGE WINDS AND UPPER LEVEL WINDS IN OPPOSITE DIRECTIONS

B. ATMOSPHERIC STABILITY AND TEMPERATURE INVERSIONS

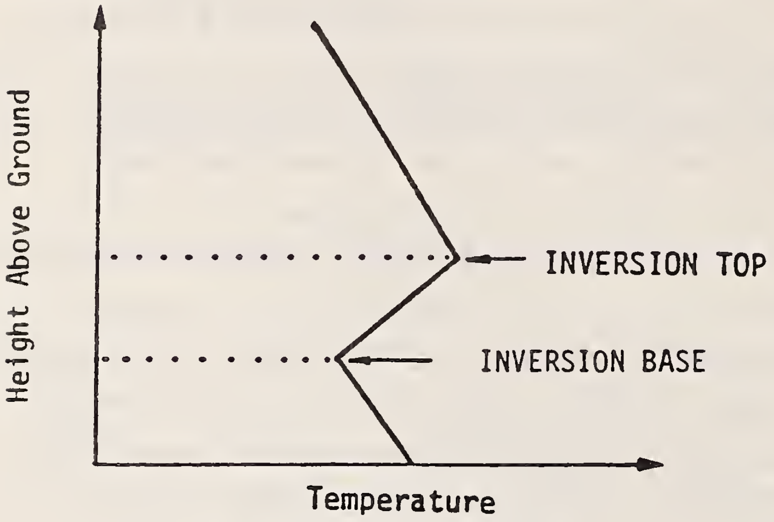
One property of the atmosphere with a great effect on air pollution is its change of temperature with height, which determines the so-called atmospheric stability. Consider a hypothetical parcel of air at ground level in a thermally insulated container. If this container is raised 100 meters above the ground and allowed to expand so that the pressure of the air inside it matches the pressure of the air around it, the temperature of the air inside it will drop. (The amount of the temperature drop varies from about 1°C for dry air to roughly 0.4°C for very humid warm air.) The temperature change of the hypothetical air parcel with height, if no energy is exchanged between it and its surroundings, is termed the adiabatic lapse rate. If the actual change of atmospheric temperature with height, or the environmental lapse rate, is less than the adiabatic lapse rate, when a parcel of air initially at the same temperature as the surrounding air is raised, it will be cooler than the air around it at its new height. Being cooler and thus more dense that its surroundings, the air parcel will tend to resist a further rise. When this condition prevails the atmosphere is termed stable, because its temperature structure retards vertical air motion. The converse condition, instability, occurs when the environmental lapse rate is greater than the adiabatic lapse rate. Under these conditions, when a parcel of air initially at the same temperature as the air around it is raised, it will be warmer than the air around it at its new height. Under these conditions, therefore, a parcel of air that is raised will tend to continue to rise. When the environmental lapse rate equals the adiabatic lapse rate, the atmosphere is said to have neutral stability. Atmospheric stability categories are discussed further in Section X.C.

The concept of atmospheric stability helps in understanding a phenomenon of great importance in air pollution studies--the so-called temperature inversion. A temperature inversion is a stable layer of air, that is, its lapse rate is less than the adiabatic lapse rate. Roughly speaking, this means that the temperature remains constant or increases with height. This is the inverse of the usual situation in the troposphere as a whole, in which the temperature decreases with height--hence, the name "inversion layer." When the bottom of such a layer coincides with the ground, it is called a "surface inversion"; otherwise, it is called an "elevated inversion." Figure 34 shows examples of temperature soundings through surface and elevated inversions. Inversions are normally characterized by their base height, thickness, and internal temperature gradient.

Inversions are important because they inhibit the mixing and dilution of pollutants. Pollutants released within a surface or elevated inversion may experience very little mixing because of the quenching effect of the stable air in the inversion layer on atmospheric turbulence. In contrast, pollutants released below an elevated inversion may diffuse rapidly upward. However, pollutant mixing is constrained by the base of the inversion,



(a) Surface Inversion



(b) Elevated Inversion

FIGURE 34. SCHEMATIC DIAGRAM OF SURFACE AND ELEVATED TEMPERATURE INVERSIONS

which effectively acts as a lid on the layer of air next to the ground. Essentially, the height of the inversion base prescribes a volume within which emissions from ground-based sources can be mixed. In general, the lower the inversion base, the smaller the volume of air available for dilution of pollutants, and hence the higher the pollutant concentrations.

Temperature inversions can be formed in several ways. When frontal activity* occurs, a temperature inversion can form near the interface between cold and warm air masses. Inversions form from advection when warm air flows over cold surfaces (i.e., snow-covered ground, an ocean or lake, or a cold air layer) or when a wedge of cool air undercuts warmer air, as in the case of sea breeze intrusions or drainage flows in mountainous terrain. Over land, surface inversions called nocturnal inversions are produced frequently by radiative cooling of the ground during clear nights. After sunrise, the sun heats the ground, which in turn heats a shallow layer of air above it. The ensuing turbulent convection gives rise to the gradual transformation of the surface inversion into an elevated inversion. Nocturnal surface inversions are usually dissipated through these processes within two or three hours after sunrise. Elevated inversions can be formed by the erosion of surface inversions due to convective mixing, sinking (subsidence) of the upper level air, which is typical of a developing high pressure system (anticyclone), radiation from the top of a cloud layer, and subsidence between convection clouds. Often, two or more of these effects operate together to produce a very persistent inversion.

Elevated inversions created from surface inversions are transient and thus of less importance in air pollution studies than elevated inversions produced by the subsidence of large scale air masses. The latter may cover regions of several thousand square kilometers and persist for several days. Inversions of this type are associated with high pressure cells and often lead to regional air pollution problems, such as those in the northeastern

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* Frontal activity refers to the collision of warm and cold air masses. The temperature discontinuity between the two is called the frontal line or frontal zone.

United States in winter and on the Pacific coast in summer. Elevated inversions formed by anticyclonic subsidence and cloud top radiation can be very persistent, leading to so-called anticyclonic gloom.

C. ATMOSPHERIC CHEMISTRY

Chemistry plays a key role in the relationship between emissions and ambient pollutant concentrations. When pollutants are emitted, they are immediately subject to not only the transport processes described above, but also a variety of chemical reactions. This section summarizes certain problems inherent in describing atmospheric chemistry, and then discusses in detail two classes of chemical transformations in the atmosphere of particular interest in transportation planning. These two are the oxidation of nitrogen oxides and hydrocarbons in the formation of photochemical oxidants, and the formation and growth of atmospheric particulates.

1. Characteristics of Atmospheric Reactions

Description of atmospheric chemical reactions is beset by several difficulties. First, there are a myriad of stable chemical species in the atmosphere. Most of these exist in very low concentrations and are thus difficult to measure or even detect. In fact, some probably remain unidentified. Second, there are very many unstable species (highly reactive, short-lived intermediates) in the atmosphere. These species are exceedingly difficult to measure because of their extremely low concentrations and high reactivities. Third, among the stable and unstable species, literally hundreds of chemical reactions could occur.

The present lack of understanding about some atmospheric reactions does not stem from the inherent complexity of the chemical reactions; in fact, most are quite simple. Rather, difficulties in measuring the rates of reactions and the lifetimes of intermediate pollutant species, and even in detecting the presence of certain species, limit man's ability to define in complete detail all of the reactions that a pollutant undergoes. Moreover, because the transformation of one species into another often entails competing reactions whose relative importance depends on many factors (e.g., temperature, available sunlight, and chemical composition of the polluted air mass), it is often difficult to determine the dominant reactions.

Besides these difficulties, the production and destruction of most pollutants of importance is highly nonlinear and is generally a function of many other variables (e.g., temperature and sunlight) that also exhibit nonlinear behavior. For example, although NO emissions are known to contribute to the formation of photochemical oxidant, under certain conditions an increase in NO emissions may actually decrease local production of ozone. In view of this incomplete understanding, it is difficult in most instances to determine with certainty the relationship between emissions and ambient air quality. Despite the many difficulties, considerable progress has been made in the last 25 years in delineating atmospheric chemical reactions. The descriptions below reflect these advances in the understanding of atmospheric chemistry.

2. The Formation of Photochemical Smog

Photochemical smog was recognized relatively recently as a type of air pollution. In the early 1950s it was discovered that nitrogen oxides play a role in the production of tropospheric oxidants [85]. Since then, intensive laboratory, theoretical, and field studies have been carried out to elucidate the nature of this pollution problem. Broadly speaking, photochemical smog refers to an atmospheric condition in which above-normal concentrations of visibility-reducing contaminants and chemical oxidants such as ozone, aldehydes, peroxyacetyl nitrate (PAN), and NO_2 are produced in the atmosphere, usually on clear, warm summer or autumn days with light winds. The most common harmful or annoying effects of photochemical smog include eye irritation, plant damage, and visibility reduction. The brown haze that accompanies smog is caused by light absorption by NO_2 and light scattering by particulates less than about 1 μm in diameter. Although photochemical smog was first identified in the Los Angeles basin, it has since been observed in numerous urban areas throughout the world [86].

The formation of photochemical smog is quite intricate, undoubtedly involving hundreds of different species and reactions. The rates of these reactions vary with concentration and, in some cases, with ambient temperature, pressure, and/or light intensity. The principal ingredients are organic compounds (e.g., paraffins, olefins, aromatics, and aldehydes), oxides of nitrogen (NO and NO_2), air, and ultraviolet light. The central component of smog formation is the NO_2-NO-O_3 cycle, depicted in Figure 35. In this cycle, ultraviolet light photolyzes nitrogen dioxide (NO_2) to form nitric oxide (NO) and an oxygen atom:

$$NO_2 \xrightarrow{h\nu} NO + O \quad . \tag{1}$$

The oxygen atom then quickly combines with an oxygen molecule from the air to form ozone:

$$O + O_2 \rightarrow O_3 \quad . \tag{2}$$

In the last reaction in the cycle, the products combine to regenerate the original reactants:

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

These three reactions are fast enough that the concentrations of NO, NO_2, and O_3 are generally close to a steady-state relationship:

$$\frac{[NO_2]}{[NO][O_3]} = \text{constant} \quad , \tag{4}$$

where the value of the constant depends on the intensity of sunlight. Higher intensities of sunlight favor NO and O_3 over NO_2 only marginally

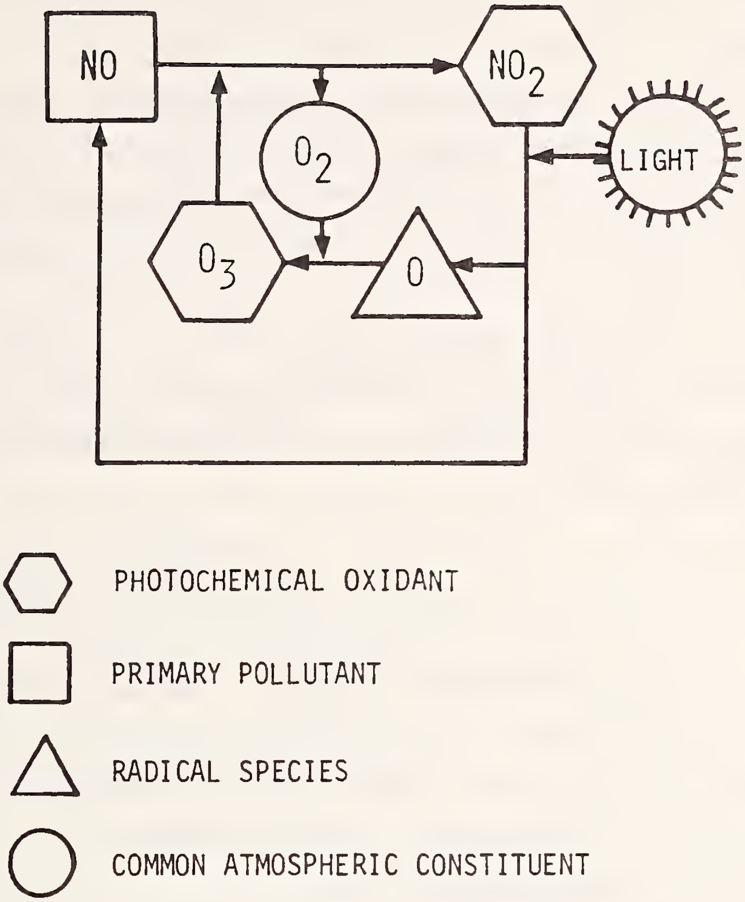


FIGURE 35. THE NO_2-NO-O_3 CYCLE

If no other reactions were important, ozone formation would be a rather simple process, and ozone concentrations would be low. In the presence of hydrocarbons, however, NO is converted to NO_2 by oxidizing radicals. A radical is a chemical species having a single unpaired electron, which causes it to be very reactive. The oxidizing radicals in smog come from the photochemical oxidation of hydrocarbons. Radicals, from the photolysis of aldehydes and other sources, participate in a chain reaction in which a hydrocarbon molecule is attacked by a hydroxyl radical ($OH\cdot$). The product is an organic radical, generally a peroxyalkyl ($RO_2^{\cdot}$) or peroxyacyl ($RCO_3^{\cdot}$) radical. The organic radical reacts with NO to yield NO_2, a hydroperoxy radical ($HO_2^{\cdot}$), and a different hydrocarbon, usually an aldehyde. The hydroperoxy radical reacts with NO to form NO_2 and $OH\cdot$.

$$HC_1 + OH\cdot \rightarrow \text{Organic Radical} \qquad (5)$$

$$\text{Organic Radical} + NO \rightarrow NO_2 + HO_2^{\cdot} + HC_2 \qquad (6)$$

$$HO_2^{\cdot} + NO \rightarrow NO_2 + OH\cdot \qquad (7)$$

The sum of these reactions is:

$$HC_1 + 2NO \rightarrow 2NO_2 + HC_2 \qquad (8)$$

Note that an $OH\cdot$ radical is consumed in Reaction 5 but generated in Reaction 7. According to Reaction 8, hydrocarbons convert NO into NO_2, which, as mentioned above, results in a higher ozone concentration. Reactions 5 through 8 are highly simplified--they omit the consumption of O_2 and production of CO_2, and they use the symbol HC to cover the complexities of hydrocarbon oxidation--but they do highlight the fact that ozone production depends largely on the concentrations of radicals and reactive hydrocarbons.

Carbon monoxide (CO) may marginally add to oxidant formation via the reaction:

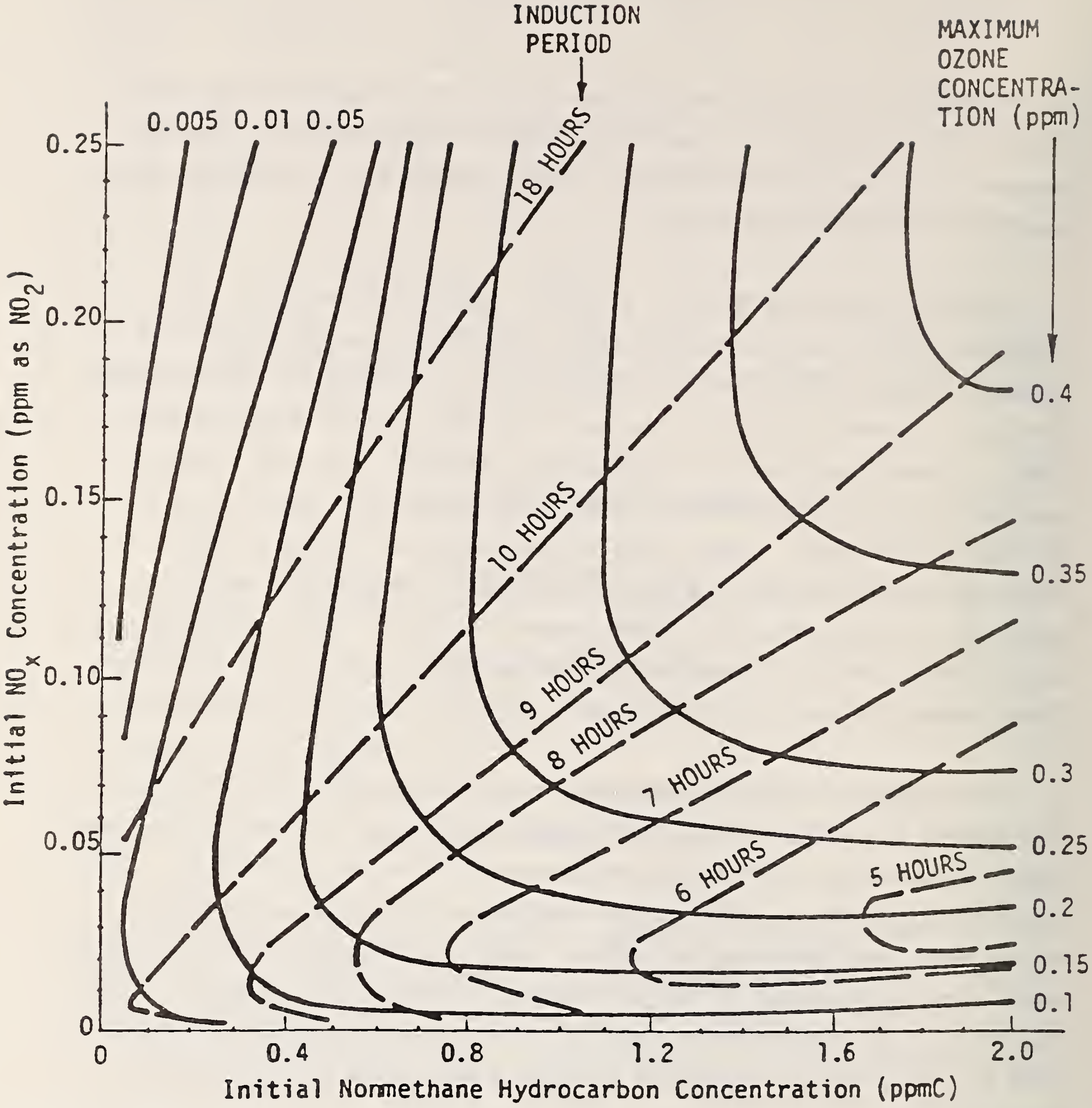
$$CO + OH\cdot \xrightarrow{O_2} CO_2 + HO_2^{\cdot} \qquad (9)$$

The $HO_2^{\cdot}$-radical from this reaction oxidizes an NO molecule to NO_2 and reforms an OH· radical as shown in Reaction 7. Reaction 9 is slow and produces only one oxidizing radical. Thus, CO has little effect on smog formation in most circumstances.

Besides reacting with NO to form NO_2, the organic radicals in Reactions 5 and 6 can react with other radicals to form peroxides and, perhaps, heavier organic acids. These acids can condense to form aerosol particles. Hydroxyl radicals can react with NO_2 to form nitric acid (HNO_3). These reactions slow hydrocarbon oxidation, and thus ozone production, by destroying radicals; thus, they are called radical sink or termination reactions. Were there no net sources of radicals these reactions would stop smog formation altogether. However, aldehydes photolyze to form peroxy and other organic radicals. Since aldehydes are both emitted into the atmosphere and formed during hydrocarbon oxidation, their photolysis builds and maintains a quantity of oxidizing radicals.

The radical termination reactions have both good and bad effects. The removal of radicals slows the production of ozone and reduces the peak ozone concentration by reducing the number of NO to NO_2 conversions. But the products of the radical removal reactions, primarily peroxides and nitric acid, are themselves oxidants. Organic acids and nitric acid from these reactions may add to the particulate concentration. Finally, slowing the rate of photochemical reaction reduces the peak ozone concentration at the expense of spreading elevated ozone concentrations over a greater area.

Figure 36 indicates the complexity of the relationship between ozone, HC, and NO_x concentrations. The solid lines in this figure are isopleths of the peak ozone concentrations in computer simulations of smog chamber experiments. (Isopleths are lines of equal concentration, just as the



Source: Ref. 87.

FIGURE 36. ISOPLETHS OF MAXIMUM ONE-HOUR-AVERAGE OZONE CONCENTRATIONS AND INDUCTION PERIODS DERIVED FROM COMPUTER SIMULATIONS

contour lines on a topographic map are lines of equal elevation.) The time from the start of the simulation to this peak, called the induction period, is indicated by a dashed line. These isopleths are based on the results of a number of computer simulations of photochemical smog formation using assumed initial concentrations of NO, NO_2, and an urban hydrocarbon mix, constant light, and constant volume. It is important to note that Figure 36 is limited in its applicability to the atmosphere because it is based on a particular hydrocarbon mix, it ignores meteorology, and it does not account for continuous emissions of fresh pollutants.

The most obvious feature of Figure 36 is the bend in the ozone isopleths that occurs at a hydrocarbon/NO_x ratio of roughly 13 ppmC/ppm as NO_2. At higher ratios ozone production in this system is NO_x-limited; the NO concentration is relatively low, and so many oxidizing radicals react with other radicals instead of converting NO to NO_2. Thus oxidizing radicals are destroyed instead of participating in the formation of ozone.

At HC/NO_x ratios less than 13, oxidizing radicals are more likely to react with NO_2 than to convert NO to NO_2. Also, the high initial concentration of NO increases the induction period. The slowing effect of NO_x on ozone formation is evident from the fact that increasing the amount of NO_x (moving toward the top of the diagram) almost invariably increases the induction period. Only in severely NO_x-limited cases (HC/NO_x > 50) does increasing the initial NO_x concentration shorten the induction period.

Another important insight obtained from Figure 36 is the nonlinearity of ozone formation. At a given HC/NO_x ratio, doubling the HC and NO_x concentrations does not usually double the resultant peak ozone concentration. The reason for this nonlinearity is that as HC and NO_x concentrations are increased, radical reactions that do not lead to ozone formation become more important. For example, the concentration of peroxyacyl nitrate (PAN), which is formed from peroxyacyl radicals and NO_2, increases more than the increase in HC or NO_x concentrations. The concentrations of hydrogen peroxide, organic acids, ketones, and many other pollutants also exhibit a greater than linear dependence on hydrocarbon and NO_x concentrations. Thus, a 50 percent reduction in HC or NO_x emissions generally results in less than a 50 percent reduction in ozone, but other noxious compounds are often reduced by more than 50 percent.

The above discussion reviews only the main features of photochemical oxidant formation. Many reaction steps that are known to occur or might occur were omitted in the interest of simplicity and generality. However, for transportation planners, familiarization with the processes identified above should be sufficient to provide a working knowledge of the principles underlying photochemical oxidant formation.

3. Aerosol Chemistry in the Atmosphere

An aerosol is a suspension of fine solid or liquid particles in air, such as smoke, haze, or fog. Aerosols can contain both primary and secondary pollutants. Primary aerosols are particulates emitted directly to the atmosphere from natural or man-made sources. Examples of primary aerosols include pollen, spores, dust, smoke, tire dust, and sea salt. In contrast, secondary aerosols derive from chemical reactions and physical mechanisms occurring in the atmosphere. Common secondary aerosols include sulfate ($SO_4^=$), nitrate (NO_3^-), and organic materials. Secondary aerosols are discussed below because of their role in visibility impairment and their possible adverse health effects; furthermore, the largest fraction of secondary aerosol mass is attributable to vehicular emissions.

Chemical and physical processes interact in the formation of secondary aerosols. Chemical processes transform some primary pollutants into secondary pollutants that can participate in aerosol formation. For instance, SO_2 can be chemically converted to SO_4 by reaction with oxidizing radicals, by oxidation in a liquid droplet in the presence of ozone, or by a number of less well understood processes involving solid or liquid particles in the atmosphere. If ammonia is also present in the air, it can react with sulfuric acid to form ammonium sulfate particles, which absorb water at moderate relative humidities and thereby increase in size.

The physical processes involved in aerosol dynamics chiefly determine the physical characteristics of the aerosol--the number of particles, the particle size distribution, particle growth and loss rates, and so forth. Physical processes important in the description of aerosol dynamics include [4]:

> Production of particles by gas phase nucleation.
> Growth of particles by reactions of gases on the surfaces of particles.
> Growth of particles by gas phase reactions and subsequent absorption of the reaction products on the particles.
> Coagulation
> Scavenging of smaller particles by larger ones during their fall.
> Gravitational settling.
> Impaction on obstacles on the earth's surface.
> Removal of particles during cloud formation or precipitation.

Obviously, the extent to which each of the above processes is significant in terms of generating or removing aerosols depends on factors including the concentrations of particles of various sizes, atmospheric mixing, and humidity. In urban atmospheres on smoggy days, for example, it is believed that aerosol formation is initiated by the condensation of gaseous organic species onto existing condensation nuclei--perhaps sea salt particles or lead aerosols from vehicular exhaust. If the concentration of water droplets (fog) is high enough, the particles may grow by coagulation and by diffusion of gaseous species to the aerosol surface, perhaps reaching a size (0.1 to 1.0 μm) sufficient to cause visibility impairment or penetration and retention of aerosol particles in respiratory passageways.

Perhaps the central difficulty in describing the behavior of aerosols is that the dynamics of both gaseous and particulate air pollutants must be understood. Because aerosol formation and growth are so strongly linked to the evolution and fate of gas phase species, knowledge of gas phase atmospheric chemistry is a prerequisite to understanding aerosols. Additional information on these subjects is given in References 88 and 89.

4. Summary of the Main Characteristics of Chemical Processes

The foregoing discussion highlighted several characteristics of chemical processes in the atmosphere. Important among these are the following:

> A large number of chemical species exist in the atmosphere, and they undergo a myriad of interrelated, competing reactions both in the gas phase and on solid and liquid airborne particles.
> The rates at which atmospheric reactions take place range from nearly instantaneous to very slow.
> While the principles of gas phase chemical reactions are essentially well understood, incomplete knowledge as to the number and types of reactions in which a particular species can be involved limits the detailed description of atmospheric chemical processes.

Chapter VIII describes how the chemical phenomena discussed above interact with physical processes at various spatial scales to produce the resultant ambient air quality.

D. REMOVAL PHENOMENA

Pollutant removal includes physical extraction from a volume of interest or chemical or physical conversion into another compound. In this discussion, the troposphere is the volume of interest; thus, a contaminant carried aloft into the stratosphere or deposited on the earth's surface can be regarded as removed. Also, an NO molecule, when converted to NO_2 through reaction with ozone, can be thought of as being removed, even though the nitrogen atom still remains in the atmosphere. Important pollutant removal processes are discussed below.

1. Gravitational Settling

Gravitational settling (or sedimentation) is an important and familiar mechanism of removal of particulates from the atmosphere. The rate at which a particulate settles depends on two opposing processes--the particulate's upward rate of motion due to turbulent diffusion (turbulent suspension) and its downward rate of settling due to gravity. A variety of factors help determine whether the settling or suspension process prevails. Three such important factors are the intensity of atmospheric turbulence and the particulate's shape and mass. For particulates smaller than approximately 0.1 μm, removal by gravitational settling is insignificant. For particulates between 0.1 and 1.0 μm, settling velocities in still air, though finite, are small compared with turbulent fluctuations in wind velocity; consequently, settling of particulates in this size range is also of limited importance. However, for particulates larger than 5 to 10 μm, the effect of gravitational settling is significant. Fly ash from power plants and lead particulates from automobiles are examples of air pollutants that are removed efficiently by gravitational settling.

2. Impaction

Another physical removal process is the impaction (or inertial deposition) of particulates on surfaces such as trees, hillsides, buildings, and the like. When air encounters an obstacle, the fluid pathlines become deformed as the air moves around the obstacle. Depending on its size, a particulate in the air flow may or may not follow the fluid pathlines around the obstacle. It will not if the particulate's inertia is sufficient to carry it across the fluid pathlines to the surface of the obstacle. Although the mechanics of surface removal due to impaction are reasonably well understood, the importance of this removal process relative to other processes is not known. Impaction is probably most effective for particulates greater than approximately 0.1 μm in diameter. Below that size, particulates can respond to turbulent wind velocity fluctuations, and they also possess less inertia.

3. Precipitation Scavenging

The cleansing of the atmosphere by precipitation is an important means of pollutant removal. Liquid precipitation can remove pollutants in two ways: rainout and washout. Rainout is the capture of pollutant gases or primary or secondary aerosols in water droplets during their formation and residence in a cloud. Washout is the scavenging of pollutants by precipitation as it falls through the atmosphere to the ground. For gaseous pollutants, essentially the same physical processes occur for both rainout and washout. For aerosols, however, differences can occur between the two scavenging mechanisms.

a. Precipitation Scavenging of Gases

Gas scavenging by falling raindrops is extremely complicated, and only its rudimentary aspects are discussed here. Consider a raindrop falling through air containing pollutant gas molecules. For the raindrop to capture a gaseous molecule through either washout or rainout, the molecule must first migrate through the atmosphere to the surface of the raindrop. Once at the surface, the gas molecule may either adhere to the gas-liquid interface or pass through it into the raindrop by convection and diffusion. Chemically reactive pollutants, such as NO_2 and SO_2, can undergo a variety of reactions inside the raindrop. Pollutants such as N_2O and methane may simply remain in solution in the raindrop, in which case their concentrations in the liquid are related to their concentrations in the atmosphere by Henry's Law.* Still other pollutants, such as NH_3, can chemically dissociate into ions in solution.

As a raindrop falls, it may encounter regions of higher or lower concentrations of gaseous pollutants and different ambient temperatures. These variations may alter the solubility of the gas in the raindrop. As a result, the concentration of a gas within a given raindrop may either increase or decrease, depending upon the ambient conditions. In some cases, the major importance of precipitation scavenging may not be in removing gaseous pollutants from the atmosphere; instead, washout and rainout might result in a redistribution of pollutants throughout the air column as sorption and desorption processes occur. As an example, precipitation falling through an elevated plume from a power plant may scavenge SO_2 from the plume only to release it at lower elevations where SO_2 desorption is the dominant process.

b. Precipitation Scavenging of Aerosols

As mentioned above, precipitation can remove aerosols by washout and rainout. In urban areas at least, rainout is probably not an important removal process for local urban aerosols because cloud formation leading to precipitation takes place at elevations above the polluted layer [89]. However, washout in such areas may be quite effective. The effectiveness of washout depends on such factors as the size distributions

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* Henry's Law states that the equilibrium concentration, C_A, of a species A in a solution (in this case, a raindrop) is proportional to the partial pressure (P_A) of A in the atmosphere around the solution; that is, $P_A = HC_A$, where H is Henry's constant.

of the aerosol and the water droplets, the solubility of the aerosol in water, the aerosol concentration in the air, and the precipitation intensity.

The removal of aerosol particles by rainout can occur through several mechanisms. They can be captured during the nucleation process by water droplets or ice crystals (hydrometeors). In a cloud, thermal and electrical forces may bring aerosol particles into contact with water droplets. Finally, as a droplet falls through the cloud, it may "sweep out" aerosol particles by interception and impaction.

Washout processes are perhaps better understood than these rainout processes. As a raindrop falls, it presents a large cross-sectional area. (Raindrops typically range from 0.03 to 0.5 mm in diameter, whereas aerosols are only as large as 5 to 10 μm.) Small particles, say less than 0.1 μm in effective diameter, will move with the air as it passes around a raindrop. This process is shown schematically in Figure 37. Larger aerosol particles possess greater inertia, and may be impacted by the raindrop and swept downward.

4. Surface Uptake of Air Pollutants

Surface uptake mechanisms, or surface sinks, are important removal processes for many pollutants. Conceptually, the removal of pollutants at the surface of the earth (by water, soil, vegetation, buildings, and so forth) can be regarded as occurring in three steps:

> Transport to the vicinity of the surface.
> Transport to the surface by molecular processes.
> Retention of the contaminants on the surface by one of several physical, chemical, or combined mechanisms.

The first step is explained by introducing the concept of the laminar sublayer. Consider wind flow over smooth, flat terrain. Examples of

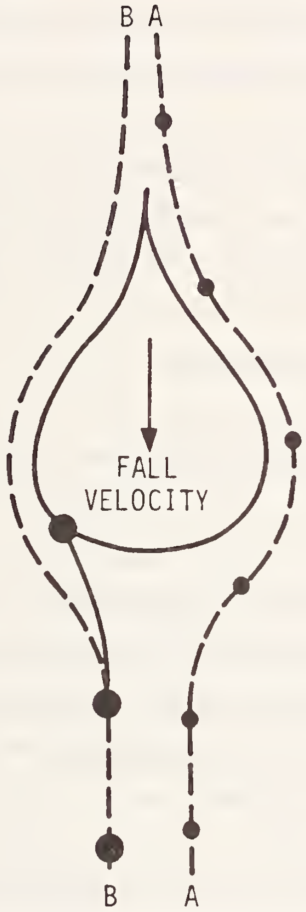


FIGURE 37. COLLECTION OF PARTICULATES BY A FALLING RAINDROP. The small particulate depicted on the pathline A-A can move with the air around the approaching droplet, whereas the larger particulate originally on pathline B-B is impacted by the raindrop.

such surfaces might be the pavement in a large parking lot or a prairie covered with snow. In general, under most atmospheric conditions, the wind flow over such surfaces will be turbulent. However, in the immediate neighborhood of the surface, the random or turbulent components of the wind are very small, and within a very thin layer next to the surface, they vanish. This layer is called the laminar (or viscous) sublayer because of the absence of turbulence in it. The rates at which mass, momentum, and energy are transferred within the sublayer are governed by the rates of molecular processes. Because turbulent eddies do not exist in the laminar sublayer, the rapid mixing and transfer of material that is characteristic of turbulent flow in the atmosphere does not take place. Of course, the boundary between the laminar sublayer and the air above it is not sharp. In reality, the two are joined by a transitional layer in which the rates of diffusion by molecular and turbulent processes are comparable.

It is easy to see how the laminar sublayer might exist on a smooth surface such as a parking lot or snowfield. It is more difficult, perhaps, to envision how such a layer might exist on an aspen leaf being violently blown by the wind. Nevertheless, it does exist. The thickness of the laminar sublayer is so small in most cases that it is impossible (or at least very difficult) to observe it experimentally. But the laminar sublayer is of decisive importance in the surface uptake of pollutants, as discussed below.

The first step, then, in the surface uptake of pollutants entails the transport of pollutants to the outer boundary of the laminar sublayer. This transport is achieved by means of the processes of advection, turbulent diffusion, impaction, and sedimentation.

Next, pollutants diffuse through the sublayer toward the surface. This diffusion takes place as a result of random collisions among the molecules in the air stream and the pollutant species themselves. In some instances, the rate at which material is transported through the laminar sublayer is slower than the rates at which pollutants are either supplied to the top of the sublayer or affixed to the ground surface. Consequently, diffusion through the sublayer under these conditions is referred to as the rate-limiting step in the surface uptake of pollutants.

Finally, removal of pollutants from the atmosphere is completed when one of several processes occurs at the surface:

- The formation of a solution on the surface.
- The chemical reaction of the pollutant gas or particulate with the surface.
- The adhesion of the gas or particulate to the surface.
- The uptake of the gas or particulate by vegetation (this includes one or more of the above processes).

When chemical reaction occurs at the surface, the rate of reaction may be slower than the rate of transfer to and through the laminar sublayer, in which case the third step in the surface uptake process is regarded as rate limiting.

Owing to the complexity of surface uptake processes, few, if any, theoretical expressions have been derived for the mass transfer coefficients of materials removed from the atmosphere by surfaces. The only readily available information on the rate of transfer to surfaces is provided by measurements of surface fluxes and deposition velocities (i.e., the effective rate at which material is deposited on the surface). These measurements have been made for a variety of surfaces under different meteorological conditions, but unfortunately, the magnitude of the deposition velocity depends on numerous variables that change with weather conditions and surface characteristics. For surface sinks involving only absorption, the deposition velocity depends on both surface composition and effective surface area. For sinks affected by diffusion rates, the effects of the overall atmospheric diffusivity, which depends on wind speed, surface roughness, and atmospheric stability, must be included. Consequently, the extrapolation of measured deposition velocities to other weather and surface conditions requires many assumptions. In summary, although many of the physical and chemical processes affecting the uptake of atmospheric pollutants have been identified, their inherent complexity and the dramatic spatial variability in the nature of the earth's surface render analytical description of surface removal processes essentially impossible.

5. Loss to the Stratosphere

With respect to the troposphere, material transported to the stratosphere can be regarded as lost or removed. In contrast to surface uptake, stratospheric removal processes must be described in a more general fashion because of the rather imprecise definition of the interface between the stratosphere and the troposphere, i.e., the tropopause.

The main pollutant removal mechanisms in the stratosphere--chemical reactions--arise from the unique chemical and physical properties of this region of the atmosphere. In the stratosphere, not only is the atmospheric pressure significantly reduced, but also there exists intense ultraviolet radiation in the wavelength band from approximately 1700 to 3400 Å. In addition, ozone, OH·, and excited molecular oxygen (O^{1D}) occur in higher concentrations there than in the troposphere. Some pollutants react rapidly under the conditions in the stratosphere. As an example, more nitrous oxide (N_2O) is emitted into the atmosphere than any other nitrogen oxide [39]. In the troposphere, N_2O is relatively inert. Due to the intense radiation at wavelengths below approximately 3400 Å and the high concentrations of O^{1D} in the stratosphere, however, N_2O photolyzes and reacts to form NO and N_2. Carbon tetrachloride and chlorofluorocarbons are examples of anthropogenic pollutants that are removed by transport to and chemical reaction in the stratosphere.

6. Tropospheric Reactions

If a particular chemical species, say a primary pollutant such as NO, reacts with another pollutant in the troposphere to form a third species, then from a practical standpoint NO is "removed" from the system. Although the nitrogen and oxygen atoms would still exist in the atmosphere, they would be in different forms. Thus, the chemical and physical properties of the NO molecule would no longer exist. Of course, if additional reactions occurred such that the nitrogen and oxygen atoms recombined to form NO, the atmospheric reaction process that led to NO formation would then be regarded as a pollutant source.

7. Summary of Important Atmospheric Removal Processes

Several physical and chemical processes effective in removing pollutants from the troposphere were identified above. Because the efficiency of a removal process for a particular pollutant depends on the physicochemical properties of that pollutant, some pollutants are removed more effectively by one mechanism than others. Table 23 identifies several common air pollutants and lists some of the processes discussed in this chapter that are effective in removing them from the troposphere.

E. SUMMARY

This chapter discusses, in general terms, the fate of air pollutants after they are emitted into the atmosphere. The fate of a particular pollutant molecule depends on how it is transported in the atmosphere, what reactions it undergoes, and what ultimately becomes of the pollutant (i.e., how it is finally removed from the atmosphere). The principles identified in this chapter are applied in the next chapter to transportation environments of interest to transportation planners. Of particular concern in that context is the manner in which various chemical and physical processes interact on different temporal and spatial scales. Thus the next chapter focuses on physical and chemical interactions on three spatial and temporal scales: microscale, mesoscale, and synoptic scale.

TABLE 27. REMOVAL MECHANISMS FOR SOME COMMON AIR POLLUTANTS

Pollutant	Major Identified Removal Mechanisms
SO_2	Precipitation scavenging; chemical reactions (primarily oxidation); absorption by soil, rocks, plants, and surface water; dry deposition
Radicals	Photochemical reactions
Organic acids	Precipitation scavenging; photooxidation; condensation onto particulates
Aerosols (particulates)	Rainout and washout, fallout, and impaction
H_2S	Oxidation to SO_2 by ozone, molecular oxygen, or atomic oxygen
NH_3	Reaction with SO_2; oxidation to nitrate; precipitation scavenging
NO	Oxidation to NO_2 by reaction with O_3 or oxidizing radicals
NO_2	Oxidation to nitrate; photodissociation to NO; precipitation scavenging; surface deposition; absorption by plants
O_3	Photochemical reactions; absorption by soil, vegetation, and water surfaces
CO	Absorption by soil; chemical oxidation; oxidation by bacteria
Reactive hydrocarbons	Photochemical oxidation
Methane	Surface uptake (biological action); slow photochemical oxidation
Fluorocarbons	Photodissociation in the stratosphere
N_2O	Photodissociation in the stratosphere; stratospheric reaction with excited molecular oxygen; absorption by surface water, soil, and vegetation

VIII PHYSICAL AND CHEMICAL PROCESSES IN VARIOUS TRANSPORTATION ENVIRONMENTS

The introduction to Chapter VII discussed some processes affecting the concentrations of air pollutants in a control volume (see Figure 26). The size of that control volume was purposely not specified because different processes are important at different spatial and temporal scales. For example, gravitational settling of lead particulates from automobile exhaust is important for a short time after emission near the roadway; in contrast, washout can affect pollutant concentrations over an entire urban area for several hours or more. In an area such as the northeastern United States, emissions from one urban area may significantly affect air quality in a city far downwind. For transportation planning, it is convenient to consider atmospheric processes at three scales: microscale, mesoscale, and synoptic scale, as defined below. This chapter examines the relative importance of various processes at these scales. Because of interactions between the processes, inherent nonlinearities in them, and incomplete understanding of them, it is impossible to identify exactly the contribution of each process to air quality. Nevertheless, by developing an understanding of the principles underlying those processes and their interactions, the transportation planner or engineer can extend them to specific air quality problems.

The microscale environment, as discussed in this chapter, includes the region from a roadway to approximately 0.5 to 1 kilometer downwind over a time scale of a few seconds to a few tens of minutes. The mesoscale environment encompasses an entire urban area and outlying suburban zones. Typical spatial and temporal scales are on the order of 1 to 100 kilometers and 1 to 24 hours. The synoptic scale (or macroscale) environment refers to a region on the order of a hundred to several thousand kilometers in length. Time scales of importance in the macroscale environment range from one to several days. The following sections identify atmospheric processes that are particularly important in each of these environments and discuss how the processes interact to affect air quality.

A. MICROSCALE ENVIRONMENT

A broad range of conditions characterize areas adjacent to roadways. The more common physical settings of roadways include: elevated, at-grade, or depressed placement of the roadway, sparse or dense vegetation, few man-made structures or tall, closely spaced buildings, flat or rugged topography, appurtenant highway structures (e.g., on-ramps, off-ramps, overpasses), and straight or curved roadway segments. As shown below, the physical setting in the vicinity of roadways strongly influences transport phenomena in the microscale environment and, to a lesser extent, the removal of contaminants from the atmosphere. Particularly important immediately downwind of roadways are the existing land use patterns and the nature of the topography.

1. Microscale Transport Phenomena

As a rule, vehicular emissions enter the atmosphere in high concentrations. The rate at which these emissions are reduced to low concentrations largely depends on the intensity of turbulent mixing encountered as they are carried downwind. The turbulence responsible for the mixing arises from the release of the emissions themselves, the motion of vehicles on the roadway, the influence of the local roadway environment on the wind, and the large-scale atmospheric motions occurring upwind and downwind of the roadway. These sources of turbulence have varying degrees of influence on the dilution of vehicular emissions.

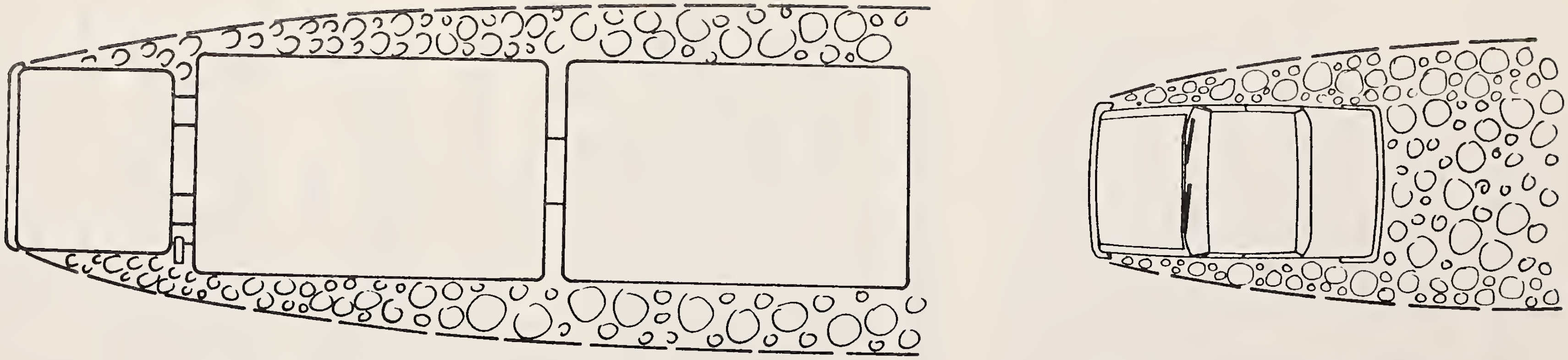
Pollutants emitted from the exhaust pipe of a moving vehicle are accompanied by heat emissions and intense, small-scale, high-frequency turbulence. While the initial turbulence, generated during the emission process, is probably insignificant in view of the other sources of turbulent mixing, the emission of heat may be important. Heat emissions cause the pollutants to become buoyant with respect to the ambient atmosphere. In the absence of countervailing effects (e.g., aerodynamic downwash in the wake of the vehicle), buoyancy causes the pollutants to rise above the roadway, allowing them to be entrained by the prevailing airflow and to be dispersed downwind.

Generally, the most significant source of turbulent mixing on the roadway is the motion of traffic. As a vehicle moves along a roadway, a turbulent wake is formed behind the vehicle. In the wake, initial dilution of exhaust emissions is greatly enhanced. While the wake region moves along the roadway with the vehicle, vortices (and turbulent eddies) shed by the vehicle propagate and diffuse down the road at a slower speed, depending on the momentum imparted to them by the passing vehicle. The intensity and scale of turbulence due to the passage of traffic depend on many factors, the most important of which are the density of traffic and the speeds and shapes of the vehicles. As the driving speed increases, a greater amount of energy is available for the generation of turbulent motion; hence, roadway mixing is enhanced at high speeds. In addition, the size of the turbulent wake is a function of the vehicle's size and the extent to which it is streamlined. Figure 38 depicts the effect of vehicle size and shape on wake formation.

A third source of turbulent motion involves the airflow over the roadway segment itself. Figure 39 shows several highway configurations. As the wind moves over the highway, it encounters a variety of protrusions or depressions on the ground surface caused by elevated or depressed roadway segments, overpasses, roadside vegetation, structures, and the like. These terrain irregularities generate atmospheric turbulence in the immediate vicinity of the roadway. Downwind of the roadway, the turbulence is manifested in wake regions, depicted for a variety of flow configurations in Figure 39.

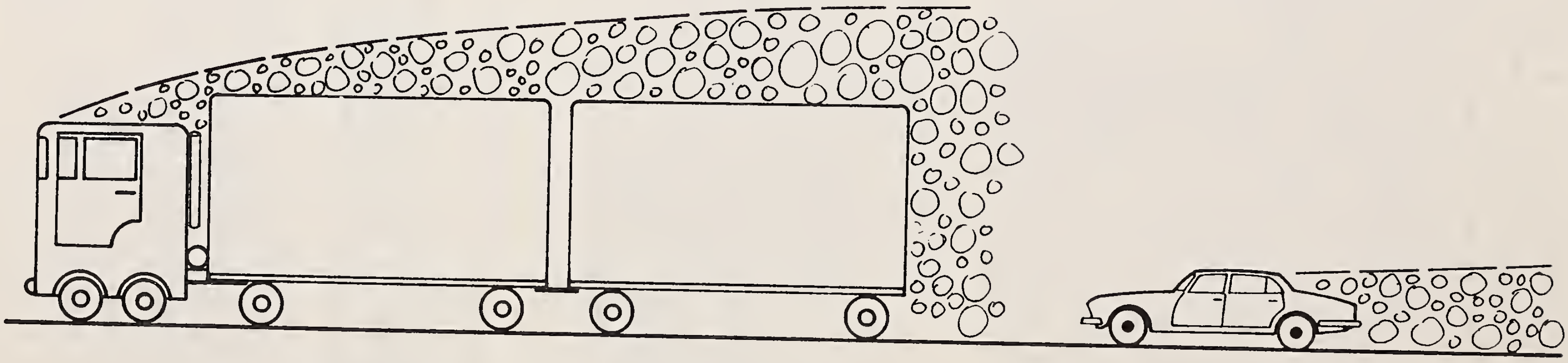
Finally, turbulence is transported to the roadway from upwind areas. Depending on many factors (e.g., upwind land use patterns, atmospheric stability, wind speed, terrain features), the level of turbulence transported into the microscale environment may vary greatly.

Collectively, turbulence due to vehicular traffic, airflow over the roadway segment, and upwind atmospheric conditions can lead to intense mixing of exhaust emissions in the vicinity of the roadway. The mixing



(a) Top View of a Bluff Tractor-Trailer Rig

(b) Top View of a Streamlined Car

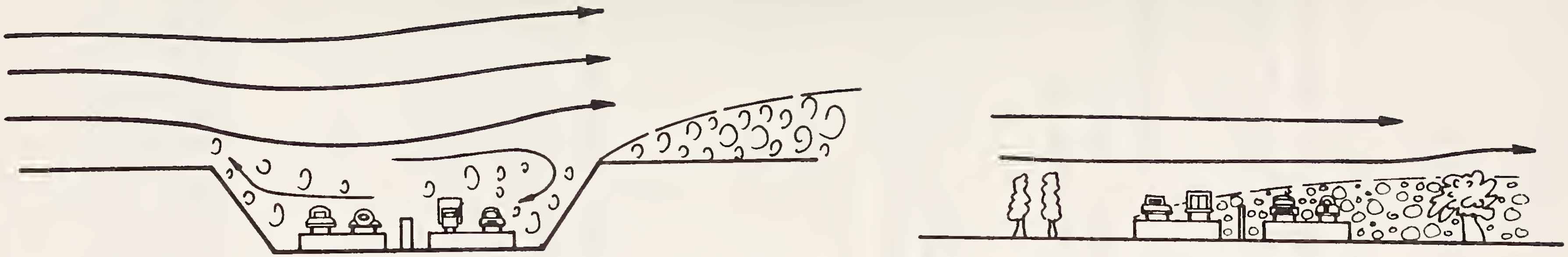


(c) Side View of a Bluff Tractor-Trailer Rig

(d) Side View of a Streamlined Car

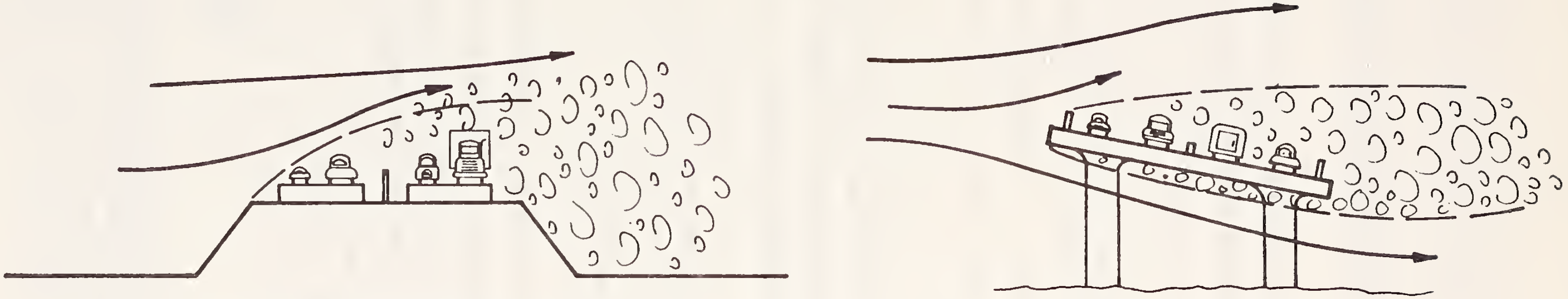
Note: "Bubbles" represent turbulent eddies, and dashed lines indicate approximate boundaries of turbulent wake regions.

FIGURE 38. REPRESENTATION OF THE INFLUENCE OF VEHICLE SIZE AND AERODYNAMIC SHAPE ON TURBULENT WAKE FORMATION



(a) Depressed Roadway

(b) Level Roadway



(c) Elevated Roadway on Fill

(d) Elevated Roadway

FIGURE 39. AIRFLOW AND TURBULENCE OVER VARIOUS ROADWAY CONFIGURATIONS

is so great, in fact, that pollutant concentrations may be reduced to nearly ambient levels within roughly 500 to 1000 meters of the roadway.

2. Important Chemical Processes in the Microscale Environment

For a chemical process to be considered important within the microscale environment, two conditions must be met: (1) Its rate must be fast relative to the time scales associated with transport and mixing in the microscale environment, and (2) the pollutants involved must be present in significant quantities. Reactions involving radicals, for example, are fast enough to satisfy the first condition, but radicals are present in low concentrations Hydrocarbon reactions, in contrast, are too slow to be of importance on the microscale, despite the relative abundance of hydrocarbons near roadways.

According to the above criteria--the speed of reaction and the quantity of reactants--there are three chemical processes that can be important at the microscale level:

- > The reaction of ozone with nitric oxide
- > The reaction of sulfuric acid with ammonia
- > Aerosol coagulation.

The ozone-nitric oxide reaction is responsible for the observed depletion of ozone in the vicinity of roadways. The photolysis of NO_2 and the reaction of NO with O_3 occur so rapidly that a photostationary equilibrium (i.e., steady-state condition) normally exists for the three species at any instant and location. Accordingly, ozone concentrations can be expressed as follows:

$$[O_3] = k \frac{[NO_2]}{[NO]} \qquad (10)$$

where k is a constant depending on solar intensity and ambient temperature.

Nitrogeneous pollutants other than NO or NO_2 react too slowly to be important on the microscale. Thus, if the ambient concentrations of O_3, NO, and NO_2 upwind of a roadway are known, then the concentrations of these species downwind can be estimated from knowledge of the emissions and transport of NO_x and Eq. (10).

The reaction of sulfuric acid with ammonia takes place according to the following reactions:

$$H_2SO_4 + NH_3 \rightarrow (NH_4)HSO_4 \qquad (11)$$

$$(NH_4)HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4 \qquad (12)$$

These reactions proceed to completion rapidly and are of interest because of possible sulfuric acid emissions from catalyst-equipped automobiles. Because both the sulfate and ammonium species are conserved (i.e., they are not converted into other chemical species during their residence in the microscale environment), and because there are no appreciable back-reactions analogous to NO_2 photolysis, the ammonia-sulfuric acid reaction is simpler to describe than the ozone-nitrogen oxide reaction mechanism.

Finally, aerosol coagulation can be an important physicochemical process in the microscale environment. Aerosol particles in automobile exhaust tend to be less than 0.1 μm in diameter, a size too small to remain in one's lungs.* However, when one such particle collides with another, they tend to coagulate, thereby increasing the average size of aerosol particles. After a few minutes of coagulation, a significant fraction of the aerosol mass resides in the 0.1 to 1.0 μm size range. Aerosol phenomena in general are poorly understood at present relative to gas phase chemistry and little data are available concerning their behavior and effects.

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* "Smoky" cars and diesel engines produce many particles much larger than 1.0 μm in diameter, but these tend to fall out in the immediate vicinity of the roadway. Moreover, they tend to be filtered out by the upper respiratory tract (nose and sinuses). Particles between 0.1 and 1.0 μm are most likely to enter and become trapped in the lungs.

3. Removal Processes in the Microscale Environment

Because of the small temporal and spatial scales associated with atmospheric processes in the vicinity of roadways, only a few removal processes are effective in providing a sink for air pollutants in this environment. Many removal processes require time for transport of the pollutants to their eventual removal sites (e.g., the stratosphere), and by the time such transfer is accomplished, the materials are likely to have been carried great distances away from the roadway. In the microscale environment, gravitational settling, impaction, washout, and chemical reactions appear to be the most effective means of pollutant removal.

Certain particulate emissions from motor vehicles are removed quite rapidly in the vicinity of roadways through sedimentation and impaction. In particular, lead and lead compounds and other particulate emissions (e.g., sulfur, bromine, chlorine) settle out rapidly if their size is sufficiently large. For example, roughly 57 percent of the lead emitted from automobiles deposits on or near roadways [90]. The remaining 43 percent, which is composed of particles with a mean diameter of 9 μm or less, is transported downwind of the roadway. As expected, with increasing distance from a roadway, there is a concomitant decrease in the number of large lead particles in the air. Sulfur-containing and other particulates also settle out in the vicinity of roadways. Generally, only the submicron-size particulates remain suspended in the air long enough for them to be transported out of the microscale transportation environment.

Precipitation scavenging of exhaust emissions may be important in some cases. For example, during periods of intense rainfall, some pollutants may be washed out in the vicinity of the roadway; however, it is difficult to estimate the percentage of pollutants removed in the microscale environment by this process because of the temporal and spatial variability of precipitation.

Removal of traffic emissions by chemical reactions may be important, depending on the particular pollutant of interest. Carbon monoxide, for example, is essentially inert over the time scales of interest in the microscale environment. In contrast, nitric oxide reacts so rapidly with ozone to form NO_2 that removal of a portion of the NO emissions is clearly evident, based on the observed depletion of ambient ozone directly downwind of the roadway. The formation of sulfate from emitted sulfur dioxide may represent another potential sink in the microscale environment, though the extent to which this occurs is not well understood at present. There is an indication that surface uptake of carbon monoxide by soil adjacent to roadways might be an important removal mechanism, but this process also requires further study.

In summary, pollutant removal mechanisms involving the fallout of large particles or the rapid reaction of traffic emissions with themselves or with ambient pollutants are important in the vicinity of roadways. Some mechanisms may be important under certain circumstances (e.g., washout and surface uptake). Others, such as loss to the stratosphere, are clearly unimportant at the microscale level.

4. Process Interactions with Emissions

The concentrations of air contaminants in the vicinity of a roadway are governed by interactions among transport phenomena, atmospheric chemistry, emissions, and removal processes. The factors that are most influential to roadway air quality include emissions rates, atmospheric temperature, solar radiation, and atmospheric dispersion. In this section, a few examples indicate how some of these physical and chemical processes influence pollutant concentrations in the microscale transportation environment.

a. Ozone Reduction Adjacent to Roadways

When nitric oxide is exhausted to the atmosphere, the pollutant encounters ambient ozone, whereupon the two species react rapidly to form NO_2. However, the extent to which NO_2 forms through nitric oxide scavenging of ozone depends on several factors, of which the most important are:

- > The mass of NO emitted to the atmosphere
- > The ambient concentration of ozone
- > The extent to which NO is mixed with ambient ozone
- > The ambient temperature
- > The intensity of solar radiation.

Each of the above factors affects the reduction of ambient ozone concentrations near roadways.

Clearly, the amount of NO emitted from a roadway has a strong bearing upon the extent of downwind ozone depletion. If traffic is sparse, the reduction in ozone due to reaction with NO will be minimal, whereas if a roadway is heavily traveled, significant amounts of NO may be released. In this latter situation, pronounced ozone depletion may be observed, as depicted in Figure 40.

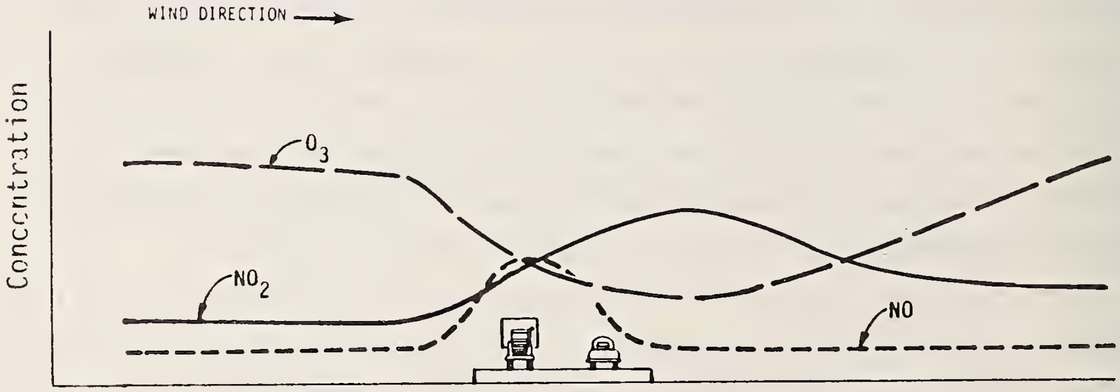


FIGURE 40. DEPLETION OF OZONE DOWNWIND OF A ROADWAY WHERE NITRIC OXIDE IS EMITTED

The extent to which atmospheric ozone is scavenged by NO emissions depends in part upon the degree to which exhaust emissions are mixed with the surrounding air. If atmospheric turbulence levels are low, the NO-ozone reaction will be diffusion-limited; that is, the reaction will proceed only as fast as the two chemical species are mixed together. Conversely, if turbulent mixing is vigorous on the downwind side of the roadway, ozone depletion may occur very rapidly.

On a bright summer day, intense solar radiation can rapidly photolyze NO_2 such that ozone is reformed in moderate concentrations downwind of the roadway. This formation of ozone would reduce the depletion of ozone near the roadway such that the net depletion would be less than that which would occur under similar conditions at night.

b. Dispersion of Emissions from Roadways

The importance of the dispersion of exhaust emissions from roadways was discussed above in terms of either promoting or inhibiting chemical reactions. Dispersion is also a key process in determining the fate of relatively inert pollutant emissions near roadways. Consider CO for example. On a hot summer day with moderate to strong winds and intense thermal mixing, carbon monoxide emissions can be dispersed very rapidly--upward by thermal convection currents and downwind by advection and diffusion. In contrast, calm nighttime inversion conditions in a transportation corridor constructed along the floor of a mountain valley could easily lead to very limited mixing and resultant high local pollutant concentrations.

B. MESOSCALE ENVIRONMENT

This discussion of the interactions among various physical and chemical processes within the mesoscale transportation environment focuses on conditions in a hypothetical urban area and its surrounding suburbs. (For brevity, the word city is used to refer to the mesoscale environment.)

Borrowing the terminology used by Myrup and Morgan [91], one may define the texture of a city as the three-dimensional geometry of the urban and suburban areas. This geometry is characterized by buildings, roadways, open space, vegetation, and so forth. The structure of the city refers to the vertical component of the city geometry, whereas fabric refers to the horizontal characteristics of the city. One might observe the structure of a city by viewing its skyline, whereas the city's fabric could be seen from an airplane. Clearly, the texture of the mesoscale environment is a complex function of city structure and fabric.

No two mesoscale environments have the same texture; each city has certain characteristics that interact uniquely with the atmosphere. However, certain city-atmosphere interactions are general enough to serve as a starting point for discussing atmospheric processes in the mesoscale environment. Some of the physical characteristics of the texture of cities that influence the transport and dispersion of air pollutants are outlined below.

1. Mesoscale Transport Phenomena Influenced by Man's Activities

The texture of a city can be thought of as being composed of a central business district and outlying business and commercial areas scattered throughout the city. Generally speaking, the outlying business areas are interconnected with each other and with the central business district by a variety of transportation corridors. The remainder of the city is normally composed of residential areas, schools, parks, open space, and perhaps a variety of agricultural and industrial activities. Typically, the structure of the city is greatest in the business districts because of a preponderance of tall office buildings, convention centers, and the like. On the fringes of the city, i.e., the suburbs, the vertical structure is generally less pronounced, reflecting a shift in land use patterns from business toward residential and open space.

The texture of the hypothetical city described above would modify the urban atmosphere in four important ways:

> A retardation of airflow over the city.
> A general heating of the atmosphere.
> A distortion of wind flow patterns throughout the city.
> An increase in atmospheric turbulence within and downwind of the city.

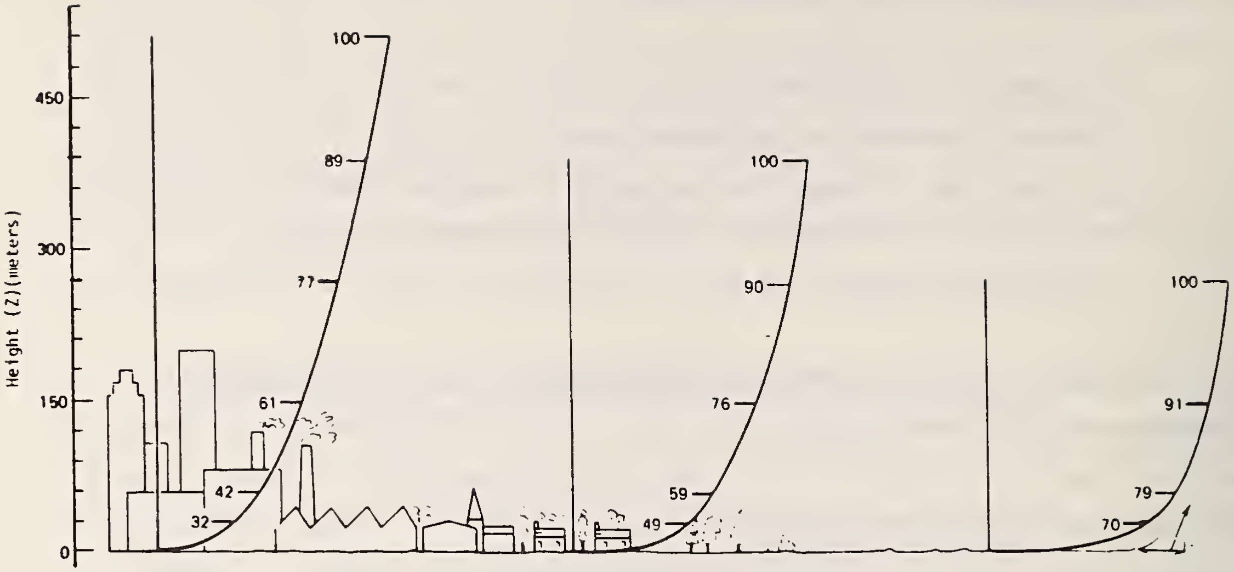
Each of these effects of man-made structures on mesoscale transport phenomena is discussed below.

a. The Friction Island Effect

As air flows over a city, the increased aerodynamic drag on the atmosphere due to the city's texture tends to reduce the speed of the wind and to increase the thickness of the planetary boundary layer over the city, as shown in Figure 41. As the surface winds over the city decrease relative to the wind on the fringes of the city, winds tend to converge in regions of maximum surface roughness. Although the existence of this so-called "friction hump" has been known for many years [92], the extent to which it modifies the mesoscale wind flow over cities is not known.

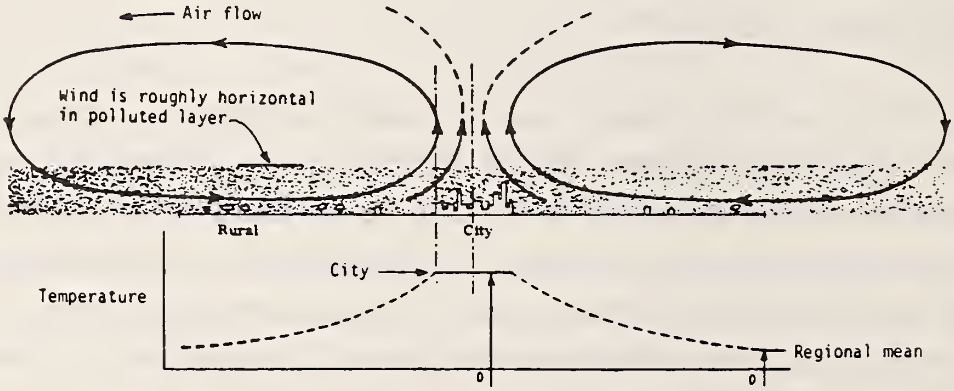
b. The Heat Island Effect

Another influence that cities have on mesoscale transport phenomena involves the so-called urban heat island effect. It is commonly observed that mean ambient temperatures are a few degrees warmer in the interior of a city than in outlying rural areas. The temperature increase within the city has been attributed to many factors, among which heat emissions from fuel combustion, space heating, and increased absorption of solar energy by pavement, buildings, vegetation, and the like are probably most important. In effect, horizontal temperature gradients due to warmer city temperatures generate secondary wind circulations, which converge at the city's interior. As shown in Figure 42, a general rising of air



Source: Ref. 93.

FIGURE 41. RETARDATION OF SURFACE WINDS OVER A CITY AND THE RESULTANT INCREASE IN THE PLANETARY BOUNDARY LAYER. Numbers represent wind speed as percent of wind speed at the top of the planetary boundary layer.



Source: Redrawn from Ref. 92.

FIGURE 42. VERTICAL SECTION OF THE URBAN HEAT ISLAND CIRCULATION PATTERN AND THE TEMPERATURE DISTRIBUTION PRODUCING IT

above the city is offset by subsiding air in rural areas. This thermally driven wind circulation is superimposed upon any wind flow over the city that may be due to synoptic weather influences. The extent to which winds due to the heat island effect are important from the standpoint of pollutant transport and dispersion within the mesoscale environment will depend on the speed of the horizontal wind flowing over the city and the magnitude of the urban-rural temperature gradient.

c. The Effects of City Texture on Wind Flow Patterns

An obvious example of the influence of city texture on the transport of air pollutants is the modification of surface winds due to man-made structures and other obstacles. Within built-up portions of the city, airflow patterns can be extremely complex because of the channeling of flow through a maze of tall office buildings, hotels, apartment buildings, and so forth. Within these so-called "street canyons," formed by tall structures on both sides of the roadway, wind flow patterns may be considerably different from those observed on the fringe of the city. As one example, consider the street canyon shown in Figure 43. In this case, pollutant emissions from the roadway might be trapped within the street canyon circulation, rather than being flushed downwind.

d. The Effects of Enhanced Atmospheric Turbulence

Turbulence levels within and downwind of a city are enhanced in two ways. First, mechanically generated turbulence is formed by the action of the wind blowing over blunt objects, such as buildings, roadway structures (see Figures 39 and 43), vegetation, and so forth. Second, thermally induced atmospheric turbulence arises as a result of heat emissions (e.g., refinery or power plant operations) and turbulent convection stemming from differential warming of surfaces throughout the city. The effect of this additional turbulence is to increase the rate at which contaminant emissions are diffused throughout the urban area.

2. Mesoscale Transport Phenomena Due to Topography

In addition to the thermal and aerodynamic effects of cities on mesoscale transport processes, the characteristics of the mesoscale environment itself play an important role in determining the fate of contaminant emissions. For the purposes of this discussion, three categories of topographical effects on mesoscale transport phenomena are defined: kinematic, dynamic, and thermal-radiational. Because of the wide range of conditions the transportation planner can conceivably be faced with in examining mesoscale air quality impacts, the discussions presented below are general.

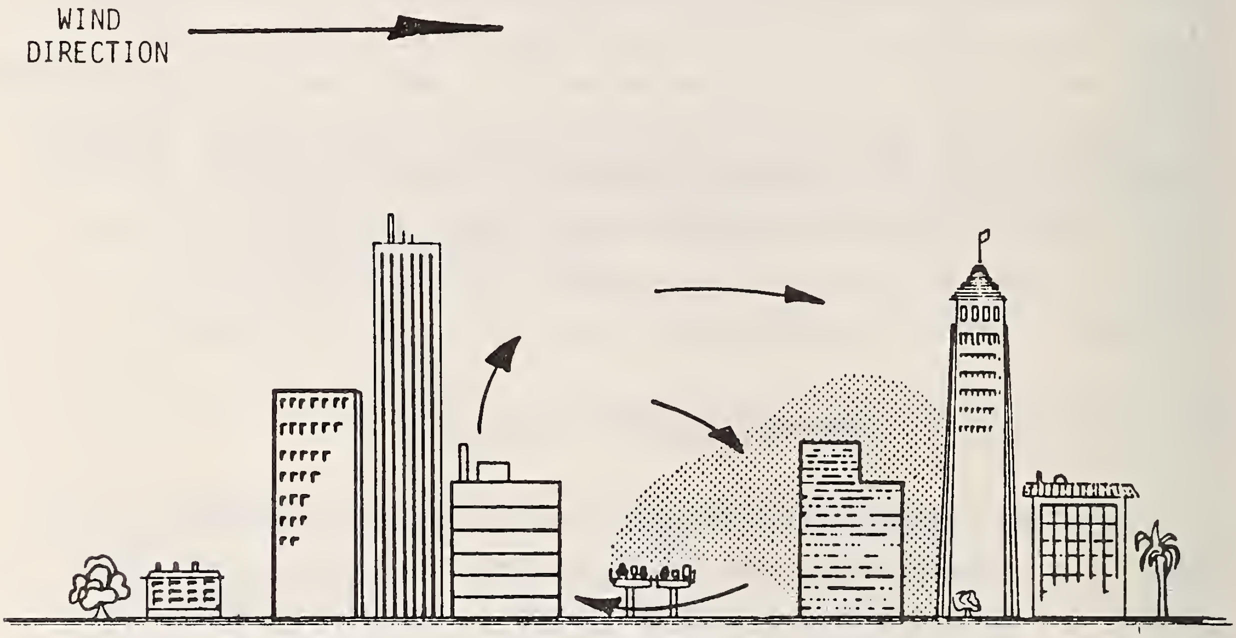


FIGURE 43. AN EXAMPLE OF ROADWAY EMISSIONS TRAPPED BY CIRCULATING WIND FLOW IN AN URBAN STREET CANYON

a. Kinematic Effects

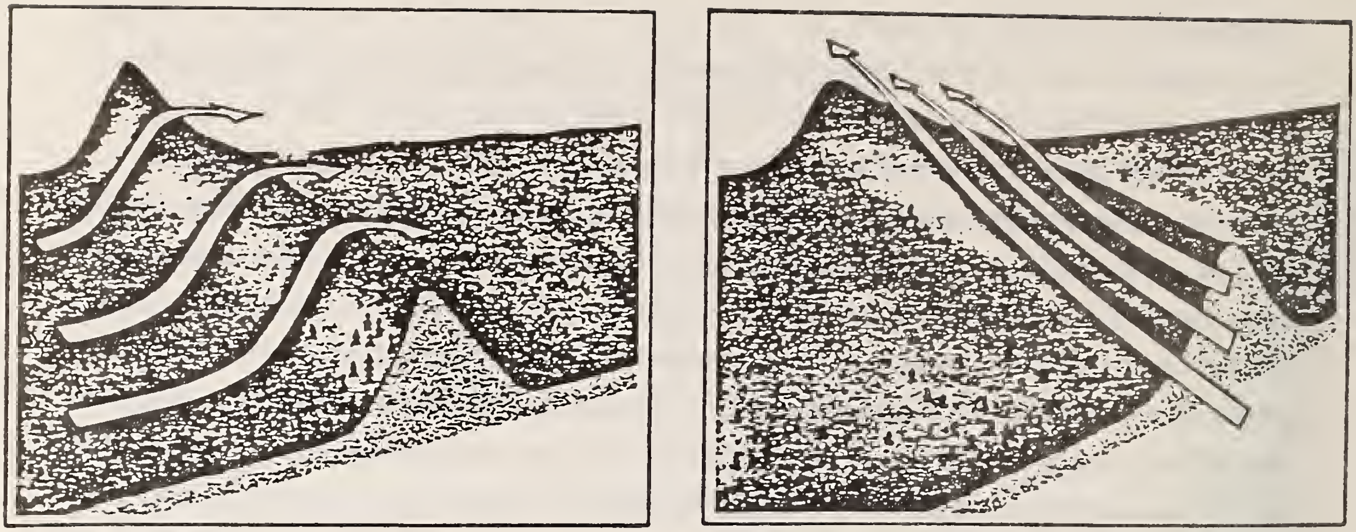
The kinematic effects of irregular terrain on atmospheric flow are probably the most well known. Horizontal airflow, either normal or oblique to a terrain barrier (e.g., a ridge), frequently results in orographic lifting, as shown in Figure 44. In addition, as shown in Figure 45, canyons and valleys tend to channel the ground-level flow within them. Often, wind flow is accelerated through mountain passes or saddles and decelerated on the leeward side (see Figure 46). This feature of the terrain-induced wind field is called gapping [94]. Another kinematic feature of the wind field is the diverting or bifurcation of airflow around a solitary terrain feature in a stable atmosphere. Figure 47 is a schematic representation of the bifurcation of a plume below an elevated inversion layer encountering isolated mountain peaks. Finally, the above kinematic effects are often superimposed upon one another, because topography rarely exhibits a simple geometric pattern. Figure 48 depicts a combination of gapping and lifting effects due to topography.

b. Dynamic Effects

Dynamic effects caused by the interaction between topography and the atmosphere are more difficult to describe than the foregoing kinematic effects. Examples of dynamic effects of topography on airflow include:

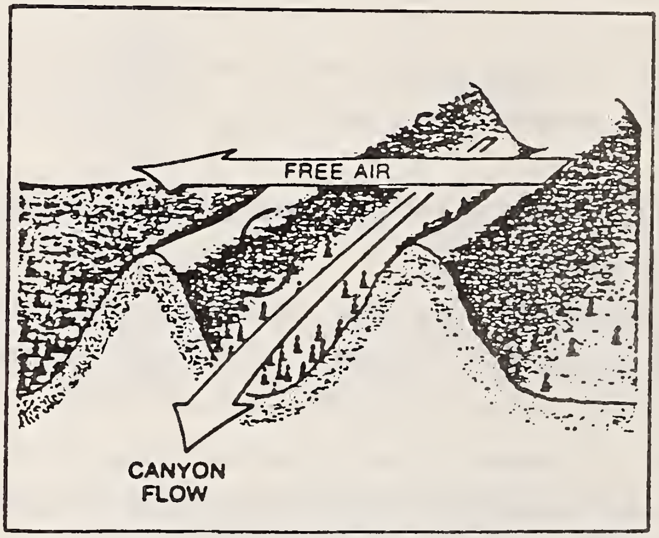
- Gravity oscillations in the lee of mountains and ridges under stable atmospheric conditions (i.e., mountain lee waves).
- Boundary layer separation over ridges and other irregular terrain features.
- Canyon circulations involving the interaction between ridgetop winds and winds within valleys and canyons.

The influence of dynamic effects due to irregular terrain on the mesoscale wind field is quite similar to that due to man-made structures. Both situations lead to an increase in the intensity of atmospheric turbulence and to distortion of the streamlines of the flow near the ground. Turbulent eddies generated downwind from terrain obstacles interact with each other, often complicating the turbulent motion. Spatial inhomogeneities in surface roughness other than the general terrain features (e.g.,



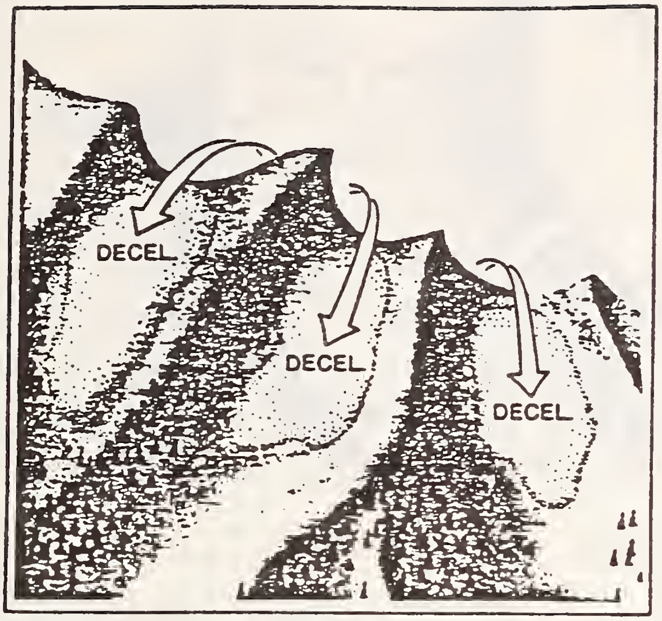
Source: Ref. 95.

FIGURE 44. OROGRAPHIC LIFTING. The maximum rate of orographic lifting occurs when the wind is perpendicular to the mountain barrier (left). This rate is reduced when the wind strikes the barrier at angles other than perpendicular (right).



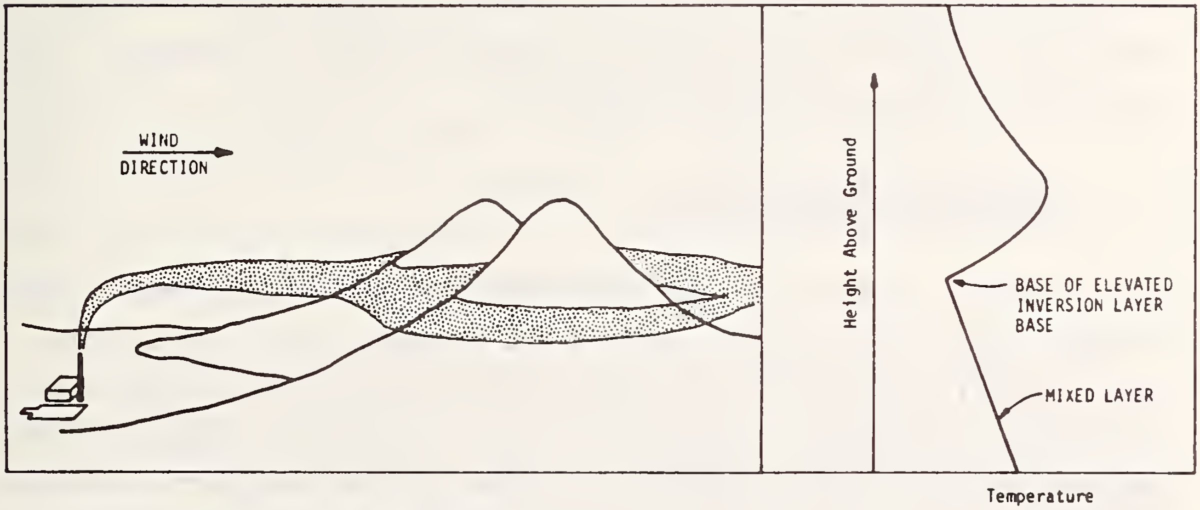
Source: Ref. 95.

FIGURE 45. CHANNELED FLOW. Flow above the ridgecrests is approximated by the free airflow. Canyons tend to deflect the wind to align with the canyon direction. Flow over the mountainside is generally irregular and unsteady.



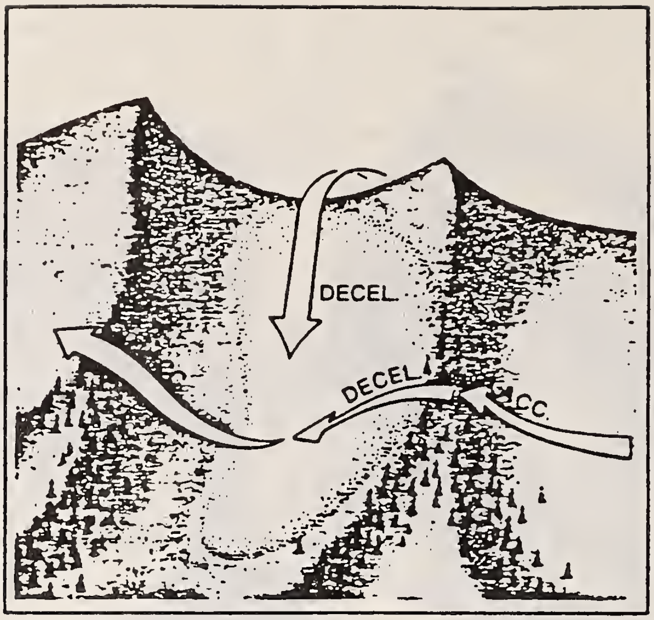
Source: Ref. 95.

FIGURE 46. GAPPING OF AIRFLOW THROUGH MOUNTAIN NOTCHES. The flow accelerates on the windward side and decelerates in the lee of the mountain.



Source: Adapted from Ref. 96.

FIGURE 47. PLUME BIFURCATION AROUND TWO ISOLATED MOUNTAINS BENEATH AN ELEVATED INVERSION LAYER



Source: Ref. 95.

FIGURE 48. SUPERPOSITION OF GAPPING AND LIFTING EFFECTS ON THE MOUNTAIN WIND FLOW

variations in ground cover, tree spacing, canopy height) generate additional mechanical turbulence, which is observed as gustiness and intermittency in wind velocities near the ground. Because turbulence is advected and diffused downwind, it is difficult to ascertain to what extent the atmospheric turbulence at a given location is produced locally or imported from upwind areas.

c. <u>Thermal-Radiational Effects</u>

Mesoscale wind circulations can also arise from thermal-radiational effects. Local wind flows in valleys and mountain passes can be generated by spatial variations in surface albedo resulting from differences in surface cover (i.e., vegetation) or slope aspect (i.e., angle of incidence of the sun's rays). These local flows further modify the flow over irregular terrain. When winds above the planetary boundary layer are light, thermally induced circulations (e.g., land-sea breezes, mountain-valley winds, slope winds) may be the dominant transport mechanism near the ground. Under stable atmospheric conditions with strong winds, however, kinematic and dynamic perturbations to the wind field far exceed thermal-radiational effects on the mesoscale.

It should be noted that thermal gradients can generate winds that are stronger than those arising from kinematic effects. An example is the Santa Ana wind in the Los Angeles basin. These effects, however, generally extend over an area larger than the mesoscale transportation environment as defined earlier. In reality, these large-scale motions, driven by differential heating and cooling of the earth's surface, give rise to the synoptic scale transport phenomena discussed later in this chapter.

In sum, the effect of topography on wind flow is to modify its speed and direction, generate waves and vortices, and augment atmospheric turbulence. These general characteristics have important bearing upon the extent to which air contaminants released within the mesoscale environment are transported and dispersed downwind.

3. Vertical Transport

Sections 1 and 2 above focused on the influences of certain characteristics of cities and topography on the transport and dispersion of pollutants in the mesoscale transportation environment. The primary emphasis was on downwind dispersion of pollutants. However, vertical transport of material is also important. A few vertical transport mechanisms that can have important effects on mesoscale air quality under certain conditions are discussed below.

A variety of mechanisms have been postulated as being responsible for the vertical transport of pollutants and the subsequent formation of layers of pollutant-laden air aloft. Of course, the extent to which a given mechanism leads to the occurrence of polluted layers aloft depends on the topography and meteorology of the region. At least three mechanisms might contribute to the vertical transport of pollutants above the base of the inversion layer in the Los Angeles basin [97]:

> Upslope flow and subsequent advection back into the inversion layer.
> Dispersion into the inversion layer through vertical transport and diffusion.
> Pollutants rising to the inversion level before the inversion base is formed from below.

Some transport mechanisms may be limited to specific geographical regions. For example, a vertical transport mechanism was postulated in connection with the Lake Michigan lake breeze in which the three-dimensional flow of the lake breeze front recirculates pollutants into the inversion layer over the lake [98]. Again, the convergence in the San Fernando Valley of two sea breeze fronts with different points of origin has been suggested as a means of vertical transport of ground-based pollutants to layers aloft over the Los Angeles metropolitan area [99]. Finally, the general rising motion associated with the urban heat island effect or converging surface wind flows may also be capable of transporting pollutants aloft.

In summary, transport phenomena occurring in the mesoscale transportation environment are governed by numerous interactions among the local meteorology, topography, and the characteristics of the urban setting. Although many of the transport mechanisms discussed above occur in all urban areas, the extent to which any single transport process is dominant can be determined only through detailed consideration of the urban area in question.

4. Important Chemical Processes in the Mesoscale Environment

Recall that in the microscale environment, only fast reactions involving pollutants present in significant quantities could be considered important because of the short duration of contaminants in that environment. However, in the mesoscale or urban environment, slow reactions can build up significant concentrations of some pollutants during the course of a day. Another important characteristic of the urban environment is the temporal variation in the production of radical species. During the day, photolysis of aldehydes and HNO_2 generates free radicals that oxidize nitric oxide, a prerequisite to ozone buildup. After sundown, the production of radicals ceases, and hence, the sustained production of ozone ceases as well.

Finally, the mixture of pollutant species present in the urban environment is different from that in the vicinity of a roadway. The mixture of hydrocarbons, nitrogen oxides, sulfur compounds, and the like near a roadway is biased toward vehicular emissions. Throughout an urban area, however, the distribution of pollutant species can be quite different. Smelters, foundries, and other heavy industries emit a wide range of inorganic gases and metal compounds to the atmosphere; petroleum refineries, cleaning operations, and chemical plants emit a spectrum of hydrocarbons, aldehydes, and other pollutants. Because these and other sources are distributed unevenly throughout the urban environment, the pollutants in the atmosphere vary from place to place. Consequently, certain chemical reactions may proceed more rapidly at some locations than others, largely because of the spatial variations in emissions. For example, within the first 25 to 30 kilometers downwind of a power plant, ozone concentrations in the plume will be rather low because of scavenging by NO emissions. However, much farther downwind, perhaps 50 to 100 kilometers, ozone might be slightly in excess of ambient concentrations under certain conditions.*

5. Removal Processes in the Mesoscale Environment

Removal processes for gaseous pollutants are more important at an urban scale than at the roadway level, despite the higher pollutant concentrations at the roadway, because the surface area and residence time of pollutants in the urban area are much greater. The urban area also contains a wider variation in surface composition than the roadway environment.

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* Although the exact conditions under which ozone formation in power plant plumes might occur are not presently known, studies suggest that it might happen if the plume has entrained air that is rich in hydrocarbons [100]; this could occur, for example, if the plume passed over a refinery or chemical processing plant.

Gravitational settling is an important mesoscale removal process. This mechanism is quite effective in removing large particulates (principally lead and lead compounds) in the immediate vicinity of a roadway, and this process continues, albeit at a slower rate, throughout the urban area as well. By the time the emissions leave the roadway most of the very large particles have settled. Consequently, gravitational settling of particulates in the mesoscale environment involves the removal of smaller particles, say in the 1 to 5 μm size range. Such particles settle more slowly than larger ones, but they can remain in the mesoscale environment long enough for settling to be significant.

The removal of particulate matter near roadways and throughout the urban area may be a significant component of the material balance for a particular pollutant. For example, of the approximately 18 metric tons per day of lead emitted into the Los Angeles basin, apparently only one-third is transported beyond the basin [90].

For some pollutants, especially large particulates, impaction may result in removal in an urban area. This possibility is enhanced by the structure of the urban environment: The large number of vertical surfaces exposed to horizontal airflow (e.g., buildings, bridges, billboards, and trees) present sites for pollutant removal through impaction. The importance of this removal mechanism is not known.

Aerosols and gaseous pollutants can be removed in significant amounts from the urban environment by precipitation scavenging. As an example, the average decrease in aerosol and pollutant gas concentrations due to rain in Frankfurt/Main, Germany, was reported to range from 24 to 73 percent [101]. These values probably overestimate the significance of scavenging as an urban pollutant sink, because clean air brought in by storms may be responsible for part of the decrease in concentrations. Nevertheless, it is clear that precipitation scavenging can be an important removal mechanism in an urban area.

It was pointed out earlier that rainout--pollutant removal within a cloud--is not the principal scavenging loss mechanism in the urban environment because cloud formation normally occurs above the inversion layer, which frequently serves as a lid on urban emissions. It is possible that rainout scavenging could occur within fog banks advected into an urban area by a sea breeze or lake breeze intrusion. However, washout is more important than rainout in the urban atmosphere.

As previously mentioned, the surface uptake of pollutants occurs in three stages: transfer to the laminar sublayer, transport through the layer, and interaction by adsorption or reaction with the surface. Within the urban environment, sufficient time is available for the first two processes to proceed. Thus, the key to the importance of surface deposition at the mesoscale is whether and to what extent physicochemical interactions between pollutants and the surface take place.

One study of surface sinks in the urban environment found that some pollutants, such as CO and NO, have low surface removal efficiencies, whereas others, such as SO_2, NO_2, and ozone, can be removed quite effectively in the urban environment. In computer simulations, reductions in one-hour-average ground-level SO_2 concentrations of between 10 to 25 percent were observed for SO_2 deposition velocities within the range of reported experimental values. Roughly similar results were obtained for urban surface sinks of ozone and NO_2 [102]. From these preliminary studies, it appears that pollutant removal in the urban environment by surface sinks may be important in accounting for the fate of pollutants. However, much remains to be learned, particularly in characterizing the texture of urban areas, before a satisfactory description of surface sinks can be obtained.

The amount of pollutants in the urban environment removed by transport to the stratosphere is probably small. Most transport to the stratosphere is caused by large-scale organized motion of the atmosphere occurring on spatial scales the size of the urban environment or larger.

The single most important removal process in the mesoscale environment appears to be chemical reactions. The discussions of atmospheric chemistry above identified chemical reactions that contribute to the removal of primary and secondary pollutants from the urban atmosphere. Important among these are:

- > The oxidation of nitric oxide to nitrogen dioxide and eventually to nitrate and nitric acid.
- > The oxidation of SO_2 to sulfates.
- > The oxidation of reactive hydrocarbons through chain reactions involving free radicals.

In sum, atmospheric reactions associated with photochemical smog formation are significant pollutant sinks in the mesoscale transportation environment.

6. Process Interactions with Emissions

The preceding discussions highlighted the physical and chemical processes that are particularly relevant to urban air quality. However, the transportation planner must not only understand the various processes, but also recognize how they interact. In large measure, these interactions govern the resultant air quality in the urban environment. Consequently, the discussion now turns to the ways in which meteorological, chemical, and emissions processes combine to produce the pollutant concentrations often seen in a large metropolitan area during periods of poor air quality.

As the basis for this discussion, consider a hypothetical air stagnation episode during the summertime in a large city. Although the episode could persist for several days, only a 24-hour period sometime during the middle of the episode will be discussed, in five segments:

Period	Hours
Midnight to sunrise	2400-0500
Sunrise to midmorning	0500-1000
Midday	1000-1400
Midafternoon to sunset	1400-1900
Sunset to midnight	1900-2400

Although the above time segments may be somewhat arbitrary, they do serve the useful purpose of presenting the sequence of events that characterizes a smoggy day. For the sake of this example, it is assumed that the urban area is under the influence of a large-scale high pressure system and its attendant subsidence inversion. Finally, it is assumed that the overall air quality and meteorology of the day can be inferred from data collected at a "representative" monitoring station located somewhere in the city. (The representativeness of monitoring stations is discussed in Chapter X.)

The example discussed below is quite detailed; hence, some understanding of the change in atmospheric temperature with height, and the effects of that change on vertical air movement, is necessary to appreciate it. Briefly, air cools as it rises and expands. If the actual decrease in temperature with height in the atmosphere is greater than that in an air parcel that is pushed upward, the air parcel will be warmer than its surroundings, and will continue to rise. In this condition the atmosphere is called unstable. If the actual decrease in temperature with height is less than that in an air parcel that is pushed upward, or if the temperature increases with height, the air parcel will be cooler than its surroundings, and will resist upward movement. In this condition the atmosphere is called stable. Finally, if the decrease in atmospheric temperature with height is the same as that in an air parcel that is pushed upwards, the parcel will have no tendency to rise or sink due to buoyancy effects. In this condition the atmosphere is neutrally stable or adiabatic. If an elevated inversion layer is present, the unstable air between it and the ground is termed the mixed layer or the mixing layer. These concepts are discussed in greater detail in Chapter VII. The reader may wish to review the relevant sections of that chapter before studying the following example, which shows how the thicknesses of the mixed layer and the inversion layer change during the day.

a. Midnight to Sunrise

At midnight, the mixed layer over the city is approximately 600 to 700 feet thick, as depicted in Figure 49. Capping this shallow mixed layer

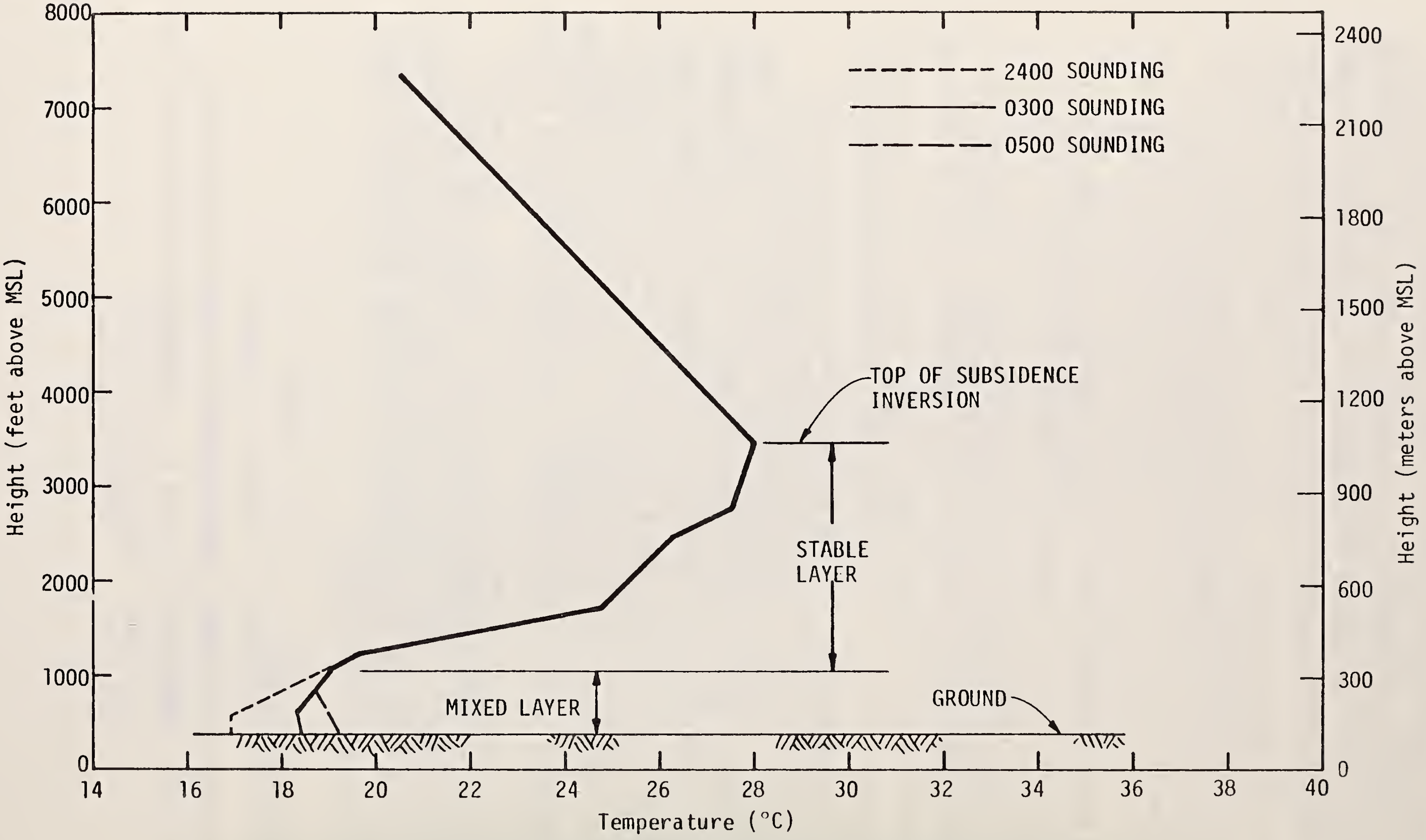


FIGURE 49. VERTICAL TEMPERATURE STRUCTURE OVER A HYPOTHETICAL CITY DURING AN AIR POLLUTION EPISODE--MIDNIGHT TO SUNRISE

is a deep, stable subsidence inversion extending up to approximately 3500 feet above mean sea level (MSL). During the night, the ground cools by emitting long wave radiation to the clear sky, and the base of the inversion gradually lowers. Pollutants near the descending inversion base become incorporated in the inversion or stable layer. By 0500, the mixed layer above the city has been reduced to roughly 100 to 500 feet in thickness. Winds during the early morning hours are light and variable, with typical speeds on the order of a few miles per hour. Turbulence levels within the mixed layer, below the inversion, are low because of the light wind speeds and weak thermally induced convection currents.

Nighttime vehicular emissions are low relative to daytime emissions. Presumably, from midnight to sunrise traffic is concentrated along major freeways and arterials, reflecting interzonal traffic arising from nighttime commercial activities (e.g., trucking), basic community support activities (i.e., police, ambulance, and fire services), and miscellaneous nighttime traveling.

Stationary sources may or may not emit pollutants during the night. Businesses that operate only during daytime (e.g., garages, dry cleaners, certain types of manufacturing processes) do not contribute to nighttime emissions. Refineries, chemical plants, packing houses, and other businesses that operate continuously do produce nighttime emissions, though some sources may run at less than full capacity at night. Point sources, such as power plant stacks, may discharge their emissions into the stable layer aloft. Depending on whether a power plant operates steadily or intermittently to meet peak demands, its emissions at night may equal its daytime emissions or be some fraction thereof.

Important chemical reactions occur during the midnight-to-sunrise period. For example, secondary pollutants (e.g., ozone and NO_2) formed from the previous day may be trapped within the stable layer as the base of the inversion lowers during the night. In such a layer aloft, ozone is essentially removed from the influence of nighttime surface NO emissions, which would otherwise scavenge it. Moreover, whatever NO remained in the stable layer from the previous day would be slowly oxidized to NO_2. Because photolysis of NO_2 does not occur at night, the NO_2/NO ratio in the stable layer above the city tends toward a higher value, which is conducive to ozone formation given adequate sunlight. At the ground, NO emissions would react with ambient ozone, decreasing the concentrations of both and increasing the NO_2 concentrations.

Generally speaking, the concentrations of all pollutants are lower at night than during other periods of the day. This is a result of the combination of low emissions rates during the night and the long time during which pollutant dispersion can take place. Figure 14 in Chapter VI presents representative diurnal variations for several pollutants in an urban area.

b. Sunrise to Midmorning

In the early morning hours before sunrise, the ground temperature is at its lowest value. At sunrise, the sun begins to heat the earth's surface, which in turn begins to heat the air above it and to set up thermal convection. By midmorning (1000), thermal convection within the mixed layer changes its atmospheric stability from slightly stable at 0500 to neutrally stable (adiabatic) at 1000. As shown in Figure 50, increasing thermal convection as the morning progresses results in the erosion of the inversion base and thickening of the mixed layer.

At sunrise, wind speeds are usually at their lowest during subsidence inversion conditions. Wind speeds generally increase in the morning hours as thermal heating becomes established. For example, a sea or lake breeze might be established if the city is located near a large body of water. Alternatively, if mountains or hills are nearby, mountain or slope winds might induce airflow over the city.

The most dramatic event during this period of the day is the increase in human activity, especially automotive traffic, in the hours just after

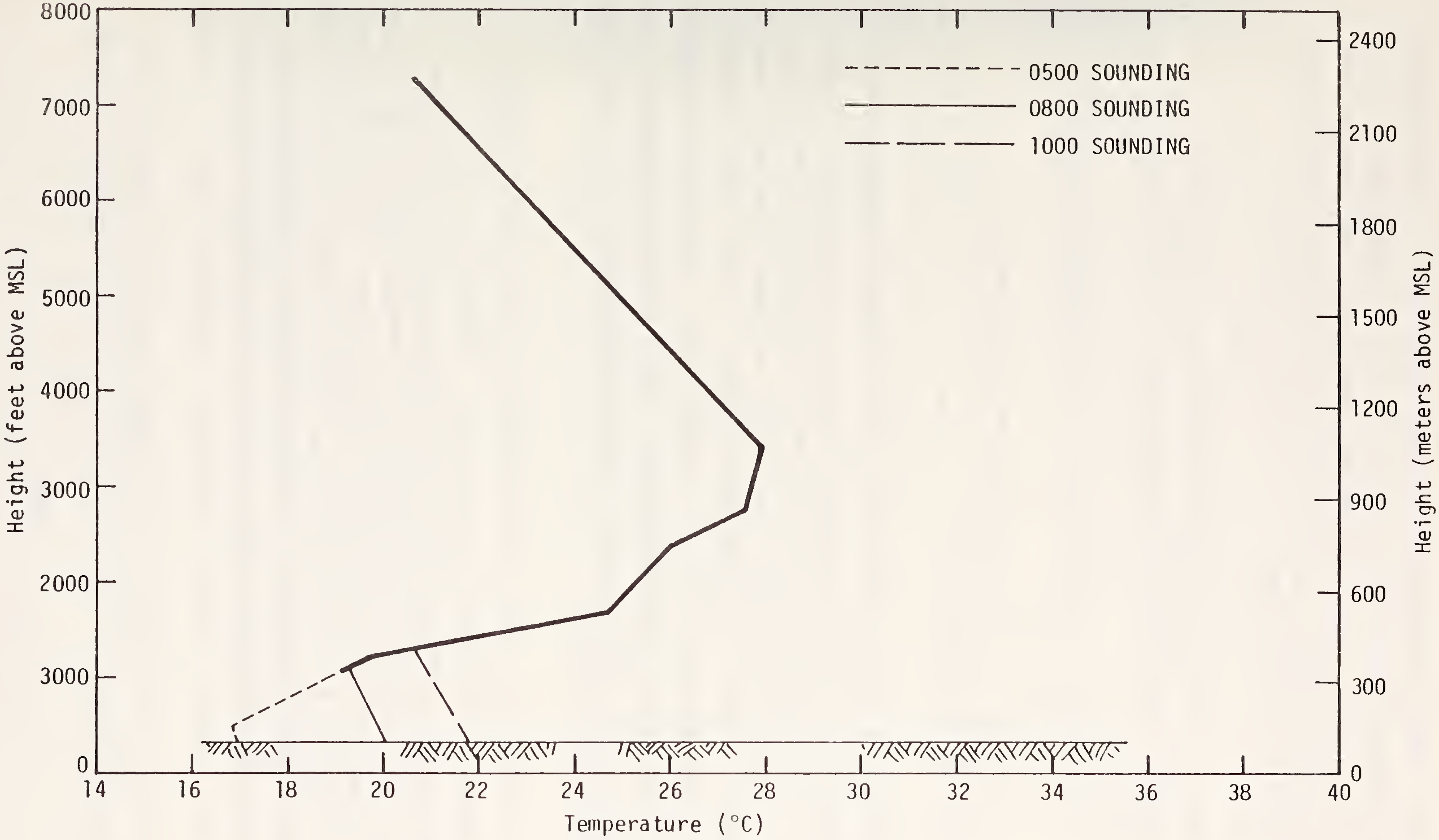


FIGURE 50. VERTICAL TEMPERATURE STRUCTURE OVER A HYPOTHETICAL CITY DURING AN AIR POLLUTION EPISODE--SUNRISE TO MIDMORNING

dawn (0600 to 0800). As shown in Figure 14 in Chapter VI, the concentrations of primary automotive pollutants, NO and CO, increase significantly during the morning rush hour. During the rush-hour period, primary pollutant concentrations reach high levels for several reasons, the most important of which are the following:

- The rate at which pollutants are emitted into the atmosphere is substantially increased because of the morning traffic.
- The low-level inversion acts as a lid on pollutants emitted into the mixed layer.
- The generally low wind speeds do not appreciably dilute the morning pollutant load.

Emissions from other sources also increase during the morning hours. In response to an increased demand for electricity, peaking power plants are run at greater capacity, resulting in a concomitant increase in NO_x (primarily NO) and SO_2 emissions. In addition, industrial sources, such as foundries, smelters, and other manufacturing activities, begin to discharge air pollutants as the day's business begins. In sum, the sunrise-to-midmorning period is characterized by a pronounced discharge of contaminants into the atmosphere, with most of them confined in the mixed layer beneath the inversion.

With the onset of sunrise and the loading of the mixed layer with large amounts of hydrocarbons, NO, and sulfur oxides from vehicular and stationary sources, several chemical reactions take place. The NO_2 initially present in the mixed layer (and in the inversion layer as well) begins to photolyze, yielding a supply of oxygen atoms. Some of the oxygen atoms will undergo a series of inorganic reactions leading to the formation of ozone and hydroxyl radicals. All three species react with hydrocarbon emissions to form a variety of free radicals, which rapidly oxidize NO to NO_2.

Air quality measurements at a monitoring station would reveal characteristic morning peaks for both NO and NO_2. As shown in Figure 14, the NO peak occurs roughly between the hours of 0600 and 0800, as does the CO peak. This concurrence is expected because both are primary pollutants emitted principally from the same source--automobiles. However, NO concentrations rapidly decline as this pollutant is oxidized to NO_2 by free radicals. CO concentrations decrease at a slower rate because CO is largely unreactive. The decrease in CO concentrations is due to lower vehicular emissions and gradual dispersion of the pollutant throughout the urban area. Roughly an hour or two after the NO peak, concentrations of NO_2 begin to rise until an NO_2 peak is observed around midmorning. At the same time, ozone concentrations are observed to increase gradually as some of the NO_2 is photolyzed.

The time differences between the NO, NO_2, and ozone peaks are commonly observed in smog chamber experiments. In the urban atmosphere, however, the decreases in NO and NO_2 concentrations cannot be explained solely on the basis of atmospheric chemistry. The rising inversion base causes some of the decrease by increasing the volume in which the pollutants may disperse. Thus, the decreases in NO and NO_2 are due partly to chemical reactions and partly to the thickening of the mixed layer. Complicating the situation further, pollutants within the inversion layer are injected into the mixed layer as convective mixing erodes the base of the inversion. As a result, urban air quality during the morning hours is determined by complicated interactions among temporally varying emissions, nonlinear atmospheric reactions, and dilution and injection effects due to the rising of the inversion base.

c. Midday

During the period from 1000 to 1400, solar radiation reaches a maximum. Thermal convection intensifies in the mixed layer, resulting in a sustained erosion of the base of the subsidence inversion. By early afternoon, the inversion base has risen to approximately 2500 feet. Because convective mixing is so strong at midday, emissions near the ground can be carried to the top of the mixed layer in as little as 10 to 20 minutes. Figure 51 presents a typical variation in the midday temperature sounding. Note that

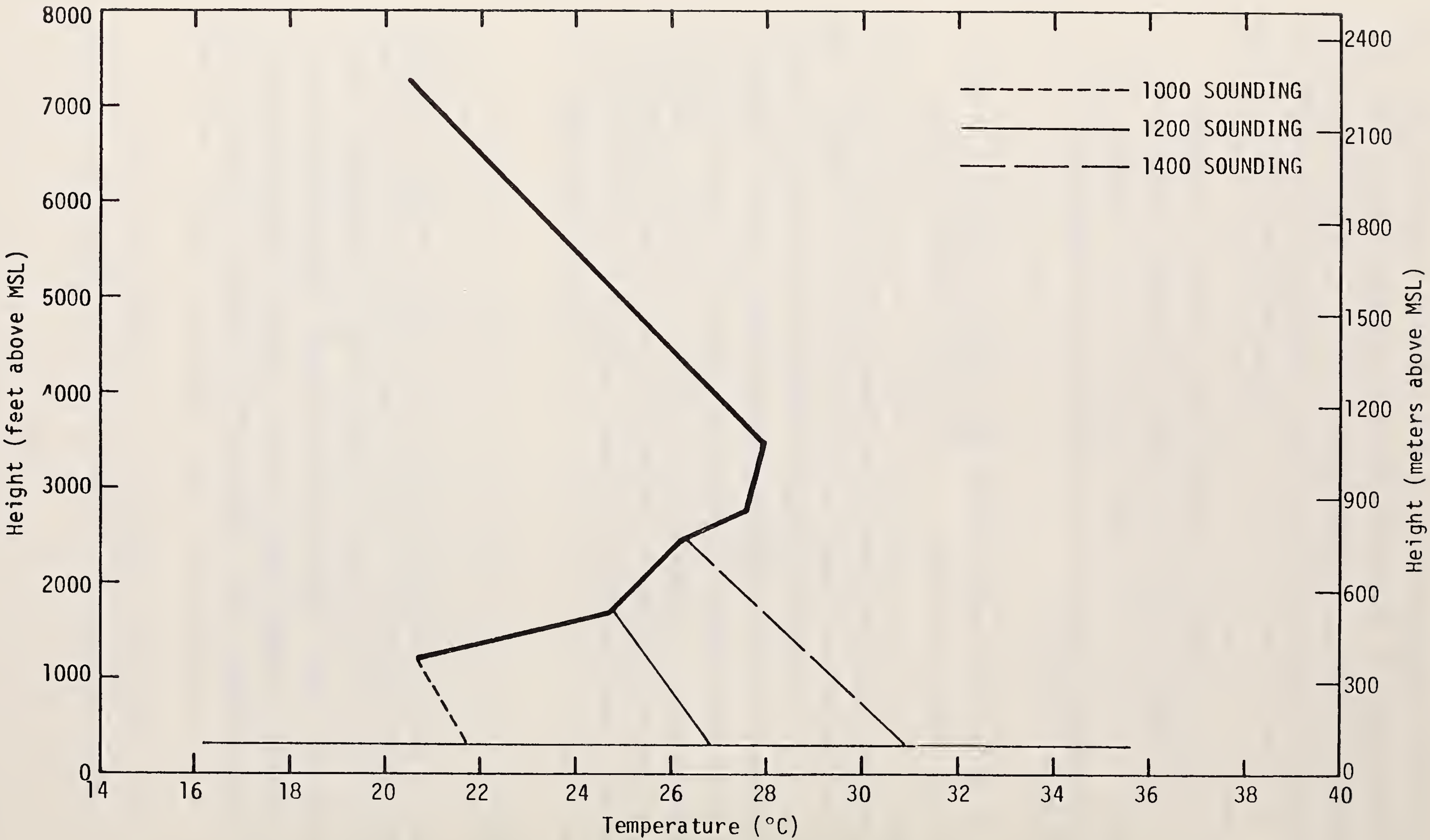


FIGURE 51. VERTICAL TEMPERATURE STRUCTURE OVER A HYPOTHETICAL CITY DURING AN AIR POLLUTION EPISODE--MIDDAY

as the day progresses the mixed layer not only thickens but also becomes more unstable because of intense solar heating of the ground.

As a rule, wind speeds are higher at midday than during the morning hours. This increase can result from local effects (e.g., surface temperature differences between the urban center and outlying rural areas) or from large-scale effects (e.g., intensification of synoptic scale temperature differences between thermal high and low pressure centers). In many large cities, the increased winds during midday are a result of sea or lake breeze intrusions, heat island effects, or mountain-valley winds. Together, the thickening mixed layer and increasing surface winds lead to enhanced pollutant dilution, or as it is sometimes called, ventilation.

Midday traffic emissions are lower than those during the morning rush hour; nevertheless, the midday traffic does contribute important amounts of primary pollutants to the atmosphere. In contrast, municipal and industrial sources emit at essentially constant rates throughout the daytime hours. Thus, although large amounts of hydrocarbons and NO are not emitted during midday, primary pollutants are still continuously discharged to the atmosphere from all sources.

Midday hours are characterized by intense photochemical activity; ultraviolet radiation reaches maximum intensity at this time of the day. Concurrent with the peak in radiation is the rapid buildup of photochemical oxidants, principally ozone. Since NO is rapidly converted to NO_2 during midmorning, the photolysis of NO_2 leads to an accumulation of ozone by midday. The newly formed ozone reacts with ambient hydrocarbons (largely derived from morning rush-hour traffic) to produce free radicals, which continue to oxidize NO to NO_2. As discussed earlier, this series of chain reactions often leads to high ozone concentrations.

While oxidant concentrations are increasing, atmospheric reactions involving sulfur oxides are also taking place. In particular, reactions involving SO_2 and a variety of free radicals formed in the photochemical smog reactions are thought to be an important pathway in the formation of SO_3 and eventually sulfates. Although there are uncertainties in the rates of certain sulfur oxidation reactions and in the relative importance of different oxidation pathways, the oxidation of SO_2 to sulfates has been observed to increase with increasing concentrations of hydrocarbons and atmospheric water droplets, and to occur mainly after the majority of the NO has been converted to NO_2. Finally, direct photooxidation of SO_2 to SO_3 also occurs, though this pathway is of secondary importance.

Air quality measurements taken at midday would typically indicate high levels of photochemical oxidants (i.e., ozone, PAN) and decreasing concentrations of CO, NO, NO_2, and reactive hydrocarbons. The decline in concentrations of these species during midday may be related to interactions among several processes, of which the following are perhaps most important:

> Thickening of the mixed layer
> Increasing daytime wind speeds
> Reduction in primary pollutant emissions
> Chemical reactions involving primary pollutants
> Surface uptake.

In contrast with the morning hours, when ambient air quality is dominated by emissions, atmospheric reactions play the key role in governing air quality during midday.

d. Midafternoon to Sunset

During the late afternoon (1400 to 1900), the supply of solar energy to the urban environment diminishes. The hypothetical temperature sounding in Figure 52 indicates that as sunset approaches, the ground surface temperature drops. This in turn reduces the intensity of thermal convection in the mixed layer. In effect, the combination of a subsiding high pressure air mass and a cooling of the ground surface tend to reduce the thickness of the mixed layer and to induce a shift from unstable to neutral or slightly stable conditions below the inversion

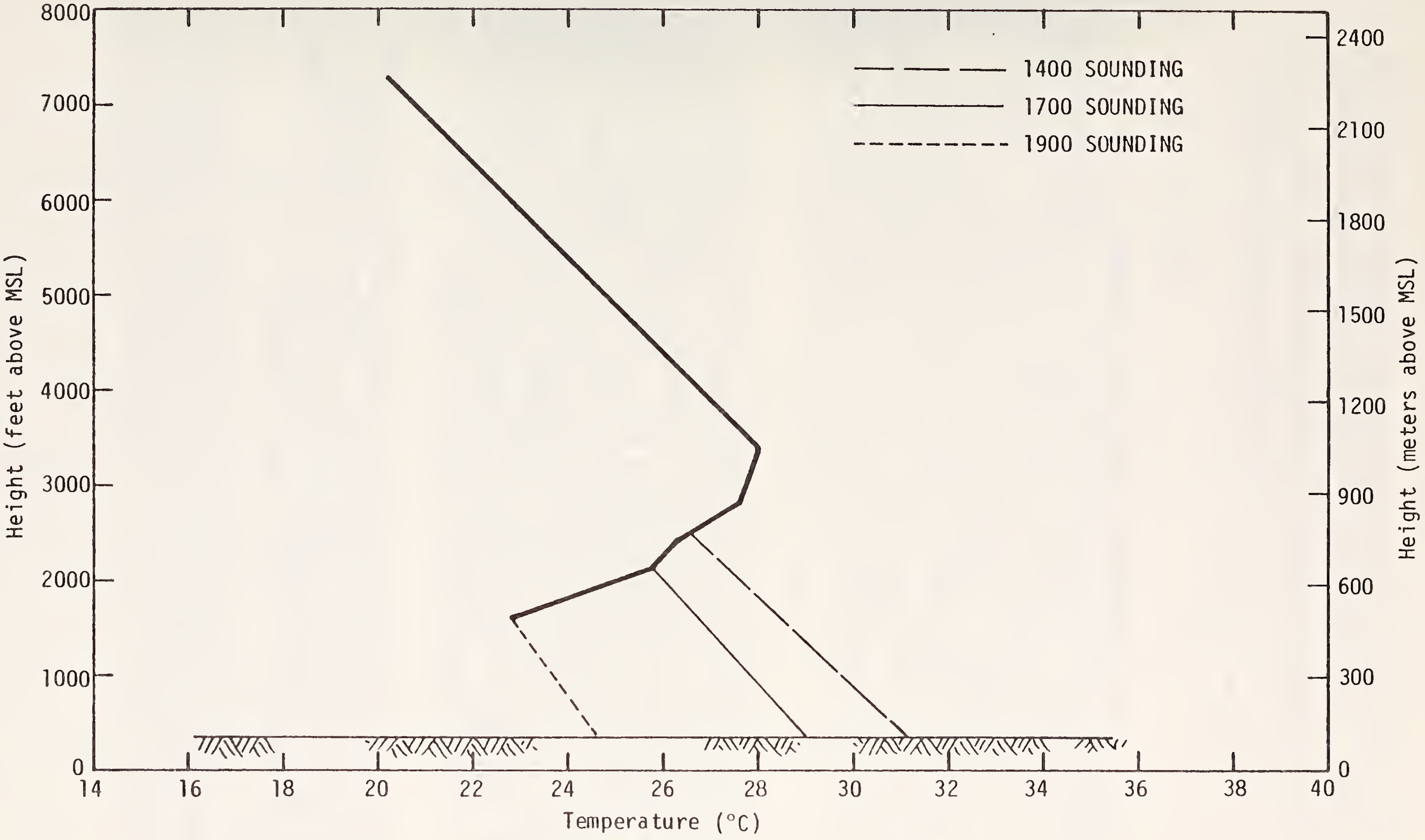


FIGURE 52. VERTICAL TEMPERATURE STRUCTURE OVER A HYPOTHETICAL CITY DURING AN AIR POLLUTION EPISODE--MIDAFTERNOON TO SUNSET

base. Also, during this period the temperature differences between urban and rural areas, water bodies, and the like are reduced, with the result that surface winds begin to diminish as sunset approaches. Thus, whatever strong ventilation effects were present at midday are gradually weakened as the winds slow down, the inversion base drops, and turbulent convection in the mixed layer decreases.

Ironically, while atmospheric conditions are becoming increasingly less conducive to the dispersion of pollutants at this time of the day, pollutant emissions begin to increase. This second peak in emissions is due principally to late afternoon (or evening) rush-hour traffic. Although it might be expected that the evening surge in traffic emissions discharges roughly the same amount of primary pollutants to the atmosphere as the morning rush, the temporal distribution of evening rush-hour emissions is more diffuse; evening rush-hour traffic is commonly spread out over several hours (say, 1600 to 2000), whereas morning traffic is largely concentrated in a few hours (perhaps 0700 to 0900).

The later afternoon hours are also characterized by a reduction in photochemical activity. With decreasing insolation, photolysis reactions slow down, and at sunset they virtually stop. Accordingly, the production of free radicals (e.g., through aldehyde photolysis) is inhibited. Near the ground, high NO emissions scavenge ambient ozone, particularly in the vicinity of large roadways. Also, to the extent that radical oxidation of SO_2 is an important mechanism, the rate of conversion of SO_2 to sulfate is slowed as a result of the decreasing supply of radicals.

Air quality observations at monitoring stations during the late afternoon reveal decreasing ozone concentrations. This trend occurs because the formation of ozone by photochemical processes decreases and the increased NO emissions scavenge the available ozone to form NO_2.

In sum, urban air quality during late afternoon hours is largely influenced by a lowering of the inversion base (and consequent trapping of pollutants in layers aloft), a reduction in wind speeds and photochemical activity, and a secondary increase in emissions. For the most part, ozone concentrations drop off sharply while CO and NO_x concentrations remain roughly constant. On a particular evening, however, atmospheric conditions could lead to a noticeable buildup of CO and NO_x.

e. Sunset to Midnight

The surface cooling trend that begins in the late afternoon continues throughout the evening. Intense radiative heat loss to the nighttime sky takes place, particularly if there is little or no cloud cover. As shown in Figure 53, the elevation of the inversion base continues to drop, reaching approximately 600 feet by midnight. Whereas a shallow nocturnal radiation inversion at the surface often forms in rural areas, urban areas generally have sufficient residual heat from various sources, such as refineries and space heating, to prevent formation of surface inversions. Thus, even at night a shallow mixed layer exists.

In the absence of weather fronts or strong surface pressure gradients, wind flow through an urban area after sunset is usually light. If the city is located near a large body of water, land breeze circulations may be set up, but the strengths of these flows are normally less than those of their daytime counterparts (i.e., sea or lake breezes), because of smaller temperature contrasts between land and water at night. If the city is adjacent to mountainous areas, as are Los Angeles, Salt Lake City, and Albuquerque, nighttime drainage (mountain) winds may be generated. These winds are also relatively light--typically on the order of 2 to 4 miles per hour.

Vehicular emissions decrease during the evening hours, as do emissions from certain municipal and industrial sources, such as incinerators, factories, cleaners, and peaking power plants. In contrast, base-loaded power plants and refineries operate at full capacity continuously. At nighttime, emissions from power plants and other elevated point sources (e.g., refinery flares) may be discharged into stable layers above the inversion base, whereas vehicular and stationary area source emissions are discharged into the shallow mixed layer.

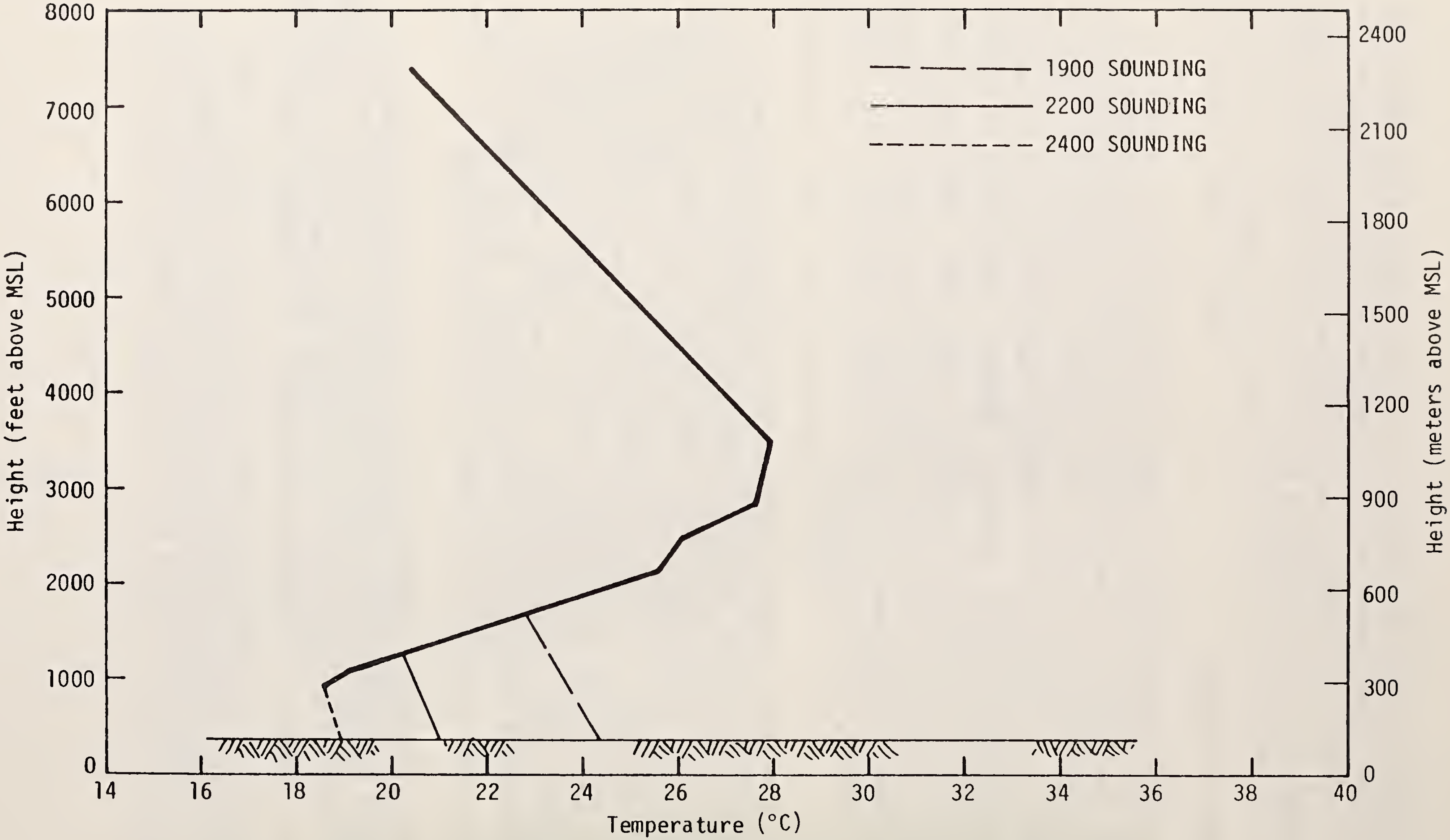


FIGURE 53. VERTICAL TEMPERATURE STRUCTURE OVER A HYPOTHETICAL CITY DURING AN AIR POLLUTION EPISODE--SUNSET TO MIDNIGHT

Atmospheric chemistry slows down considerably after sunset. In particular, photochemical reactions, such as NO_2 photolysis, essentially stop. However, ambient ozone remaining from the day's photochemical activity can react rapidly with fresh NO emissions to form NO_2, which can further react with ozone to form NO_3. Ambient hydrocarbons, such as olefins, may react with ozone to form products such as aldehydes.

As a result of the trend toward stable stratification of the nighttime atmosphere, a certain amount of layering occurs in which some strata contain higher concentrations of a given pollutant than other strata. For example, vehicular emissions may lead to layers near the ground that contain high (relative to overall nighttime conditions) concentrations of NO and reactive hydrocarbons. Aloft, layers of ozone, NO_2, and less reactive hydrocarbons might exist. The extent to which these layers mix, thereby leading to the depletion of ozone and the oxidation of NO to NO_2, depends on the degree of mixing among the various strata.

In summary, pollutant concentrations in the late evening gradually decrease in magnitude. By midnight, concentrations may be only slightly higher than their minimums over the entire day. Processes that contribute to the buildup of high concentrations of secondary pollutants (e.g., increased vehicular emissions and photochemical reactions) are not important between sunset and midnight. Atmospheric dispersion is reduced as a result of light winds and a shallow, stably stratified mixed layer. The importance of surface sinks (though still a factor in removing pollutants) diminishes because of the reductions in pollutant concentrations and in the effectiveness of transport processes that carry pollutants to surfaces.

Many processes were found to be important in the example just presented--inversion phenomena, wind transport, solar radiation, nighttime atmospheric chemistry, and others. Additional complexities could have been added to this example, such as precipitation scavenging. Thus, the ultimate effect of urban vehicular emissions on air quality is a very complicated problem.

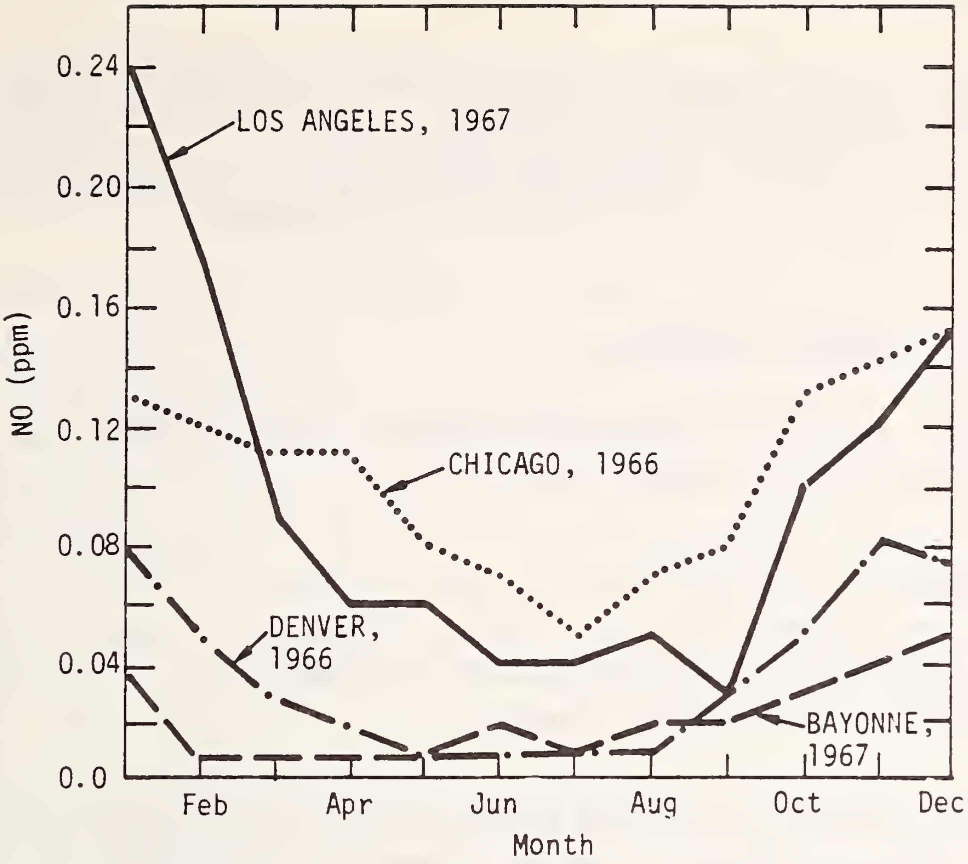
The foregoing discussions have focused on events that might occur in a typical urban area during a summer smog episode. But the transportation planner is also concerned with the interaction of various processes at other times of the year. Consequently, certain seasonal patterns in primary and secondary pollutant concentrations in metropolitan areas are discussed below.

Figures 53 and 54 present mean monthly NO and NO_2 concentrations at four urban sites. Average urban NO concentrations are typically higher during the late fall and winter than at other times of the year, perhaps largely because of the decreased overall atmospheric mixing and reduced solar radiation (which drives photochemical processes). Another factor contributing to high monthly average NO concentrations is the increased NO emissions from power generating and heating sources during the cold autumn and winter months.

The monthly variation in NO_2 concentrations is less distinct than for NO, as shown in Figure 54. Los Angeles, for example, experiences minimum NO_2 concentrations during the summer, whereas Chicago has its maximum then. Although more NO is converted to NO_2 during the summer months as a result of increased photochemical activity, sinks for NO_2, such as atmospheric reactions and surface uptake, may be large enough to compensate for the additional NO_2. The rate of disappearance of NO_2 due to various phenomena may determine the seasons during the year when maximum NO_2 concentrations will occur. In the case of Los Angeles and Chicago, it is clear that such factors as the area's climatology and the nature and distribution of emissions sources play an important role in the seasonal variation of NO and NO_2 concentrations.

C. MACROSCALE ENVIRONMENT

In the macroscale environment, atmospheric processes that occur over time periods of from one to several days are important. This implies a



Source: Ref. 64.

FIGURE 54. MONTHLY MEAN NO CONCENTRATIONS AT FOUR URBAN SITES

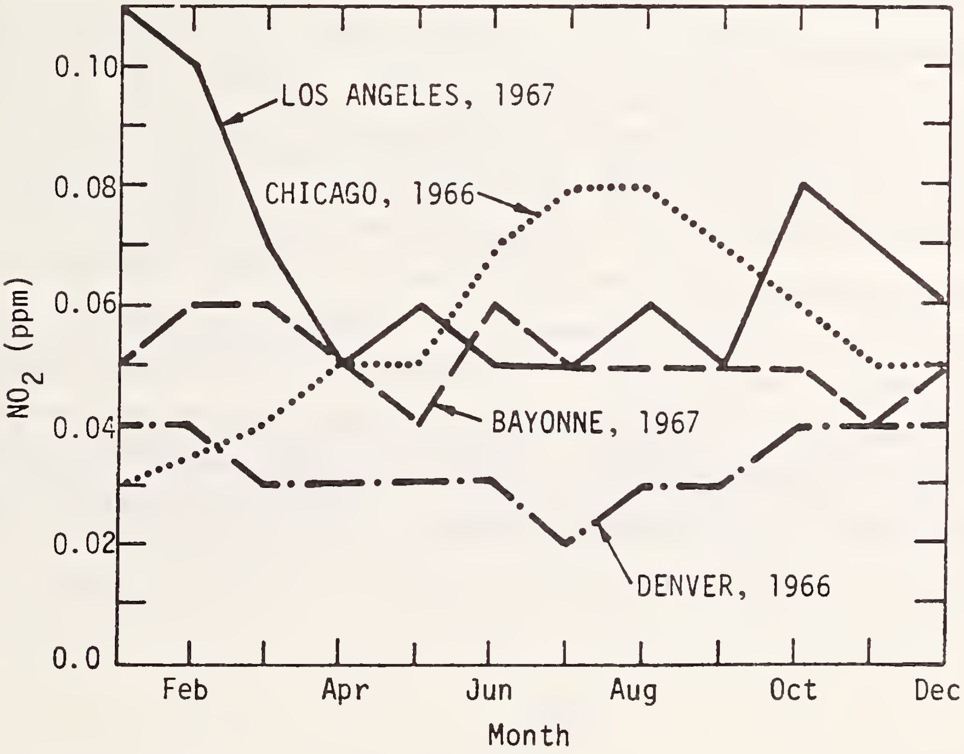


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FIGURE 55. MONTHLY MEAN NO_2 CONCENTRATIONS AT FOUR URBAN SITES

large geographical extent, roughly a hundred to several thousand kilometers horizontally and the thickness of the troposphere vertically. It is clear that consideration of the air quality impacts in regions of this size must encompass a wide range of geographical and land use conditions.

1. Macroscale Transport Phenomena

Four general categories of macroscale transport (often referred to as long range transport) can be identified:

- > Transport in the surface layer
- > Transport in layers aloft
- > Transport between the troposphere and stratosphere
- > Transport in large-scale air masses.

Although clear distinctions among the above categories may not be possible in all cases, they do provide a convenient framework for the discussions that follow.

a. Transport in the Surface Layer

Strictly speaking, surface layer transport refers to the advection and diffusion of pollutants beneath an inversion layer. Surface layer transport is a dominant process at the mesoscale level during the course of a day, but it is somewhat less important on the macroscale level. One of the reasons for this is that variations in the thickness of the mixed layer over a few days and over large geographical regions can be considerable. Moreover, under certain circumstances, such as a ground-based nocturnal inversion, the mixed layer does not exist. But relaxing the definition of surface layer transport to include the transport of pollutants in the lowest layer of the atmosphere (i.e., that which is characterized by surface wind measurements) gives a more suitable description of this transport process. As discussed earlier, pollutants transported in the surface layer are close to sources of emissions and surface pollutant sinks. Thus, surface layer transport significantly affects air quality in the macroscale environment.

An example of macroscale transport in the surface layer is the so-called urban plume. Numerous studies have reported the existence of a large, diffuse plume containing high (relative to background air) concentrations of secondary pollutants downwind of metropolitan areas. Capped by an elevated inversion, the urban plume can be observed large distances downwind. Under some conditions the St. Louis urban plume, for example, remained clearly distinguishable from ambient air as far as 160 km downwind [103]. Other studies have documented surface layer transport of pollutants from large northeastern cities up to 250 to 400 km [104]. Apparently, the strength and direction of the wind, the height of the inversion, and the type of surface (i.e., bodies of water, prairie lands, rolling hills, rugged mountains) over which the plume is carried largely determine the distance over which the urban plume can be distinguished from the ambient air.

The surface layer can be viewed as a link between ground-based emissions and pollutant concentrations aloft. Ground-level emissions are advected and diffused within the surface layer, and they can also undergo chemical reactions. The extent to which pollutant concentrations are altered in layers aloft depends largely on the rate at which pollutants are transported from sources upward through the surface layer or, conversely, downward from layers aloft to surface sinks.

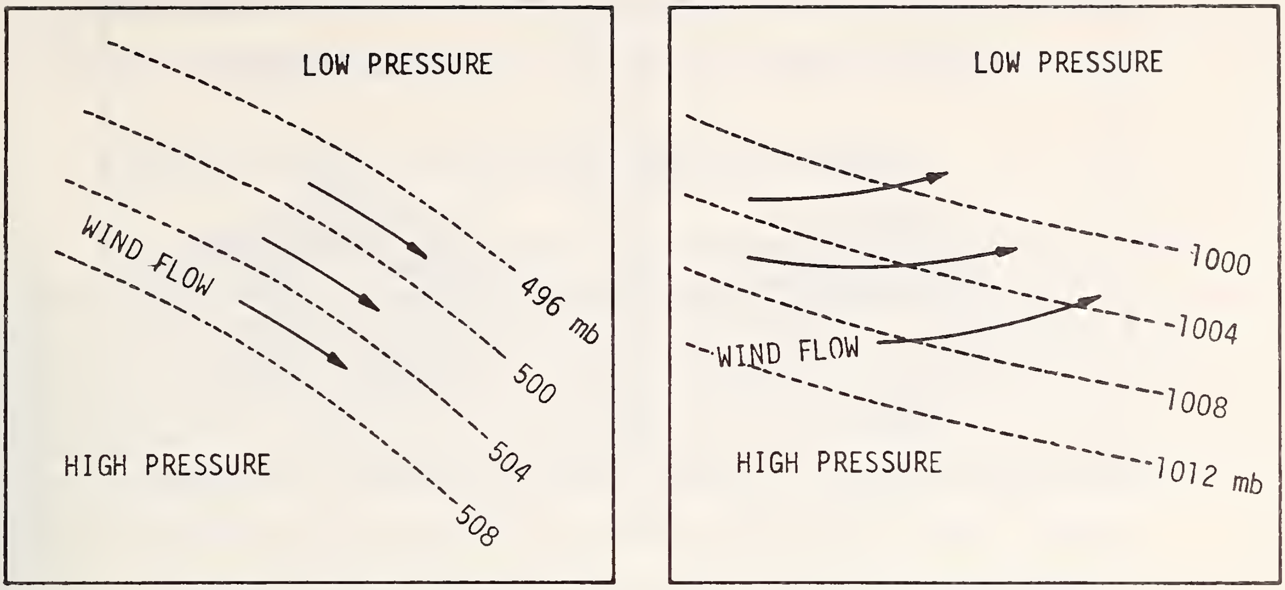
b. Transport in Layers Aloft

Another important macroscale transport mechanism is the conveyance of pollutants in layers of air aloft. A layer aloft can be defined as a stratum of air having different characteristics (e.g., concentrations) from the strata above and below it. Typically, these differences arise because of the presence of a temperature inversion, often accompanied by a shear in wind speed or direction. Conceptually, one might envision a layer aloft as the air within or above an elevated temperature inversion that caps the surface layer.

Transport in layers aloft can be an important transport mechanism for several reasons. First, wind speeds in layers aloft are frequently larger than those of surface winds; thus, pollutants can be carried greater distances downwind. Second, if the direction of the wind aloft differs from that of the surface winds, identification of the sources of pollutants in the layer aloft and prediction of their destinations are difficult. Third, as discussed later, pollutants in layers aloft are isolated from new surface emissions and surface sinks; thus, chemical transformations during transport in layers aloft can be quite different from those in the surface layer. Finally, because of the generally greater stability and hence, less atmospheric turbulence in layers aloft, pollutants are not dispersed as readily as they are in the surface layer.

An earlier discussion of transport phenomena in the mesoscale environment identified several mechanisms that form polluted layers aloft. This section concerns the physical driving forces that give rise to the transport of pollutants in layers aloft.

Perhaps the most familiar cause of wind aloft is the dynamic interaction between high and low pressure cells in the atmosphere. If the earth did not rotate, winds over flat terrain would go directly from regions of high pressure to regions of low pressure. But, because the earth rotates, upper level winds (observed from the ground) appear to be deflected to the right in the northern hemisphere. This deflection is due to the so-called Coriolis force. Thus, at high altitudes, the wind flows nearly parallel to the isobars (contours) of equal atmospheric pressure). Near the ground, surface friction retards the wind, thus creating the planetary boundary layer, and causes the winds to flow across the pressure contours from regions of high to low pressure. These generalized wind patterns are shown in Figure 56. The clockwise turning



In Upper Air

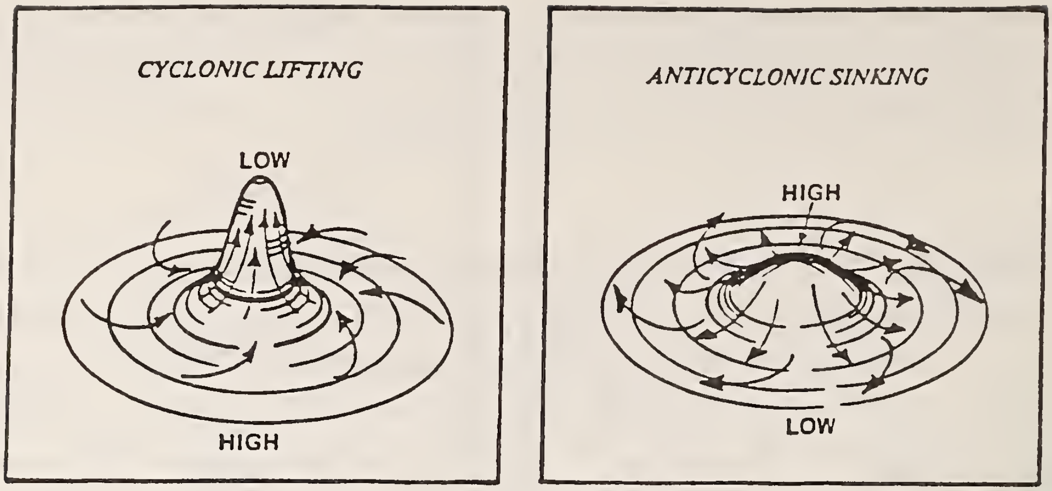
At Earth's Surface

Source: Adapted from Ref. 95.

FIGURE 56. WIND FLOW ALONG PRESSURE CONTOURS IN THE UPPER AIR AND ACROSS PRESSURE CONTOURS AT THE EARTH'S SURFACE. Note: A millibar (mb) is a unit of pressure; standard atmospheric pressure at sea level is approximately 1013 millibars.

of the wind with increasing height (Ekman spiraling) occurs throughout the depth of the planetary boundary layer. At the top of the boundary layer, the wind is virtually unaffected by terrain; the wind speed and direction are governed largely by the magnitude of the pressure gradient at that level and the effects induced by the earth's rotation.

Pollutants emitted from ground-level sources can be carried aloft by many mechanisms, some of which have been discussed earlier. Once contained in a layer aloft, they can be transported great distances from their source regions, depending on the intensity of and spacing between the high and low pressure cells. Figure 57 shows the wind flows associated with both cyclonic and anticyclonic systems. Slowing moving (quasi-stationary) systems of this type are capable of transporting airborne pollutants over distances between 100 to 1000 km. (Large frontal systems are discussed later in this section.)



Source: Ref. 95.

FIGURE 57. CYCLONIC LIFTING (CONVERGENCE) AND ANTICYCLONIC SINKING (DIVERGENCE). The diameter of the inflow or outflow region is between 100 and 1000 km.

One particularly interesting long range transport mechanism, the so-called nocturnal jet, involves the interaction between atmospheric pressure gradients (due to high and low pressure systems) and radiative temperature inversions. Although the existence of the nocturnal jet has been known for many years, it is still not fully understood. Apparently, the jet is primarily related to large-scale thermal and pressure patterns. During the day, convective mixing in the surface layer distributes the effects of surface frictional drag almost uniformly throughout the lower depths of the planetary boundary layer. However, shortly after sunset, as the ground cools by radiative heat loss, the surface frictional drag that was present near the top of the boundary layer during the daytime is significantly reduced. Essentially, flow at the surface and flow aloft become decoupled with the result that a nocturnal jet forms near the top of the planetary boundary layer. Nocturnal jets have been observed at several locations in the United States, including the San Joaquin Valley in California [105] and Cedar Hill, Texas [106]. Although more remains to be learned about this phenomenon, it appears that nocturnal jets are potentially capable of transporting pollutants long distances. One study, for example, suggested that pollutants from cities as far south as Dallas can be transported into Wisconsin by nocturnal jets within the inversion layer [98].

c. Transport Between the Troposphere and Stratosphere

Investigations carried out over the last two decades have shown that stratospheric and tropospheric air undergo continuous exchange. It has been estimated that as much as 70 percent of the total stratospheric air mass mixes with the troposphere annually [107]. As a result, pollutants discharged into the troposphere may eventually reach the stratosphere, and stratospheric pollutants (of which ozone and radioactive debris are most important) may be mixed down into the troposphere.

Mechanisms that lead to the transport of pollutants between the troposphere and stratosphere include [78]:

- Seasonal adjustments in the height of the tropopause (i.e., the boundary between the troposphere and stratosphere).
- Mean meridional circulation.
- Turbulence at the level of the tropopause.
- Thunderstorms that penetrate into the stratosphere.
- Cyclogenesis (i.e., the formation of high or low pressure systems).

The first two of the above processes occur over relatively large temporal and spatial scales. Their importance to ground-level air quality is probably limited to a slight modification of seasonal and regional background air pollutant concentrations. Turbulence at the tropopause, generated by frontal activity, may mix pollutants vertically, but the extent to which this mechanism transfers large amounts of pollutants is not known. However, cyclogenesis and thunderstorms can be important contributors to short-period high ground-level ozone concentrations because the downdrafts associated with these phenomena are capable of transporting ozone from high to low altitudes with relatively little dilution or chemical scavenging [78].

d. Transport in Large-Scale Air Masses

Representative spatial scales for transport in surface layers and layers aloft are on the order of the dimensions of cyclonic and anticyclonic weather systems (see Figure 57). This section discusses transport of an even larger scale, the global movement of entire synoptic scale air masses by complex dynamic and thermal effects. These air masses can extend over many states and have lifetimes ranging from one to a few weeks.

A good example of the capacity of large-scale air masses to transport pollutants is provided by a study of a two-week air pollution episode over the eastern half of the United States in June and July of 1975 [108]. On the basis of nationwide visibility, ozone, and sulfate aerosol data and synoptic weather maps, the following long range transport sequence was deduced. At the beginning of the regional episode, a maritime air mass was transported northerly from the Gulf of Mexico across Louisiana, Arkansas, Illinois, and Indiana. Upon reaching the Great Lakes region, the air mass stagnated, accumulating a load of pollutants from the heavily industrialized northeastern region of the United States. At the same time, tropical storm Amy was advancing up the northeast Atlantic coast, thereby preventing eastward escape of the hazy, polluted air mass. Slowly, the air mass drifted westward, passing over Missouri and Kansas. However, another synoptic air mass, this one advancing from Canada toward the Great Lakes, collided with the polluted air mass and during the following two days moved the hazy air mass across the southeastern portion of the United States to Florida. Examination of surface visibility, ozone, and sulfate data at eastern locations during the episode confirmed the hypothesis that multistate-scale haziness can be caused by the accumulation of pollutant emissions in one region and their subsequent transport over a large distance. In the example above, emissions from the Great Lakes region were shown to contribute to high secondary pollutant concentrations in Alabama and Florida--a distance of roughly 1500 km.

2. Important Chemical Processes in the Macroscale Environment

The distinguishing characteristic of chemical processes on the synoptic scale is that reactions take place in what is known as an "aged" air mass. By the time an air mass reaches the synoptic scale, it has experienced most of its chemical reaction potential. The more reactive hydrocarbons have been oxidized, leaving only methane and other low-reactivity hydrocarbons. Nitrogen oxide concentrations are low, and most of the NO_x has been converted to HNO_3, which is removed by precipitation scavenging and surface uptake. Hydrocarbon-to-NO_x ratios are high relative to common urban values, though, as noted above, the hydrocarbons are of low reactivity. In short, most of the primary pollutants have been converted to slowly reacting secondary species or stable end products by the time an air parcel reaches the synoptic scale. Of course, if the air mass receives an input of fresh emissions from either man-made or natural sources, the hydrocarbon-NO_x-SO_x chemistry can become more active.

3. Removal Processes in the Macroscale Environment

The ultimate fate of anthropogenic or natural air pollutants is largely governed by removal processes that occur in the macroscale, or regional, environment. As a result of the generally low pollutant concentrations and long time periods associated with this environment, the various removal mechanisms discussed earlier in this chapter become more nearly equal in terms of providing sinks for airborne contaminants.

By the time pollutants are carried far downwind of an urban source area (and hence can be considered in the macroscale environment), most of the particulate matter derived from vehicular emissions (e.g., lead) is in the submicron size range. The heavier particles would have been removed by gravitational settling and impaction near roadways and throughout the urban area. Accordingly, the rate at which individual particles settle out of the atmosphere or are removed by impaction on surfaces on a regional scale is reduced because of the small particle sizes.

Precipitation scavenging on the macroscale level occurs both as rainout and as washout. In this environment, pollutants are transported aloft by thermal convection and turbulent diffusion to altitudes at which cloud formation phenomena occur. Once condensation nuclei within the cloud acquire sufficient water in either solid or liquid phase to enable them to fall, the precipitation elements (raindrops, ice crystals, or snowflakes) pass through the cloud, intercepting additional moisture and gas or aerosol contaminants. This process of rainout occurs until the precipitation emerges from the cloud, at which point scavenging by washout can proceed.

Obviously, pollutant scavenging by rainout and washout is only important if precipitation occurs. In light of the dramatic spatial variability of precipitation across the United States, the importance of this removal mechanism varies from region to region. One might reasonably expect that precipitation scavenging is a more important mechanism in the Pacific Northwest than in the very dry regions in the Southwest. (Compare, for example, the mean annual precipitation in Seattle, Washington, of over 100 inches with the mean of less than 2 inches in Death Valley, California.)

Removal of pollutants by surface uptake processes is greatly enhanced by the long time periods and the wide range of surfaces that exist in the macroscale environment. Pollutant gases and aerosols are transported to surfaces such as soil, vegetation, rocks, and water. Although it is difficult to quantify precisely the surface uptake of pollutants (by either precipitation scavenging or dry deposition processes), particularly at the regional level, surface uptake is the main means whereby pollutants are eventually removed from the troposphere.

Tropospheric pollutants can also be lost to the stratosphere. In the regional environment, large-scale atmospheric motions are capable of carrying pollutants to great elevations. Pollutants transported to the top of the troposphere may continue up into the stratosphere. Once in the stratosphere, they may react and be removed as discussed earlier. Although stratospheric removal of pollutants (e.g., fluorocarbons) is known to exist, the magnitude of this sink remains uncertain.

A final removal mechanism in the macroscale environment is chemical reactions within the troposphere. This pollutant sink is less important on the macroscale than in the urban environment. By the time pollutants reach the macroscale environment, they have been diluted to very low concentrations. Thus, the rates of reaction are also reduced. If low concentrations of certain pollutants from an urban area (NO_2, for example) encounter a fresh source of emissions (reactive hydrocarbons, perhaps), then removal by chemical reactions can assume greater importance.

4. Process Interactions with Emissions

Recall that at the microscale level, the degree of turbulent mixing and the rate of chemical reactions had the greatest effects on ambient air quality near roadways. In the urban environment, several other factors were found to be important, including solar insolation, the temporal variation in the mixed layer, and the temporal distribution of emissions. As the temporal and spatial scale of the transportation environment under consideration increases, the number and complexity of process interactions increase as well. It is not surprising, then, that on the regional, or macroscale, level, nearly all of the chemical and physical processes identified in Chapter VII have some bearing on ambient air quality. In the interest of simplicity, however, the following discussion of macroscale interactions presents a general example that embodies many of the important interactions that can occur on the regional level. This example portrays the long range transport of photochemical oxidant and its precursors from an urban area to a rural mountainous area far downwind (perhaps 1000 km or more). Although the long range transport of pollutants may take place in the surface layer, in a layer aloft, in large-scale air masses, or perhaps in occasional wind phenomena such as a nocturnal jet, it is assumed in the example that the urban emissions are transported in a layer aloft.

Recalling the discussion of typical events during an urban smog episode, suppose that various pollutants are trapped within an elevated inversion over an urban area during the afternoon and evening hours, when the inversion base drops. These pollutants might include ozone, NO, NO_2, SO_2, a variety of hydrocarbon species, radicals, and the like. If the upper level winds are strong, the pollutants in (and above) the stable layer might be transported downwind of the urban area. As they travel downwind overnight, the pollutants are dispersed only slightly because:

- Thermally induced turbulence and mixing in the planetary boundary layer decrease at night.
- The layers aloft are far removed from ground sources of mechanical turbulence.
- Stable strata decrease atmospheric turbulence within the inversion.

[Of course, if significant wind shear (in speed, direction, or both) existed within the inversion layer, then pollutants in the layer aloft might experience enhanced dispersion.] The result of these physical processes is the creation and maintenance of a layer of pollutants aloft, which is then transported downwind at night with very little dispersion.

Photochemistry ceases when the sun sets, thus virtually eliminating all sources of radicals. Olefins, which can react with ozone to produce a small amount of radicals, are usually depleted by the end of the day because of their high reactivity. In short, the chemistry that produces oxidants is terminated during the night. No ozone can be generated because no NO_2 photolysis occurs. Shortly after sunset, the remaining ozone and NO can react until one or the other is exhausted. This reaction is so rapid that its rate is controlled by atmospheric mixing.

Radicals disappear at night as well. The rates of disappearance are not completely known, but the more reactive ones, such as $OH\cdot$ and oxygen atoms, disappear rapidly. The fate of peroxy radicals such as $HO_2^{\cdot}$ and $RO_2^{\cdot}$ is uncertain because their main daytime reaction is with NO. The NO concentration decreases at night, however, because of its reaction with ozone and the elimination of its primary source within the polluted layer aloft, the photolysis of NO_2.

By morning, the polluted air layer may have traveled as far as 300 to 500 km downwind of the urban area where it was formed. Along the way, it is isolated from fresh emissions, except perhaps for emissions from an elevated point source, such as a power plant plume, which might be capable of penetrating the inversion base. After sunrise, however, NO_2 begins to photolyze, thereby leading to the series of chain reactions involving ozone formation, ozone scavenging by NO, and subsequent photolysis of additional NO_2. In addition, the remaining hydrocarbons and aldehydes participate in the ensuing photochemical reactions. Aldehydes remaining from the previous day's photochemical activity have special significance in the morning because their photolysis leads to radical formation after the sun rises.

Generally speaking, an increase in ozone concentrations would be observed in the polluted air layer. However, the amount of increase depends on the amount of NO_x and the HC/NO_x ratio remaining as the sun rises. This ratio governs the amount of ozone formed only if sufficient NO_x is present to photolyze at a significant rate. A typical value of NO_x, which is barely significant, is about 2 to 3 ppb.

Now, suppose that the elevated air mass reaches a mountainous region with dense spruce, fir, and pine forests. During the growing season, especially around midday, natural hydrocarbon emissions can be expected from the forest. Although the types of hydrocarbons and the amounts in which they are emitted by foliage are not well understood at present, it has been estimated that in some instances hydrocarbon concentrations from natural emissions can be high as 0.6 ppmC [78]. If convective mixing due to thermal heating of the mountain slopes is sufficient to erode the base of the elevated temperature inversion, then natural hydrocarbon emissions will be mixed upward and pollutants in the aged air mass will be brought down. The result of this exchange can be quite important. In particular, if sufficient NO_2 and aldehydes exist in the polluted layer aloft in the morning, photolysis of these species will provide radicals that can initiate photochemical chain reactions. If the fresh supply of hydrocarbons is mixed with the initiating radicals, a series of reactions may occur in which many radicals are formed. Ultimately, ozone generation could occur, and damage to vegetation in the mountainous area might result.

Concurrent with the possible formation of oxidants in this example is the removal of pollutants by scavenging, surface uptake, and other mechanisms. The extent to which oxidant concentrations change depends on whether removal processes or formation processes are dominant. Thus, the fate of air pollutants on the synoptic scale depends on nearly all of the physical and chemical atmospheric processes identified in the previous chapter.

D. SUMMARY

This chapter discusses the relative importance of several physical and chemical phenomena with respect to three transportation environments--the microscale, mesoscale, and macroscale (synoptic). Within each environment, processes that are influential in the link between pollutant emissions and ambient air quality are identified. Although it is impossible to rank all of the phenomena in order of their importance to concentrations in each of the three environments, certain processes can be said to strongly influence the relationship between emissions and air quality at each scale.

In the vicinity of a roadway (microscale environment) over temporal scales of a few tens of minutes, the following processes are important:

> Rapid mixing of emissions and ambient pollutants due to atmospheric turbulence generated by traffic and by airflow across the highway and appurtenant structures.
> Rapid chemical reactions involving ozone and NO.
> Deposition of heavy particulate matter, such as lead, immediately downwind of the roadway.

Over the course of a day in the urban (mesoscale) environment, the following processes are particularly important:

> Horizontal advection and vertical diffusion of pollutants throughout the urban environment.
> Limitation of the volume available for dilution of pollutants by a capping temperature inversion.
> Diurnal variation in the amount of sunlight available for initiation and maintenance of photochemical reactions.
> Large spatial variability in the composition of pollutants emitted from various urban emissions sources.
> Pollutant removal due to chemical conversion to secondary pollutants, precipitation scavenging, and surface uptake.
> Chemical reactions leading to the formation of photochemical oxidants and particulate sulfate.

On the synoptic scale (macroscale environment), the dominant atmospheric processes include:

> Long range advective transport of polluted air masses.
> Chemical interactions between the pollutants in aged air masses and fresh emissions.
> Removal processes involving precipitation scavenging and surface uptake.

For transportation planning and engineering, the most important pollutant at the microscale is generally CO; at the mesoscale, oxides of nitrogen, hydrocarbons, and oxidants; and at the synoptic scale, oxidants. Although SO_x and particulates do present problems at various scales, the contribution of motor vehicles to these problems is minor.

Clearly, the dominant physical and chemical processes and the pollutants likely to be of greatest interest differ from one transportation environment to another. One consequence of this dependence upon temporal and spatial scales is that air quality models and other techniques used to relate emissions to air quality are generally developed for a specific environment. Thus, one might speak of a microscale model, a mesoscale model, or a macroscale model. Each of these generic types of models represents the physical and chemical processes of greatest importance at the particular scale of interest. The next chapter addresses in detail how the atmospheric processes and interactions discussed in this chapter are represented in various types of air quality models.

IX AN ASSESSMENT OF AIR QUALITY MODELS

Chapters VII and VIII discussed physical and chemical processes that are known to influence air quality. Because of the complexities of those processes and their interactions, predicting the pollutant concentrations that will result from the emissions of an array of sources is difficult. However, the need for quantitative relationships between emissions and air quality has been evident for some time, and considerable effort has been devoted to the development of suitable air quality prediction techniques or air quality models. The purpose of this chapter is two-fold: first, to identify techniques possibly of value to transportation planners and engineers, and second, to assess the merits of various techniques.

This chapter focuses on concepts for air quality modeling rather than on particular air quality models. This treatment permits examination of the strengths and weaknesses inherent in each concept without describing individual air quality models, of which there are many. (The Appendix lists a number of air quality models and references in which they are described.) Examples of each modeling concept are presented, however. Considerable attention is given to the adequacy of a particular modeling concept for treating the physical and chemical processes discussed in Chapters VII and VIII. Clearly, a poor representation of an important process will limit the utility of a particular modeling concept. Of course, omission or less than adequate treatment of processes of secondary importance may not markedly affect overall utility.

A. TYPES OF AIR QUALITY MODELS

Air quality models can be segmented into two main groups--physical models and mathematical models--as shown in Figure 58. Mathematical models

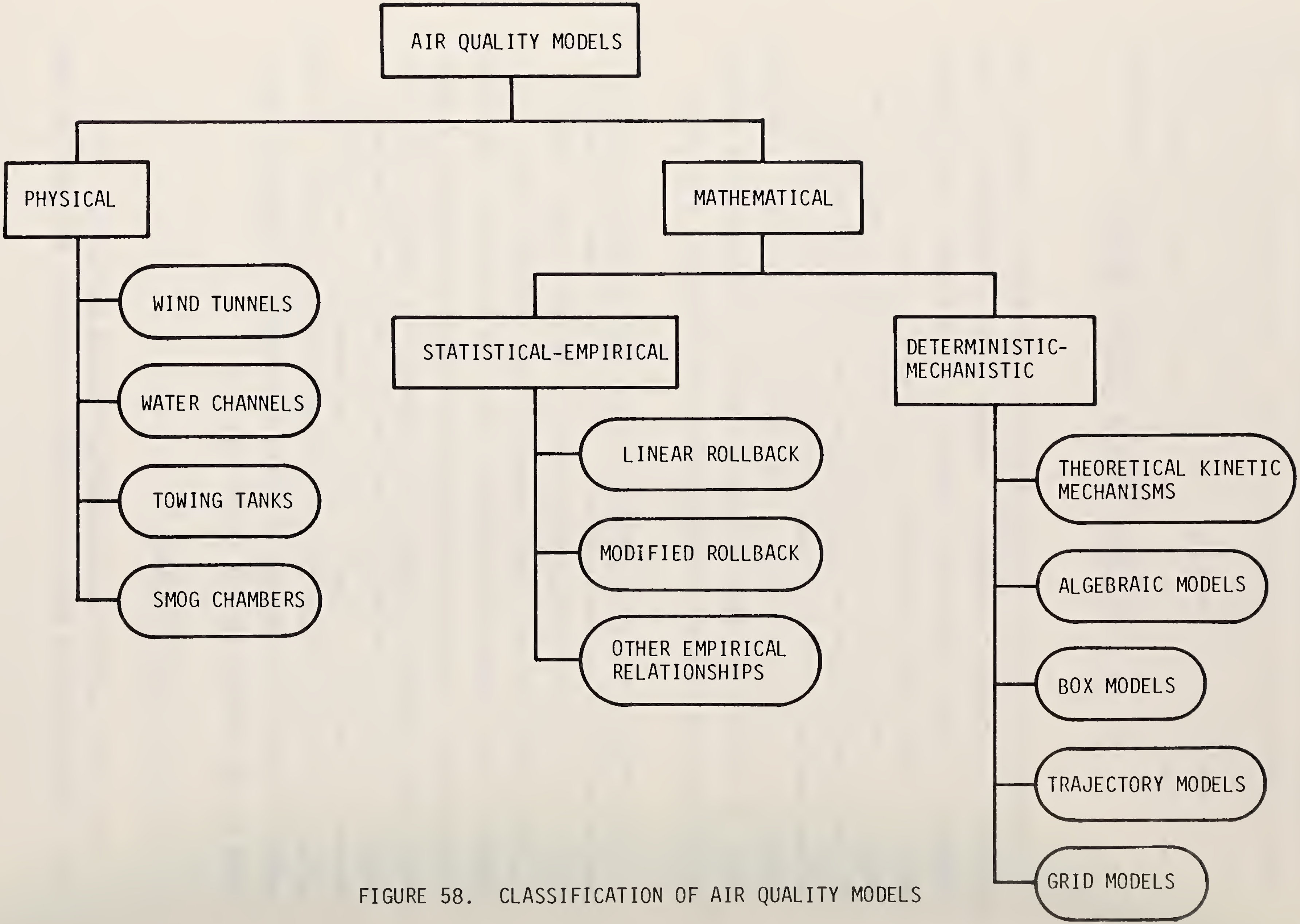


FIGURE 58. CLASSIFICATION OF AIR QUALITY MODELS

generally consist of a number of equations describing some physical and chemical atmospheric processes; the solution of these equations provides a relationship between emissions and air quality. In contrast, physical models are laboratory-scale apparatuses capable of reproducing, to some extent, various processes that actually take place in the atmosphere. Physical models are discussed only briefly in Section IX.F because of their limited utility to transportation planners.

Mathematical models can be classified as either statistical-empirical or deterministic-mechanistic [109]. Each of these categories encompasses several modeling concepts, as shown in Figure 58. Models in the former category are generally based on a statistical analysis of historical air quality data and some simplifying physical or chemical assumptions. Development of these types of models has been hindered by the lack of suitable data bases. Routine air monitoring networks are now operating in most areas, however, and in the future they should provide the inputs required by these models. Deterministic-mechanistic models attempt to describe mathematically the physical and chemical processes that occur in the atmosphere. As a result, they are often referred to as physicochemical models. The complexity of a physicochemical model is generally related to its degree of sophistication in the treatment of relevant atmospheric processes. The following sections highlight the features of the modeling concepts within two categories as shown in Figure 58.

B. STATISTICAL-EMPIRICAL MODELS

1. Linear Rollback

The linear rollback concept is the simplest relationship between emissions and air quality. This concept is based on the premise that pollutant concentrations above background levels are directly proportional to emissions. That is, a reduction in emissions rates at some time in the future will lead to a proportional reduction in the magnitude of peak air pollutant concentrations. Theoretically, linear rollback is valid only if:

> The pollutant of interest is inert (often assumed for CO) or undergoes first order chemical reaction (often assumed for SO_2).
> Emissions from all sources are increased or decreased uniformly with no alteration to the relative spatial or temporal distribution of emissions.
> Meteorological conditions and background concentrations remain constant.

In some cases, linear rollback may be useful when emissions from all mobile and stationary sources are expected to change by the same percentage.

One important limitation of this concept is that emissions must be altered uniformly. Thus, one should avoid applying linear rollback if the spatial distribution of emissions will change, such as may occur from transportation projects. Efforts to overcome this limitation have been reported [110], but the methodology becomes much more complicated and one must be able to assess the effects of all upwind sources on air quality at the point of interest. Also, the use of rollback is severely restricted if only selected sources are to be controlled. In this case, one of the following conditions must be met for rollback to be valid:

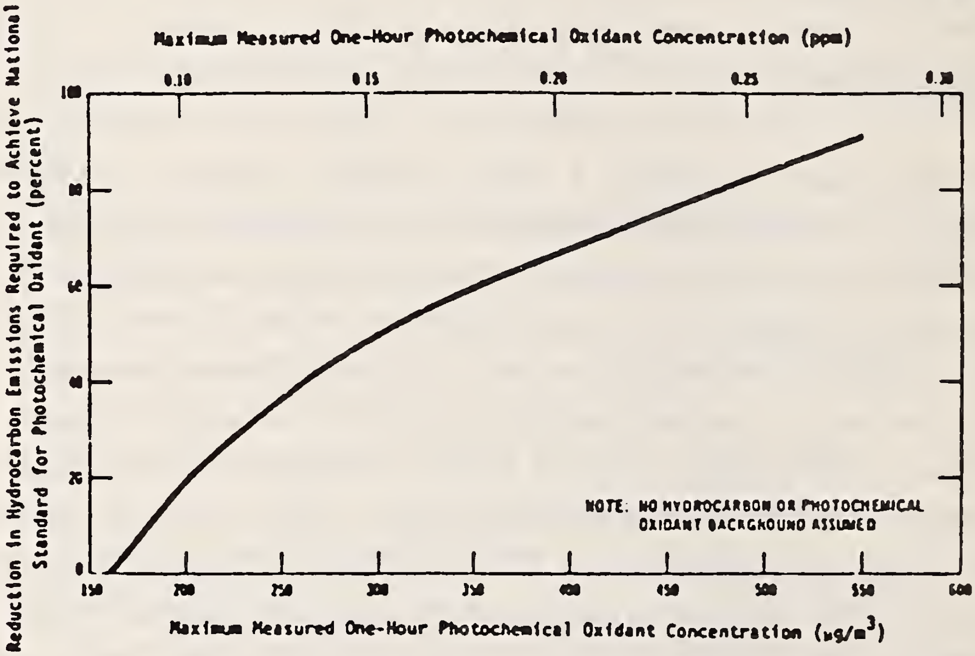
> The type of source controlled must be by far the greatest, so that other sources can be ignored.
> The type of source controlled must have the same temporal, spatial, and vertical distribution of emissions as the average of all other sources.
> There must be complete mixing within a fixed finite volume of air (the size of the urban area), with no exchange with surrounding areas. For treating ozone, this mixing must occur on a time scale that is short compared with the time of formation of peak ozone levels. The "formation half-life" of ozone in urban areas is typically less than two hours.

Another issue is the suitability of linear rollback for reactive pollutants. In the past, attempts were made to relate oxidant (or ozone) concentrations to hydrocarbon emissions using linear rollback. However, it is well known that the oxidant-precursor relationship is not linear and is dependent on the ambient concentrations of NO_x as well as hydrocarbons. Similarly, NO_2 concentrations are a function of not only NO_x emissions but also hydrocarbon emissions. Because NO_x emissions consist primarily of NO, NO_2 is essentially a result of the oxidation of NO. In addition, in smog chamber experiments the sum of the NO and NO_2 concentrations after several hours of irradiation is usually significantly less than the initial NO_x concentration, indicating that other nitrogenous products are formed in smog chambers. It can be argued that a reduction in NO_x emissions would tend to reduce the amount of NO that can be oxidized to NO_2, but the relationship between NO_x emissions and NO_2 concentrations is nevertheless nonlinear and will be influenced by meteorological as well as chemical factors. In summary, transportation planners should probably not use the linear rollback concept for reactive pollutants such as O_3 and NO_2.

2. Modified Rollback

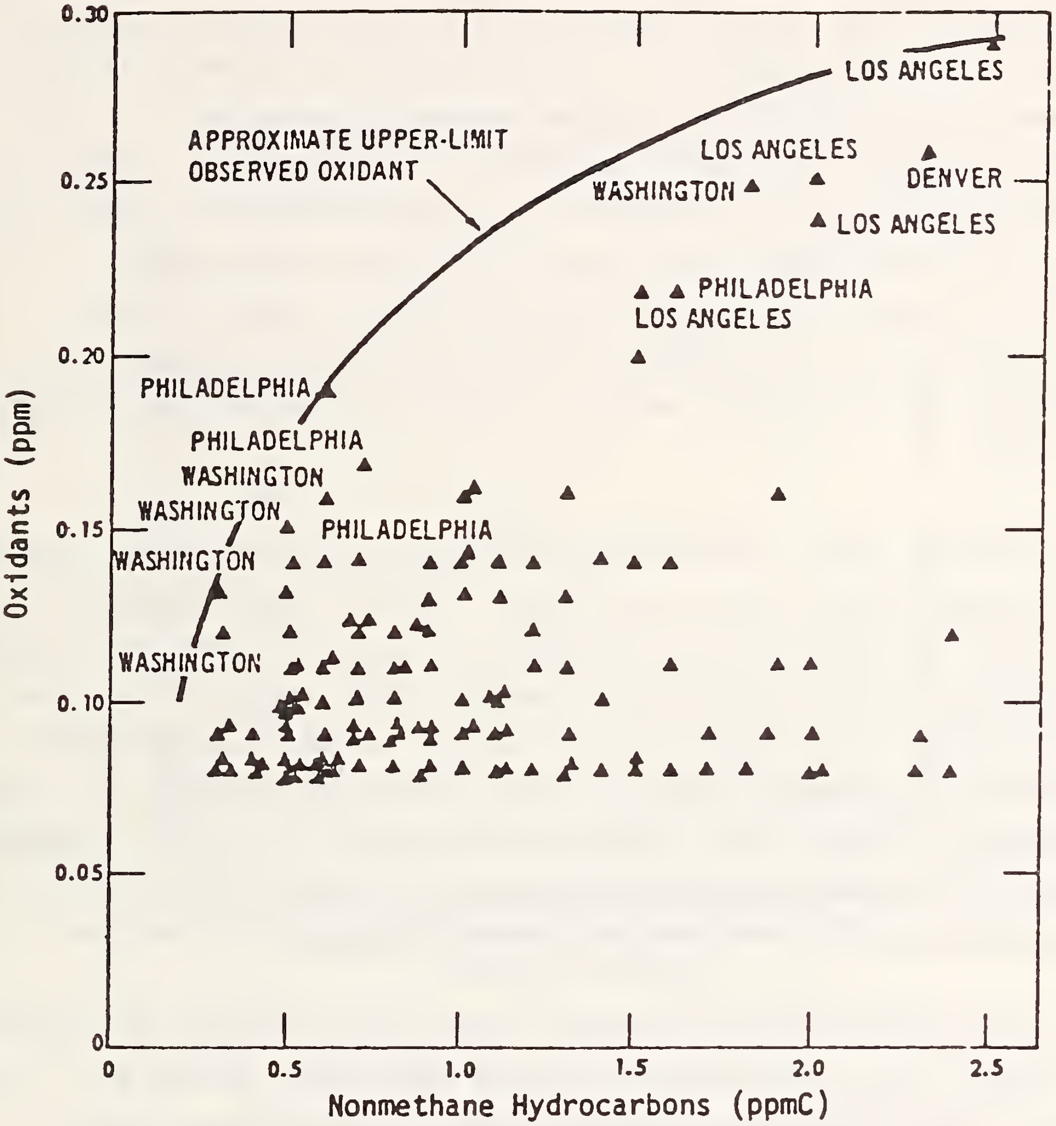
Recognizing the limitations of linear rollback, several investigators have attempted to develop modifications of it for characterizing the nonlinear oxidant-precursor relationship. The key element of modified rollback is the attempt to relate observed concentrations of precursors (hydrocarbons and/or NO_x) to the resulting oxidant concentrations through the use of statistical analyses of ambient monitoring data or, in some instances, smog chamber data. It is assumed that the ambient concentrations of precursors are proportional to the corresponding emissions. Thus, given an estimate of present precursor concentrations and an estimate of present and future precursor emissions, one can estimate future precursor concentrations. In most modified rollback techniques it is then a simple matter to read the resulting predicted oxidant concentration from a graph.

Perhaps the most well-known modified rollback method is the so-called Appendix J relationship. As shown in Figure 59 this relationship is essentially a plot of the percentage reduction in hydrocarbon emissions required to attain the national oxidant standard in a given area as a function of the maximum one-hour-average oxidant concentration observed in that area. The relationship was developed from daily measurements in four cities (Washington, Philadelphia, Denver, and Los Angeles) of 6 to 9 a.m. average nonmethane hydrocarbon concentrations and the subsequent maximum one-hour-average oxidant concentrations, which are illustrated in Figure 60. In the analysis of the data, an upper limit curve shown in Figure 60 was drawn such that, for any measured 6 to 9 a.m. hydrocarbon concentration, all of the observed oxidant concentrations were below that curve. Given the upper limit curve, the percentage reduction in hydrocarbon concentration needed to ensure compliance with the national oxidant standard (0.08 ppm) is calculated as a function of the maximum oxidant concentration. This reduction in hydrocarbon concentration is assumed to equal the required percentage change in hydrocarbon emissions, as shown in Figure 59.



Source: Ref. 38.

FIGURE 59. THE APPENDIX J RELATIONSHIP



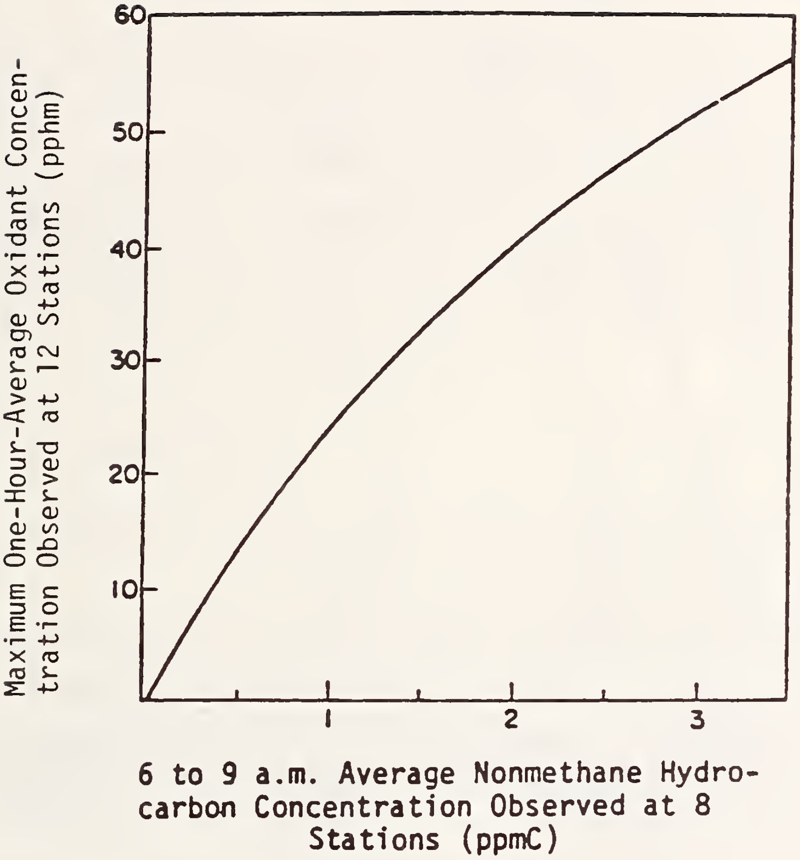
Source: Ref. 111.

FIGURE 60. MAXIMUM DAILY ONE-HOUR-AVERAGE OXIDANT CONCENTRATION AS A FUNCTION OF 6 TO 9 A.M. AVERAGE NONMETHANE HYDROCARBON CONCENTRATION. Data from Continuous Air Monitoring Program stations in Washington, Philadelphia, and Denver, June through September, 1966 through 1968; Los Angeles, May through October, 1967.

An important criticism of the Appendix J relationship is that the hydrocarbon and corresponding oxidant concentrations used to derive it were measured at the same site. From the discussion in the previous two chapters, it is clear that emissions of precursors at one location are generally not responsible for the oxidant concentrations at that location except when air stagnation conditions persist. This shortcoming was addressed in developing an upper limit curve for the Los Angeles basin by using the 6 to 9 a.m. average nonmethane hydrocarbon concentration (as measured at eight stations) and the highest one-hour-average oxidant concentration at any site in the basin [112]. This upper limit curve is illustrated in Figure 61. Analysis of upper limit curves derived for various cities confirms the variability of the oxidant-precursor relationship from one city to another due to the differences in emission patterns and meteorological conditions.

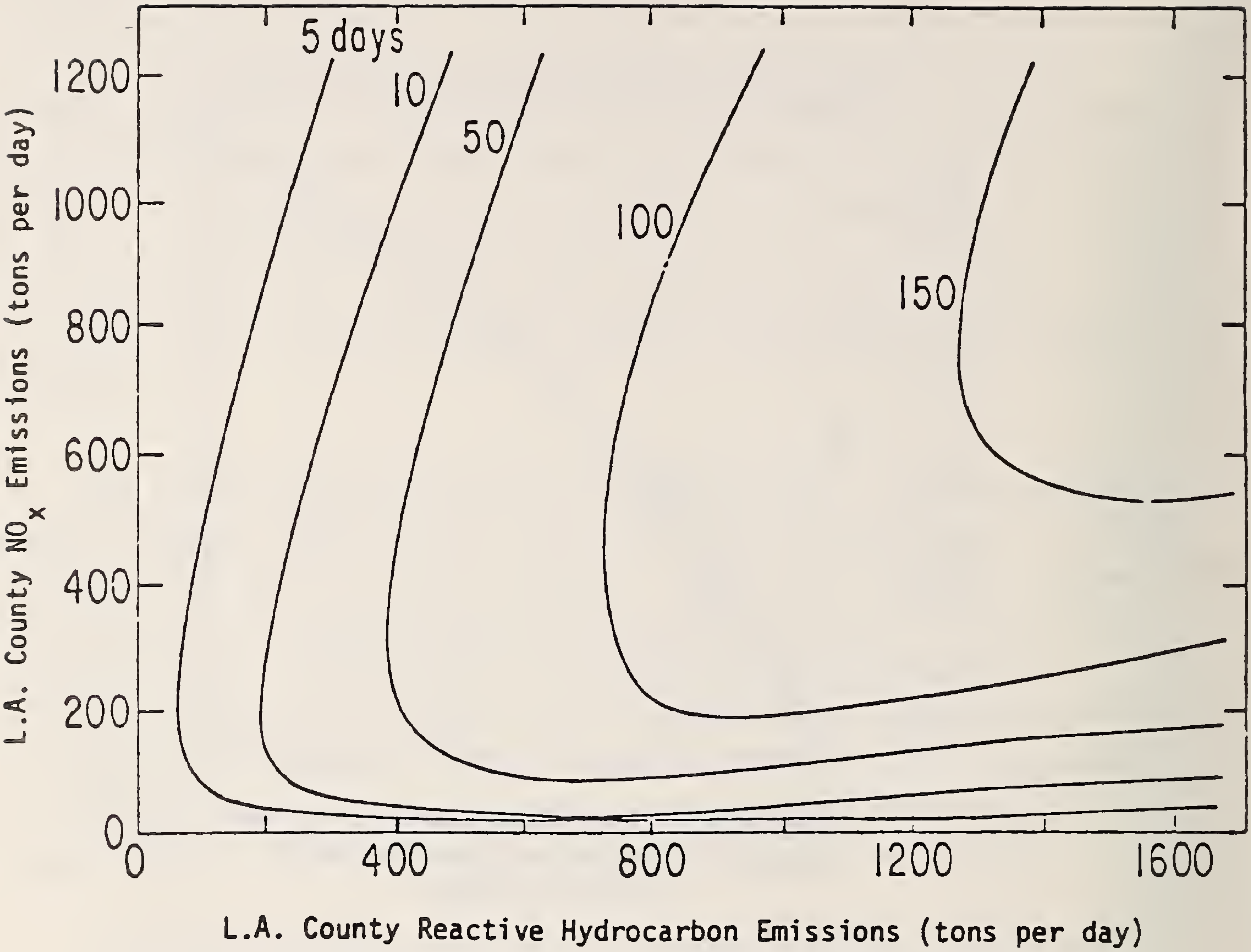
Note that linear rollback and the modified rollback methods discussed above completely ignore the role of NO_x. Its role was considered in a study that used five years of monitoring data for calculating the joint frequency distribution of morning hydrocarbon and NO_x concentrations in downtown Los Angeles [113]. By examining the corresponding oxidant concentrations downwind of the downtown station, it was possible to calculate the probability of exceeding the California state oxidant standard (0.10 ppm). Assuming a linear relationship between ambient precursor concentrations and precursor emissions, the rollback plot shown in Figure 62 was derived.

The modified rollback techniques cited above illustrate the variety of analyses that can be carried out using ambient air quality data. In general, these relationships were developed for reactive pollutants--namely oxidant and NO_2--and are purportedly applicable to urban-scale air quality problems. No studies have been reported wherein these techniques have been applied to either microscale or macroscale problems. Although they are relatively easy to use once they have been developed, they are all subject to the following limitations:



Source: Ref. 112.

FIGURE 61. UPPER LIMIT OXIDANT CURVE DERIVED FROM MONITORING DATA TAKEN IN THE SOUTH COAST AIR BASIN



Source: Ref. 113.

FIGURE 62. EXPECTED NUMBER OF DAYS PER YEAR WITH 0.10 PPM OR HIGHER OXIDANT CONCENTRATIONS IN CENTRAL LOS ANGELES AS A FUNCTION OF NO_x AND REACTIVE HYDROCARBON EMISSIONS

> They do not account for the effects of spatial or temporal changes in emissions.
> They do not explicitly consider meteorological factors.
> They do not account for the effects of background pollutant concentrations.
> They do not reflect the influence of changes in hydrocarbon reactivity on oxidant production.

In general, the modified rollback techniques discussed above are the result of attempts to derive simple statistical relationships between precursor concentrations and reactive pollutant concentrations. It is not clear that such statistical relationships can adequately describe the complicated interactions of the physical and chemical processes known to take place in the atmosphere. Accordingly, these methods are likely to be of only very limited value to the transportation planner.

3. Other Empirical Relationships

As mentioned previously, statistical air quality models have received little attention as a result of the paucity of historical air quality data. However, routine air monitoring in the Southern California area (mainly Los Angeles) has yielded a data base extending back over 15 years. The length of the historical record coupled with the large number of monitoring sites has motivated several investigators to initiate developmental efforts leading to the formulation of statistically based air quality models.

As an example of one empirical modeling approach, the terms of the conservation of mass equation were used to suggest statistical predictors for the concentrations of NO, NO_2, O_3, and CO [114]. In effect, conservation equations were written for each species consisting of linear sums of terms reflecting the influence of emissions, advection, vertical diffusion, and chemistry. In particular:

> Emissions of CO and NO were assumed to be proportional to the mean traffic density in area of interest.

> Advective transport was assumed to be proportional to wind speed.

> Vertical diffusion was linearly related to the depth of the mixed layer raised to a power.

> Chemical production (or decay) rates of NO, NO_2, and O_3 were derived from a three-step "lumped parameter" reaction set, which reflects the influence of hydrocarbon concentration and solar radiation. CO was assumed to be inert.

The coefficients of the emissions, advection, and vertical diffusion terms were determined statistically from available observational data. Solution of the governing equations resulted in predicted one-hour-average concentrations for the four pollutants. The strength of this model is that an attempt has been made to parameterize important elements of the physical and chemical processes. However, the model lacks spatial resolution, and thus, is most applicable to isolated regions in which emissions do not vary spatially.

C. DETERMINISTIC-MECHANISTIC MODELS

A large number of the air quality models currently available can be categorized as deterministic-mechanistic. The term deterministic applies because these models predict a specific outcome (in this case, air pollutant concentrations) given certain model inputs. In contrast, some statistical models provide predictions expressed in terms of probabilities of occurrence. The term mechanistic applies because many of these models contain a system of equations representing various chemical reactions which, in the aggregate, is known as a kinetic mechanism.

Within the deterministic-mechanistic category, models may be regarded as either kinetic mechanisms or physicochemical models. The former are based upon sets of mathematical equations representing the chemical reactions that take place in a volume of air such as a smog chamber.

Physicochemical models are generally more complex. They involve (to varying degrees of thoroughness) descriptions of many of the physical and chemical atmospheric processes discussed in Chapters VII and VIII. Kinetic mechanisms are often tested and refined with laboratory smog chamber data and then modified for inclusion in a physicochemical model.

The fundamental basis of all physicochemical model concepts is the atmospheric diffusion (or species continuity) equation. As discussed in Chapter VII, several important physical and chemical processes affect pollutant concentrations, including:

- Wind transport
- Turbulent diffusion
- Removal process (to surfaces or the stratosphere)
- Chemical reactions
- Emissions.

The species continuity equation is essentially a mass balance in which each of the above processes is represented in mathematical terms. Central to the derivation of this equation is the notion that the concentration of a given pollutant within an arbitrary volume in the atmosphere depends on competing processes, as shown in Figure 26. Different processes are important in different situations. In the case of carbon monoxide, for example, transport and diffusion are more important than chemical reactions. In contrast, ozone concentrations depend as much on chemical as on meteorological processes. As shown below, one of the distinguishing features of any physicochemical air quality model is the extent to which each atmospheric process is accounted for in its formulation.

Physicochemical models can be classified as either Eulerian or Lagrangian, depending upon the coordinate system used. The Eulerian model concept involves a coordinate system fixed with respect to the earth within and through which pollutants are emitted, carried and diffused by the wind, react, and are eventually removed from the atmosphere. The Lagrangian concept employs a different frame of reference--one that moves with a parcel of air. Despite the different frames of reference, both model concepts account, at least in principle, for the same physical and chemical processes. Eulerian model concepts include the algebraic, box, and grid models. Trajectory air quality models embody the Lagrangian concept.

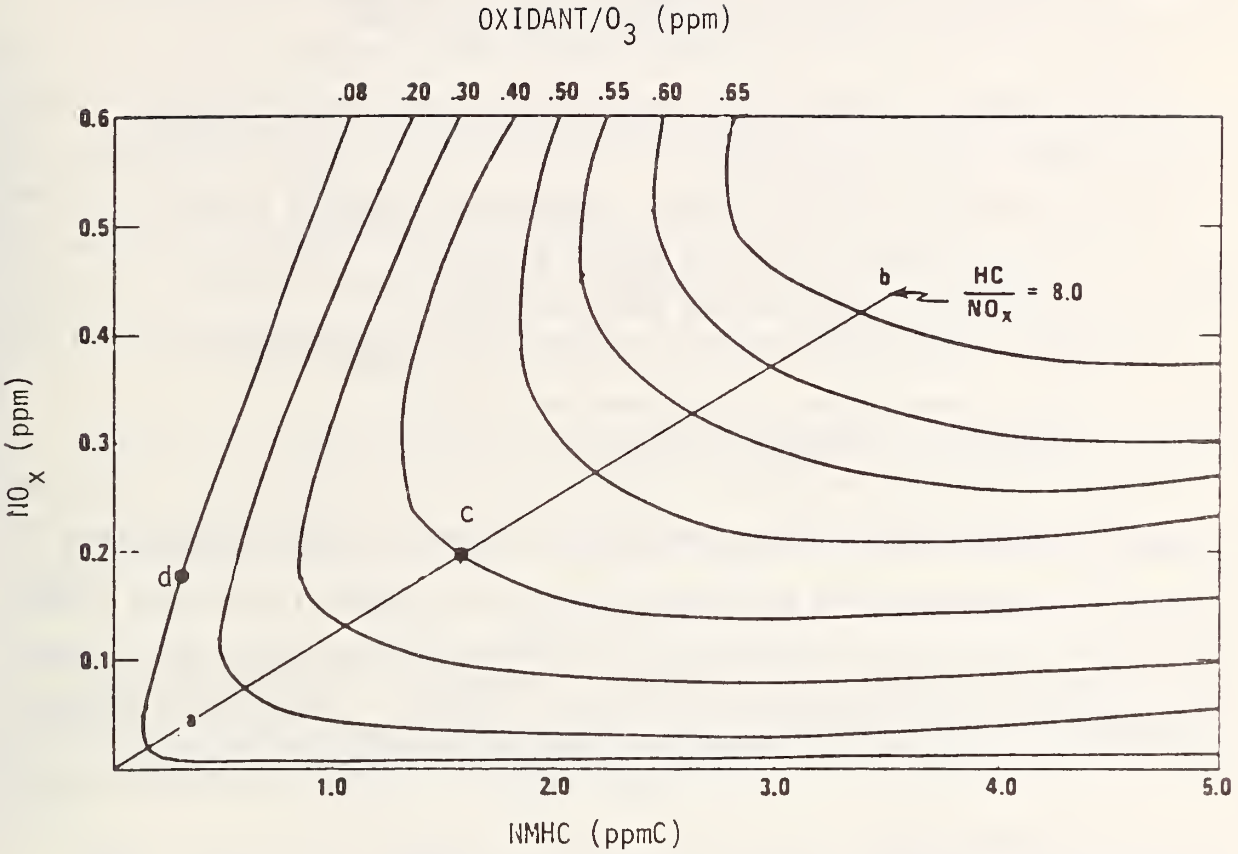
Kinetic mechanisms and physicochemical models are discussed in the following subsections in order of (generally) increasing level of detail in the treatment of atmospheric processes.

1. Kinetic Mechanisms

a. Model Concept

Among the main drawbacks of the modified rollback techniques discussed earlier is that, being inherently stochastic in nature, they provide predictions of limited utility. For instance, their predictions cannot account for temporal variations in emissions or changes in meteorology. To surmount these limitations, a model concept has been developed based on the cause-effect relationship in smog chamber experiments between oxidant (O_3) and its precursors [115,116,117]. One model embodying this concept is commonly referred to as EKMA (Empirical Kinetic Modeling Approach).

EKMA was developed as follows. First, an explicit chemical kinetic mechanism for propylene, butane, and NO_x was developed to simulate the reactions taking place in a smog chamber containing automotive exhaust and nitrogen oxides. The mechanism was then used with a variety of initial hydrocarbon (propylene and butane) and NO_x concentrations to predict the maximum ozone concentrations that would form during a hypothetical 0800-1800 time period. The results of many simulations were used to construct isopleth diagrams similar to that shown in Figure 63.



Source: Adapted from Ref. 118.

FIGURE 63. OXIDANT/O_3 ISOPLETH DIAGRAM OF THE TYPE USED IN THE EMPIRICAL KINETIC MODELING APPROACH (EKMA)

b. Operational Features

To date, development of the EKMA model concept has resulted in both generalized and site-specific approaches. In the generalized approach, an ozone isopleth is generated based on the following:

- A constant dilution rate of 3 percent per hour (to account for arising inversion).
- A diurnal variation of solar radiation equivalent to that at Los Angeles during the summer solstice.
- No emissions added during the simulation.
- Initial hydrocarbon and NO_x concentrations based upon 6 to 9 a.m. measurements at the area of interest.
- Simulation from 0800 to 1800.

However, because dilution rates, emissions, sunlight, the reactivity of hydrocarbon emissions and the entrainment of pollutants from layers aloft vary from city to city, one form of the EKMA method was developed to generate site-specific (and day-specific) ozone isopleths. This method accepts the following features to characterize the area and day of interest:

- Dilution rate.
- Emissions rates.
- Radiation level appropriate for the geographical location and time of year.
- Reactivity of the hydrocarbon mixture.
- Entrainment of pollutants from layers aloft as the inversion rises.

In short, the site-specific EKMA method permits the user to select the set of conditions most representative of the area under study and then develop the corresponding isopleth diagram.

A number of schemes have been suggested for relating isopleth diagrams to the real atmosphere. In the procedure shown in Figure 63, one first draws a ray through the origin of the chart (say, line a-b) corresponding to the current hydrocarbon/NO_x ratio (in the example, HC/NO_x = 8 ppmC/ppm). (The hydrocarbon/NO_x ratio may be calculated from 6 to 9 a.m. ambient air quality measurements or from appropriate emissions estimates.) One then finds the point on the ray corresponding to the current maximum one-hour-average oxidant concentration (point c in the figure, at O_3 = 0.40 ppm.) A point on the isopleth corresponding to the desired oxidant concentration is then selected (point d on the 0.08 ppm isopleth). Due consideration must be given to the NO_x reductions (if any) required to satisfy the NO_x air quality standards. The percentage changes in hydrocarbon and NO_x concentrations are calculated from the coordinates of points c and d. These percentage changes in concentrations are assumed to be equal to the corresponding percentage changes in hydrocarbon and NO_x emissions.

Clearly, the EKMA approach generates a great deal of information about the role of precursors in forming oxidant. To determine the analogous information experimentally would require many costly smog chamber experiments.

The EKMA method is discussed in greater detail in several references [115-120]. The EPA gives procedures for the use of the method for both the generalized and site-specific approaches [115].

Very recently the EKMA model concept has been extended to the analysis of ambient NO_x concentrations [121]. Although preliminary, the results of this study suggest that the EKMA concept may be of value in defining NO_2-precursor relationships and in comparing predicted impacts with present or proposed NO_2 standards.

c. Limitations of the Model Concept

Several key aspects of the EKMA model concept inherently limit its range of application [119, 120]. First, and of particular relevance to transportation planning, is the EKMA method's lack of spatial or temporal resolution. This restricts the usefulness of the method in evaluating alternative emissions control strategies and in evaluating the subregional impacts of new emissions sources. Second, the method, as currently designed, requires that a new isopleth diagram be developed for each change in hydrocarbon reactivity due to emissions control measures. Thus, the effects of changes in hydrocarbon reactivity can be assessed, but with somewhat greater effort than that required for evaluating overall reductions in emissions. Finally, the suitability of EKMA for assessing the effectiveness of emissions control strategies is difficult to determine in advance. Because the approach is intended to be used for making relative rather than absolute predictions, the extent to which the method is appropriate for a given area cannot be judged by merely comparing ozone concentrations predicted by EKMA based on measured HC and NO_x concentrations with the corresponding measured ozone concentrations. Only after an emissions control strategy has been implemented and a sufficiently long period of time has elapsed can accuracy of the technique be determined.

d. Typical Applications

Notwithstanding the above limitations and others pointed out in the literature, the EKMA method can be helpful in certain situations. For example, a regional planning agency may find it useful in determining regional reductions in hydrocarbon and NO_x emissions applicable to all major sources in order to achieve region-wide compliance with air quality standards. If, however, the emission reductions specified are not fairly uniform over the region, spatial and temporal resolution in the air quality analysis becomes necessary, and the EKMA method is not suitable. Although the EPA does not presently proffer the EKMA method as a screening procedure, the method does appear to have potential for aiding in the determination of whether additional monitoring data are needed for an air quality analysis, whether more sophisticated modeling techniques are needed, or both [120].

2. Algebraic Models

a. Model Concept

This class of models is based upon a simplified form of the atmospheric diffusion equation. If meteorological and emissions processes (e.g., winds and dispersion rates) do not vary with time and the most important physical processes governing the fate of emitted pollutants are downwind transport, crosswind dispersion, and vertical dispersion, then the diffusion equation can be reduced to a form that can be solved algebraically. The most familiar formulation of this model concept is the Gaussian model, in which the distribution of pollutants at any cross section of a plume downwind of its source is assumed to be normal, or Gaussian. Largely because of the mathematical simplicity of the Gaussian probability distribution function, this model concept has been used extensively.

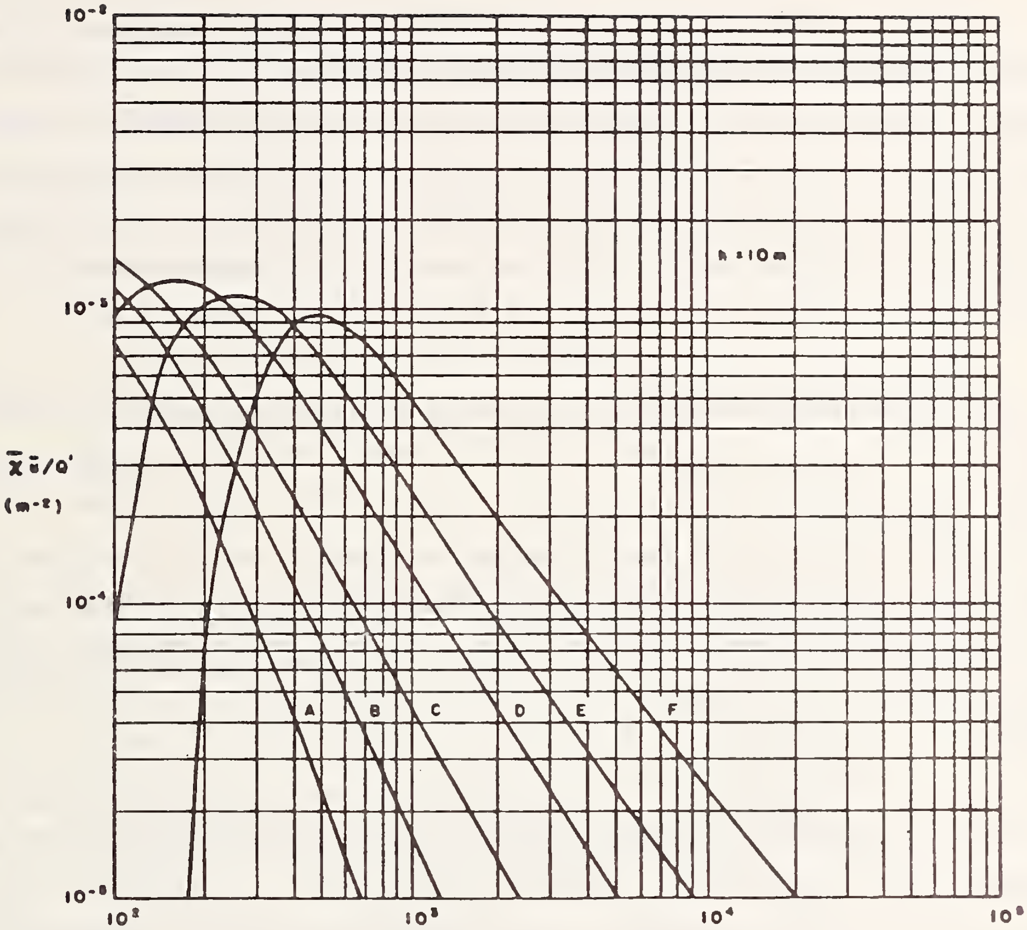
Other procedures for describing particle spread statistics, or diffusion rates, have also been used. Among these are K-theory, in which the rate of pollutant diffusion is assumed to be proportional to the spatial gradient in its concentration, and statistical theories, in which pollutant diffusion rates are empirically related to experimental results in which the motions of individual fluid particles are known. Due to its widespread usage, the Gaussian model is the only type of algebraic model discussed below.

b. Operational Features

Due to the simplicty of the Gaussian concept, it is possible to use Gaussian models without recourse to computers or extensive data bases. In fact, solutions can be obtained with pocket calculators or nomographs. For example, the nomograph in Figure 64 contains a series of curves corresponding to ground-level pollutant concentrations (normalized by the emissions rate and mean wind speed) as a function of distance downwind of the source. The curves labeled by capital letter correspond to the Pasquill atmospheric stability categories, which are determined on the basis of average wind speed, cloud cover, and qualitative estimates of solar radiation intensity. (See Chapter X for further details.) Thus, the data requirements needed to operate Gaussian models are minimal. (Data needs for verification purposes, however, are greater; they are discussed later in this section.)

Gaussian models were originally intended to be applied to short term averaging periods (say, 3 to 10 minutes) because most field measurements of pollutant concentrations used to derive Gaussian dispersion parameters were conducted for short term averages. However, the model is also applied to longer periods, frequently up to an hour or more. Even longer averaging times can be accommodated by running the model for one hour at a time for the desired interval. In this case, dispersion estimates are modified to account for longer periods by empirical relationships such as those presented in Ref. 122.

The basic Gaussian concept has been extended to include a number of dispersion situations, including emissions from a line source (highway) and ground-based area sources. Although the simplicity of the model concept remains in these varied applications, from an operational standpoint it is often desirable to solve the algebraic equation on a computer, thereby avoiding numerous, tedious calculations.



Source: Ref. 122.

FIGURE 64. NORMALIZED GROUND-LEVEL AVERAGE CONCENTRATION FOR AN EFFECTIVE SOURCE HEIGHT OF 10 M AS A FUNCTION OF DISTANCE FROM THE SOURCE. (A-F are atmospheric stability categories defined in Chapter X.)

c. Examples of Gaussian Models and Typical Applications

A number of computational algorithms (or computer codes) embodying the basic Gaussian model concept have been developed. These algorithms have been called Gaussian models in the literature even though, strictly speaking, they are merely different computational procedures for implementing the same basic Gaussian model [123]. Nevertheless, the various algorithms are called models in the following discussion in keeping with convention.

As indicated above, Gaussian models have been developed for a wide variety of air quality problems. For elevated single or multiple point sources, models such as Valley, CRSTER, PTMAX, PTDIS, PTMTP, NOAA, and Short Z are available from federal agencies, such as the EPA or NOAA, or from private organizations [123,124]. Models applicable to stationary area sources include RAM, TEM, CDM, AQDM, and TCM [125-127]. Gaussian models applicable to roadways are Caline 2, HIWAY, Airpol-4, and TRAPS [124, 128-130].

The above models and others founded on the Gaussian concept are used to predict short term average concentrations (say, 1 to 3 hours or 24 hours) as well as annual averages. The models are used to study pollutants that are either chemically inert or can be treated as linearly reactive, such as CO, SO_2, particulates, and heavy metals.

Owing to their algebraic form, these models are relatively inexpensive to use. Since only a pocket calculator or nomograph is used, only a short time is needed to obtain a solution. Solving more detailed Gaussian models that compute long term average pollutant concentrations from a number of sources may necessitate the use of a computer, but typically the computing costs of one model run are on the order of a few tens of dollars.

d. Limitations of Gaussian Models

The most frequently used air quality model is the Gaussian, probably because, being based on algebraic equations, it is easy to solve. The model requires relatively little data and has modest computing requirements. However, to develop models of such simplified character, many assumptions concerning the behavior of the atmosphere must be made. Some of these assumptions are common to all physicochemical models, but many are unique to simplified models. Some assumptions impose severe restrictions on the range of applicability of this model concept. Thus, while the Gaussian is attractive because of the simplicity in its formulation and use, it may provide poor representations of atmospheric processes in some circumstances.

The limitations of the Gaussian model have been discussed by a number of investigators [83,131,132]. Among the more important limitations of the model concept are the following:

- It represents a steady-state solution of the atmospheric diffusion equation; thus, it does not allow for the modeling of periods in which the wind changes frequently with time.
- It assumes a uniform windfield. Thus, it cannot take into account spatial variations in wind speed or direction at a given time. This is particularly a problem in situations involving irregular topography or complex meteorological regimes (e.g., land-sea breeze transitions, drainage flows, upslope winds).
- It includes dispersion parameters established empirically for meteorological regimes and terrain that do not necessarily resemble those common to the site of interest. Moreover, measurements of dispersion rates have been made primarily for from ground-level sources are likely to be quite different from dispersion rates aloft.

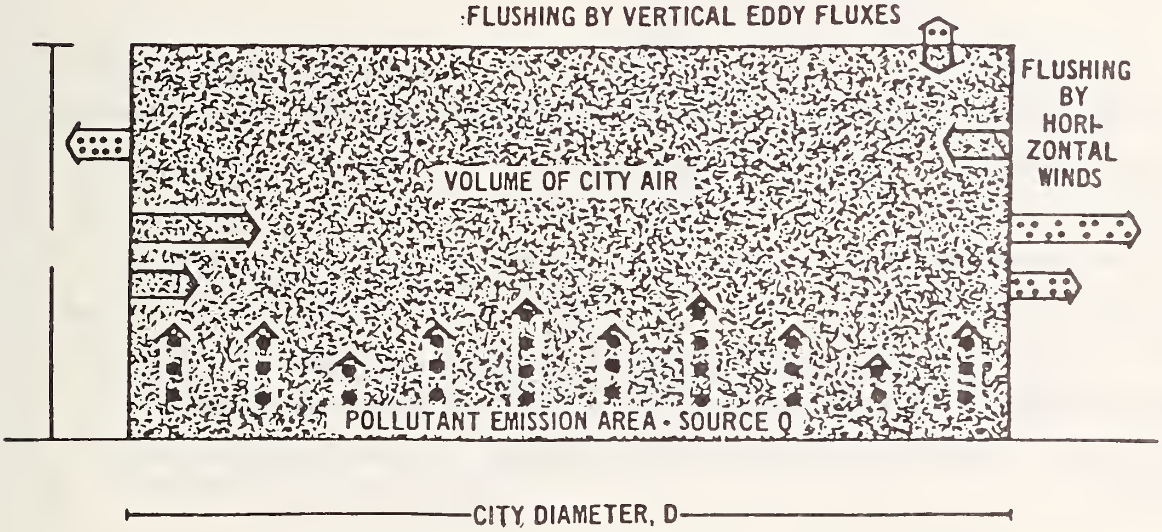
- It does not account for variations in atmospheric diffusion rates with height. Including the height-dependent dispersion rate is often important because turbulence is suppressed near the ground and may be suppressed in the vicinity of stable layers aloft.
- Dispersion parameters are based on gross stability categories, whereas the stability of the atmosphere varies spatially and temporally, sometimes at scales smaller than those characteristic of the steady-state assumption.
- Finally, the model is limited to the treatment of inert or linearly reactive pollutants. If an air quality analysis is concerned with primary pollutants such as CO, SO_2, or primary particulates, this restriction presents no problem; but the model concept is incapable of treating secondary pollutants such as oxidants, NO_2, and particulate sulfate.

In short, the Gaussian model concept represents a tradeoff between ease of application and potential degradation in model performance due to the approximations inherent in its formulation. In cases where emissions and meteorological conditions do not vary greatly, and dispersion rates can be based on measurements made at similar sites, the model may prove to be useful. It is a particularly good candidate for providing screening estimates of the magnitude of an air quality problem. However, if secondary pollutants, complex terrain, or complicated meteorological conditions prevail, the Gaussian model may prove to be inadequate. In such cases, models that accommodate temporal and spatial variations in meteorological fields and chemical reaction processes may be necessary.

3. Box Models

a. Model Concept

Fundamental to the box model concept is the assumption that pollutant concentrations in a volume of air, or "box," over an urban area are spatially homogeneous and instantaneously mixed. Under this assumption, pollutant concentrations can be described by a simple balance between the rates at which they are transported in and out of the air volume, their average rates of emission from sources within the volume, the rate at which the volume expands or contracts, the rates at which pollutants flow out the top of the volume, and the rates at which pollutants decay. In a sense, the box model concept is related to the grid model concept (discussed later) in that grid models are composed of a large array of small boxes. Figure 65 identifies the major features of the box model concept. Although the box model concept was originally developed to apply to inert pollutants, some attempts have been made to extend it to treat nonlinear photochemical reaction processes. This aspect of the model concept is discussed later.



Source: Adapted from Ref. 133.

FIGURE 65. SCHEMATIC ILLUSTRATION OF A BOX MODEL OF URBAN DIFFUSION

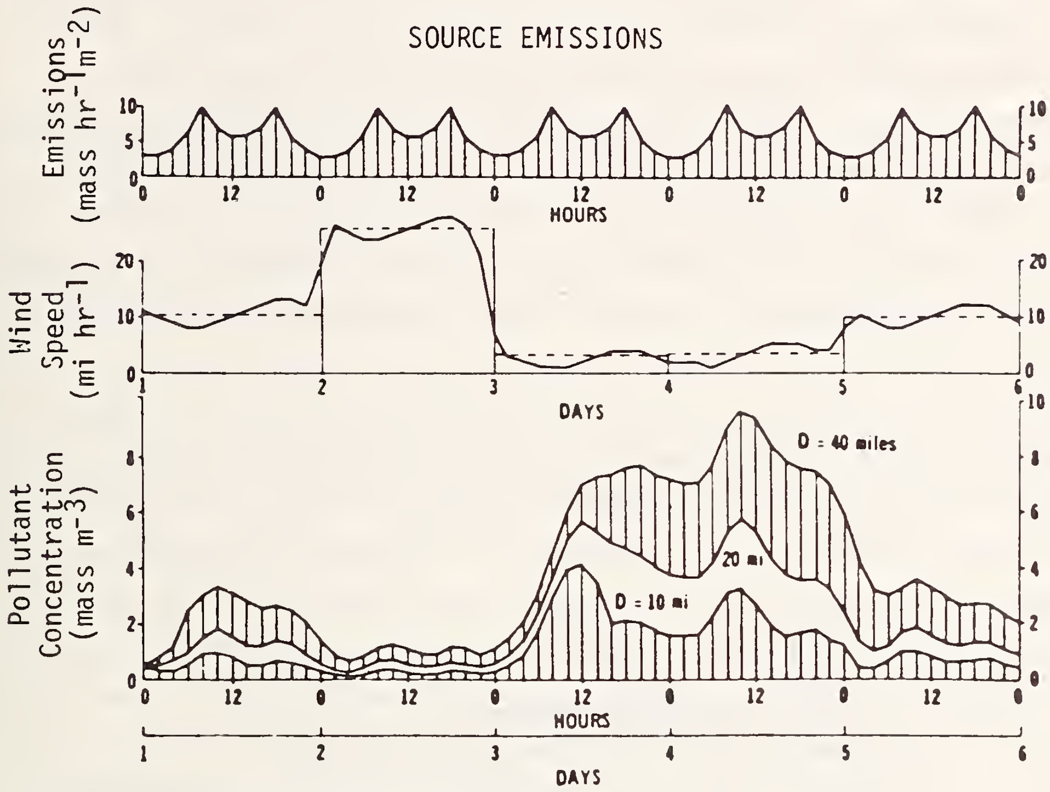
b. Operational Features

Although the theoretical basis for box models can be traced to the atmospheric diffusion equation, the assumptions inherent in its formulation lead to a very simple model equation. For chemically inert pollutants, the surface concentration is proportional to local emissions and inversely proportional to the bulk wind speed. The constant of proportionality is assumed to depend on atmospheric stability. Thus, given an average wind speed and emissions rates, a simple calculation yields an estimated average pollutant concentration. For reactive pollutants--including NO, NO_2, and O_3--the box model equations are nonlinear algebraic expressions solvable by hand or with a computer. Whether inert or reactive pollutants are being simulated, both the data needs and computational expense of box models are small.

The output of a box model is a single pollutant concentration, which is taken to be representative of the average concentration within the box for the interval of interest. This interval can range from one hour to one year. A series of short term box model calculations can be used to generate a temporal plot of pollutant concentrations. For example, Figure 66 shows concentrations of a primary pollutant predicted by a box model for the same wind speeds and emissions per unit area in cities of three diameters: 10, 20, and 40 miles. Pollutants are retained for a longer time within the larger cities, leading to higher average concentrations.

c. Examples of Box Models

Several models employing the box concept have been developed in recent years. Among the earliest were the models developed for use in simulating the fate of chemically inert pollutants in urban areas [133,134]. Later, attempts were made to include chemically reactive species, using a simplified set of nonlinear algebraic equations. Very recently, box models have been developed that include state-of-the-art photochemical kinetic mechanisms, continuous emissions, dilution, and varying solar radiation. Because they entail the solution of coupled nonlinear differential equations, models in the latter category must be solved on a computer.



Source: Adapted from Ref. 133.

FIGURE 66. CALCULATED TRENDS OF POLLUTANT CONCENTRATIONS IN RESPONSE TO INDICATED EMISSIONS AND WINDS.

d. Limitations of Box Models

Immediately apparent from the above discussion is the fact that box models lack spatial resolution. Thus, the model concept cannot be used in situations where the meteorological or emissions patterns vary significantly across the modeling region. This limitation is of greatest concern when the air quality problem at hand involves heterogeneous emissions and pollutant distributions or reactive pollutants.

The combined effects of local emissions patterns and meteorological conditions generally give rise to significant spatial variations in pollutant concentrations. Note, for example, that the volume of air within which the smog is trapped in Los Angeles has a horizontal dimension perhaps 200 times as large as its vertical dimension. As a result, pollutant concentrations are highly nonuniform in the long, shallow region [135]. Moreover, vehicular emissions are generally greater in the central business district than in outlying suburban areas. Major freeways and large stationary sources (e.g., power plants and refineries) also contribute to the spatial variation in emissions. Local meteorological conditions influence the dispersion of pollutants downwind of each source. Typically, pollutant concentrations at the upwind edge of an urban area are smaller than those at the downwind edge.

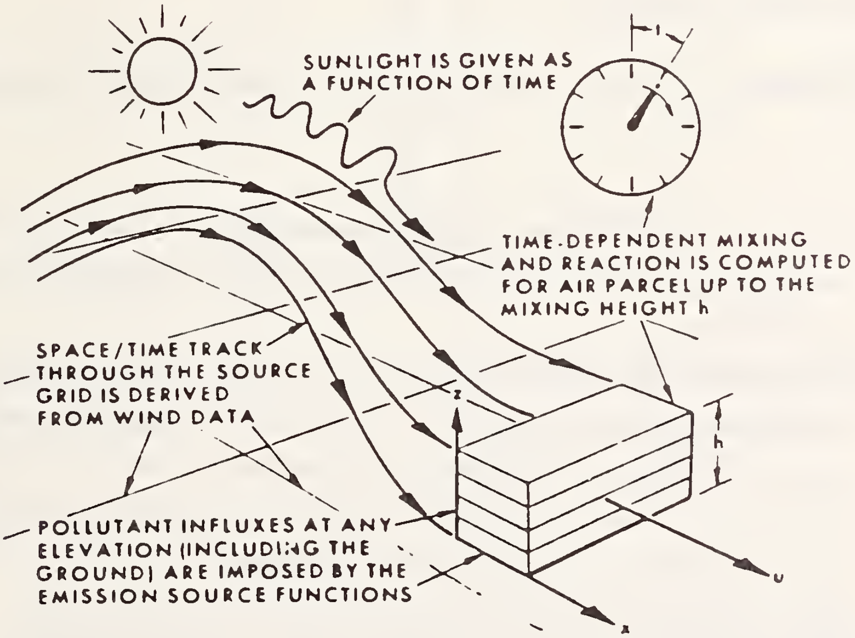
If pollutants are not uniformly distributed over the region to which the box model is applied, two sources of error are introduced into the predicted concentrations. First, the calculated mass of pollutants advected out of the region may be incorrect because the actual concentrations at the downwind edge of the region may, in reality, be different from the spatially averaged value used by the model. Second, calculated net reaction rates may be in error because spatially averaged concentrations are used in the rate expressions. If pollutants are not uniformly distributed over the region, then chemical reactions will proceed at different rates in different areas. Under such circumstances, net reaction rates cannot be determined correctly through the use of spatially averaged concentrations [136].

Clearly, box models cannot be used to assess the effectiveness of emissions control strategies that lead to spatially inhomogeneous emissions. Likewise, they cannot be used to predict the magnitude and location of the maximum ozone concentration in a given region. However, there is the possibility that photochemical box models, which treat continuous emissions, dilution, and other factors, can be used to obtain order of magnitude estimates of the pollutant burden in an urban area [137] and may also be useful in estimating long term air quality trends.

4. Trajectory Models

a. Model Concept

Like other physicochemical air quality models, trajectory models are based on the atmospheric diffusion equation, but they use what is sometimes called a moving-coordinate approach to describe pollutant transport. These models simulate a hypothetical column or parcel of air. From a specified starting point, the column moves under the influence of the local meteorological conditions. For example, if the wind speed is two miles per hour, then after one hour the column would have moved two miles from its original position in the direction in which the wind was blowing. Emissions are injected into the parcel and undergo vertical mixing. Concurrently, chemical reactions take place in the parcel. Figure 67 presents a schematic representation of the trajectory model concept.



Source: Ref. 138.

FIGURE 67. SCHEMATIC REPRESENTATION OF THE TRAJECTORY MODEL CONCEPT

Several basic assumptions must be invoked in formulating a trajectory model [139]:

> The horizontal diffusion of pollutants into the air parcel along its sides can be neglected.
> The parcel is advected by a mean wind velocity that is constant with height.
> The vertical component of the wind velocity can be neglected.
> The volume of the parcel is constant and is unaffected by horizontal convergence and divergence of the wind field.
> The average wind velocities obtained from measurements are representative of the winds that would affect the movement of the parcel.

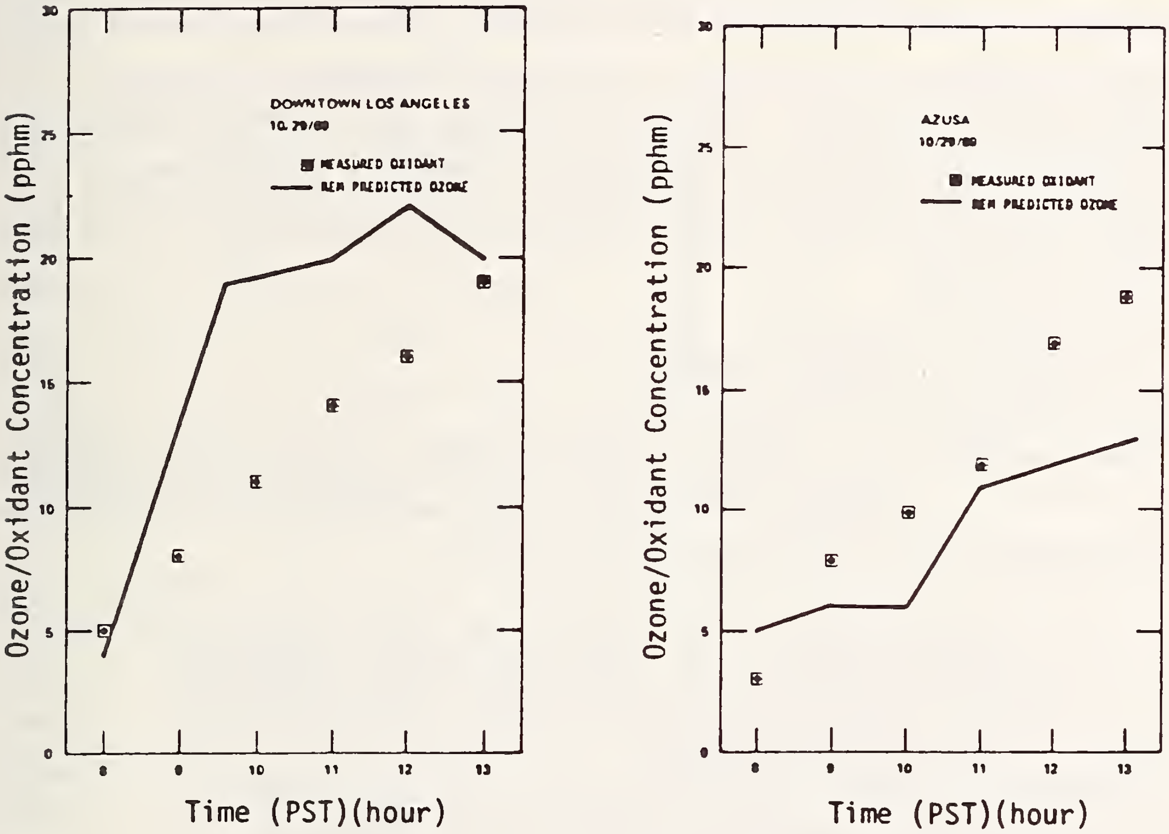
Each of these assumptions somewhat limits the validity of trajectory model predictions, depending on the characteristics of the particular problem being considered.

b. Operational Features

In general, trajectory models require the following types of input data:

> Emissions--The rates at which hydrocarbons, NO_x, and CO are emitted into the parcel from the various sources along the trajectory.
> Meteorological data--Wind speed and direction measurements to determine the movement of the parcel; vertical temperature soundings to determine the height of the air column.
> Ultraviolet radiation--Measurements to provide estimates of rate constants for photolysis reactions.

Although these data need be prepared only along the trajectory to be modeled, general application of a trajectory model to an urban area usually requires that emissions and meteorological data be assembled for a significant portion of the region. Because the trajectory model concept retains certain of the diffusion and reaction terms in the atmospheric diffusion equation, a computer must be used to operate the model. Examples of output from the REM trajectory model are given in Figure 68.



Source: Ref. 140.

FIGURE 68. COMPARISON OF REM OZONE PREDICTIONS AND ACTUAL OXIDANT OBSERVATIONS AT TWO STATIONS IN THE LOS ANGELES BASIN

c. Examples of Trajectory Models

Examples of trajectory models include DIFKIN [141] and REM [140], which are basically one-dimensional (streamwise) advective models. In REM, the parcel is completely mixed through its entire depth, whereas in DIFKIN, the vertical column of air is divided into a stack of cells that may exchange diffusive fluxes but that maintain their individual integrities as they are advected together. Both models consider only one trajectory at a time, so no horizontal pollutant diffusion can be computed (since concentrations outside the trajectory are not known). Furthermore, wind shear and vertical advection cannot be treated in either model. Both models compute trajectories from winds interpolated from observations taken at a limited number of stations, and both use complex sets of kinetic equations for the description of chemical reactions.

d. Limitations of Trajectory Models

Some assumptions that must be invoked to derive trajectory models were listed earlier. An extensive examination of the implications of these assumptions resulted in the following conclusions [142].

> For a parcel passing over line and area sources, neglect of horizontal diffusion would cause errors in the predictions of less than about 10 percent.

> Neglect of vertical winds can have a significant effect on predictions, depending on the amount of convergence and divergence in the wind field.

> Neglect of wind shear can have a substantial impact on predictions; errors on the order of 50 percent may be incurred.

Regions in which significant vertical wind motion has been observed include the San Fernando Valley [99] and St. Louis [143]. Significant variations of wind speed and direction with height have also been reported [144]. Clearly, a trajectory model could not be applied in areas of rough or complex terrain, where the winds usually have a significant vertical component and considerable variation in the horizontal components with height.

Although one study [142] indicated that horizontal diffusion can usually be neglected, in some instances it cannot. For example a trajectory that narrowly misses a large emissions source (e.g., a power plant or refinery) cannot account for the horizontal diffusion of pollutants that will, in reality, be transported into the air parcel. Under such circumstances errors in prediction of as much as 30 to 40 percent may result [141].

The method for determining the trajectory velocity presents another technical difficulty. Two different velocities, one spatially averaged and the other temporally averaged, can sometimes be obtained from the same data set [145]. Meteorological data usually consist of one-hour-average wind velocities obtained from a network of fixed stations. Trajectory models, however, require some estimate of a time-varying, spatially averaged wind velocity; so the values obtained from the measurement network are combined, ambiguously, to construct the required spatial averages. The extent to which they represent actual trajectory velocities is questionable.

As noted earlier, the convergence and divergence of the horizontal wind are phenomena commonly observed in urban areas. A trajectory parcel placed in such a field would soon be distorted. For example, during the Los Angeles Reactive Pollutant Program (LARPP) in Los Angeles [146], tetroons* released together were observed to move several kilometers apart within a few hours. Since in trajectory models it is assumed that the volume of the air parcel does not change as it is advected, serious errors in the concentration predictions can result from distortion of the parcel.

Since trajectory models follow a parcel of air along its trajectory, they compute the time history of concentrations within that parcel. The

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* A tetroon is a balloon used to study air currents above ground level.

location of the parcel on a grid map is not an independent variable; indeed, location is an output result. Consequently, it can be very difficult to compare trajectory model predictions with typical aerometric data, which are measured at fixed points. Trajectory model results are somewhat comparable in form to smog chamber results, though the experimental conditions in a smog chamber include unique chamber wall effects and cannot duplicate the complex variations in emissions and dilution that each passage along an atmospheric trajectory would entail.

Finally, because trajectory models give results only on the path traversed by the air parcels, and because these results include a time dependency, this type of model does not permit direct analysis of spatial variability. Instead, such models can be used to compute results at various points--random origin points--that terminate their particular trajectories at the same time. This technique provides a limited degree of spatial resolution.

5. Grid Models

a. Model Concept

Grid models, the most sophisticated class of air quality models developed to date, are based on a stationary two- or three-dimensional array of grid cells, within which pollutants are emitted, transported from cell to cell, diffused by turbulence, undergo chemical reactions, and are removed from the grid region by rain, adsorption on the ground, and other means. The complete atmospheric diffusion equation forms the theoretical basis for the grid model concept. As a class, grid models provide a higher level of detail in the treatment of relevant atmospheric processes than any other class of model.

b. Operational Features

Various types of grid models have been developed. They differ primarily in the number of atmospheric processes accounted for, the level of sophistication in the treatment these processes, and the numerical procedures used to solve the governing conservation equations. Two early three-dimensional grid models for photochemical pollutants differed primarily in the method used in the solution of these equations. One used finite difference procedures for integration of the governing equations [147], whereas the other used particle-in-cell techniques [148]. Two less-general grid models have also been developed. One is a two-dimensional cell model that is based on the solution of ordinary differential equations derived from the species conservation equations. Although it is essentially a dynamic mass balance formulation, this model possesses many of the characteristics of the more general grid models [149,150]. The other is a full grid model for sulfur dioxide, which is treated as a linearly reactive species [151]. Although this model has not been modified to include photochemical reactions, it does have the potential for such extension.

Grid models are the most widely applicable form of physicochemical model, and they are particularly well suited to the examination of regional air pollution problems. Because concentration predictions are available for numerous locations (both at the ground and aloft) throughout the day and night, these models are well suited to the analysis of regional and subregional impacts due to variations in emissions rates or locations of sources. For example, using grid models it would be possible to develop strategies to control only those emissions directly responsible for the maximum ozone concentrations in a region. In general, grid models can be applied to any situation where sufficient data are available to derive the required inputs.

Concomitant with the complexity and sophistication of grid-based photochemical models are large computing and data base requirements. For example, Table 28 identifies meteorological, emissions, and air quality data inputs required to operate one complex photochemical grid model. Other grid models may not require all of the input data listed in the table, but grid models as a class require more data then any of the models discussed thus far.

TABLE 28. DATA-DEPENDENT INPUTS REQUIRED BY A COMPLEX PHOTOCHEMICAL GRID MODEL

	Spatial and Temporal Resolution				
Description	xy	xyz	z	t	Remarks
Meteorology					
Horizontal (u-v) winds (m/sec)		x		x	The vertical component, w, is computed by the airshed model, rendering the resultant wind field mass consistent
Reference height of surface wind monitoring stations (m)	x				Used in the diffusivity algorithm
Diffusion break (m)	x			x	Elevation at which the stability structure of the atmosphere changes markedly (e.g., an inversion or thermal internal boundary layer)
Top of modeling region (m)	x			x	
Ground-level temperatures (°C)	x			x	Not absolutely essential to model operation
Atmospheric pressure (mb)				x	
Temperature gradient below diffusion break (°C/m)				x	Used in plume rise calculations
Temperature gradient above diffusion break (°C/m)				x	Used in plume rise calculation
Water concentration in the atmosphere (ppm)				x	Used in kinetic module
Exposure (stability class)				x	Used in diffusivity algorithm
Radiation intensity factor (per min)					Used in kinetic module
Air quality					
Initial conditions (pphm)		x		x	Required for NO, NO_2, O_3, HNO_2, H_2O_2, olefins, paraffins, aldehydes, aromatics, PAN, SO_2, $SO_4^=$, and CO
Boundary conditions (pphm)		x		x	Required for same species as above
Concentrations above top of modeling region	x			x	Required for same species as above
Surface concentrations at several locations within modeling region (ph)	x			x	Required for verification and evaluation of model performance (same species as above)
Surface characteristics					
Surface roughness (cm)					Used in diffusivity, surface sink, and microscale algorithms
Vegatation factor (fraction of alfalfa absorption)	x				Used in surface sink algorithm

TABLE 28 (Concluded)

Description	xy	xyz	z	t	Remarks
Emissions					
Lumped ground-level emissions from traffic, area sources, airports, etc. (g/hr)	x			x	Required for NO, NO_2, O_3, HNO_2, H_2O_2, olefins, paraffins, adehydes, aromatics, PAN, SO_2, $SO_4^=$, and CO
Elevated stationary point source emissions (g/hr)					Emissions from tall stacks for the above species are required
Elevated mobile source emissions (g/hr)		x		x	Emissions from aircraft takeoffs and landings for the above species are required (as appropriate)
Location and height of elevated point source emissions (m)		x			Required for computation of effective stack heights
Location of aircraft flight areas (m)		x		x	Requirement depends on magnitude of aircraft emissions
Heat flux from elevated point sources (MW)				x	Used in plume rise algorithm
Roadway emissions rates from autos (g/hr)	x			x	Required for NO, NO_2: used in the treatment of subgrid-scale (minoscale) phenomena
Roadway microscale parameter (m/sec)	x			x	Parameter given by $\sum_i n_i v_i$ where i = vehicle type, n_i = number of vehicles in category i, and v_i = speed of vehicles in category i

Source: Ref. 152.

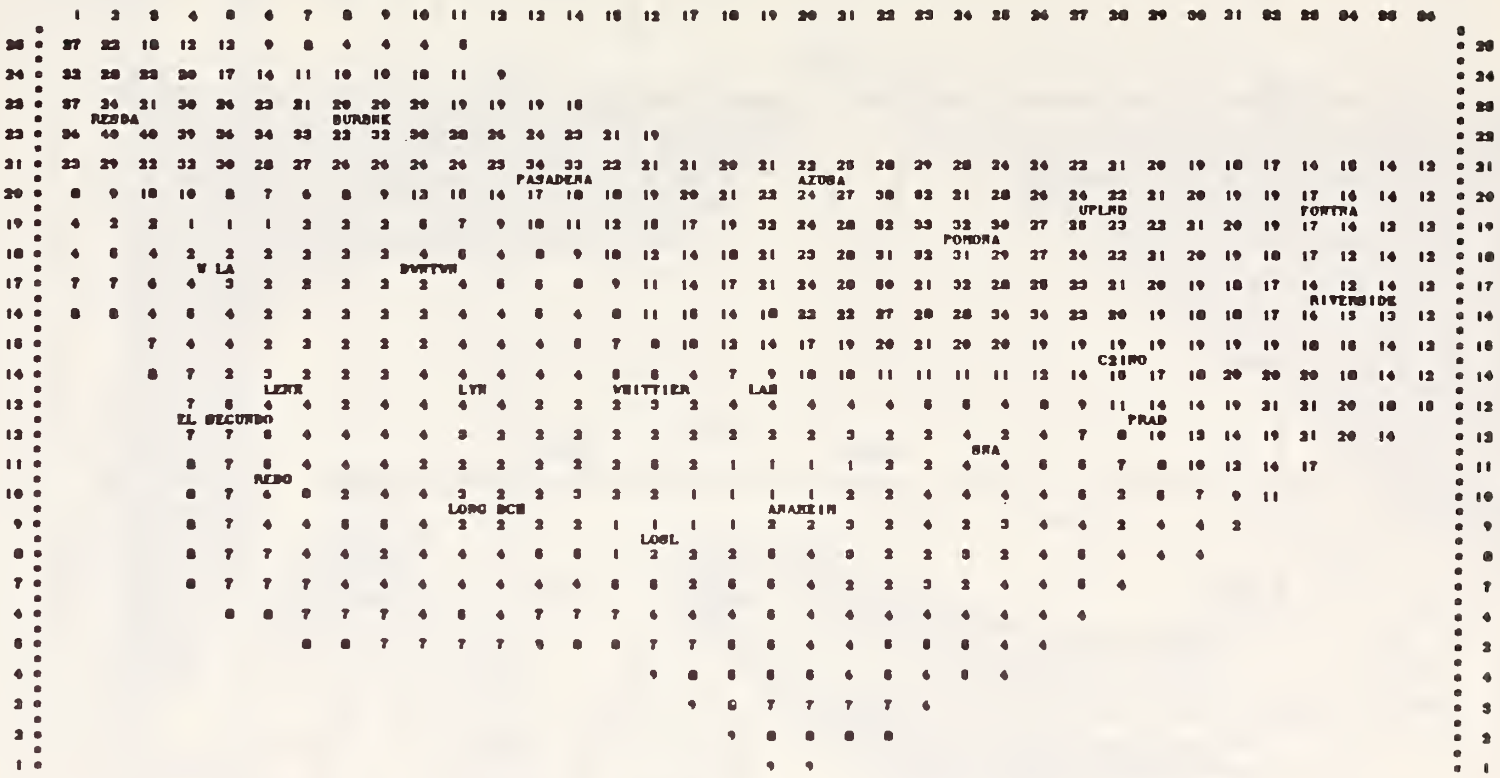
c. Examples of Grid Models and Their Applications

Currently available grid models have already been mentioned [147-151]. One of the distinguishing features in the application of grid models is the vast amount of output information available. Typically, for each hour of the computer simulation, average pollutant concentrations at ground-level cells and cells aloft are calculated. Thus, one can obtain pollutant concentration fields (see Figure 69) or isopleths of ground-level concentrations. These forms of model output are useful in locating the spatial maximum concentrations and spatial gradients in pollutant concentrations. Furthermore, the ground-level maps permit one to resolve apparent discrepancies between prediction and measurement such as might occur where systematic biases in wind direction shift the location of the simulated pollutant cloud slightly away from its actual location. Grid model predictions can also be compared with measurements at a monitoring station. Finally, grid models afford detailed evaluation of emissions control strategies. Figure 70 shows isopleths of the predicted increases in NO concentrations (above base case values) that might result from a new source of emissions.

d. Limitations of Grid Models

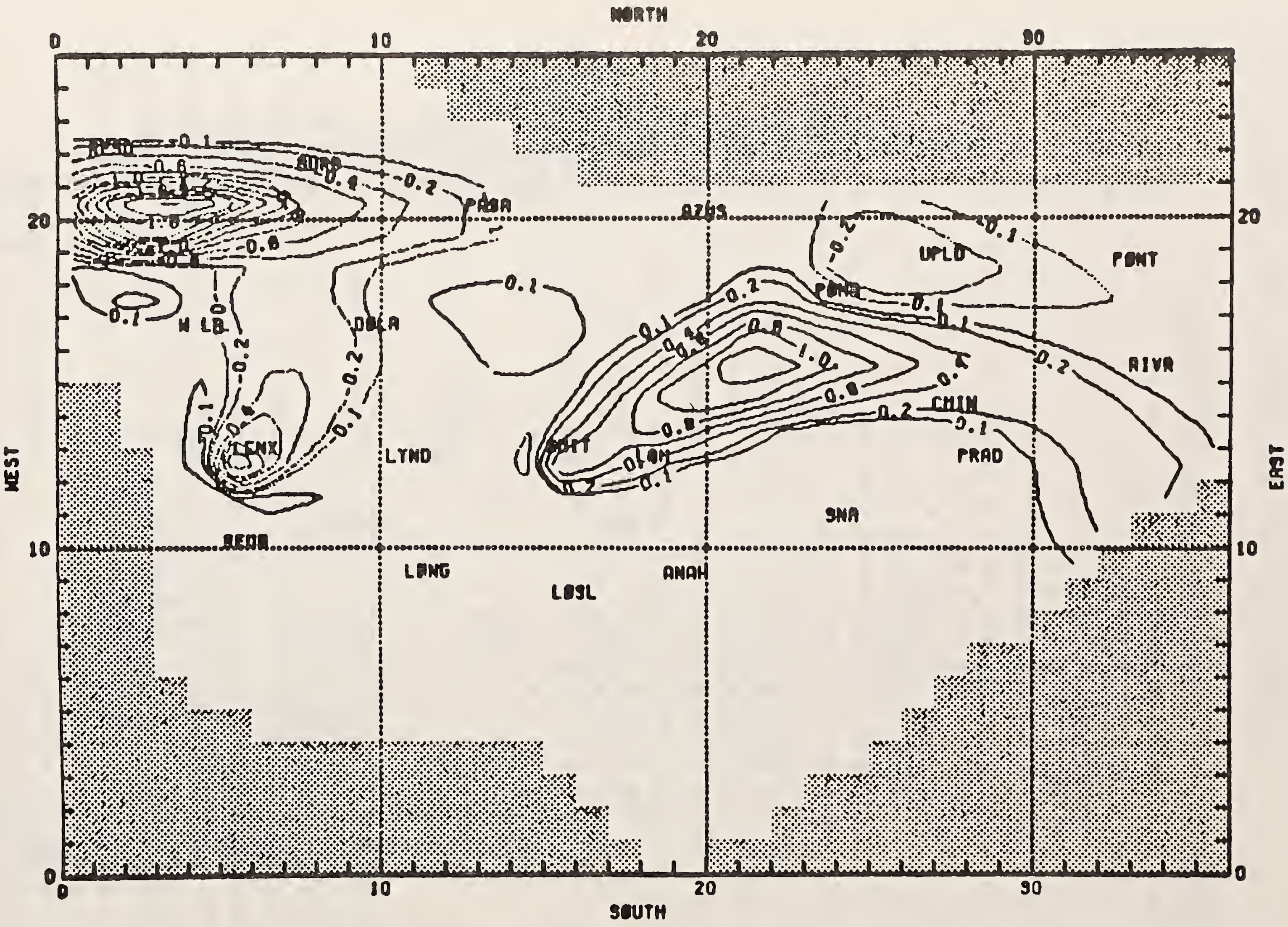
Every air quality modeling concept suffers certain limitations; grid models are no exception. A potentially important technical limitation of grid models is that the atmospheric diffusion equation is difficult to solve accurately. In particular, conventional finite difference techniques introduce a pseudo-diffusion effect as a result of poor treatment of advective transport. The net effect is to smooth out concentration variations. The magnitude of the error depends primarily on [142]:

> The emissions pattern.
> The wind speed and the relative magnitude of physical diffusion.



Source: Ref. 153.

FIGURE 69. EXAMPLE OF OUTPUT OBTAINED FROM A GRID MODEL APPLIED TO THE LOS ANGELES BASIN. The figures represent average predicted ground-level concentrations of ozone (in pphm) between 12:00 a.m. and 1:00 p.m. PST on 4 August 1975.



Source: Ref. 154.

FIGURE 70. ISOPLETHS OF CHANGES IN O_3 CONCENTRATIONS (in pphm) FROM BASE CASE DUE TO RELOCATION OF A REFINERY FROM GRID LOCATION (16,13) TO (6,13)

> The grid size.
> The finite difference scheme selected.
> The length of simulation time.

Although it is almost impossible to eliminate numerical diffusion in grid models, errors can be reduced to an acceptable level for most applications by selecting an appropriate grid size and finite difference scheme.

Another important limitation of grid models is the cost of data preparation, simulation, and analysis of results. The computing demands of some of the newer models nearly exceed the capabilities of even the largest computers. Computing costs for an urban area such as Los Angeles, California, may run as high as $1,000 to $2,000 for a 24-hour simulation. Preparing an adequate data base for these models may cost from as little as $10,000 up to $200,000, depending on the amount of available data and the availability of monitoring equipment and personnel. Because the amount of output information available from these complex models is very large, statistical methods are often needed to interpret the output.

Finally, grid models, as currently designed, are generally not capable of resolving pollutant concentrations at the microscale--that is, at scales smaller than the size of the grid cell. Thus, important local effects, such as the depletion of ozone by reaction with NO near roadways and the high pollutant concentrations in the immediate vicinity of point sources, tend to become obscured by the averaging of pollutant concentrations over the grid cell volume. Although research is under way to incorporate microscale effects into grid models, this aspect of the model concept is at present a potential limitation in some air quality applications.

D. ESTIMATED ACCURACY OF THE VARIOUS MODEL CONCEPTS

To establish the accuracy of an air quality model, one must typically carry out a verification study. The objective of verification is to determine whether the model under consideration adequately reproduces pollutant concentrations for the set(s) of conditions to which it is applied. The data requirements for a verification study are twofold: First, necessary input data to run the model must be supplied and second, monitoring data must be available to check the model's output. Previous model verification studies have varied considerably in the amounts of data used for verification.

Errors in model predictions are the result of inaccuracies in model inputs and inadequacies in the model formulations. In addition, model predictions may fail to match measured concentrations because of errors in the measurements. A well-designed verification study takes proper account of all of these kinds of discrepancy. Unfortunately, only a few of the studies reported in the literature were conducted in a way that permits identification of possible weaknesses in model formulation. Accordingly it is extremely difficult to determine whether the cause of observed discrepancies between measurements and predictions is inadequacies in the input data, the model, or both.

In general, verification procedures have consisted of a comparison of some kind between measured and calculated pollutant concentrations. Comparisons can be made at the locations of pollutant monitors, where measured concentrations are available. They can be made qualitatively, using graphical techniques such as scatter plots, or quantitatively, using statistical procedures. (These topics are discussed in Chapter X).

Two aspects of pollutant concentration variations should be accounted for. First, a model should correctly predict the amounts of pollutants formed (as indicated by pollutant concentrations). Second, the model should account satisfactorily, as far as its formulation permits, for both spatial and temporal trends in pollutant concentrations.

Because field measurements serve as the basis for assessing model accuracy, estimates of model performance based upon comparisons between measurement and prediction should be considered in light of the nature of the data base. In some instances a data base may closely resemble those meteorological and emissions conditions for which a particular model concept is best suited. Verification efforts with this type of data base might result in a high level of predictive accuracy. In contrast, if the data base is substantially different from the conditions for which the model concept is best suited, the model is likely to be judged inadequate. Thus, a model that undergoes verification with a data base that does not "stress" the model may be thought to be a fairly good predictor, when in fact its accuracy may be far less when applied to a different set of conditions. This aspect of model verification points out an extremely important caveat that must be understood when assessing model accuracy. A statement of model accuracy is heavily dependent upon the nature and quality of the data and the performance measures used in evaluating the model results. It is quite likely that a model might give predictions that are accurate to within ± 50 percent under some conditions, but only to within ± 100 percent under others.

Based upon a recent review of the model verification literature [152] it is possible to make the following very general estimates of the accuracy of concentrations predicted by different model concepts:

Model Concept	Estimated Accuracy
Statistical-Empirical	A factor of 10
Algebraic (Gaussian)	A factor of 2 or 3
Physicochemical (grid or trajectory)	± 30 to 50 percent

It is emphasized that the above are merely estimates. Current research supported by the EPA has as its aim the determination of standards of model performance and procedures for evaluating model performance [152]. Hopefully, this work, when completed, will lead the way to a clearer understanding of the accuracy of alternative model concepts.

E. SUITABILITY OF ALTERNATIVE MODELS FOR ESTIMATING AIR QUALITY IN TRANSPORTATION ENVIRONMENTS

The air quality model concepts introduced in the preceding section were developed to meet a variety of needs. Clearly, no single model is suited to all possible applications. In addition, none of the models yet developed embodies all of the pertinent atmospheric processes. This section discusses alternative model concepts in the context of the three transportation environments identified in Chapter VIII, namely microscale, mesoscale, and synoptic scale. The range of air quality analysis problems encountered in each environment and candidate model concepts for each environment are identified.

1. Microscale Air Quality Analysis

a. Types of Problems To Be Addressed

The air quality analysis problems encountered in the microscale environment are closely related to the dominant chemical and physical processes at that scale. Recall from Chapter VIII that among the most important processes in the microscale environment are:

- > Rapid mixing of emissions and ambient pollutants due to turbulence generated by traffic and air flow across the highway and appurtenant structures.
- > Rapid chemical reactions involving ozone and NO.
- > Deposition of heavy particulate matter, such as lead, immediately downwind of the roadway.

Because the temporal and spatial scales are small compared to the mesoscale and synoptic scale environments, the range of air quality problems is somewhat narrow. Of principal interest are the concentrations of CO, hydrocarbons and particulates (i.e., lead) immediately downwind of roadways, intersections, parking lots, and so on. However, NO_2 concentrations may also be of interest, particularly if ozone-rich air encounters an area of high vehicular emissions, such as a freeway. (Recall that NO_2 is formed rapidly due to the NO-ozone reaction.)

Examples of the type of analysis problems common to the microscale transportation environment include:

- Determination of ground-level CO concentrations at receptors downwind of a roadway. A receptor location might be a sidewalk, toll booth, or playground.
- Determination of ground-level CO concentrations at receptors at various locations within and surrounding a large shopping center, downtown mall, or sports/entertainment complex.
- Determination of downwind NO_2 concentrations attributable to vehicular NO emissions.

Normally, the formation of photochemical oxidant and aerosols (sulfates, nitrates, and others) is not of concern in the microscale environment due to the length of time required for their formation.

b. Available Model Concepts

Several models have been applied to microscale transportation problems; others are being developed. Perhaps the simplest modeling approach is the use of the rollback concept, in which the percent increase (decrease) in future CO concentrations at a receptor is assumed to be proportional to the increase (decrease) in emissions. Although rollback is easy to use, concentration data at key receptors under worst case conditions must be available. Moreover, rollback is based on the assumption that the emissions source distribution does not change spatially or temporally in future years. Due to these limitations and the availability of alternative models, rollback is not ordinarily the recommended approach.

The Gaussian model concept is the most widely used technique for analyzing roadway or other microscale impacts. A number of line source models have been developed and applied to a variety of situations. Among the more familiar Gaussian models for highway applications are CALINE 2, HIWAY, AIRPOL-4, and TRAPS. These models are good candidates for screening analysis; numerical models, described below, would ordinarily be used for more refined analysis.

Grid models are also available for use in microscale analyses. Although grid models have not been applied to roadway and local source situations as has the Gaussian model, in recent years a few grid models have been developed for these applications [155-157].

2. Mesoscale Air Quality Analysis

a. Types of Problems To Be Addressed

Certain atmospheric processes are of greater importance when the focus of the air quality analysis shifts to the mesoscale. As with the microscale, horizontal advection and vertical diffusion of pollutants are key processes. The following other factors also come into play:

- > Limitation of the volume available for dilution of pollutants as a result of a capping temperature inversion.
- > Diurnal variation in the amount of sunlight available for initiation and maintenance of photochemical smog reactions.
- > Large spatial variability in the composition of emissions from various urban sources.
- > Pollutant removal due to chemical conversion to secondary pollutants, precipitation scavenging, and surface uptake.
- > Chemical reactions leading to the formation of photochemical oxidants and particulate sulfate.

At the mesoscale (or urban scale), both primary pollutants such as CO, hydrocarbons, and particulates and secondary pollutants--particularly photochemical oxidants and sulfate--are of concern. At this scale a range of air quality problems is encountered. For example:

> What is the maximum one-hour-average oxidant concentration expected to occur under worst case meteorological conditions if a particular emissions control strategy is invoked?

> Where and at what time of day does the oxidant maximum occur?

> What percentage of an urban area can be expected to experience ozone concentrations above a specified level (say, 0.08 ppm) if a particular emissions control strategy is adopted?

> What is the impact of a major new source such as a shopping center or freeway interchange on urban oxidant, NO_2, and sulfate concentrations and ground-level concentrations downwind of the source?

> What change in daily average CO, SO_2, or $SO_4^=$ concentrations might be expected over an area from imposition of a proposed emissions control strategy?

Of course, many other analysis problems can also arise.

b. Available Model Concepts

The number of modeling concepts available for mesoscale air quality studies is large. At one end of the spectrum of complexity are the simple statistical-empirical models, which are potentially useful in estimating general trends in ambient air quality. Next are the line and area source Gaussian models, which have been used widely in urban areas, focusing on single and multiple point and area sources for both short and long term averaging periods. Gaussian model applications have been confined primarily to CO and SO_2 impact studies. For oxidants and other secondary pollutants, the EKMA method and trajectory and grid models represent alternative modeling approaches. In short, all of the model concepts introduced earlier have potential application in mesoscale studies. The decision as to which model is best suited to the problem at hand is based largely upon the extent to which the model concept properly accounts for the relevant processes in the mesoscale environment.

3. Synoptic Scale Air Quality Analysis

a. Types of Problems To Be Addressed

At the synoptic scale (also called the regional scale or macroscale), the atmospheric processes of greatest importance include:

> Long range advective transport of polluted air masses.
> Chemical interactions between pollutants in aged air masses and fresh emissions.
> Removal processes involving precipitation scavenging and surface uptake.

Because the time and space scales are so large compared to the microscale environment, for example, certain processes, such as the initial dispersion of emissions, are not of major importance at the synoptic scale. Basically, the processes of greatest concern are those governing the ultimate fate of pollutants.

Several questions may be raised concerning the impact of emissions on regional air quality. One of the more important ones addresses the role that urban hydrocarbon and NO_x emissions play in the formation of elevated oxidant concentrations in rural areas. Although the causes of these elevated concentrations have yet to be determined, accumulating evidence implicates urban sources as the primary contributor to ambient ozone concentrations well above air quality standards in synoptic scale environments. Central to this question is the uncertainty as to whether emissions controls in an urban area, while seemingly yielding a net improvement in ambient pollutant concentrations in that area, may actually lead to increased oxidant concentrations farther downwind. Another synoptic scale problem of interest is the fate of sulfur-bearing pollutants. (Although mobile sources are not the primary emitter of sulfur oxides, they do contribute a non-negligible portion of the sulfur oxides emissions inventory.) Specifically, over time scales of one to a few days, what is the rate at which anthropogenic SO_2 emissions are converted to sulfate, and how and where are these sulfates ultimately removed from the atmosphere?

b. Available Model Concepts

In contrast to the wide variety of air quality modeling concepts suited for mesoscale analysis, there are essentially only two concepts that have proven useful in synoptic scale studies--the grid and trajectory concepts.

Several models have been developed based on the trajectory concept, both in the United States and in Europe. Many of the differences between the models lie in their prescriptions of the transport wind, diffusion rates, surface deposition rates, emission sources, and solution techniques. Several grid models have also been developed for synoptic scale analyses, and they too are characterized by different levels of detail in the treatment of advection, diffusion, removal, and atmospheric chemistry.

F. PHYSICAL MODELS

At present, physical models have limited utility for assessing the air quality impacts of transportation projects. Physical models that have been employed in the study of air pollution include wind tunnels, water channels, towing tanks, and smog chambers. A wind tunnel consists of a fan to draw air through a duct system as well as various heating and mechanical elements to control the characteristics of the flow field. Both water channels and towing tanks generally use water as the fluid medium, but they are distinguished by the manner in which the flow field is generated. In a water channel, a pump at one end of the apparatus maintains the flow. In a towing tank, an object is moved through still water. Thus, the "flow field" is caused by moving an object through the fluid rather than forcing the fluid past a stationary object. Finally, a smog chamber is a vessel in which air pollutants are mixed, irradiated, and allowed to undergo chemical transformations.

Wind tunnels, water channels, and towing tanks differ from smog chambers in that they attempt to simulate atmospheric flow characteristics Neutral atmospheric stability is most readily simulated in wind tunnels and water channels, and a thermally stratified atmosphere can be simulated by filling a towing tank with stratified layers of salt water. The accuracy of physical models depends on appropriate simulation of the scales of atmospheric motion. In most circumstances, it is not possible to scale all phenomena correctly, and thus, the investigator is forced to compromise. Clearly, it would be difficult to simulate anything but the simplest atmospheric chemical process in a water channel or towing tank. The feasibility of studying photochemical processes in a wind tunnel has been discussed [158], but no successful experiments have been reported to date. The following studies are representative of uses of these types of physical models:

> Wind tunnel experiments to determine the characteristics of a plume from a point emissions source in the lee of a mountain ridge [159].

> Wind tunnel experiments to examine the influence of stack height and local building characteristics on ground level pollutants concentrations resulting from the emissions of a point source [160].

> Wind tunnel experiments to study the influence of the urban heat island effect on air flow over a city [161].

> Towing tank experiments to characterize the dispersion of a point source plume in stably stratified flow over complex terrain [96].

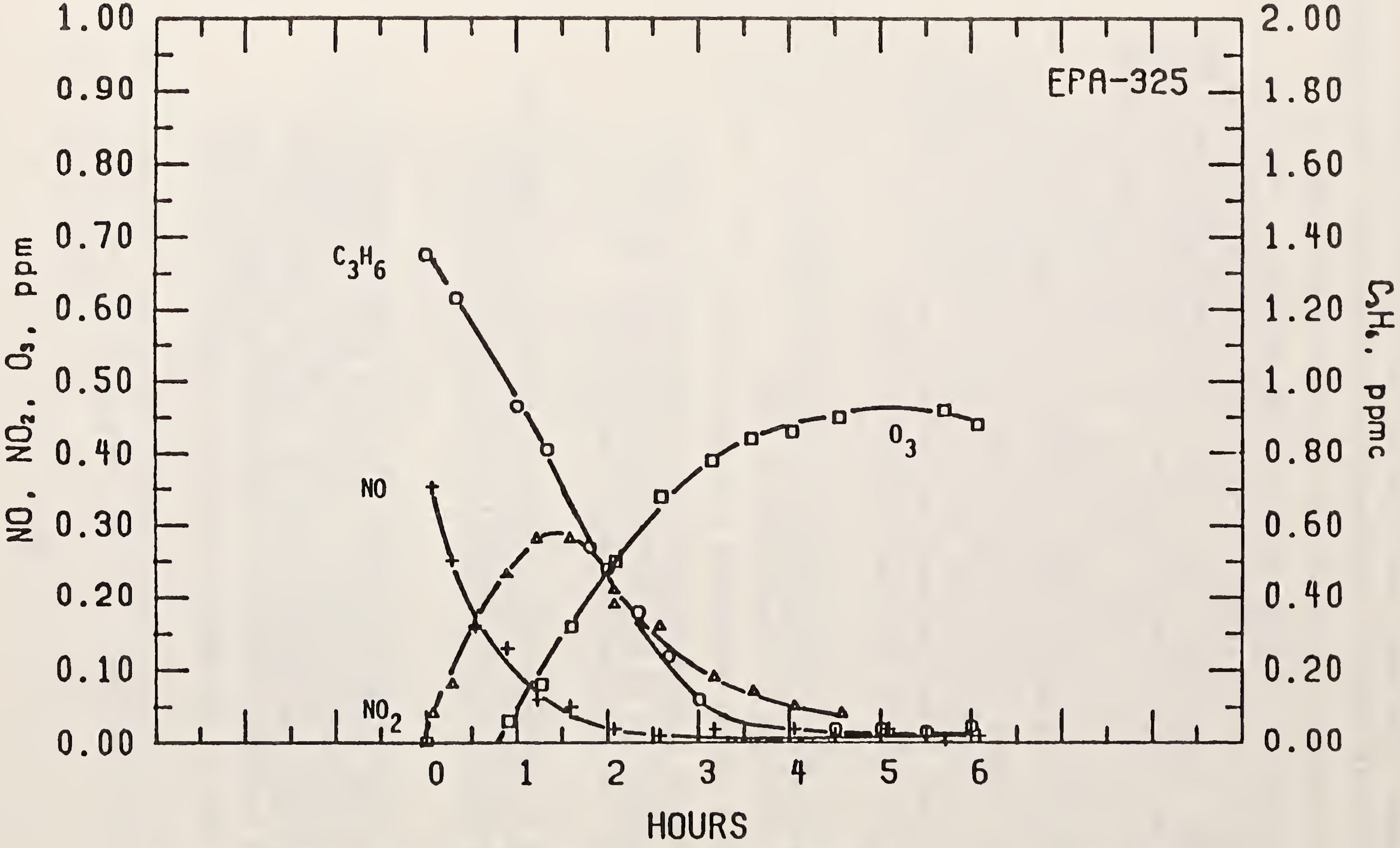
Actual examples of a wind tunnel, water channel, and towing tank can be seen at the EPA's Fluid Modeling Facility in Research Triangle Park, North Carolina [162].

Smog chamber experiments have played an important role in improving our understanding of the chemical transformations that take place in the atmosphere. In a typical experiment, pollutants are injected into the chamber at concentrations similar to those observed in the atmosphere. They are then constantly mixed and allowed to react under controlled conditions of temperature, pressurs, and light. Pollutant concentrations within the chamber are measured as a function of time. The results of a typical smog chamber experiment involving the irradiation of propylene and NO_x is presented in Figure 71. For additional realism, an outdoor chamber has been constructed that employs actual sunlight to irradiate the pollutants [163]. Moreover, provisions have been made to allow air in the chamber to be exchanged with clean air to simulate dilution effects such as those observed in the atmosphere when an inversion rises during the morning. Representative smog chamber studies include:

> An evaluation of the influence of hydrocarbon and NO_x concentrations on ozone production [164].
> Outdoor chamber experiments to assess the effect of nonmethane hydrocarbon reductions on NO_2 production [163].
> An examination of the interrelationship between SO_2 oxidation and photochemical smog formation [165].

An important limitation of smog chambers is that the smog chamber walls produce effects that are not representative of actual atmospheric situations.

Physical models cannot currently serve as a general predictive tool for use by transportation planners. They are useful in studying critical details of physical and chemical processes, but wall effects and the inability to adequately simulate the interactions of emissions, meteorological, chemical, and removal processes are important limitations.



Note: Initial conditions were 0.40 ppm NO_x, 0.04 ppm NO_2, and 1.35 ppmC propylene.

Source: Ref. 163.

FIGURE 71. TYPICAL RESULTS OF A SMOG CHAMBER EXPERIMENT INVOLVING THE IRRADIATION OF PROPYLENE, NO, AND NO_2

G. SUMMARY

This chapter focuses on the many physical and mathematical techniques that are available for use in establishing the relationships between emissions and ambient air quality. Physical models, while an interesting approach to the problem, do not appear at this time to be widely useful in air quality analysis. Mathematical models, however, appear to have a wide range of application and to offer the best prospects for estimating future air pollution concentrations. Currently, most research is directed at developing improved mathematical models rather than improving physical models.

The field of mathematical air quality simulation modeling is evolving rapidly. Accordingly, no attempt has been made here to single out specific models as best suited for particular applications. Rather, the underlying model concepts have been stressed. This approach allows the transportation planner or engineer to identify the appropriate concept to apply to a given situation. Information on specific state-of-the-art models is available from EPA reports and the general technical literature. As understanding of atmospheric processes is advanced, specific air quality models can be expected to improve substantially.

It is worth noting that the EPA continues to play a leading role in the development and updating of air quality models. It also provides recommendations concerning the uses of models for various applications. In some instances, models developed for very specific purposes or models very recently developed are not included in the EPA's catalog of recommended models. This is not to say that such models are inappropriate; in fact, the EPA suggests that if the models recommended in its guidelines are found to be inappropriate, other, perhaps more sophisticated and specialized, models should be considered.

Finally, with respect to the issue of model accuracy, it is presently not possible to give unequivocal statements as to the accuracy of model concepts or specific computational algorithms. Hopefully, increasing interest and research in model validation and evaluation of model performance measures will lead to more precise estimates of model accuracy. For the present, model accuracy can only be estimated on the basis of limited comparisons between model predictions and experimental data. It should be kept in mind that some models include a margin of safety; that is, they are based on assumptions that generally lead to conservative estimates of pollutant concentrations because they tend to overpredict slightly.

X THE DESIGN AND USE OF AIR QUALITY MONITORING PROGRAMS

The cornerstone of air quality analysis in the transportation planning process is the collection of data that accurately represent air quality and meteorological conditions in the area that might be affected by a transportation planning decision. To examine air quality impacts one must usually begin by characterizing current air quality through the implementation of a monitoring program and then use a predictive method to determine the additional effect of a proposed transportation plan. Most often, the predictive method will require meteorological data. This chapter is included to provide the highway planner or engineer with an understanding of the methods used to monitor pollutant concentrations and meteorological conditions.

The collection of meaningful and reliable data requires selection, first, of appropriate monitoring sites and, second, of appropriate measurement devices (with their attendant data reduction requirements). The monitoring network chosen should produce data that accurately characterize air quality throughout the region being studied, over an appropriate time scale. Since concentrations of pollutants fluctuate from point to point in both time and space, and since many air quality control requirements call for measurements that are averaged in space or time or both, the choice of monitoring sites and measurement methods, which have characteristic response times of their own, can significantly influence the results of the monitoring program. Because of these considerations, the design of a monitoring program requires careful examination of the program goals, the spatial scale of the region being monitored, the measurement techniques to be used, and the reporting requirements for the information obtained. This chapter discusses each of these issues in turn, after the overview in the next section.

A. GENERAL CONSIDERATIONS

Air quality monitoring programs have four main applications:

- Assessment of compliance with air quality standards. Compliance with federal and state regulations defining acceptable air quality is determined using data collected by monitoring stations.
- Determination of long term air quality trends. Analysis of historical records of air quality measurements enables evaluation of the effectiveness of air pollution control strategies.
- Acquisition of a data base for development and validation of an air quality model.
- Estimation of the air quality impacts of planned new facilities. Monitoring studies provide baseline pollution concentrations that can be considered when planning the construction of a new facility, such as a highway.

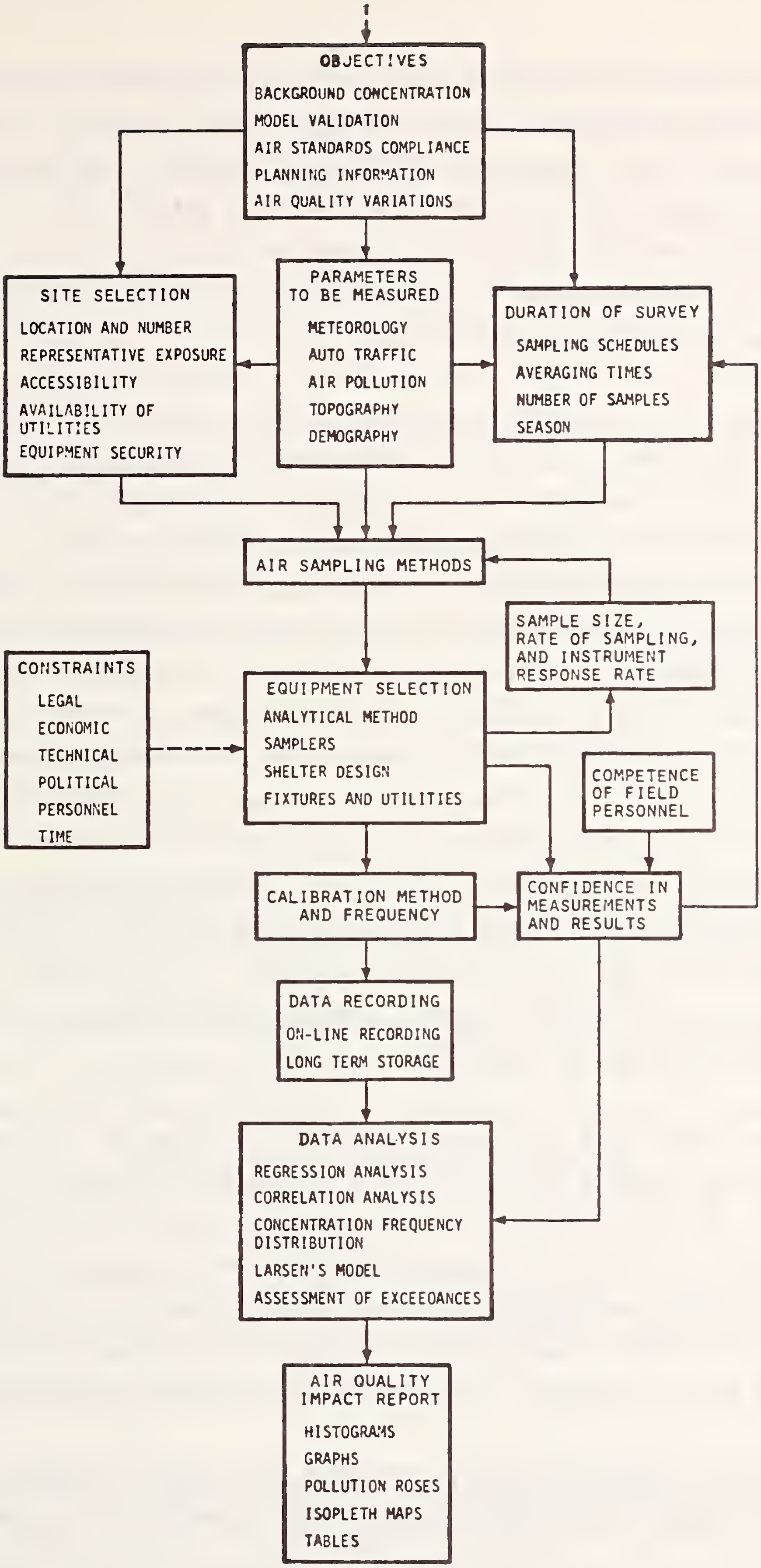
Although a particular monitoring program may be intended to fulfill the needs of more than one of these applications, the planned uses of the program greatly influence its design.

Program design considerations can be divided into four main steps:

- Determination of which parameters to measure.
- Selection of analytical measurement methods.
- Siting and structural design of the monitoring network.
- Selection of data reporting and analysis techniques.

Figure 72 illustrates a procedure for designing an air quality monitoring program.

The number and identity of the pollutants to measure depends on the objectives of the study. This choice affects the selection of analytical methods to some extent. Many monitoring analyzers are capable of measuring more than one pollutant, and it is usually cost-effective to choose the one that can cover the required set of pollutants. Since multipurpose machines tend to be



Source: Adapted from Ref. 166.

FIGURE 72. PROCEDURE FOR DESIGNING AN AIR QUALITY MONITORING PROGRAM

more expensive than single-purpose ones, however, the former should be used only when their full capabilities are needed. The purpose of the study also dictates which, if any, meteorological parameters need to be monitored along with the pollutant concentrations. For instance, determination of compliance with a National Ambient Air Quality Standard does not require any meteorological data, but the validation of a complex air quality model could require extensive meteorological measurements.

The selection of analytical methods presents a difficult series of decisions. For any given pollutant, a large number of analytical instruments are available, based on many different principles. They range from very simple to highly complex and from relatively inexpensive (hundreds of dollars) to expensive (tens of thousands of dollars). They can require manual operation, or they can operate automatically for months without attention, recording data in machine-readable form. Even when a particular instrument has been selected, the associated hardware of samplers, pumps, and data recorders needs consideration. Also, the frequency of calibration should be set according to the needs of the chosen machine. In choosing a set of analytical tools, one should evaluate the network requirements so that the selected instrumentation will have the right balance between simplicity of operation and accuracy, between ruggedness and sensitivity, and between cost and utility. For meteorological monitoring, the variety of instruments available is not as great, but the correct balance is still needed between demands and resources to ensure deployment of the most cost-effective network.

The deployment of a monitoring network is governed by the spatial scale required of the output data. The uses of the data can range from concern about a particular location (calling for many closely spaced measurements) to a requirement for a region-wide study (necessitating data typical of a large area, specifically excluding small perturbations from local sources). On a temporal scale, data requirements can range from one-hour-average concentrations to annual averages, depending on the pollutant species of concern.

Monitoring sites are selected visually by trained personnel to best represent air quality on a scale appropriate to the goal of the monitoring program. Once the sites have been selected, the manner in which the instruments are to be installed is considered. Such considerations as the appropriate elevation for placement, required shelters for proper "surroundings," and prevention of vandalism enter into this decision.

Data reduction, analysis, and reporting can be accomplished through various methods to produce the final results from the study. Monitoring hardware that is used for continuous monitoring usually gives output in the form of an analog voltage signal. This signal must be interpreted correctly with respect to the electrical zero and span of the instrument before it is converted to concentration units. Drift in zero and span values should be checked periodically and allowed for in presenting the results. Many monitoring instruments produce output signals on strip charts, which can be converted to periodic pollutant concentrations (digitized) either manually or automatically using an electronic digitizer. In either case, careful quality control procedures should be followed to ensure high quality data (see Ref. 167). Automatic digitizers do not have transcription problems, but care must be taken to identify each data record correctly.

Data must be reported with the appropriate precision. The reporting standards for different pollutants suggested by the EPA are presented in Table 29.

In the data analysis, many levels of sophistication are possible, from simple data tabulations to complex statistical procedures, as described later. For large data bases and complex statistical analyses, a computer is an almost indispensable tool. However, care should be taken to see that it is used just as a tool and not as a substitute for careful consideration of the data.

Each of the elements in this general overview of the main considerations in monitoring program design is discussed in more detail below.

B. MONITORING GOALS

Assessing the air quality impact of the construction of a proposed highway requires data on three levels. Before the project is started, the existing air quality must be assessed, and an air quality model can be used to predict the impact of the proposed construction. Monitoring data are needed to

TABLE 29. SUGGESTED REPORTING ACCURACY FOR RAW DATA

Pollutant	Number of Decimal Places	
	$\mu g/m^3$	ppm
Suspended particulate matter	0	--
Benzene-soluble organic matter	1	--
Sulfates	1	--
Nitrates	1	--
Ammonium	1	--
Sulfur dioxide	0	2
Nitrogen dioxide	0	2
Nitric oxide	0	2
Carbon monoxide	1	0
Total oxidants	0	2
Total hydrocarbons	1	1
Ozone	0	3
Methane	1	1

Source: Ref. 167.

validate the model to be used. Then, after the proposed facility is built, subsequent analysis is needed to assess compliance with ambient air quality standards. Although the model can be used to check compliance, some external confirmation may also be required. These assessments require an air quality monitoring program. In current practice monitoring is seldom performed after the facility is built.

1. Assessing Existing Air Quality

To assess existing air quality, one should take a sufficient number of measurements to define long term concentrations adequately while also noting daily, weekly, or seasonal fluctuations. Equipment should be selected according to the criteria discussed above. Measurement of peak concentrations is essential because violations of air quality standards are most likely to occur during these peaks. Ideally, the monitoring program should extend throughout the possible area of impact of the proposed construction project. If this is not possible because of limitations of time or resources, measurements should at a minimum be made in the vicinity of current peak pollutant concentrations and also where the peak impact from the project is expected to occur. In addition, measurements should also be required in areas where sensitive populations are likely to be exposed (e.g., parks, hospitals, schools). The meteorological conditions under which the peak values occur should also be noted. Such information can both give insight into the possible causes of high pollutant concentrations and indicate the appropriate set of meteorological conditions to use in model runs for assessing the impact of the project.

The EPA has defined categories of sites (peak, neighborhood, and background) for different purposes. Peak stations are used to determine compliance, neighborhood stations help assess typical exposures, and background stations provide information on pollutants transported into the region. Note that within a category there may be more than one type of station, such as CO peak stations in street canyons and highway corridors.

2. Assessing Compliance with Air Quality Standards

In the final analysis, pollution levels must conform to the requirements of the National Ambient Air Quality Standards, which were promulgated to protect public health and welfare. The standards for various pollutants are based on different averaging times (see Table 1), which impose requirements on monitoring programs that depend on the pollutant of interest. Whatever the pollutant being monitored, measurements should adequately reflect the period specified in the standards.

3. Monitoring To Obtain Data for Air Quality Models

Mathematical models are used to predict pollutant concentrations in situations where insufficient or no measurements are available. As indicated above, they can be used to predict the impact of proposed construction, with considerable influence on the decision whether to proceed with the project. In view of this potential influence on the decision-making process, it is essential that the model merit the greatest possible confidence. For this reason, air monitoring programs are frequently undertaken to validate a model. Such monitoring programs can be directed toward two ends:

> Confirming predictions of the model, for instance, the accuracy of the peak concentrations and their locations.

> Providing measurements to correct the model when its assumptions have been violated, for instance, when a planned highway is to be elevated or depressed.

A monitoring program to validate a model differs from one designed to assess general air quality both in the deployment of the monitors and in the variables monitored. For model validation, the monitors should be deployed to account for small-scale effects as well as general levels. The variables measured should include all those that appear as either input to or output from the model. Wide ranges of the input variables, including both meteorological and emissions data, should be considered to ensure that the model can reliably predict pollutant concentrations under a wide variety of conditions.

C. MEASUREMENT TECHNIQUES

This section describes the equipment and techniques used to collect air quality and meteorological data. Both the different types of instrumentation used and the principles of operation of each are presented. Although this discussion may appear to include greater detail than others in this report, the information may serve as useful reference material since it is not readily available in this format elsewhere.

1. Air Quality

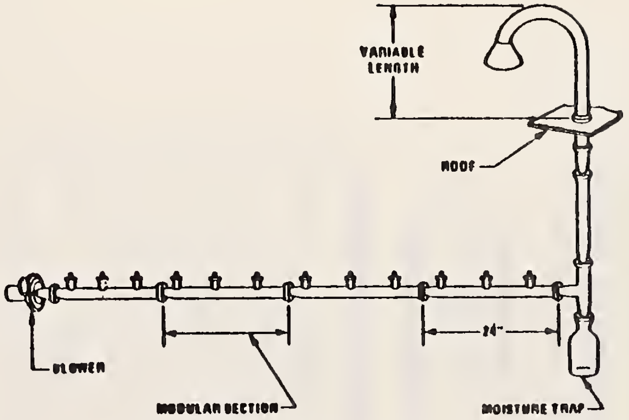
The main pollutants of interest to transportation planners are likely to be carbon monoxide, hydrocarbons, nitrogen oxides, and oxidants. All methods for measuring these pollutants follow the same steps: obtainment of a sample of air, its analysis using some calibrated procedure, and recording and interpretation of the data. However, the techniques used for each stage vary greatly. This section first discusses the types of hardware and software used to carry out the various tasks of the analysis, and then details the chemical and physical principles behind the available analysis instruments, indicating which methods are applicable to each pollutant.

a. Air Samplers

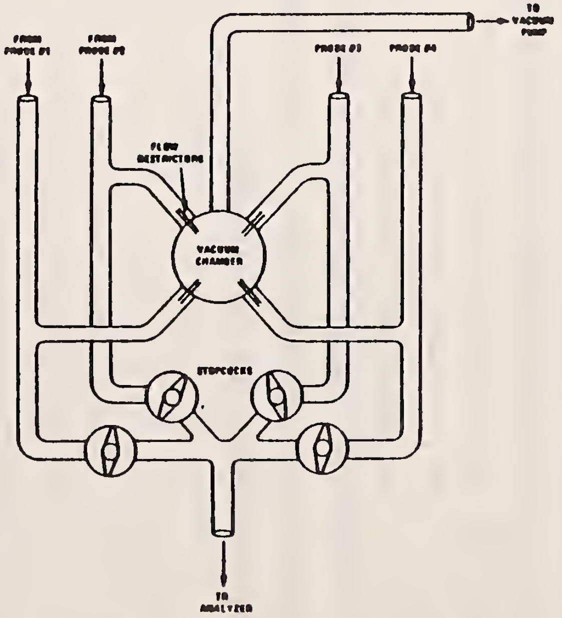
Three sampling procedures are in general use: continuous sampling, intermittent sampling, and integrated grab sampling. The type of air sampler and method of sampling chosen depend on many factors:

> The pollutant being studied, if it is reactive, can impose a requirement that the time between sample collection and analysis be short.
> The analytical method to be used determines the size of the sample required.
> The number of samples required during the monitoring study indicates whether automatic methods are desirable.
> The desired averaging time of the concentration required determines the period over which the sample must be collected.

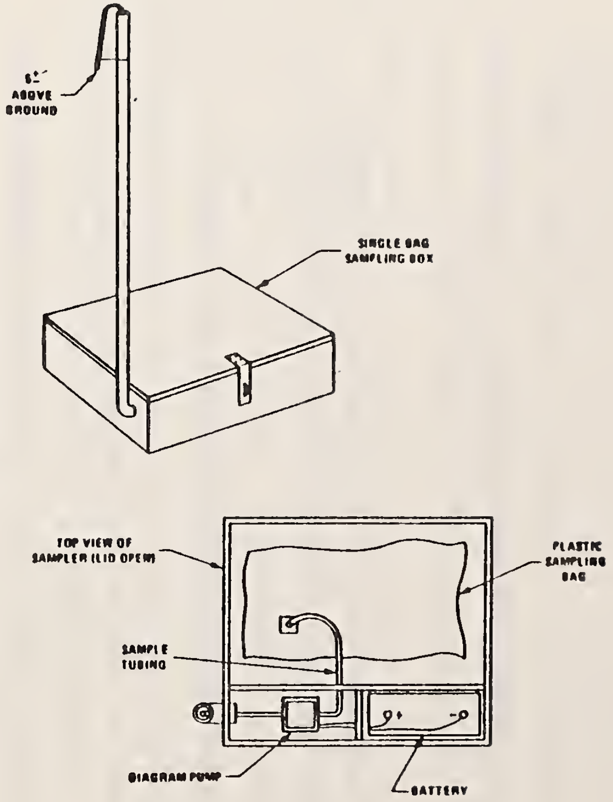
In continuous sampling, the air to be analyzed is continuously drawn through a manifold, which has sampling ports. Intermittent sampling affords an opportunity to sample many locations; air is drawn to the analyzer from many probes in turn, so that concentration measurements are made for each. In integrated grab sampling, air is drawn through a collection device for a given amount of time, so that the total sample collected is representative of pollutant concentrations averaged over the period. The collection device can be a bubbler containing an absorbing solution, a filter paper (for particulates), or a plastic bag. Figure 73 shows schematic representations of each of these types of sampler.



(a) Sampling Manifold for Continuous Air Monitoring



(b) Intermittent Sequential Sampling Manifold



(c) Single Bag Air Sampling Box for Integrated Bag Samples

Source: Ref. 168.

FIGURE 73. SCHEMATIC OF THE THREE MAIN TYPES OF SAMPLERS

b. Calibration Procedures

Collection of high quality data in a monitoring program requires accurate knowledge of the relationship between the instrument reading and the true concentration of the pollutant in the sample. This relationship is established through periodic instrument calibration. For a primary calibration, the instrument must be standardized against the EPA reference method for the given pollutant [169]. These methods, listed in Table 30, have been judged by the EPA to give reliable and accurate analyses.

The calibration procedure consists of introducing samples with known concentrations of pollutant into the instrument and to a reference method setup. To ensure the acceptability of the results, one should use concentrations that span the range of values likely to be encountered while monitoring. The standard gas mixtures are generated using one of three means: permeation tubes, gas generators, or certified gas mixtures purchased in cylinders. A permeation tube consists of the pollutant contained in liquid form in a tube with a permeable plug. By holding the tube at a constant temperature, one can obtain a constant rate of diffusion from the tube, and when this gas is mixed with a constant flow of clean air, a constant concentration results. The EPA specifies the methods by which references gases for calibration are to be generated; they are also given in Table 30.

The test results from the instrument are plotted against the reference method results to give a calibration curve. This curve can then be used to convert future results from that instrument to true concentration values.

TABLE 30. EPA-RECOMMENDED METHODS FOR CALIBRATION

Pollutant	Federal Reference Method for Calibration[*]	Test Gas Generation Method[†]	Verification[†]
Photochemical oxidants (corrected for SO_2 and NO_2)	KI colorimetric	Ozone generator[§]	Gas phase titration[**]
Carbon monoxide	Certified gas cylinder	Cylinder of CO in air or nitrogen	NBS certified[††]
Nitrogen dioxide	NaOH colorimetric	Permeation tube[§§][***]	Gas phase titration[**]
Nitric oxide	--	Cylinder of 100 ppm NO in prepurified nitrogen	Gas phase titration[**]
Nonmethane hydrocarbons	Certified gas cylinder	Cylinder of methane in zero air	NBS certified[††]

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[*] As recommended in the Federal Register, Vol. 36, p. 8186 for calibrating methods of measurement of "criteria pollutants."

[†] Preferred method of generating test atmospheres as published in the Federal Register, Vol. 40, p. 7053 (18 February 1975).

[§] As described in the Federal Register, Vol. 36, No. 228 (25 November 1971).

[**] As described in Section 7.1 of the Federal Register, Vol. 38, No. 110 (8 June 1973).

[††] If NBS (National Bureau of Standards) standards are not available, obtain two standards that agree within 2 percent from independent sources, or obtain one standard and submit it to an independent laboratory for analysis, which must agree within 2 percent of the supplier's nominal analysis.

[§§] As described in Ref. 170.

[***] As described in Ref. 171.

Source: Ref. 168.

c. Analysis Methods

The analysis procedures and instruments available to measure the concentrations of gaseous air pollutants range widely both in basic principles of operation and in price. A comprehensive study of analytical methods has been published by the Lawrence Berkeley Laboratory [172]. The proper choice of a set of instruments for an air monitoring survey can be made only after the scope and purpose of the project have been fully defined. This subsection briefly describes the main techniques of analysis that are used with air monitoring instrumentation and shows which techniques are applicable to the various automobile-emitted pollutants. The analytical techniques used with commercially available instruments are given in Table 31 along with the applicability of each to automotive pollutants.

Colorimetry. Colorimetric analyzers, which are used for many pollutants, are based on the reaction of the pollutant with a reagent in a specially prepared solution to produce a colored species. A spectrophotometer is used to measure the absorbance of the solution at a particular wavelength, and the absorbance is used to calculate the concentration of the colored species. Colorimetric analyzers have the advantages of simplicity of operation, high sensitivity, and (provided that proper procedures are followed) specificity. Their disadvantages include the sensitivity of the color-forming reactions to external influences, such as temperature and pH, long development times, fading, and interferences.

Spectroscopy. All spectroscopic analytical techniques utilize the measurement of the absorption spectrum of the pollutant under study in some way. However, with this common base, spectroscopic techniques vary as follows:

> Nondispersive absorption spectroscopy. Instruments based on this principle use broadband absorption in a particular portion of the spectrum--ultraviolet, visible, or infrared. Typical bandwidths are on the order of a few micrometers.

TABLE 31. ANALYTICAL TECHNIQUES FOR AIR QUALITY DETERMINATION AND THEIR APPLICABILITY TO VARIOUS POLLUTANTS

Technique	NO_2	Oxidant	CO	Hydrocarbons
Colorimetry	✓	✓	✓	
Nondispersive spectroscopy				
Infrared	✓		✓	✓
Ultraviolet	✓			
Dispersive spectroscopy				
Infrared	✓		✓	✓
Ultraviolet	✓	✓	✓	✓
Second derivative spectroscopy	✓	✓		
Correlation spectroscopy	✓			
Chemiluminescence	✓	✓		
Bioluminescence	✓		✓	
Gas chromatography			✓	✓
Catalytic oxidation			✓	✓
Amperometry	✓	✓	✓	
Ion selective electrodes	✓			
Electrochemical cells	✓		✓	

These instruments are somewhat sensitive to interferences, particularly from water vapor; auxiliary absorption cells or optical filters are commonly used to filter out radiation at interfering wavelengths.

> Dispersive absorption spectroscopy. Dispersive absorption spectrometers measure the absorption of gases at any set wavelength within their range, rather than the broad range of wavelengths used by the nondispersive instruments. They are thus extremely flexible and not limited to one pollutant. However, in a gas mixture with many components, absorption bands can overlap, and these instruments may lose their specificity.

> Second-derivative spectroscopy. Second-derivative spectrometers operate on the spectrum of the species under study to change the output signal electronically to one that is proportional to the second derivative of the transmission-wavelength function. These instruments have not been extensively evaluated, but they do have multiparameter capability.

> Correlation spectroscopy. Correlation spectrometers use the correlation between received radiation and a reference characteristic of a specific pollutant. These instruments are applicable to remote measurements and point measurements. The advantages of this method include high specificity and the capability for remote use. The disadvantages are high cost and a need to know pathlengths to obtain results in parts per million.

Chemiluminescence. Chemiluminescent analyzers are based on reactions of the pollutant under study that produce radiant emissions. The emitted radiation is detected by a photomultiplier. Chemiluminescent analyzers have many advantages, including continuous operation, fast response, high sensitivity and selectivity, and good reliability. The disadvantages include the need for pumps and for a supply of the necessary reagent, and the temperature sensitivity of the photomultiplier tube (this can be compensated for by electronic circuitry).

Bioluminescence. Monitors based on this principle operate in a manner similar to chemiluminescent analyzers, but the radiation comes from microorganisms. Some of these instruments have multiparameter capability, but they have problems with sensor lifetimes and they are quite expensive.

Gas chromatography. Gas chromatographs are well known analytical tools in the chemistry research laboratory. They pass a mixture of gases through a tube (column) with a high surface-to-volume ratio. The column can be packed or coated with various substances, and the differential absorption-desorption of the various components in the mixture to be analyzed causes them to emerge from the column at different times. They are then detected and recorded electronically. The type of detector most commonly used is the flame ionization detector, which is sometimes used alone to analyze mixtures containing hydrocarbons. The gas chromatography analysis technique has great specificity, and it can be manually or automatically operated.

Catalytic oxidation. This analysis technique consists of passing the pollutant-containing gas over an oxidizing catalyst bed and measuring the heat produced. The sample must be pretreated to remove interferences, and water can deactivate the catalyst. The two pollutants that can be measured using this technique are CO and hydrocarbons, and they can interfere with each other unless operating conditions are carefully chosen.

Amperometry. Amperometric analyzers measure the current necessary to maintain a constant halogen ion concentration in an analysis cell. In one type, iodide ions are oxidized to triiodide, which is reduced back by an electric current. The current required to maintain a constant iodide concentration is proportional to the amount of iodide oxidized. Although these instruments offer the advantage of low maintenance, many potential interferences need to be overcome with selective filters.

Ion selective electrodes. These analyzers use electrodes to detect pollutants. The electrodes are constructed using liquid ion exchangers to be sensitive to one ion in particular. In addition to specificity, this technique offers rapidity of response.

Electrochemical cells. Analyzers of this type oxidize or reduce the pollutant at a sensing electrode and measure the resulting current. They are simple to operate and have low maintenance and rapid response, but they have problems with interferences and temperature dependence (though the latter can be overcome electronically).

2. Meteorological Variables

The meteorological variables of interest in an air monitoring study include:

- > Wind speed
- > Wind direction
- > Atmospheric stability
- > Solar radiation
- > Temperature
- > Mixing depth.

Each is discussed separately below.

a. Wind Speed

There are several types of instruments that measure wind speed (called anemometers): pressure plate, bridled cup, pressure tube, hot wire or heated thermometer, and rotating anemometers. The last, which is the most common, is shown in Figure 74. In these anemometers, a propeller, a windmill, or a cup arrangement is rotated by the wind and the speed of rotation is related to wind speed. Various forms of anemometers are available having a wind range of operating characteristics, particularly with respect to their sensitivity. In general, the more sensitive the anemometer (that is, the lower the wind speed at which it responds), the less rugged it is and the less it is able to operate for long periods with little attention.

Thus, the choice of an anemometer is governed by the needs of the monitoring program. If a study of microscale effects is being made, an anemometer that is capable of responding rapidly to fluctuations in wind speed and that has the sensitivity to measure very low wind speeds is required. If a larger scale study is contemplated, for which larger scale average wind speed measurements are needed without short term fluctuations being recorded, the use of a heavier, more slowly responding anemometer is appropriate.

The output from an anemometer can be expressed in terms of wind speed or wind run,* and it can be electrically, mechanically, or manually recorded. Wind run records are useful when long term average wind speeds are required. Some form of machine recording is essential if the instrument is to be left unattended for long periods of time.

b. Wind Direction

Wind direction measuring instruments generally employ some form of wind vane (see Figure 75) mounted asymmetrically about a pivot, which aligns itself according to the wind direction. The trade-offs between ruggedness and sensitivity that apply to anemometers also apply to wind vanes. The output can be recorded by many different means--electrical or mechanical and automatic or manual.

It is sometimes desirable to measure the direction of the vertical wind component when atmospheric stability is to be determined. For this purpose, a bivane, which measures both directions simultaneously, is used.

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* Wind run is the distance traveled by a parcel of air in one unit of time.

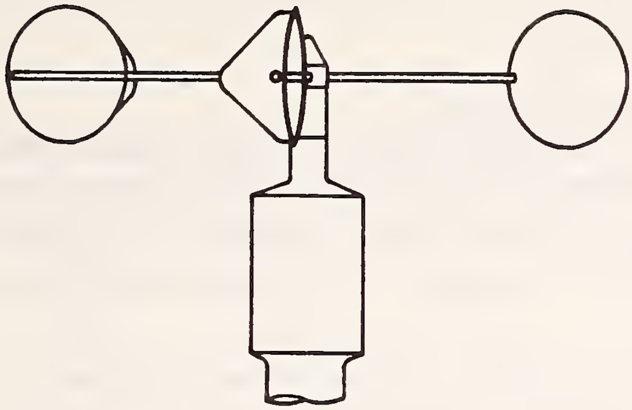


FIGURE 74. SKETCH OF A ROTATING ANEMOMETER

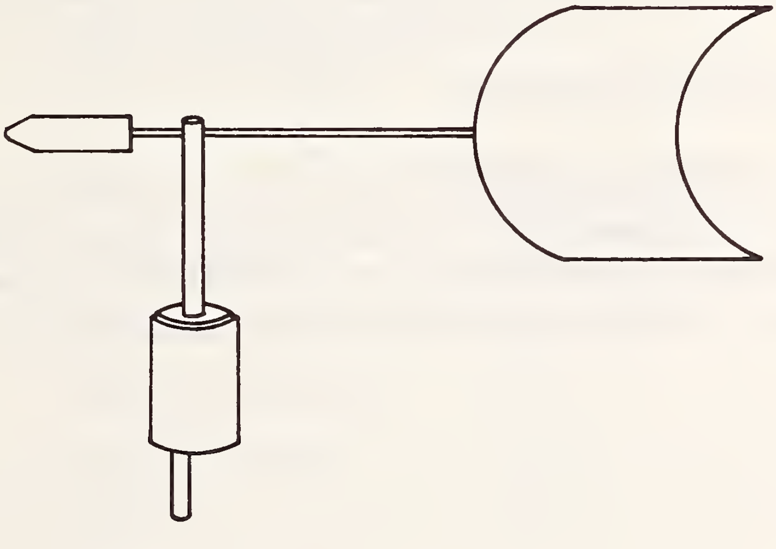


FIGURE 75. SKETCH OF A WIND VANE

c. Atmospheric Stability

Atmospheric stability has a great effect on the dispersion of pollutants, as discussed in Chapter VII. It is usually defined in terms of six categories, ranging from Category A (very unstable) to Category F (moderately stable) [173]. Stability categories are based on one of four measurements:

> Surface wind speed and insolation (see Table 32).

> Standard deviation of the lateral wind direction (see Table 33). This standard deviation is estimated from the range of horizontal wind directions.

> Standard deviation of the vertical wind direction. This can be measured with the bivane instrument described above or directly with a sigma meter.

> Vertical temperature gradient of the atmosphere. This gradient can be measured using several techniques--lidar, acoustic radar, radiosonde, aircraft, wiresonde, or an instrumented tower. The latter two methods are suitable only if the gradient close to the ground is of interest. (The atmospheric stability category depends on the vertical temperature gradient for reasons discussed in Section VII.B.)

d. Solar Radiation Measurements

Solar radiation is measured by one of two instruments: the pyrheliometer and the net radiometer. The pyrheliometer uses a thermopile, whereas the net radiometer measures the net radiation flux on a horizontal surface. The latter instrument cannot be used during rain.

TABLE 32. PASQUILL'S ATMOSPHERIC STABILITY CATEGORIES

Surface Wind Speed (m/sec)	Insolation			Nighttime Conditions	
	Strong	Moderate	Slight	Thinly Overcast or ≥ 4/8 Low Cloud	≤ 3/8 Low Cloud
<2	A	A-B	B	--	--
2-3	A-B*	B	C	E	F
3-5	B	B-C*	C	D	E
5-6	C	C-D*	D	D	D
>6	C	D	D	D	D

Note: "Strong" insolation corresponds to sunny midday in midsummer in England, and "slight" insolation to similar conditions in midwinter. Night refers to the period from one hour before sunset to one hour after dawn. The neutral category D should also be used, regardless of wind speed, for overcast conditions during day or night and for any sky conditions during the hour preceding or following night as defined here.

* For double categories, use the average of the two values.

Source: Ref. 168.

TABLE 33. PASQUILL'S STABILITY CATEGORIES RELATED TO THE STANDARD DEVIATION OF THE LATERAL WIND DIRECTION

Category	Description	Standard Deviation of the Lateral Wind Direction (degrees)
A	Extremely unstable	25.0
B	Moderately unstable	20.0
C	Slightly unstable	15.0
D	Neutral	10.0
E	Slightly stable	5.0
F	Moderately stable	2.5

Source: Ref. 168.

e. Location of Meteorological Instruments

The correct location of meteorological instruments is critical to obtaining proper measurements. In measuring wind speed, for example, the interaction of the airflow with the terrain must be taken into account when locating anemometers. An instrument located close to a terrain feature such as a building or a tree will measure the effect of that feature on the airflow. In some cases, this is desirable, but if measures of general airflow are required, the instrument must be located on a mast or tower sufficiently far away from such terrain features. A typical mast height is 10 meters. The influence of a roughness feature extends approximately to its height in the upwind and vertical directions and 5 to 10 times its height in the downwind direction. In some situations, the local terrain is so complex that many instruments are necessary to characterize general air movements adequately.

If measures of wind speed are available at elevations different from that at which speeds are required (e.g., for microscale studies), the measurements can be converted using the expression

$$u = u_r Z^a$$

where u is the wind speed at height Z, u_r is the wind speed at some reference height (usually one meter above the ground), and the exponent a is an empirically determined constant that depends on the vertical temperature structure of the atmosphere and the roughness of the ground surface.

D. MONITORING SITE LOCATION

In discussions of the spatial distribution of air pollutants, it is conventional to consider different scales based on the horizontal concentration gradients. For the purposes of this section, the three scales defined in Chapter VIII, namely, microscale, mesoscale, and synoptic scale (or macroscale), are used. In a different context, other divisions might be more appropriate.

The term microscale is used to describe effects that occur on a scale of up to 1 kilometer. This scale would correspond with a small air mass in which relatively large concentration gradients may exist. Such conditions typically exist very near a pollution source or near a topographical feature that has a large effect on airflow.

The term mesoscale refers to effects that occur over intermediate distances between 1 and 100 kilometers. This description covers fairly large regions and applies to situations where a mass of pollutants is fairly well dispersed or a group of small emissions sources is spread over a fairly large area. Pollutant concentrations can vary considerably over such an area, but microscale variations as defined above are excluded from consideration.

The term macroscale is used to describe effects that occur on a spatial scale greater than mesoscale effects, that is, larger than 100 kilometers. For example, rural background effects in areas with no substantial contributions from urban areas are defined on this scale.

The boundaries between the scales defined above are by no means sharp. However, air quality models are usually designed to model air quality problems at one scale in particular, with provisions sometimes to accommodate other effects.

A comprehensive regional monitoring program will consist of a network of stations designed to detect macroscale and mesoscale effects. An example of such a network is given in Figure 76, which shows the meteorological and air quality stations in the Los Angeles area. Monitoring for microscale effects is normally undertaken on a case-by-case basis, and such monitors are placed temporarily in appropriate locations. Careful location of monitoring probes is necessary to obtain proper results from a monitoring program. Poor siting could result in the measurement of microscale effects when mesoscale measurements are required, with the result that incorrect conclusions are drawn. The location of air pollutant monitors has received much attention from the EPA, which has issued many reports on this subject [e.g., 174-176].

The following subsections discuss the specific considerations for network design that apply to each of the main pollutants of concern to transportation planners.

1. Carbon Monoxide

Since CO is not subject to any long term standard, determination of seasonal CO trends and effects is generally not an issue in placing network monitors. The standards for CO are based on one-hour and eight-hour averaging times. The one-hour standard is typically violated during the morning rush hour under the condition of a low inversion. These violations thus occur at the locations of peak rush-hour traffic. Violations of the eight-hour standard, however, tend to occur in the evening and overnight and not near the locations of traffic peaks. Thus, the design of a totally adequate network for CO is very difficult. Since CO is a primary pollutant emitted directly from automobiles, and since it is inert, microscale effects on CO concentrations can be important. A peak station site should be adjacent to the street being studied. In street canyons the highest CO concentrations are frequently observed on the upwind side of the street as illustrated in Figure 77. Concentrations are reduced to near the urban background level at a distance of 200 to 300 feet from the roadway [82].

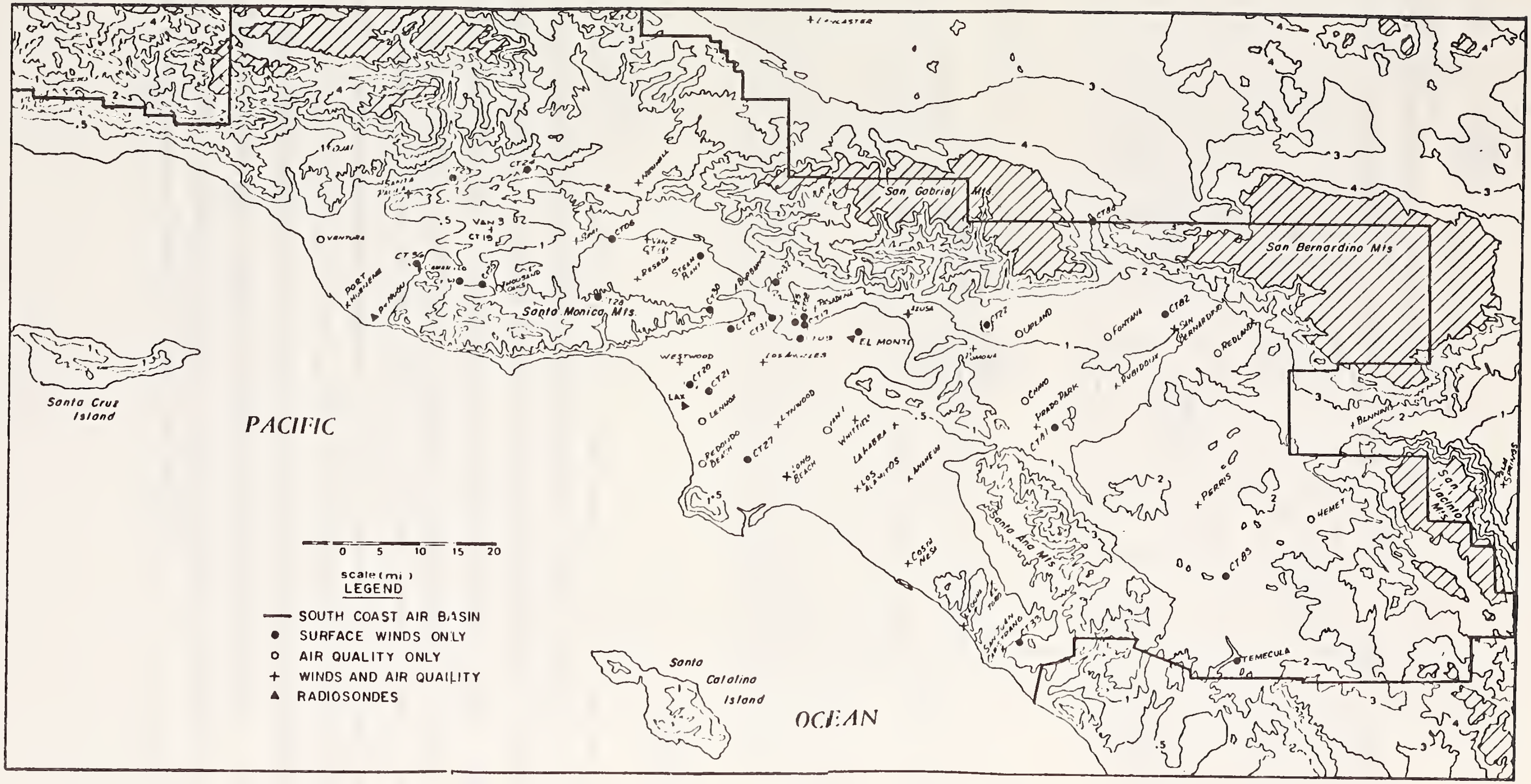
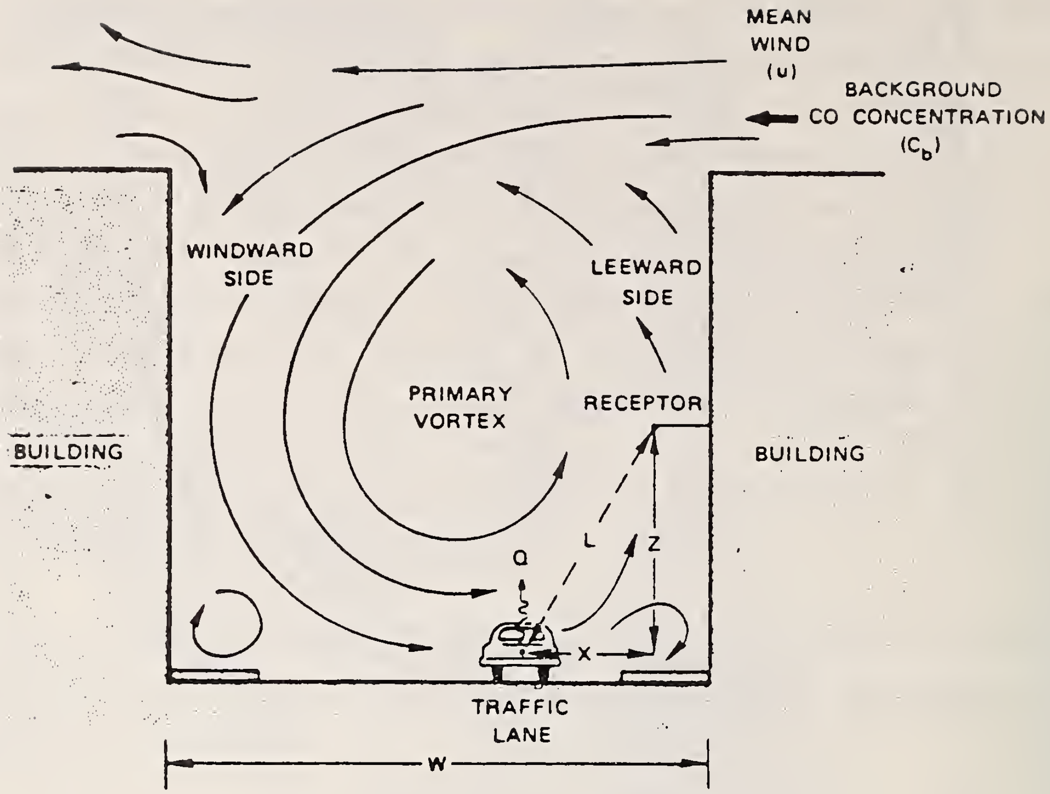


FIGURE 76. METEOROLOGICAL AND AIR QUALITY MONITORING STATIONS IN THE LOS ANGELES AREA IN JUNE 1974



Source: Ref. 177.

FIGURE 77. SCHEMATIC OF CROSS-STREET CIRCULATION IN A STREET CANYON

2. Oxidants

In the past it was assumed that, since photochemical oxidants are secondary pollutants, they would be spread relatively uniformly over large areas, and so relatively few monitors would suffice to establish concentrations. Other studies have shown, however, that concentrations can vary markedly over an urban area, with peak concentrations displaced from the area of maximum precursor emissions [178]. Moreover, photochemical oxidants are subject to microscale effects around roadways owing to the scavenging effect of NO emissions. Thus, it is useful to employ a photochemical model to indicate locations where oxidant monitoring would be advisable. The locations of the probes are not as important as they are for CO because oxidants are generally well mixed vertically. Monitors should not be located too near a highway because of the NO scavenging effect.

3. Nitrogen Dioxide

NO_2 is subject to an annual standard, but it exhibits short-term fluctuations in concentration because of its formation in photochemical reactions. The peak concentrations of NO_2 occur at different times of the day during the year, indicating different rates of reaction. Thus, peak concentrations will occur in different locations, making the placing of probes more difficult. NO_2 concentrations are generally monitored in a downtown area where microscale effects may be important. Additional guidance on placement, particularly for the assessment of mesoscale concentrations, can be obtained from the application of a photochemical model.

4. Particulates

For background measurements of particulates, a uniform distribution of monitoring sites in the study area is appropriate because particulates are a ubiquitous problem. Additional monitoring near roadways may be appropriate to measure the effect of reentrained dust. Particulate monitors have often been placed on rooftops of tall buildings, but it can be argued that this procedure does not adequately represent population exposure.

5. Sulfur Dioxide

The configuration of a sulfur dioxide monitoring network is usually similar to that for particulates, since these pollutants have many common sources. However, SO_2 is subject to shorter term standards. In a region dominated by area sources, the locations of the maxima for long and short averaging times are likely to coincide, whereas when large point sources are dominant, the short term maxima are likely to occur at different locations from the long term maxima. The total network is usually uniformly distributed, with one or more sites in areas of anticipated highest concentrations to monitor compliance with air quality standards. The locations of these maxima can be identified through consideration of emissions inventories or through air quality models.

E. INTERPRETATION OF MONITORING DATA

Upon completion of an air quality monitoring program, one is faced with a formidable volume of data. The uses to which these data are applied have been described--for example, assessing compliance with standards, identifying trends, and model development. This section describes the procedures used to bridge the gap between the raw data and the questions that the monitoring program was originally designed to answer. The discussion begins with techniques that are used to summarize data in characterizing air quality and then continues with descriptions of the statistical procedures for comparing air quality with standards and for using data for model input.

1. Data Summaries

Data summaries make large amounts of data easier to appreciate by highlighting their general features. Summary techniques include:

- Cross tabulations
- Histograms
- Frequency distributions
- Trend graphs
- Correlation plots
- Isopleth maps.

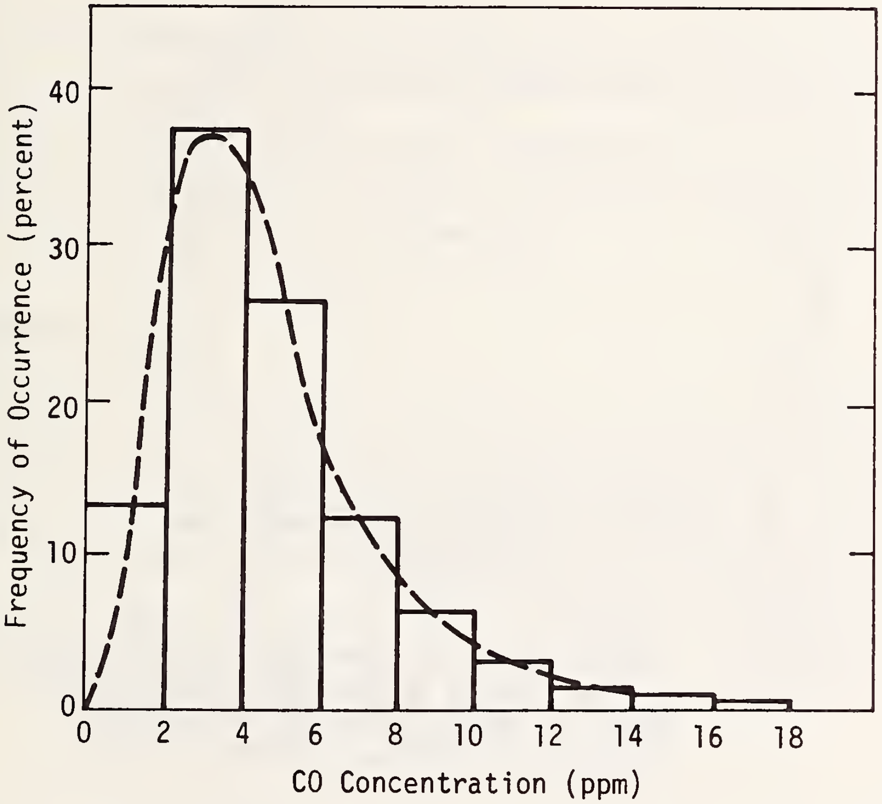
Each is discussed below.

a. Cross Tabulation

Tabulations of data can be readily prepared by computer once the data are entered. Tabulation is not the most lucid way of presenting data, but a carefully designed table can highlight the pertinent features of a data set. For instance, a table listing pollutant concentrations at all hours of the day, with different days presented side by side, can show differences in diurnal variations through a period of time. Cross tabulation of meteorological data with air quality data can be used to show relationships between the two. Most frequently, data tables are used in the appendix to a report to support conclusions and graphical descriptions in the main text.

b. Histograms

Histograms display the relative frequency of occurrence of different air pollutant concentrations, as shown in Figure 78. These diagrams enable easy visual estimates of average values and the range of values within a data set to be made. The number of intervals into which the data are divided should be chosen to strike a balance between detail in the histograms and the labor required for their preparation.

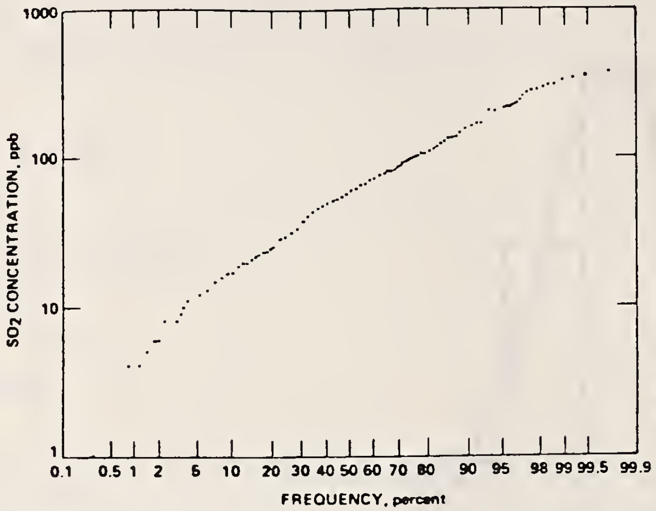


Source: Ref. 166.

FIGURE 78. EXAMPLE OF A HISTOGRAM: ONE-HOUR AVERAGE CO CONCENTRATIONS IN WASHINGTON, D.C. (CAMP) FROM 1962 THROUGH 1968

c. Frequency Distributions

Cumulative frequency distribution plots are commonly used in examining data sets. In such plots, each point represents the percentage of data values that are less than a given pollutant concentration. The plots for air quality data are generally made on lognormal probability graph paper, on which the concentration axis is logarithmic and the frequency axis is chosen such that if the data follow a lognormal distribution (the most commonly assumed statistical distribution for air pollutants), the points will fall along a straight line (see Figure 79).



Source: Ref. 179.

FIGURE 79. EXAMPLE OF A FREQUENCY DISTRIBUTION GRAPH: SULFUR DIOXIDE MEASUREMENTS FOR 1968 (24-HOUR) AT CAMP STATION IN PHILADELPHIA PLOTTED ON LOGNORMAL PROBABILITY PAPER

d. Trend Graphs

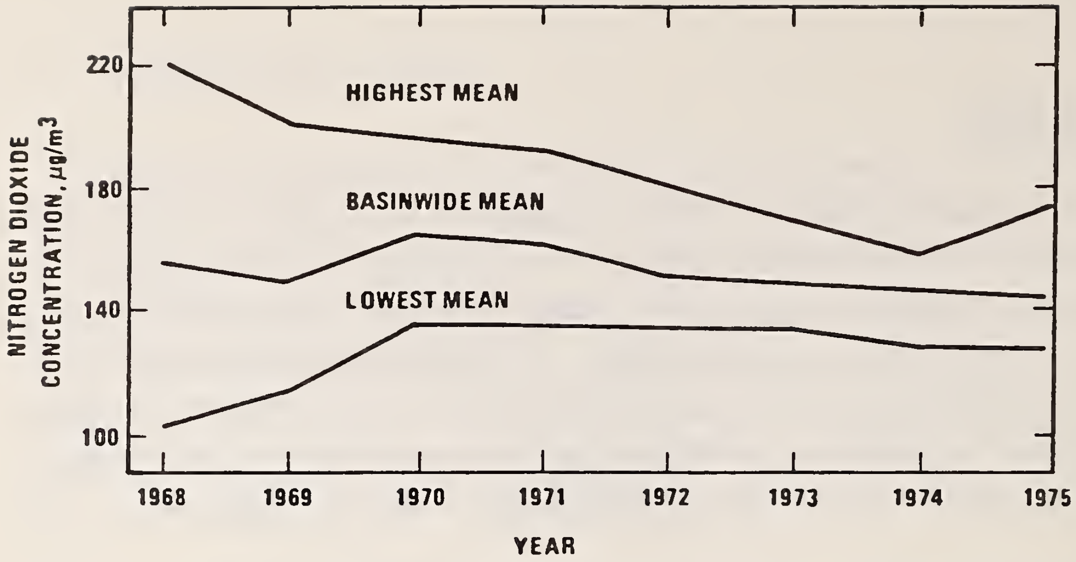
These plots are used to illustrate trends in air quality or population exposure to air pollutants with time. These trends can be traced over hourly, daily, seasonal, or any other appropriate time span, depending on the analysis being done. Such plots can illustrate whether air quality is improving or deteriorating in a particular location, and they can be used to demonstrate the need for further air quality regulation or the success of currently imposed regulations. Examples are shown in Figure 80.

e. Correlation Plots

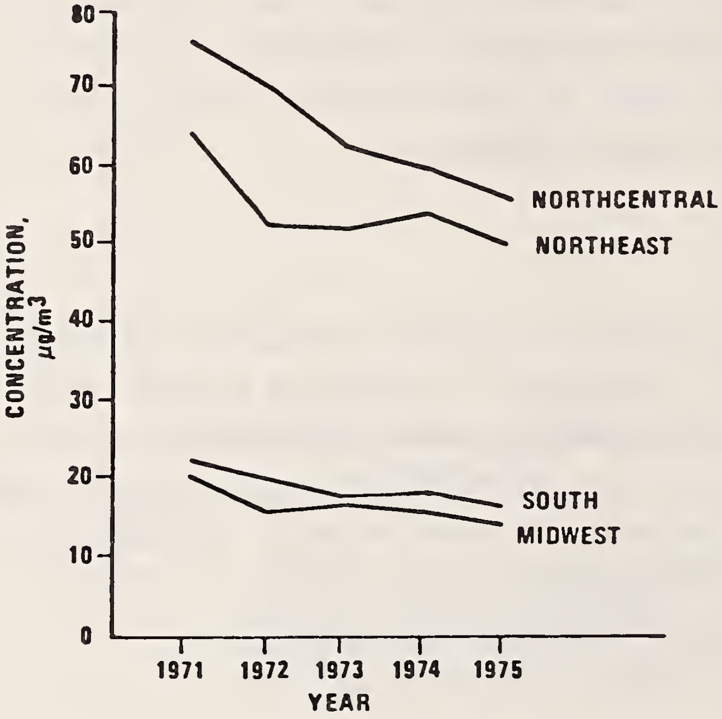
In correlation graphs, air quality data are plotted against some variable to illustrate a correlation between them. For instance, pollutant concentrations may be plotted against meteorological variables, such as wind speed and mixing depth, or other variables, such as distance from a source. Examples are shown in Figure 81.

f. Isopleth Maps

Isopleth maps are used to illustrate the spatial variations of pollutant concentrations. The contours on these maps represent equal concentrations in the same way in which contours represent elevation on topographic maps. Isopleth maps can be prepared by hand or by computer, though computer preparation requires access to plotting hardware. An example of an isopleth map is shown in Figure 82.



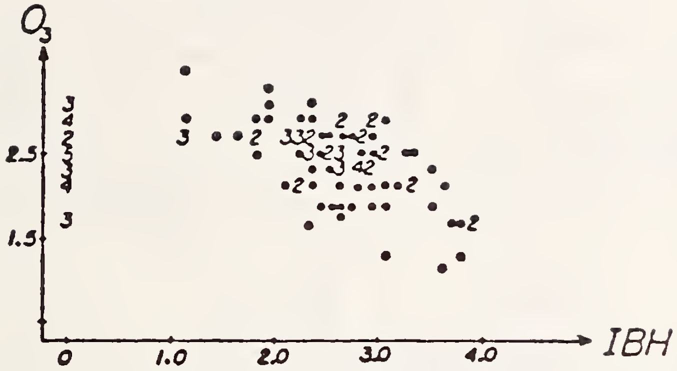
(a) Annual Mean Nitrogen Dioxide Levels in the Los Angeles Basin



(b) Ninetieth Percentile Trends for Sulfur Dioxide by Geographical Region

Source: Ref. 167.

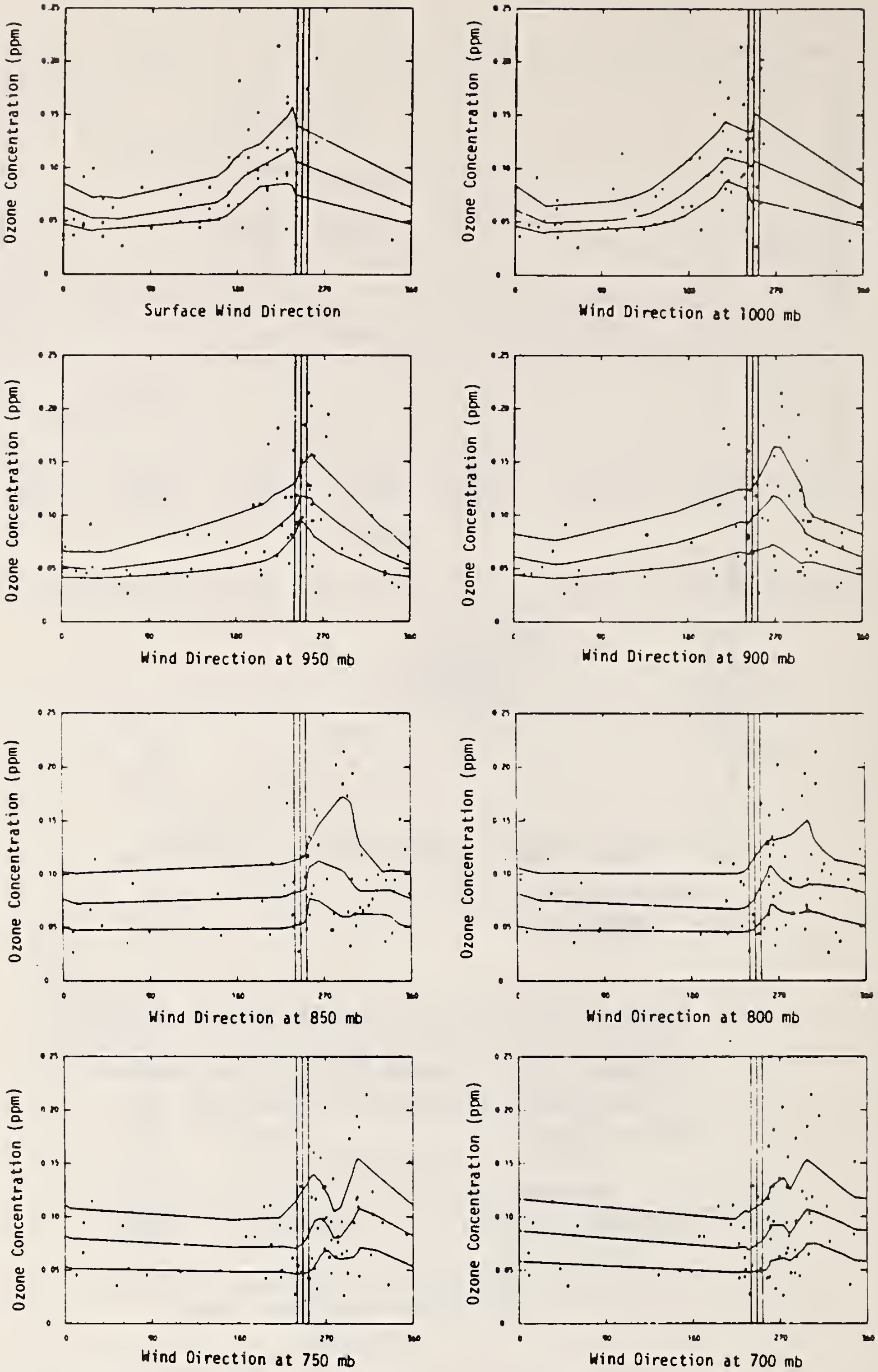
FIGURE 80. EXAMPLES OF TREND GRAPHS



Source: Ref. 114.

(a) Daily Maximum Hourly Readings of O_3 As a Function of Inversion Base Heights, July-October, 1970 (Logged Data). The numbers in the diagram give the frequencies at those points.

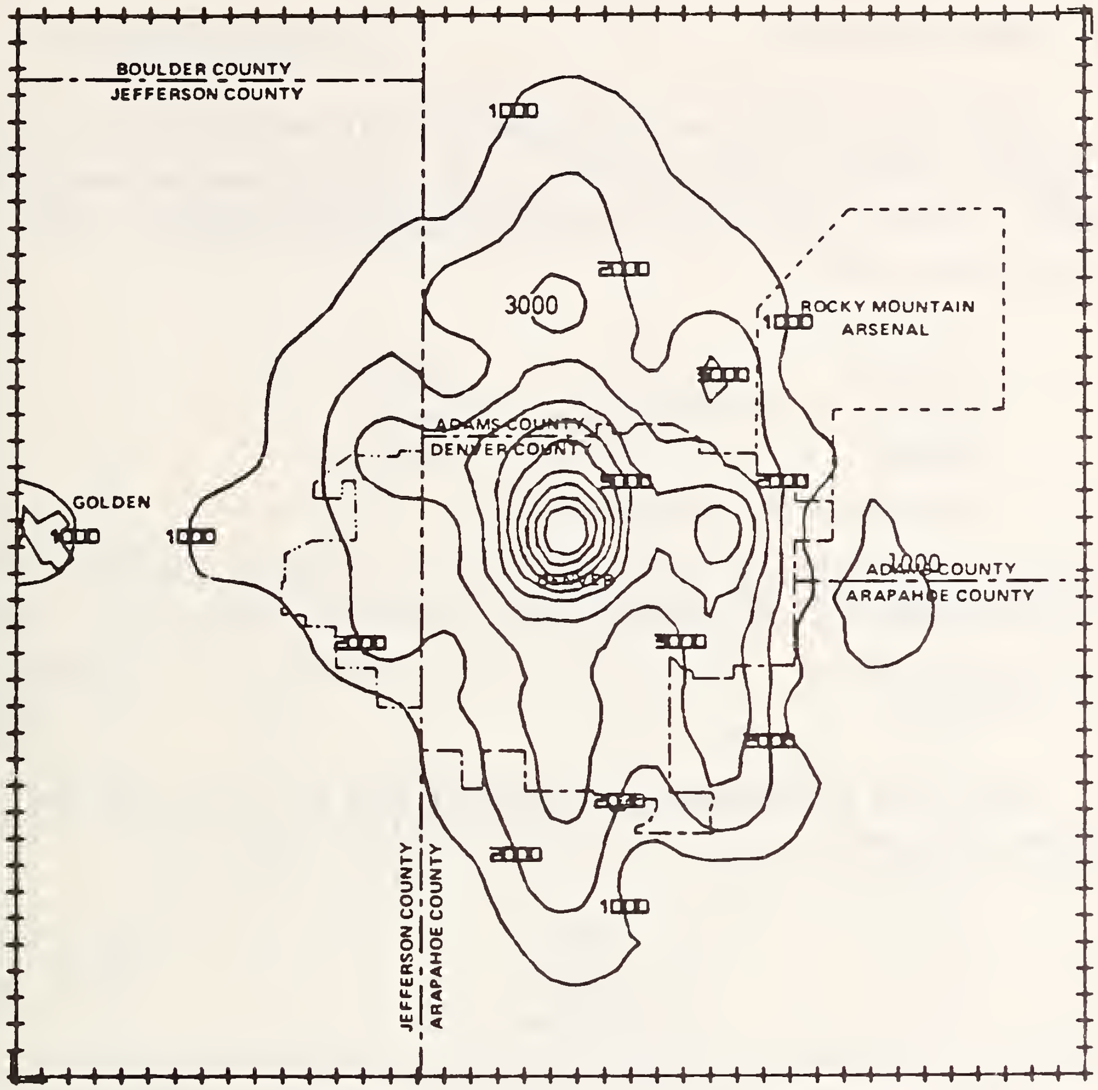
FIGURE 81. EXAMPLES OF CORRELATION PLOTS



Source: Ref. 180.

(b) Daily Maximum Ozone Concentrations (in ppm) in Fall River, Massachusetts Plotted Against Each of Eight Wind Directions from Chatham, Massachusetts, Measured at Different Heights, Ranging from Ground Level to 700 mb. Wind direction means the direction from which the wind is coming, with 0° denoting north and 180° denoting south. Curves of moving statistics are superimposed. The three vertical lines on each plot show the direction of of Chatham and Fall River from the New York City metropolitan area.

FIGURE 81 (Concluded)



City Denver Year 1970 Strategy Uncontrolled
Pollutant CO Case 2 Time Period 8 hour Total
Units $mg/m^3 x10^3$ Federal Standard 10 mg/m^3

Source: Ref. 181.

FIGURE 82. EXAMPLE OF AN ISOPLETH MAP: CO CONCENTRATIONS IN DENVER IN 1970

2. Data Statistics

Under this heading, we include methods that characterize data sets through a number or a set of numbers. They are all based on statistical theory; however, most do not require any complex calculations. The techniques include:

> Averages
> Measures of variation
> Maxima
> Time series and trend analysis.

These techniques are described below.

a. Averages

One of the simplest ways to describe a data set is by using its average, defined by

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} ,$$

where $\bar{x}$ = the average, x_i = the individual data values, and n = the number of data points. Another way of characterizing the general concentration level in a data set is to use the median, which is the concentration value above which 50 percent of the data values lie. Since air pollution concentration data are often considered to be lognormally distributed, a frequently used average is the geometric mean, defined by

$$GM = \exp\left(\frac{\sum_{i=1}^{n} \log x_i}{n}\right)$$

b. Measures of Variation

In addition to knowing the mean of a set of data, it is often of interest to have a measure of the variation about the mean. This measure is provided by the standard deviation:

$$S = \left[\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n} \right]^{1/2}$$

Another measure often used is the range, which is just the difference between the maximum and minimum values of the data. A third measure, which corresponds to the geometric mean, is the geometric standard deviation, defined by

$$GSD = \exp \left[\frac{\sum_{i=1}^{n} (\ell n \; x_i - \ell n \; GM)^2}{n} \right]^{1/2}$$

c. Maxima

The National Ambient Air Quality Standards are written in terms of the second-highest value in a specified time period. Thus, there is a need to identify the maximum concentration and the second-highest concentration. The value obtained for the latter depends on the sampling frequency: Frequent sampling yields higher values, as illustrated in Table 34.

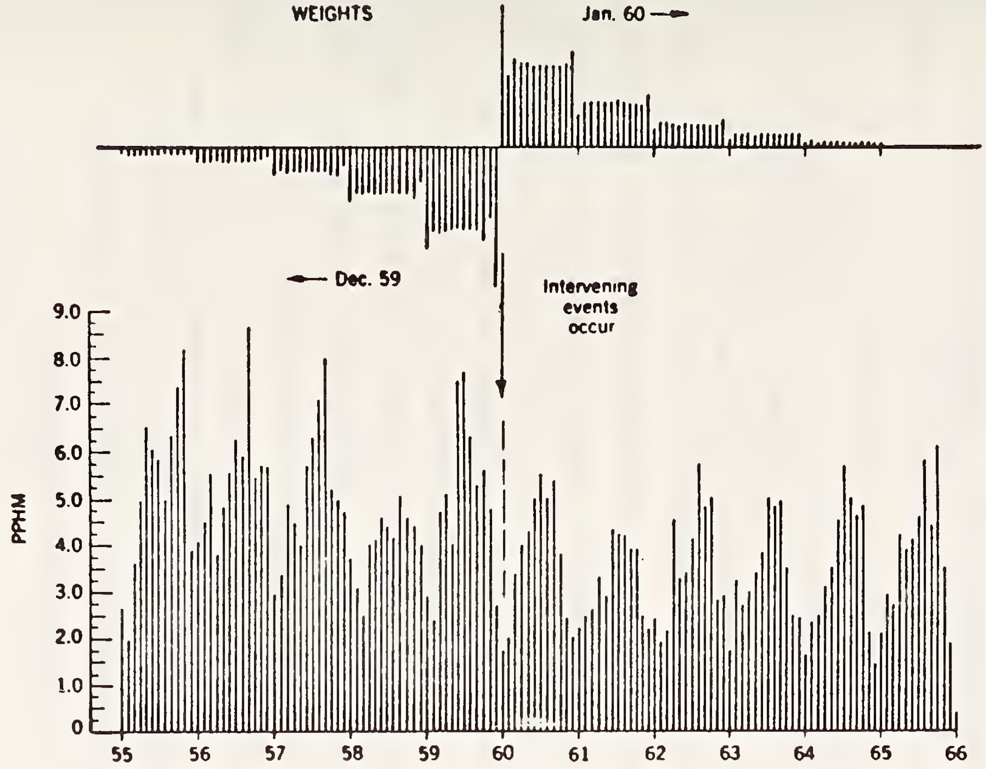
d. Time Series and Trend Analysis

The statistical theory required for these techniques is advanced, but these methods can produce important results when applied properly. For instance, the technique of intervention analysis was used to show the improvement in summer ozone concentrations in downtown Los Angeles that occurred as a result of events in 1960 (see Figure 83) [182-184].

TABLE 34. MAXIMUM AND SECOND-HIGHEST VALUES FOR VARIOUS SAMPLING SCHEMES (PHILADELPHIA, 1969)

Sampling Schedule	Observations	Maximum	Second Highest
Everyday	365	325	244
Every Sixth Day	61	219	215
"	61	195	171
"	61	244	238
"	61	215	211
"	61	325	234
"	60	239	205
Every Fifteenth Day	25	205	176
"	25	325	207
"	25	239	191
"	25	219	196
"	25	234	165
"	24	201	198
"	24	215	211
"	24	195	183
"	24	188	173
"	24	195	169
"	24	160	154
"	24	244	199
"	24	215	201
"	24	179	171
"	24	238	205

Source: Ref. 185.



Source: Ref. 184.

FIGURE 83 . EXAMPLE OF TIME SERIES AND TREND ANALYSIS GRAPH: MONTHLY AVERAGES OF O_3 IN DOWNTOWN LOS ANGELES (JANUARY 1955 TO DECEMBER 1965) AND WEIGHT FUNCTION FOR DETERMINING THE CHANGE IN 1960

3. Comparison of Data with Standards

Air quality data are extremely important in assessments of compliance with air quality standards, since the most direct and satisfactory way to demonstrate compliance or noncompliance is by using a complete data record in which the data are appropriate to the standard. If the data are unsatisfactory in some way (i.e., if data are missing or if the data averaging time is not that required by the standard), other methods need to be invoked. A simple method for predicting maximum concentrations and converting data for one averaging time to another is given in Ref. 13. This method is based on the assumption that air pollution concentration data for any averaging time are distributed lognormally. The first step in this method is to calculate the parameters that define the concentration distribution, namely, the geometric mean and the geometric standard deviation. These should be determined graphically, from a probability plot on lognormal graph paper [13]. Knowing the geometric mean and the standard geometric deviation, one can calculate the expected maximum annual average concentration. If the data set is incomplete, this method still allows prediction of the expected annual maximum. The geometric mean and standard geometric deviation are calculated from the data that are available, and these parameters are then used as above to calculate the expected annual maximum concentration. Care must be taken that the data are representative [for example, they should not all be from months when high (or low) pollution is expected]. Since this method allows monitoring data obtained at any averaging time to be reevaluated for any other averaging time, it provides a means of evaluating compliance with standards written for different averaging times. It may also reduce the amount of data required to characterize air quality in a region for pollutants that closely follow the lognormal distribution.

In comments on the interpretation of air quality data with respect to the NAAQS, it was pointed out that the use of a running average concentration over a time period may give maximum values that are higher than those calculated using discrete, nonoverlapping time intervals [186]. The differences between these two methods of calculating averages can also lead to greater observed exceedances of the NAAQS. This situation can result when the 8-hour running average exceeds the NAAQS for a 9- to 15-hour period. Use of nonoverlapping time intervals might indicate that the second-highest value did not exceed the standard. Another problem in assessing compliance with the NAAQS is that of sampling frequency. The calculated probability of detecting two or more days when the standard is exceeded at a site for various sampling frequencies, assuming that exceedances and monitoring are randomly distributed, is shown in Table 35.

TABLE 35. PROBABILITY OF SELECTING TWO OR MORE DAYS WHEN A SITE EXCEEDS THE STANDARD

Actual Number of Excursions	Sampling Frequency (days/year)		
	61/365	122/365	183/365
2	0.03	0.11	0.25
4	0.13	0.41	0.69
6	0.26	0.65	0.89
8	0.40	0.81	0.96
10	0.52	0.90	0.99
12	0.62	0.95	0.99
14	0.71	0.97	0.99
16	0.78	0.98	0.99
18	0.83	0.99	0.99
20	0.87	0.99	0.99
22	0.91	0.99	0.99
24	0.93	0.99	0.99
26	0.95	0.99	0.99

Source: Ref. 186.

The reliability of a monitoring system (as measured by the percentage of valid data it collects) has a great influence on both the probability of detecting an exceedance and on the reliability of estimation of the true extreme values. One study showed that if there were 10 exceedances in a year, a 70 percent reliable system would have a 99 percent probability of detecting at least 2 [187]. However, such a system would have only a 38 percent chance of detecting 8 of 10, and only 3 percent of detecting all 10. Thus, the probability that the highest observed concentration is the actual maximum is very small, even for a 70 percent reliable system.

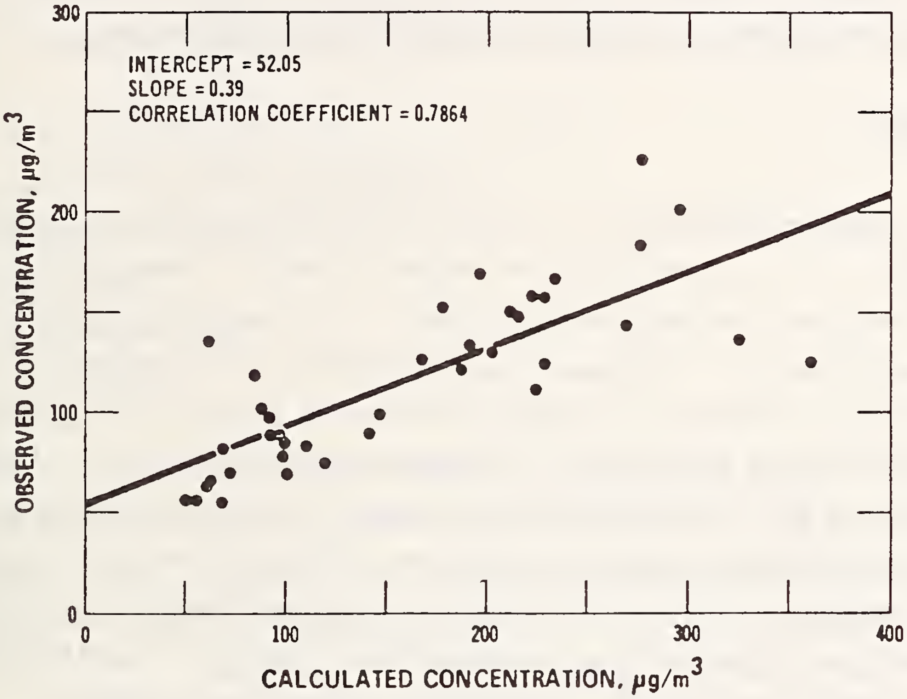
4. Model Development and Validation

As noted above, air quality monitoring data are frequently collected for the purpose of developing and validating AQSMs. In this application, actual data from the monitoring network are compared with the values predicted by the model. If the predicted values are close to the observed ones, the model can be considered as valid for calculating other concentrations where measurements were not made. These comparisons between observed and predicted concentrations can be made either graphically (see Figure 84) or statistically.

In the statistical approach, the most common methods used in validation studies are correlation and regression analysis. The correlation or linear association between two data sets is given by the correlation coefficient, ρ, defined by

$$\rho = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\left[\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2\right]^{1/2}} \quad .$$

A high correlation between observed and predicted values indicates a high degree of validity for the model. A low correlation does not necessarily indicate that the model is defective, however. Many possible sources of error are implicit in both the observed values and the model predictions. The former can be subject to instrumental errors, and the latter can have errors in input values as well as deficiencies in formulation. Errors are normally relatively large at low concentrations because such amounts cannot be measured accurately. This problem is usually not of concern since most applications focus on elevated concentrations. Another potential problem is that the predictions can be out of phase on the time axis with the observations, which could result in low observed correlation but may not indicate a serious defect in the model.



Source: Ref. 127.

FIGURE 84. GRAPHICAL COMPARISON OF PREDICTED (SOLID LINE) AND OBSERVED (DOTS) SO_2 CONCENTRATION IN ST. LOUIS FROM 1 DECEMBER 1964 THROUGH 28 FEBRUARY 1965

The technique of regression analysis is often used to establish a relationship between observed and calculated concentrations. It is assumed that a linear relationship of the form $y = a + bx$ exists between the observed values y and the calculated values x. Regression analysis is used to evaluate the coefficients a and b. This relationship then provides a means of converting calculated concentrations into values that correspond with the measured ones. Use of the regression analysis procedure enables statistical tests to be made of the significance of the linear relationship between measured and computed values.

F. SUMMARY

This chapter discusses the design and implementation of air monitoring networks. It is clear from the range of topics covered that this activity requires the application of many skills and disciplines to obtain useful results. Although highway planners will seldom, if ever, be called upon to design a mesoscale monitoring program, background information on such programs is included because planners will frequently be required to work with mesoscale air quality data. In contrast, microscale monitoring programs are far more likely to be instituted by highway planning personnel; the material contained herein is intended to provide the planner with an understanding of the air quality monitoring issues that are involved in planning construction projects.

APPENDIX
A LIST OF AIR QUALITY MODELS

This appendix lists some air quality models in each of six classes:

- > Statistical-empirical
- > Theoretical kinetic mechanisms
- > Algebraic models
- > Box models
- > Trajectory models
- > Wind models.

Within each class, models are listed in alphabetical order. A reference is cited for each model if possible, and the source, or model developer, is listed if that information is not apparent from the reference. Although this appendix lists all models with which the authors are familiar, it may not be inclusive. Inclusion of a model in this list should not be construed as an indication of the model's usefulness, state of development, or availability. Some of the models listed herein are the products of groups no longer active in air quality modeling. Nevertheless, this list provides highway planners and engineers with a list of many, perhaps most, of the air quality models in existence.

TABLE A-1. A LIST OF SOME AIR QUALITY MODELS

(a) Statistical-Empirical Models

Model	Source	Reference
"Appendix J" Modified Rollback	--	40 C.F.R. §51.14(c)(4)(1975)
Bailey	--	B. S. Bailey (1975), "Oxidant-HC-NO_x Relationships from Aerometric Data--L.A. Studies," Scientific Seminar on Automotive Pollutants, 10-12 February 1975, Washington, D.C.
Caporaletti et al. (SDAIR)	--	J. M. Caporaletti et al. (1974), "Photochemical Air Quality Prediction Model for Complex Source Evaluation and Land Use and Transportation Planning," Appendix II to a report for the Office of Environmental Management, County of San Diego, by the Department of Chemistry and Energy Center, University of California at San Diego, La Jolla, California.
Hamming	--	W. Hamming et al. (1973), "Motor Vehicle Control and Air Quality: The Path to Clean Air for Los Angeles," 66th Annual Meeting, Air Pollution Control Association, 24-28 June 1973, Chicago, Illinois.
Kinosian and Paskind	--	J. J. Paskind and J. R. Kinosian (1974), "Hydrocarbons, Oxides of Nitrogen and Oxidant Relationships in the Atmosphere Over California Cities," 67th Annual Meeting, Air Pollution Control Association, 9-13 June 1974, Denver, Colorado.

TABLE A-1 (continued)

Model	Source	Reference
Linear Rollback	--	Environmental Protection Agency (1974), "Applying Atmospheric Simulation Models to Air Quality Maintenance Regions," Report 450, in "Guidelines for Air Quality Maintenance Planning and Analysis," EPA-450/4-74-013 (OAQPS No. 1.2-031) Vol. 12, Office of Air Waste Management and Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.
Merz et al.	--	P. H. Merz, L. J. Painter, and P. R. Ryason (1972), "Aerometric Data Analysis, Time Series Analysis and Forecast, and an Atmospheric Smog Diagram," *Atmos. Environ.*, Vol. 6, pp. 319-342.
Schuck and Papetti Modified Rollback	--	E. A. Schuck and R. A. Papetti (1973), "Examination of the Photochemical Air Pollution Problem in the Southern California Area," Appendix D to EPA Region IX Technical Support Document for the Metropolitan Los Angeles Intrastate Air Quality Control Region Transportation Control Plan Final Promulgation, Environmental Protection Agency, Research Triangle Park, North Carolina.

TABLE A-1 (continued)

Model	Source	Reference
Tiao et al.	--	G. C. Tiao, M. S. Phadke, and G.E.P. Box (1975), "Some Empirical Models for the Los Angeles Photochemical Smog Data," Paper 75-51-5, 68th Annual Meeting, Air Pollution Control Association, 15-20 June 1975, Boston, Massachusetts.
Trijonis	--	J. C. Trijonis (1974), "An Economic Air Pollution Control Model Application: Photochemical Smog in Los Angeles County in 1975," Environ. Sci. Technol., Vol. 8, p. 811.

TABLE A-1 (continued)

(b) Theoretical Kinetic Mechanisms

Model	Source	Reference
Empirical Kinetic Modeling Approach [EKMA](Dimitriades-Dodge)	--	Environmental Protection Agency (1977), "Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors," EPA-450/2-77-021a, Research Triangle Park, North Carolina. M. C. Dodge (1977), "Combined Use of Modeling Techniques and Smog Chamber Data To Derive Ozone-Precursor Relationships," International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings: Volume II, EPA-600/3-77-001b, p. 805, Environmental Protection Agency, Research Triangle Park, North Carolina. B. Dimitriades (1977), "An Alternative to the Appendix J Method for Calculating Oxidant- and NO_2-related Control Requirements," ibid., p. 871. B. Dimitriades (1977), "Oxidant Control Strategies, Part 1: An Urban Oxidant Control Strategy Derived from Existing Smog Chamber Data," Environ. Sci. Technol., Vol. 11, p. 80. G. Z. Whitten, and H. Hogo (1978), "User's Manual for a Kinetics Model and Ozone Isopleth Plotting Package," Final Report under EPA Contract 68-02-2428 by Systems Applications, Incorporated, San Rafael, California.

TABLE A-1 (continued)

Model	Source	Reference
Systems Applications, Incorporated, EKMA	--	G. Z. Whitten, M. Meldgin, and P. M. Roth (1977), "A Preliminary Evaluation of the Potential Influence of Varying HC/NOx Ratios on the Design of Oxidant Control Strategies," EF77-33R, Systems Applications, Incorporated, 950 Northgate Drive, San Rafael, California.

TABLE A-1 (continued)

(c) Algebraic Models

Model	Source	Reference
Aerovironment	--	P.B.S. Lissaman (1973), "A Simple Unsteady Model Explicitly Incorporating Ground Roughness and Heat Flux," 66th Annual Meeting of the Air Pollution Control Association, 24-28 June 1973, Chicago, Illinois.
Air Quality Display Model (AQDM)	TRW Systems Group, Redondo Beach, California	J. E. Sparks (1975), "Survey of Environmental Protection Agency Air Pollution Computer Program," Annual Simulation Symposium, Tampa, Florida.
Air Quality Implementation Planning Program (AQIPP)	TRW Systems Group, Redondo Beach, California	J. E. Sparks (1975), "Survey of Environmental Protection Agency Air Pollution Computer Program," Annual Simulation Symposium, Tampa, Florida.
Air Quality Short Term Model (AQSTM)	--	Illinois Environmental Protection Agency (1976), "Air Quality Short Term Model," Springfield, Illinois.
APRAC	Stanford Research Institute, Menlo Park, California	W. Johnson, F. L. Ludwig, and A. Moon (1970), "Development of a Practical Multipurpose Urban Diffusion Model for Carbon Monoxide," *Proceedings of Symposium on Multiple-Source Urban Diffusion Models*, No. AP-86, Environmental Protection Agency, Research Triangle Park, North Carolina.
APRAC-1A	Stanford Research Institute, Menlo Park, California	R. L. Mancuso, and F. L. Ludwig (1973), "User's Manual for the APRAC-1A Urban Diffusion Model Computer Program," EPA-650/3-73-001 (NTIS PB 213091), Environmental Protection Agency, Research Triangle Park, North Carolina.

TABLE A-1 (continued)

Model	Source	Reference
Climatological Dispersion Model (CDM)	Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina	A. D. Busse and J. R. Zimmerman (1973), "User's Guide for the Climatological Dispersion Model," EPA-R4-73-024, Environmental Protection Agency, Research Triangle Park, North Carolina.
ERTAQ	Environmental Research & Technology, Inc., 2030 Alameda Padre Serra, Santa Barbara, California	--
HIWAY	Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina	J. R. Zimmerman and R. S. Thompson (1975), "User's Guide for HIWAY, A Highway Air Pollution Model," EPA-650/4-74-008, Environmental Protection Agency, Research Triangle Park, North Carolina.
NOAA Dispersion Model	--	G. E. Start, N. R. Ricks, and C. R. Dickson (1974), "Effluent Dilutions Over Mountainous Terrain," Technical Memorandum ERL-ARL-51, Environmental Research Laboratories, National Oceanic and Atmospheric Administration, Idaho Falls, Idaho.
Plume Fumigation Model (PFM)	--	P. M. Roth et al. (1975), "An Examination of the Accuracy and Adequacy of Air Quality Models and Monitoring Data for Use in Assessing the Impact of Significant Deterioration Regulations on Energy Developments," EF75-58R, Systems Applications, Incorporated, San Rafael, California.

TABLE A-1 (continued)

Model	Source	Reference
PTDIS (DBT-43)	Meteorology Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina.	D. B. Turner and H. D. Busse (1973), "User's Guides to the Interactive Versions of Three Point Source Dispersion Programs: PTMAX, PTDIS, and PTMTP," 21ADN, Environmental Protection Agency, Research Triangle Park, North Carolina.
PTMAX (DBT-13)	Meteorology Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina.	D. B. Turner and H. D. Busse (1973), "User's Guides to the Interactive Versions of Three Point Source Dispersion Programs: PTMAX, PTDIS, and PTMTP," 21ADN, Environmental Protection Agency, Research Triangle Park, North Carolina.
PTMTP (DBT-51)	Meteorology Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina.	D. B. Turner and H. D. Busse (1973), "User's Guides to the Interactive Versions of Three Point Source Dispersion Programs: PTMAX, PTDIS, and PTMTP," 21ADN, Environmental Protection Agency, Research Triangle Park, North Carolina.
PTMTP-W (DBT-51W)	--	Environmental Protection Agency (1975), "User's Manual for Short-Term Models," Region III, Atlanta, Georgia.
Real Time Air Quality Simulation Model (RAM)	--	D. B. Turner and J. H. Novak (1977), "User's Guide for RAM," Environmental Protection Agency, Research Triangle Park, North Carolina.

TABLE A-1 (continued)

Model	Source	Reference
Short-Z	H. E. Cramer Company, Inc., 540 Arapeen Drive, University of Utah Research Park, Salt Lake City, Utah	H. E. Cramer, H. V. Geary, and J. F. Bowers (1975), "Diffusion-Model Calculations of Long-Term and Short-Term Ground Level SO_2 Concentrations in Allegheny County, Pennsylvania," EPA-903/9-75-018, Environmental Protection Agency, Research Triangle Park, North Carolina.
Single Source (CRSTER) Model	Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina	Environmental Protection Agency (1977), "User's Manual for Single Source (CRSTER) Model," EPA-450/2-77-013 (NTIS PB 271360), Research Triangle Park, North Carolina.
Texas Climatological Model (TCM)	--	R. A. Porter and J. H. Christiansen (1976), "Two Efficient Gaussian Plume Models Developed at the Texas Air Control Board," *Proceedings of the Seventh NATO/CCMS International Technical Meeting on Air Pollution Modeling*, Airlie House, Virginia (September 1976).
Texas Episodic Model (TEM)	--	R. A. Porter and J. H. Christiansen (1976), "Two Efficient Gaussian Plume Models Developed at the Texas Air Control Board," *Proceedings of the Seventh NATO/CCMS International Technical Meeting on Air Pollution Modeling*, Airlie House, Virginia (September 1976). J. H. Christiansen (1976), "User's Guide to the Texas Episodic Model," Texas Air Control Board, Austin, Texas.

TABLE A-1 (continued)

Model	Source	Reference
Valley (C9M3D)	Meteorology Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina	E. W. Burt (1975), "Description of the Valley Model (C9M3D)," Environmental Protection Agency, Research Triangle Park, North Carolina. Environmental Protection Agency (1975), "Evaluation of Selected Air Pollution Dispersion Models Applicable to Complex Terrain," EPA-450/3-75-059, Research Triangle Park, North Carolina.

TABLE A-1 (continued)

(d) Box Models

Model	Source	Reference
CHEMK	--	G. Z. Whitten and J. P. Meyer (1976), "CHEMK: A Computer Modeling Scheme for Chemical Kinetics," CS75-70R2, Systems Applications, Incorporated, San Rafael, California.
Gifford-Hanna	Atmospheric Turbulence and Diffusion Laboratory (ATDL) National Oceanic and Atmospheric Administration, Oak Ridge, Tennessee	S. R. Hanna (1973), "A Simple Model for the Analysis of Chemically Reactive Pollutants," *Atmos. Environ.*, Vol. 7, pp. 803-817.
MODKIN	--	D. C. Whitney (1974), "MODKIN: A Computer Program for the Automatic Construction of Chemical Kinetics Mechanisms and Solution of Their Governing Equations," R73-51, Systems Applications, Incorporated, San Rafael, California.

TABLE A-1 (continued)

(e) Trajectory Models

Model	Source	Reference
ARTSIM	Environmental Research & Technology, Inc., 2030 Alameda Padre Serra, Santa Barbara, California	Environmental Research & Technology, Inc. (1977), "Lagrangian Photochemical/Diffusion Model", 2030 Alameda Padre Serra, Santa Barbara, California
ATRAJBOX	Environmental Research & Technology, Inc., 2030 Alameda Padre Serra, Santa Barbara, California	--
DIFKIN	General Research Corporation, Santa Barbara, California	J. R. Martinez, R. A. Nordsieck, and M. A. Hirschberg (1973), "User's Guide to Diffusion/Kinetics (DIFKIN) Code," General Research Corporation, Santa Barbara, California.
GRC	General Research Corporation, Santa Barbara, California	A. Q. Eschenroeder and J. R. Martinez (1971), "Concepts and Applications of Photochemical Smog Models," Tech. Mem. 1516, General Research Corporation, Santa Barbara, California.
LAPS	Environmental Research & Technology, Inc., 2030 Alameda Padre Serra, Santa Barbara, California	R. A. Nordsieck (1977), "A Local Air Pollution Simulator (LAPS); Volume I, User's Guide," Environmental Research & Technology, 2030 Alameda Padre Serra, Santa Barbara, California.

TABLE A-1 (continued)

Model	Source	Reference
Reactive Environmental Simulation Model (REM)	Pacific Environmental Services, Inc., 2932 Wilshire Boulevard, Santa Monica, California	L. G. Wayne, A. Kokin, and M. I. Weisburd (1973), "Controlled Evaluation of the Reactive Environmental Simulation Model (REM)," EPA-R4-73-013a, Environmental Protection Agency, Research Triangle Park, North Carolina.
Reactive Plume Model (RPM)	Systems Applications, Inc., 950 Northgate Drive, San Rafael, California	M. K. Liu, M. A. Yocke, and P. Mundkur (1975), "Numerical Simulation of Reactive Plumes," 68th Meeting of American Institute of Chemical Engineers, Los Angeles, California. M. K. Liu et al. (1976), "The Chemistry, Dispersion, and Transport of Air Pollutants Emitted from Fossil Fuel Power Plants in California," Systems Applications, Incorporated, San Rafael, California.
TRAJ	Systems Applications, Incorporated, 950 Northgate Drive, San Rafael, California (in preparation)	

TABLE A-1 (continued)

(f) Grid Models

Model	Source	Reference
Buoyant Plume Model (BPM)	Systems Applications, Incorporated San Rafael, California	M. K. Liu et al. (1976), "The Chemistry, Dispersion and Transport of Air Pollutants Emitted from Fossil Fuel Power Plants in California," EF76-18R, Systems Applications, Incorporated, San Rafael, California.
Denver Air Quality Model (DAQM)	Systems Applications, Incorporated San Rafael, California	G. E. Anderson et al. (1977), "Air Quality in the Denver Metropolitan Region: 1974-2000," EPA-908/1-77-002, Environmental Protection Agency, Region VIII, Denver, Colorado.
DEPICT (Detailed Examination of Plume Impact in Complex Terrain)	Science Applications, Incorporated, 875 Westlake Boulevard, Westlake Village, California	R. C. Sklarew and J. C. Wilson (1976), "Applications of DEPICT to the Garfield, Navajo, and Ormond Beach Air Quality Data Bases," Science Applications, Incorporated, Westlake Village, California. R. C. Sklarew, J. C. Wilson, and A. Fabrick (1976), "Evaluation of Air Quality Models: Point Source Models," Science Applications, Incorporated, Westlake Village, California.
EGAMA	Environmental Research & Technology, 2030 Alameda Padre Serra, Santa Barbara, California	B. A. Egan and J. R. Mahoney (1972), "Numerical Modeling of Advection and Diffusion of Urban Area-Source Pollutants," J. Appl. Meteor., Vol. 11, pp. 312-322. B. A. Egan and J. R. Mahoney (1972), "Applications of a Numerical Air Pollution Transport Model to Dispersion in the Atmospheric Boundary Layer," J. Appl. Meteor., Vol. 11, pp. 1023-1039.

TABLE A-1 (continued)

Model	Source	Reference
IBM Plume Model	IBM Research Center, Monterey and Cattle Roads, San Jose, California	C. C. Shir (1972), "Numerical Investigation of the Atmospheric Dispersion of Stack Effluents," IBM Journal of Research, Vol. 16, pp. 171-179.
Intera Model	Intera Environmental Consultants, 2000 West Loop South, Suite 2200, Houston, Texas	Environmental Protection Agency (1976), "Evaluation of Selected Air Pollution Dispersion Models Applicable to Complex Terrain," EPA-450/3-76-059, Office of Air and Waste Management, Research Triangle Park, North Carolina.
Livermore Region Air Quality Model (LIRAQ)	Lawrence Livermore Laboratory, University of California, Livermore, California	J. B. Knox et al. (1974), "Development of an Air Pollution Model for the San Francisco Bay Area," UCRL-51537, Lawrence Livermore Laboratory, University of California, Livermore, California. M. C. MacCracken and G. D. Sauter, eds. (1975), "Development of an Air Pollution Model for the San Francisco Bay Area," UCRL-51920, Vol. 1, Lawrence Livermore Laboratory, University of California, Livermore, California.
PIC	Systems, Science, and Software San Diego, California	R. C. Sklarew, A. J. Fabrick, and J. E. Prager (1971), "A Particle-In-Cell Method for the Numerical Solution of the Atmospheric Diffusion Equation, and Applications to Air Pollution Problems--Final Report," EPA Contract No. 68-02-0006, Environmental Protection Agency, Research Triangle Park, North Carolina.

TABLE A-1 (continued)

Model	Source	Reference
Plume Dispersion Model (PDM)	Systems Applications, Incorporated San Rafael, California	M. K. Liu et al. (1976), "The Chemistry, Dispersion and Transport of Air Pollutants Emitted from Fossil Fuel Power Plants in California," EF76-18R, Systems Applications, Incorporated, San Rafael, California.
Systems Applications Airshed Model-I	Systems Applications, Incorporated San Rafael, California	S. D. Reynolds, P. M. Roth, and J. H. Seinfeld (1973), "Mathematical Modeling of Photochemical Air Pollution--I: Formulation of the Model," Atmos. Environ., Vol. 7, pp. 1033-1061.
Systems Applications Airshed Model-II	Systems Applications, Incorporated San Rafael, California	S. D. Reynolds et al. (1977),"Continued Research in Mesoscale Air Pollution Simulation Modeling," EPA-600/4-76-016a,b,c,d, and three volumes in preparation, Environmental Protection Agency, Research Triangle Park, North Carolina.
TAPAS (Topographic Air Pollution Analysis System)	--	M. A. Fosberg and D. G. Fox (1978), "A Topographic Air Pollution Analysis System," to be submitted to Atmos. Environ. M. A. Fosberg and D. G. Fox (1977), "An Air Quality Index to Aid in Determining Mountain Land Use," Proc. Fourth National Conference on Fire and Forest Meteorology, pp. 167-170, Gen. Tech. Rep. RM-32, Forest Service, U.S. Department of Agriculture.

TABLE A-1 (concluded)

Model	Source	Reference
TAPAS (Topographic Air Pollution Analysis System) (continued)	--	M. A. Fosberg et al. (1976), "Nonturbulent Dispersion Processes in Complex Terrain," Atmos. Environ., Vol. 10, pp. 1053-1055.
		M. A. Fosberg, W. E. Marlatt, and L. Krupnak (1976), "Estimating Airflow Patterns Over Complex Terrain," Research Paper No. 162, Forest Service, U.S. Department of Agriculture.
		D. G. Fox et al. (1976), "An Experimental Study of Mountain Meteorology," Proc. Third Symposium on Atmospheric Turbulence Diffusion and Air Quality, American Meteorological Society, Boston, Massachusetts.

GLOSSARY

Å. Angstrom; equal to 10^{-1} nanometers or 10^{-10} meters.

Absorption. A process in which a substance (or energy) penetrates and is nearly uniformly distributed within a suitable gas, liquid, or solid substance.

Accuracy. A measure of how close a measurement is to the actual value.

Acetylene. H-C≡C-H; a light, relatively unreactive hydrocarbon found in the atmosphere whose major source is automobile exhaust. Because of its inertness to photochemical reactions, it is commonly used as an indicator of mobile source (auto) pollution.

Adiabatic process. A process in which heat is neither given to nor taken from a system.

Adsorption. A process in which a substance is collected on a suitable interface between a gas, liquid, or solid and a liquid or solid.

Advection. Transport of material (e.g., pollutants) by the wind.

Aerometric. Referring to measurement in the atmosphere (e.g., of wind velocity, sunlight intensity, or pollutant concentration).

Aerosol. A suspension of fine solid or liquid particles in the air, such as smoke, haze, and fog; also, the particles that make up this suspension.

Age (of an air mass). The amount of chemical reaction that has been experienced by an air mass as compared with the amount of reaction possible. An "aged" air mass has experienced most of its "chemical reaction potential."

Air parcel. Any air mass that is assumed to retain its identity; i.e., to be relatively free of mass interchanges with its surroundings.

Air quality data base. A collection of information about ambient pollutant concentrations that existed within an area during a particular time period.

Air quality model. A relationship between pollutant emissions and pollutant concentrations.

Air quality monitor. A device for measuring pollutant concentrations.

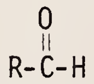
Air quality standard. A legal requirement on air quality, usually expressed in terms of a maximum allowable pollutant concentration averaged over a specified interval.

Airshed. A geographical region in which the air flow patterns are such that emissions sources within the region affect primarily the receptors within the region, and these receptors are affected primarily by those sources.

Air stagnation index. A measure of atmospheric diffusion and transport representing the degree of approach to stagnation (zero dispersal) conditions.

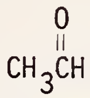
Albedo. Fraction of light reaching a surface that is reflected.

Aldehyde. A partially oxidized hydrocarbon with the structure



$$\mathrm{R}\text{-}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\text{-}\mathrm{H}$$

where R is a hydrogen atom or organic group, i.e., acetaldehyde,

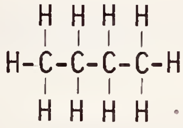


$$CH_3\overset{\overset{O}{\|}}{C}H \quad .$$

Aldehydes are formed by oxidation of hydrocarbons and are easily oxidized. Aldehyde photolysis produces radicals.

Algorithm. A calculation procedure used to solve a problem.

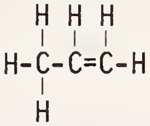
Alkane. A hydrocarbon containing only carbon-hydrogen and carbon-carbon single bonds, e.g., butane,



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array} \quad .$$

Alkanes of low molecular weight are colorless, flammable gases that react slowly in photochemical oxidant formation.

Alkene. A hydrocarbon containing one or more carbon-carbon double bonds, e.g., propylene,



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & = & C & - & H \\ & & | & & & & & & \\ & & H & & & & & & \end{array} \quad .$$

Alkenes are also called olefins. Low molecular weight alkenes are colorless, flammable gases that react rapidly in photochemical oxidant formation.

Aloft. At a height (variably defined) above the surface.

Ambient. Pertaining to conditions near a point of interest as they would be without any purely local disturbance.

Ambient concentration. The concentration of a substance at some point as it would be without any local sources or sinks of that substance.

Ambient monitoring. Systematic measurements of the characteristics (e.g., pollutant concentration and wind velocity) of the air at a fixed location.

Anomalous concentration. A concentration that is much higher or much lower, relative to the usual variations, than the concentration a short distance or a short time away.

Anthropogenic. Resulting from man's activities.

Anticyclone. A large system of winds rotating about a high pressure center.

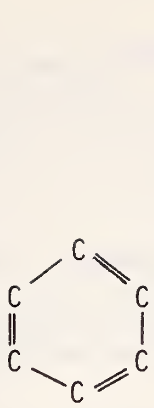
Appendix J. An empirical curve relating maximum oxidant concentrations to 6 a.m. - 9 a.m. hydrocarbon emissions. This curve was formerly recommended by the EPA for calculating hydrocarbon emissions reductions necessary to meet air quality standards.

AQCR. Air Quality Control Region; a region designated by the EPA that has significant air pollution or the potential for significant air pollution. The region includes all the counties that are affected by or have sources that contribute directly to the air quality of the region.

Area oxidant plume. A plume formed downwind of an area source of oxidant precursors.

Area source. The agglomeration of many point sources, such as home heaters, that have low emissions rates, are spread over a large area, and are to numerous to treat individually.

Aromatic. Containing a benzene ring:



Aromatic hydrocarbons are more stable than olefins, which also have double bonds.

Arterial. A large, well-traveled street, usually with traffic signals and without limited access.

atm. Atmosphere; the nominal atmospheric pressure at sea level is 1 atm.

Atmospheric stability. The resistance to or enhancement of vertical air movement caused by the vertical temperature profile. See Temperature inversion.

Background concentration. Pollutant concentration in the absence of effects from local anthropogenic emissions.

Base year. The year associated with data used as a common reference point for comparison with data collected in other years.

Boundary conditions. The values of a variable at each point along the boundaries of a region being analyzed. Such values are necessary to determine the solution within the region.

Box model. A mathematical model that assumes that all emissions and reactions take place in a single well-mixed air parcel in which all conditions are homogeneous.

Calibration. Adjusting the output of a measuring device with a known sample: e.g. setting a scale at 100 pounds while a standard 100 pound weight is being weighed.

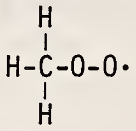
CAMP. Continuous Air Monitoring Program; a network of air monitoring stations in the major U.S. urban areas set up by the EPA to measure the variables associated with air pollution.

Catalytic converter. An emissions reduction device, commonly used on motor vehicles, intended to catalyze the chemical conversion of a pollutant to a less harmful compound.

C.F.R. *Code of Federal Regulations*; the codification of the regulations published in the Federal Register by the executive departments and agencies of the federal government.

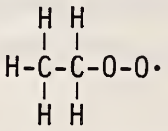
Chain reaction. A reaction that is initiated by one or more of its products. It is thus self-sustaining; e.g., $A + B \rightarrow C + A$, where A is regenerated and can again react with B to form more C.

Chemical notation. A complete symbol, such as O_2 or NO_2, represents a molecule. A subscript indicates a repetition; e.g., O_2 is a molecule made from a combination of two oxygen atoms. A dot indicates the presence of an unpaired electron in a chemical species; hence, the species is a radical (e.g., $OH\cdot$). A single line indicates a single chemical bond, and a double line represents a double bond. R- represents a hydrocarbon chain. For example, $RO_2^{\cdot}$ could be



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}O{-}O\cdot}$$

or



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}O{-}O\cdot}$$

,

among others.

Chemical reaction. A change in the chemical structure of a molecule.

Chemical symbols. Abbreviations for chemical substances:

CO = carbon monoxide
HNO_2 = nitrous acid
$HO_2^\cdot$ = hydroperoxy radical
H_2O_2 = hydrogen proxide
NO = nitric oxide
NO_2 = nitrogen dioxide
NO_3^- = nitrate
$OH\cdot$ = hydroxyl radical
PAN = peroxyacetyl nitrate
PPN = peroxypropyl nitrate
$RCO_3\cdot$ = peroxyacyl radical
$RO\cdot$ = alkoxyl radical
$ROO\cdot$ = alkylperoxy radical
SO_2 = sulfur dioxide
$SO_4^=$ = sulfate

Chemical transformation. Same as "Chemical reaction."

Chemiluminescent. Of or relating to a chemical reaction producing light, e.g., the reaction of ethylene with ozone.

Chemiluminescent method. The method of measuring ozone by measuring the light emitted from the reaction between ozone and ethylene. The intenisty of the light is proportional to the ozone concentration.

Clean Air Act. A federal law regulating air pollution; when amended in 1967, it required that the Secretary of Health, Education, and Welfare developed and issue air quality criteria necessary to protect public health and welfare.

Clean Air Amendments. The 1970 Amendments to the Clean Air Act redefine the strategy of the Act and call for every state to submit an implementation plan to the EPA describing the control strategies to be used to attain compliance with National Ambient Air Quality Standards.

cm. Centimeter; 1 cm equals 0.39 inches.

Coagulation. Physical agglomeration of particles into larger particles.

Cold start. Starting a motor vehicle with a cold engine.

Collector. A road connecting a residential area with an arterial or freeway.

Colorimetric. Of or relating to measurement based on color changes caused by chemical reaction.

Complex organic molecule. An organic molecule having many carbon atoms, side chains, and often inorganic components such as nitrate or sulfate.

Confidence interval. The interval in which a particular percentage of values is expected to fall based on previous experience, a limited sample of values, or mathematical analysis of the situation. For example, a 95 percent confidence interval of ±0.07 ppm means that 95 percent of all the measurements are expected to fall within ±0.07 ppm of the average (or actual) value.

Continuous control. A control strategy that is applied constantly, in contrast with intermittent control.

Control strategy. Actions planned or taken to reduce the concentration of pollutants in the air.

Coriolis force. The conservation of angular momentum acting on a mass at the earth's surface that is moved north or south (i.e., closer to or further from the earth's axis of rotation). In the Northern Hemisphere, masses moving north or south tend to curve to the right.

Correlation coefficient. A measure of the extent to which two variables or two sets of data are related linearly.

Coulometric. Of or relating to measurement of the number of electrons or total charge transferred as a result of a chemical reaction.

Criteria pollutant. A pollutant for which the EPA has established an NAAQS; i.e., oxidant, NO_2, SO_2, CO, HC, or TSP.

Cyclone. A large system of winds or a storm rotating about a low pressure center.

Diurnal. Related to a 24-hour period; e.g., diurnal variations in oxidant concentration.

Driving cycle. A profile of velocity versus time, specified for determining vehicular emissions rates.

Dustfall. The amount of particles settling out of the atmosphere.

Dynamic field calibration. Determination of the response of a measurement instrument located at a monitoring site to a known time-varying input signal.

EKMA [Empirical Kinetic Modeling Approach]. An air quality model based on ozone isopleth diagrams.

Emissions factor. The rate of pollutant emissions under specified conditions.

Emissions inventory. A complete list of sources and rates of pollutant emissions within a specified area and time interval.

Emissions rate. The rate at which pollutants are emitted into the atmosphere by one source or a combination of sources.

Emissions standard. A legal limit on a rate of emissions.

Empirical. Determined from or based on observation rather than physical law.

Entrainment. The drawing of material into an air mass as a consequence of the movement of that air mass.

EPA. U.S. Environmental Protection Agency.

Episode. A period of time when low wind speeds combine with limited mixing depths to create conditions favorable for high pollutant concentrations.

Episode alert. Public notification of a high level of pollution, usually accompanied by a warning to people with respiratory disease to stay indoors and by a request to motorists and industry to reduce emissions of pollutants.

Equivalent method. A method of sampling and analyzing the ambient air that is so designated by the EPA because of its equivalence to the federal reference method for the pollutant analyzed. Equivalence is demonstrated through a series of EPA-designated comparison tests.

Eulerian. Having a coordinate system fixed with respect to the earth's surface. Compare Lagrangian.

Exceedance (oxidant). An observed occurrence of oxidant concentration higher than the specified maximum one-hour average. An exceedance of the oxidant NAAQS more than once per year is a violation.

Exercise (of a model). Carrying out a simulation using full inputs and initial conditions.

Federal reference measurement principle. Refers to the principle of measurement required under Code of Federal Regulations, Title 40, Section 50.9 for automated ozone ambient analyzer or monitoring methods. For ozone, this principle is based on the observation of chemiluminescence due to the ozone-ethylene reaction.

Fed. Reg. Federal Register; a daily (weekday) publication of new public regulations and legal notices issued by federal agencies.

Fine scale. Small spacing, generally a mile or less, between data points determining the spatial resolution of a model.

Finite difference method. A method for solving differential equations by converting continuous equations into equations that are evaluated only at specific points in time and space. The finite difference method is numerical and is amenable to computer solution.

Flux. The rate per unit area at which material or energy moves. Often it is measured relative to the mean motion.

Frequency analysis. A study of the frequency of occurrence of various levels of a given variable in a data set.

Frequency distribution. A curve of the percentage frequency of occurrence of each value that a variable may take on.

Friction island effect. The reduction of surface wind speeds in an urban area caused by greater surface roughness due to buildings and other structures.

Frontal zone. The region of relatively sharp changes of temperature, humidity, and the like, between two large air masses. A frontal zone is often characterized by clouds and precipitation.

Gas chromatography. A method of analyzing the components of a mixture of gases based on the difference in adsorption of different gases on specially selected filter materials.

Gas phase reaction. A chemical reaction occurring between gaseous species.

Gaussian model. A pollutant dispersion model based on the Gaussian dispersion equation, which assumes a constant fractional decrease in concentration per unit distance from a stationary or moving center of dispersion.

Geometric mean. The n^{th} root of the product of a series of n numbers.

Geostrophic layer. The portion of the troposphere, beginning at roughly 500 m above ground level, in which air flow is not affected by the roughness of the earth's surface.

Global maximum. The highest value observed or calculated if the value at every point in the space of interest were known.

GMT. Greenwich Mean Time; the time according to a 24-hour clock in Greenwich, England. GMT, which is eight hours later than Pacific Standard Time, is used as a worldwide standard for timing weather observations.

Gravitational settling. Removal of particles from the atmosphere through the action of gravity.

Grid model. An air quality model in which all relevant equations are solved at a number of discrete points that represent points on a grid covering the region of interest.

Half-life. The time required for a quantity to decrease to half its original amount (as by chemical reaction).

HC. Hydrocarbon.

Heat island effect. The effect of an urban area on air flow due to its greater heat emissions than surrounding rural areas.

Henry's Law. A physical law stating that the equilibrium partial pressure of a volatile substance above a solution is proportional to the percentage of molecules of that substance in the solution.

Heterogeneous reaction. A chemical reaction between reactants that are in different physical states; e.g., some reactions that the place on the surface of a dust particle involve both a gas and a solid.

$h\nu$. The energy contained in a photon of light; h is Planck's constant, and ν is the frequency of the light.

Hydrocarbon-rich. Having a higher concentration of hydrocarbons that can react with the available reactants in a particular system; having too much hydrocarbon for the fastest production of ozone for a particular photochemically active atmosphere.

Hydroxyl. A radical containing a single oxygen and a single hydrogen atom ($OH\cdot$) that is formed in reactions involving water or organic molecules. The hydroxyl radical is very reactive and is believed to play a major role in photochemical smog.

Indirect control. Control of air quality by altering activities that influence the rate and distribution of emissions (e.g., traffic patterns, land use). Indirect control contrasts with direct control at the source of the emissions (e.g., devices on automobiles or smokestacks).

Initial conditions. The values of a variable at each point of a region at a specified starting time that are necessary to determine a solution at subsequent times.

Insolation. Rays of the sun that reach the surface of the earth; the delivery rate of solar energy per unit surface area.

Interference. The portion of a measurement due to the influence of a substance or effect that is not meant to be included in the measurement.

Intermittent control. A control strategy that is applied only during those meteorological conditions that lead to smog episodes.

Inversion. A thermal gradient created by warm air situated above cooler air. An inversion suppresses turbulent mixing and thus limits the upward dispersion of polluted air.

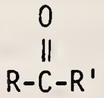
Inversion base. The lowest altitude of the thermal gradient that forms an inversion.

Isopleth. A line connecting points of equal value, e.g., a contour line connecting points of equal elevation on a topographic map, or an isotherm connecting points of equal temperature on a weather map.

Isoprene. A diolefin whose chemical symbol is C_5H_8.

Joint distribution frequency. The distribution of the frequency of occurrence of two variables having values greater than some set of value combinations.

Ketone. A partially oxidized hydrocarbon with the structure:



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}R' \quad .$$

where R and R' are hydrocarbon groups (not hydrogen). Compare with Aldehyde.

Kinetic mechanism. A set of chemical reactions and rate constants intended to represent some chemical process. Because of incomplete knowledge, kinetic mechanisms contain uncertainties regarding the values of rate constants and the products of particular reactions.

km. Kilometer; equivalent to 0.62 miles.

km^2. Square kilometer; equivalent to 0.386 square miles.

Lagrangian. Having a coordinate system that moves with respect to the earth's surface. Compare Eulerian.

Lag time. The time interval for an instrument between a step change in input concentration and the first observable corresponding change in response.

Lake breeze. A light wind blowing from a lake to surrounding land areas during the day due to temperature differences between land and water. Compare Land breeze, Sea breeze.

Land breeze. A light wind blowing from land to a large body of water at night due to temperature differences between land and water. Compare Lake breeze, Sea breeze.

LARPP. Los Angeles Reactive Pollutant Program: an intensive study of atmospheric pollutant concentrations carried out in the fall of 1973 in Los Angeles.

Layer aloft. A layer of air that can be differentiated from the air above and below it, as by an inversion.

Level of service. A measure of the level of traffic congestion on a roadway, defined in Reference 29.

Line source. A long, narrow source of emissions such as a roadway or railroad.

Link. A portion of a road in a highway network.

LIRAQ. Livermore Regional Air Quality Model; a grid-based physicochemical model developed by Lawrence Livermore Laboratory to predict pollutant concentrations in the San Francisco Bay region, described in Ref. 20.

Local meteorology. The weather conditions, temperature, wind velocity, mixing height, cloud cover, and so forth, that exist in a particular urban or rural area.

Lognormal distribution. A statistical distribution in which the logarithm of the random variable follows a normal distribution.

Long range transport. Atmospheric transport of pollutants over long distances (e.g., 100-1000 km) with relatively little dispersion.

Macroscale. See Synoptic scale.

mb. Millibar; a unit of pressure equal to 10^3 dyne/cm^2. Atmospheric pressure equals 1.013×10^3 mb.

Mean. The arithmetic average; i.e., the sum of the values divided by the number of the values.

Measurement drift. The tendency of the output of a measuring instrument to increase or decrease over time though the input is constant. For example, a thermomenter may read 75.0° at noon, 75.1° at 1:00 p.m., and 75.2° at 2:00 p.m. even though the actual temperature does not change. See also Zero Drift and Span Drift.

Measurement noise. Random fluctuations in the electrical signal from a measurement device.

Measurement principle. The basic chemical or physical phenomenon that is the basis for a measurement method.

Measurement specificity. The degree to which a measurement reflects the value for only the substance or effect of interest and does not include interference from other substances or effects.

Median. The data point in a set of data points that has a value such that half the data points have smaller values and half have larger values.

Mesoscale. Literally "middle scale" between microscale and macroscale, involving distances of 1 to 100 kilometers and times of 1 to 24 hours.

Meteorological variables. Wind speed and direction, mixing depth, temperature, pressure, degree of turbulence, sunlight intensity, humidity, and precipitation; also, the variation of these parameters.

Methane. The simplest hydrocarbon (CH_4); the major component of natural gas.

Methyl. A radical containing a carbon atom and three hydrogens ($CH_3^{\cdot}$).

Microscale. Small scale, involving distances up to approximately 1 km and times up to a few tens of minutes.

$\mu g/m^3$. Micrograms per cubic meter.

Mixed layer. Layer of air near the ground where turbulent mixing of pollutants occurs. It is limited by an inversion base, if one is present.

Mixing depth. The depth of the mixed layer.

Mobile source. A moving vehicle that emits pollutants. Such sources include automobiles, trucks, trains, ships, and farm equipment.

Modal emissions factors. Vehicular emissions factors for individual modes of operation, e.g., accelerate, cruise, decelerate, idle.

Monitoring network. An array of measurement devices designed to characterize regional air quality and, in some cases, meteorology.

Monitoring site. The location of a measurement device in a monitoring network.

NAAQS. National Ambient Air Quality Standards; established by the EPA to protect human health (primary standards) and to protect property and aesthetics (secondary standards).

Natural sink. Natural process that removes pollutants from the atmosphere.

Natural source. A source of pollutant emissions unrelated to man's activities, e.g., a volcano.

Negative interference. Phonomenon that consistently causes a measurement to be lower than the true value.

NMHC. Nonmethane hydrocarbons, typical determined by measuring total hydrocarbons and methane and subtracting. NMHC is commonly reported because methane reacts slowly in photochemical oxidant formation.

Nocturnal inversion. A surface-based temperature inversion formed at night by radiational cooling of the earth's surface and, hence, the the air near the surface.

Nocturnal jet. A high-velocity wind observed to occur at night within inversion layers.

Nonmethane hydrocarbon. A hydrocarbon other than methane. See NMHC.

Non-ozone-specific method. A method that measures the concentration of a group of oxidants (the exact group depends on the method), rather than just the concentration of ozone.

Normal distribution. The Gaussian or "bell curve" distribution.

NO_x-poor. Having less NO_x than would be required for the fastest production of ozone for a particular concentration of hydrocarbons; same as "hydrocarbon-rich."

Nucleation. Formation of a droplet by collection of water vapor on a particle.

Olefin. A hydrocarbon containing a carbon-carbon double bond. See Alkene.

Oxidation. Partial or complete loss of an electron from an atom in a chemical reaction. For example, in the reaction

$$2CO + O_2 \rightarrow 2CO_2 \quad ,$$

the carbon atoms are oxidized because some electrons initially at those atoms are pulled further from the carbon atoms by the oxygen atoms. Oxygen atoms attract electrons more stongly then almost all other atoms, hence, a reaction with oxygen is usually an oxidation. Compare Reduction.

Ozone (O_3). A strong photochemical oxidant whose molecules consist of three bound oxygen atoms, O-O-O.

PAN. Peroxyacetyl nitrate, $CH_3C(O)OONO_2$, an oxidant normally found in photochemical smog and believed to cause eye irritation.

Paraffin. A hydrocarbon containing only hydrogen and carbon and having no double or triple bonds. See Alkane.

Parcel trajectory. The path taken by a volume of air as it is advected by the wind.

Particle-in-cell technique. A method for solving fluid flow and turbulent diffusion problems on a digital computer that represents the distribution of fluid or pollutants as a collection of Lagrangian mass points that move through a network of Eulerian grid cells.

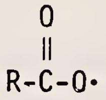
Particulates. Microscopic particles suspended in air. See Aerosol.

Pasquill stability class (or category). A standard classification scheme for atmosphere stability.

Peroxide. A molecule containing an oxygen-oxygen single bond, e.g., hydrogen peroxide, H-O-O-H.

Peroxy. A radical containing two oxygen atoms (-O-O·) A hydroperoxy radical has the formula $HO_2^{\cdot}$.

Peroxyacyl. A radical whose chemical structure is



$$R\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}O\cdot \quad ,$$

where R is an organic group.

Peroxyalkyl. A radical whose chemical structure is

$$R\text{-}O\text{-}O\cdot \quad ,$$

where R is an organic group.

Photochemical aerosol. Liquid and solid particles (usually less than 10 μm in diameter) that are formed in the atmosphere through processes that are affected by the presence and intensity of light.

Photochemical reactions. Chemical transformation whose character, rates, or both are affected by the presence and intensity of light.

Photochemical smog. The atmospheric condition that results when hydrocarbons and nitrogen oxides emitted into the atmosphere react in the presence of sunlight to form other pollutants, such as oxidants, PAN, and aerosols.

Photodissociation. See Photolysis.

Photolysis. The decomposition of a chemical compound by light.

Physicochemical model. A mathematical model that explicitly accounts for both physical and chemical processes in its formulation.

Pibal. A pilot balloon, which is released and optically tracked to determine winds.

Planetary boundary layer. The lower part of the atmosphere (from the ground surface to less than one mile above) in which wind patterns are affected by drag against the earth's surface.

Plume. The spreading pollutants emitted by a fixed source, such as a smokestack.

Point stationary source. A pollutant source that is fixed to the ground and that releases pollutants through a relatively small area (e.g., a smokestack).

ppb. Parts per billion (10^9) by volume.

pphm. Parts per hundred million (10^8) by volume.

ppm. Parts per million (10^6) by volume.

ppmC. Parts per million carbon; ratio of the volume of hydrocarbons to 1 million parts of air that would result if all carbon atoms were in the form of methane.

ppt. Parts per trillion (10^{12}) by volume.

Precipitation scavenging. Removal of a pollutant from the atmosphere by precipitation, by either nucleation around the pollutant in the formation of precipitation or scavenging of the pollutant by precipitation as it falls.

Precision. A measure of the reproducibility of measurement of the same quantity made at different times. A measurement may be precise but not accurate if some fault, such as zero error, is present.

Precursor. A chemical compound that leads to the formation of a pollutant, e.g., hydrocarbons and nitrogen oxides are precursors of photochemical oxidant.

Primary. Injected into the atmosphere rather than formed in the atmosphere.

Primary standard. A National Ambient Air Quality Standard set to protect human health.

Pristine. Undegraded by man's activities.

Quality assurance program. The program implemented as part of a measurement program to (1) identify and quantify sources of variability, (2) delineate operating procedures, (3) establish quality control checks and performance standards, (4) eliminate determinate errors and minimize indeterminate errors, and (5) operate and maintain a primary standards laboratory.

Quality control program. The program applied to routine systems in order to evaluate and document the ability of a function, activity, or person to produce results that are valid within predetermined limits.

Radiation flux. The amount of light energy per unit area per unit of time.

Radical. A chemical species having an unpaired electron. Radicals are very reactive.

Radical transfer. Transfer of an unpaired electron from one molecule to another.

Radiosonde. A light electronic device that senses temperature, humidity, and pressure and transmits this information on a radio signal. Radiosondes are designed to be carried aloft (into the atmosphere) beneath a buoyant balloon.

Radiosonde soundings. Free flights of radiosonde-equipped balloons during which information is transmitted to ground-level radio equipment as the balloons rise in the atmosphere. This information includes temperature, humidity, and pressure at various altitudes.

Rainout. The removal of a pollutant from the air in a cloud during the process of precipitation. Compare with Washout.

Random error. An error that follows a statistical distribution and that cannot be predicted or corrected.

Rate constant. A constant of proportionality that relates the rate at which the concentration of a species changes with time to the concentration of the reactant species at any particular time. For example, for the reaction A + B → products, the rate constant k is given by $(dc_A/dt)/c_A c_B$, where c_A is the concentration of A.

Rawinsonde. A radiosonde balloon that is tracked by radar to estimate wind velocity.

Reactive hydrocarbon (RHC). A hydrocarbon that readily combines with radicals and thereby contributes to the production of ozone.

Reduction. Partial or complete gain of an electron by an atom in a chemical reaction. For example, in the reaction

$$2CO + O_2 \rightarrow 2CO_2 \quad ,$$

the oxygen atoms in the O_2 molecule are reduced because they attract electrons from the carbon atoms. Compare oxidation.

Reference method. A method required by EPA regulations to be used for measuring the concentration of a pollutant to ascertain whether an area is in violation or in compliance with the air quality standard for that pollutant.

Regression analysis. The construction of a relationship between a set of predictor variables and a predicted variable. The procedure, which involves the use of past measurements, is based on minimization of the sum of the squared errors in prediction.

Reliability. The extent to which a model, experiment, or test will yield the correct results for a variety of trials.

Removal process. A process that removes a pollutant from the atmosphere.

RH. Relative humidity.

RHC. Reactive hydrocarbon; see the definition of the full term.

Rollback relationship. An oxidant prediction relationship that consists of a plot of expected oxidant concentrations as a function of hydrocarbon concentrations or emissions. It is used to estimate the reduction in emissions necessary to meet air quality standards.

Scavenging. Removal of a pollutant from the atmosphere, particularly by precipitation or chemical reaction.

sec. Seconds.

Secondary. Produced in the atmosphere rather than directly emitted.

Secondary standard. A National Ambient Air Quality Standard set to protect human welfare and aesthetics. Secondary standards are generally more stringent than primary standards.

Sensitivity analysis. A test of a model using different input and parameters to discover what effects changes in their values have on model predictions.

Simulation model. A mathematical description of real physical and/or chemical process. The responses of the model to input variations are analogous to those of the real processes.

Sink. A process that removes pollutants from the atmosphere.

Smog chamber. An experimental apparatus used to study the chemical reactions that take place in a polluted atmosphere. Such a chamber may have controllable inlets for introducing pollutants and outlets for removing samples. It can also be artificially illuminated to simulate sunlight.

Solar radiation. Energy emitted by the sun that reaches the earth as ultraviolet, visible, and infrared light.

Sounding. Measurement of meteorological properties, such as temperature or wind velocity, during a vertical transit of the atmosphere.

Span drift. The percentage change in the response of a measuring device to a pollutant concentration that registers high in the range of the instrument over a 24-hour period of continuous, unadjusted operation.

Span error. An error in the response of a measuring device to a pollutant concentration that registers high in the range of the measurement device.

Spatial resolution. A measure of the precision with which two points separated in space are distinguished from one another. In air pollution models, it is the characteristic distance over which major dependent variables, such as wind and emissions, are averaged.

Spatial scale. The distance over which significant changes of phenomena are being studied.

Spent air mass. An air mass containing nearly completely reacted pollutants.

Stable layer. A layer of air in which very little mixing takes place.

Stable layer aloft. A layer of air at least 100 feet thick, located 500 to 5000 feet above the ground, in which little or no mixing takes place.

Standard deviation. The square root of the variance. The standard deviation is a measure of the spread in a set of measurements of a single parameter.

Standard geometric deviation. A measure of the variability in a set of data; it is defined as

$$\exp\left[\sum_{1}^{N} \frac{(\ln x_i - \ln M_g)^2}{N}\right]^{1/2} ,$$

where $x_1, x_2, \ldots, x_N$ are the data with geometric mean M_g.

State implementation plan. The strategy to be used by a state to control air pollution so that the National Ambient Air Quality Standards will be met. EPA regulations require that each state devise such a plan or the EPA will impose its own plan for that state.

Stationary source. A source of pollutants that is immobile. Such sources include industrial complexes, power plants, and individual heating units. Aircraft are sometimes also included in this category because they are a significant pollutant source only near airports.

Statistical model. A statistical relationship between a set of predictor variables and a predicted variable.

Steady-state assumption. The assumption that a system or variable remains unchanged with the passage of time because of the equality of input to and outflow from the system.

Stratosphere. A layer of the atmosphere immediately above the troposphere; it extends to a height of roughly 50 kilometers, and it is characterized by little variation in temperature, low air pressure, and the absence of clouds.

Stratospheric intrusion. The transport of ozone from the stratosphere into the troposphere.

Subsidence inversion. A type of temperature inversion associated with high-pressure systems in which a thermal gradient is established by the heating due to compression of an air parcel as it decends.

Sulfur oxide (SO_x). Any of several oxides of sulfur, such as sulfur dioxide (SO_2).

Surface flux. The rate per unit area at which some quantity passes through or is emitted from a surface.

Surface layer. The layer of air near the ground, generally 1 to 100 meters deep, where surface features (e.g., trees, buildings) affect atmospheric turbulence and diffusion.

Surface removal rate. The rate at which pollutants are removed through reactions with, adsorption on, or absorption by surfaces.

Surface roughness. The characteristic height of obstructions in the path of the wind near the surface, such as the heights of trees and buildings.

Surface sink. A surface that removes pollutants from the air by reaction or absorption.

Synoptic scale. Large scale, involving distances of 100 to several thousand kilometers and times of one to several days. Also called Macroscale.

Systematic error. A nonrandom error that is caused by some inherent characteristic of a device or by flaws in analysis.

Temperature field. The distribution of temperatures over some area or within a volume.

Temperature gradient. Change of the ambient temperature as a function of distance (either vertical or horizontal).

Temporal resolution. A measure of the precision with which two points separated in time are distinguished from one another. In air pollution models, it is the characteristic time over which major dependent variables, such as winds and emissions, are averaged.

Texture. The surface roughness of a city.

THC. Total hydrocarbon (i.e., reactive plus nonreactive).

Tracer. A substance used to follow the path of a physical, chemical, or biological process.

Trajectory model. A mathematical model designed to follow a single parcel of air along a trajectory determined by the wind.

Transport. Movement of pollutants or other material in the atmosphere from one location to another.

Tropopause. The (approximate) interface between the troposphere and the stratosphere at which the vertical temperature gradient changes sign (positive in the stratosphere and negative in the troposphere) and through which exchange of air between the two spheres is inhibited.

Troposphere. The lower layer of the atmosphere, 10 to 15 kilometers deep, where most of the processes commonly considered "weather" occur.

TSP. Total suspended particulate matter.

Turbulence. Irregular air motion, characterized by a number of eddies of varying size.

Turbulent wake. The area of turbulence caused by a moving vehicle.

Ultraviolet light. Light of a wavelength in the range of 40 to 4000 Angstroms (10^{-10} meters). These wavelengths are shorter (corresponding to higher frequences) than those of visible light.

Unreactive hydrocarbon. A hydrocarbon that reacts much slower than the organic compounds that influence the production of smog. Unreactive hydrocarbons thus have little effect on oxidant production.

Urban air parcel. An air mass that has passed over an urban area and that contains anthropogenic pollutants.

Urban plume. A very large plume whose source is an entire city or metropolis. It can be transported to the countryside downwind.

UV. Ultraviolet light (see the definition of the full term.)

Validity. The extent to which a model or relationship actually predicts the real-world behavior of a system.

Variance. A measure of variability in a data set. The variance is given by

$$\frac{\sum_{1}^{n} (x_i - \bar{x})^2}{n - 1}$$

where $x_1, x_2, \ldots, x_n$ are the data points and $\bar{x}$ is their mean value.

Velocity field. The distribution of flow velocities over some area or within a volume.

Ventilation. The transport of air thorugh a given region. The rate of ventilation is equal to the mixing depth times the transport wind speed.

Venting. Movement of pollutants in the vertical direction--generally caused by convection or wind convergence.

Verification study. An experiment designed to provide data that can be used to verify the predictions or computations of a mathematical or graphical model.

Vertical sounding. Same as Sounding.

VMT. Vehicle miles traveled.

Volumetric. Pertaining to measurement of or within a volume.

Washout. The removal of pollutants from the air beneath the clouds by precipitation. Compare with Rainout.

Wind field. The same as Velocity field.

Wind shear. The spatial variation of wind velocity. It is frequently used to mean the variation of wind velocity with height above the ground.

Zero air or zero gas. A gas that contains none of the substance that is being measured and that is used to calibrate a measurement device at the null condition.

<u>Zero drift</u>. The change in reading of a measuring instrument with zero input over 12- or 24-hour periods of unadjusted operation.

<u>Zero error</u>. The error in the reading of a measuring instrument with zero input.

REFERENCES

1. R. I. Pollack et al., "Highway Air Quality Impact Appraisals," Volume II, "Guidance for Highway Planners and Engineers," EF78-34R,

   prepared for the U.S. Department of Transportation, Federal Highway Administration, by Systems Applications, Incorporated, San Rafael, California.

2. "Air Quality Criteria for Carbon Monoxide," AP-42, U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Washington, D.C. (1970).

3. "Trends in the Quality of the Nation's Air," Environmental Protection Agency, Washington, D.C. (1977).

4. J. H. Seinfeld, Air Pollution: Physical and Chemical Fundamentals (McGraw-Hill Book Company, New York, New York, 1975).

5. "Emissions Forecasting Methodologies," California Air Resources Board, Evaluation and Planning Department, Sacramento, California (1974). (NTIS PB 237 870).

6. P. Kunselman et al., "Automobile Exhaust Emission Modal Analysis Model," Calspan Corporation, Buffalo, New York (1974).

7. J. C. Murchio, Cooper, and DeLeon, "Asbestos Fiber in Ambient Air of California," California Air Resources Board, Sacramento, California (1973).

8. "Air Quality Criteria for Particulate Matter," AP-49, U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Washington, D.C. (1969).

9. J. R. Goldsmith, "Effects of Air Pollution on Human Health," in Air Pollution: Volume I, Air Pollution and Its Effects, A. C. Stern (Academic Press, New York, New York, 1968).

10. G. M. Hidy et al., "Characterization of Aerosols in California (ACHEX)," Vol. IV, California Air Resources Board, Sacramento, California (1975).

11. J. T. Peterson and E. C. Flowers, "Urban-Rural Solar Radiation and Aerosol Measurements," Meteorology Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

12. "Air Quality Criteria for Photochemical Oxidants," AP-63, U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Washington, D.C. (1970).

13. R. I. Larsen, "A Mathematical Model for Relating Air Quality Measurements to Air Quality Standards," AP-89, Environmental Protection Agency, Office of Air Programs, Research Triangle Park, North Carolina (1971).

14. "1974 National Emissions Report," Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1976).

15. H. S. Johnston and E. Quitevis, "The Oxides of Nitrogen with Respect to Urban Smog, Supersonic Transports, and Global Methane," Fifth International Congress of Radiation Research, 14-20 June 1974, Seattle, Washington.

16. C. W. Spicer, D. W. Joseph, and G. F. Ward, "Final Data Report on the Transport of Oxidant Beyond Urban Areas," EPA Contract 68-02-2241, Battelle Columbus Laboratories, Columbus, Ohio (1976).

17. H. Reiquam, "Sulfur: Simulated Long Range Transport in the Atmosphere," Science, Vol. 170, p. 318 (1970).

18. "Oxidant Air Pollutant Effects on a Western Coniferous Forest Ecosystem," Statewide Air Pollution Research Center, University of California, Riverside, California (1973).

19. G. Likens and F. H. Bormann, "Acid Rain: A Serious Regional Environmental Problem," Science, Vol. 184, pp. 1176-1179 (1974).

20. "Development of an Air Pollution Model for the San Francisco Bay Area," UCRL-51537, Lawrence Livermore Laboratory, Livermore, California (1974).

21. J. P. Killus et al., "Continued Research in Mesoscale Air Pollution Simulation Modeling: Volume V--Refinements in Numerical Analysis, Transport, Chemistry, and Pollutant Removal," EF77-142, Systems Applications, Incorporated, San Rafael, California (1977).

22. T. A. Cahill and P. J. Feeney, "Contribution of Freeway Traffic to Airborne Particulate Matter," Crocker Nuclear Laboratory, Department of Physics, University of California, Davis, California (1974) NTIS PB-231617.

23. "Mobile Source Emissions Factors, Interim Document," Office of Transportation and Land Use Policy, Environmental Protection Agency, Washington, D.C. (1977).

24. G. R. Cass, "Lead as a Tracer for Automotive Particulates: Projecting the Sulfate Air Quality Impact of Oxidation Catalyst Equipped Cars in Los Angeles," Environmental Quality Laboratory, California Institute of Technology, Pasadena, California (1975).

25. "Compilation of Air Pollutant Emissions Factors," AP-42, Main Volume (1972) and Second Edition of Supplement 5 (1975), Environmental Protection Agency, Research Triangle Park, North Carolina (1972).

26. "A Study of Emissions from Light Duty Vehicles in Six Cities," APTD-1497, Environmental Protection Agency, Office of Air and Water Programs, Office of Mobile Source Air Pollution Control, Certification and Surveillance Division, Ann Arbor, Michigan (1973).

27. M. G. Jacko and Ducharment, "Emissions Measurements from Brake and Clutch Linings from Selected Mobile Sources," Report 68-04-0020, Bendix Center, Southfield, Michigan (1973).

28. "EMFAC3: Motor Vehicle Emissions Factor Estimates for California," California Air Resources Board, Air Quality Modeling Section, Sacramento, California (1976).

29. "Highway Capacity Manual," Special Report 87, Highway Research Board Division of Engineering and Industrial Research, National Academy of Sciences--National Research Council, Washington, D.C. (1966).

30. S. D. Reynolds et al., "Further Development and Validation of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants," Systems Applications, Incorporated, San Rafael, California (1973).

31. J. C. Cosby, "Heavy Duty Vehicle Driving Pattern and Use Survey, Final Report, Part 1, New York City," Wilbur Smith and Associates, Columbia, South Carolina (1973) NTIS PB-221656.

32. "Transportation Control Strategy Development for New York Metropolitan Area," TRW Transportation and Environmental Operations, McClean, Virginia (1972).

33. A. C. Stern et al., Fundamentals of Air Pollution (Academic Press, New York, New York, 1973).

34. "Monthly Energy Review," NTIS UB/B/127-76/009, Federal Energy Administration, Washington, D.C. (1976).

35. "Guide for Compiling a Comprehensive Emissions Inventory," APTD-1135, Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1973).

36. "Census of Agriculture," U.S. Department of Commerce, County Data Bureau of the Census, Washington, D.C. (1969).

37. "County Business Patterns," U.S. Department of Commerce, Bureau of the Census, Washington, D.C. (1970).

38. Code of Federal Regulations, Title 40, "Protection of the Environment," Parts 50-69 (U.S. Government Printing Office, Washington, D.C., 1975).

39. K. H. Rasmussen, M. Taheri, and R. L. Kabel, "Sources and Natural Removal Processes for Some Atmospheric Pollutants," EPA-650/4-74-032, Center for Air Environment Studies, Pennsylvania State University, University Park, Pennsylvania (1974).

40. G. M. Hidy, "Removal Processes of Gaseous and Particulate Pollutants," in Chemistry of the Lower Atmosphere, D. J. Rasool, ed., pp. 121-176 (Plenum Press, New York, New York, 1973).

41. P. S. Liss and P. G. Slater, "Flux of Gases Across the Air-Sea Interface," Nature, Vol. 247, pp. 181-184 (1974).

42. V. J. Linnebom, J. W. Swinnerton, and R. A. Lamontagne, "The Ocean as a Source for Atmospheric Carbon Monoxide," J. Geophys. Res., Vol. 78, pp. 5333-5340 (1973).

43. J. C. McConnell, M. B. McElroy, and S. C. Wofsy, "Natural Sources of Atmospheric CO," Nature, Vol. 233, pp. 187-188 (1971).

44. R. A. Rasmussen and F. W. Went, "Volatile Organic Material of Plant Origin in the Atmosphere," Proc. of the National Academy of Sciences, Vol. 53, pp. 215-220 (1965).

45. R. S. Davis et al., "Hydrocarbon Background Levels at Two Rural Sites in Tidewater, Virginia," preprint, Old Dominion University, Norfolk, Virginia (1975).

46. A. R. Bandy, "Studies of the Importance of Biogenic Hydrocarbon Emissions to the Photochemical Oxidant Formation in Tidewater, Virginia," Scientific Seminar on Automotive Pollutants, 10-12 February 1975, Washington, D.C.

47. G. R. Rossknecht, W. P. Elliott, and F. L. Ramsey, "The Size Distribution and Inland Penetration of Sea-Salt Particles," J. Appl. Meteor., Vol. 12, pp. 825-830 (1973).

48. H. R. Pruppacher, "The Role of Natural and Anthropogenic Pollutants in Cloud and Precipitation Formation," in Chemistry of the Lower Atmosphere, D. J. Rasool, ed., pp. 1-67 (Plenum Press, New York, New York, 1973).

49. R. A. Rasmussen, "Recent Field Studies," Scientific Seminar on Automotive Pollutants, EPA-600/9-75-003, 10-12 February 1975, Washington, D.C.

50. L. A. Ripperton and J.J.B. Worth, "Chemical and Environmental Factors Affecting Ozone Concentration in the Lower Troposphere," Department of Environment Science and Engineering No. 234, University of North Carolina, Chapel Hill, North Carolina (1969).

51. E. Robinson and R. C. Robbins, "Gaseous Nitrogen Compound Pollutants from Urban and Natural Sources," J. Air Poll. Contr. Assoc., Vol. 20, pp. 303-306 (1970).

52. J. P. Lodge, Jr., and J. B. Pate, "Atmospheric Gases and Particulates in Panama," Science, Vol. 153, p. 408 (1966).

53. C. E. Junge, "Recent Investigations in Air Chemistry," Tellus, Vol. 8, p. 127 (1956).

54. J. L. Hamilton, J.J.B. Worth, and L. A. Ripperton, "An Atmospheric Physics and Chemistry Study on Pike's Peak in Support of Pulmonary Edema Research," Research Triangle Institute, Research Triangle Park, North Carolina (1968).

55. Research Triangle Institute, "Investigation of High Ozone Concentration in the Vicinity of Garrett County, Maryland and Preston County, West Virginia," EPA R4-73-019, Research Triangle Institute, Research Triangle Park, North Carolina (1973).

56. J. C. McConnell and M. B. McElroy, "Odd Nitrogen in the Atmosphere," J. Atmos. Sci., Vol. 30, pp. 1465-1480 (1973).

57. J. C. McConnell, "Atmospheric Ammonia," J. Geophys. Res., Vol. 78, pp. 7812-7821 (1973).

58. E. Eriksson, "The Yearly Circulation of Chloride and Sulfur in Nature: Meteorological, Geochemical, and Pedological Implications," Tellus, Vol. 12, pp. 63-109 (1960).

59. W. W. Kellogg et al., "The Sulfur Cycle," Science, Vol. 175, pp. 588-596 (1972).

60. R. E. Stoiber and A. Jepsen, "Sulfur Dioxide Contributions to the Atmosphere by Volcanoes," Science, Vol. 182, pp. 577-578 (1973).

61. P. J. Crutzen, "Minor Constituents in the Stratosphere and Troposphere," Pure and Appl. Geophys., Vol. 196-108, pp. 1385-1399 (1973).

62. W. L. Chameides and J.C.G. Walker, "A Photochemical Theory of Tropospheric Ozone," J. Geophys. Res., Vol. 81, No. 3, pp. 413-420 (1973).

63. Climatic Atlas of the United States (U.S. Department of Commerce, Washington, D.C., 1968).

64. "Air Quality Criteria for Nitrogen Oxides," U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Washington, D.C. (1971).

65. "Air Quality Criteria for Hydrocarbons," AP-64, U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Washington, D.C. (1970).

66. "Air Quality Criteria for Sulfur Oxides," AP-50, U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, Washington, D.C. (1969).

67. "National Air Quality and Emissions Trends Report," U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1975 and other years).

68. "Monitoring and Air Quality Trends Report, 1973," EPA-450/1-74-007, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1974).

69. R. B. Husar et al., "Ozone in Hazy Air Masses," in Proc. of the International Conference on Photochemical Oxidant and Its Control, EPA-600/3-77-001b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1977).

70. R. A. Cox et al., "Long Range Transport of Photochemical Ozone in North-Western Europe," Nature, Vol. 255, pp. 118-121 (1975).

71. C. E. Junge, Air Chemistry and Radioactivity (Academic Press, New York, New York, 1963).

72. L. A. Cavanagh, C. F. Schodt, and E. Robinson, "Atmospheric Hydrocarbon and Carbon Monoxide Measurements at Point Barrow, Alaska," Environ. Sci. Technol., Vol. 3, pp. 251-257 (1969).

73. "Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies," EPA-650/4-74-036, Research Triangle Institute, Research Triangle Park, North Carolina (1975).

74. R. A. Rasmussen, R. B. Chatfield, and M. W. Holdren, "Hydrocarbon Species in Rural Missouri Air," Washington State University, Pullman, Washington (1977).

75. R. D. Cadle, "Particulate Matter in the Lower Atmosphere" in Chemistry of the Lower Troposphere, D. J. Rasool, ed., pp. 69-120 (Plenum Press, New York, New York, 1973).

76. C. W. Spicer et al., "The Transport of Oxidant Beyond Urban Areas," Battelle Columbus Laboratories, Columbus, Ohio (1975).

77. J. S. Sandberg et al., "Sulfate and Nitrate Particulates as Related to SO_2 and NO_x Gases and Emissions," Bay Area Air Pollution Control District, San Francisco, California (1975).

78. T. N. Jerskey et al., "Sources of Ozone: An Examination and Assessment," EF76-110R, Systems Applications, Incorporated, San Rafael, California (1976).

79. "Monitoring and Air Quality Trends Report, 1974," EPA-450/1-76-001, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1976).

80. "National Air Quality and Emissions Trends Report, 1975," EPA-450/1-76-002, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

81. L. W. Chaney, "Carbon Monoxide Automobile Emissions Measured from the Interior of a Traveling Automobile," Science, Vol. 199, pp. 1203-1204 (1978).

82. "Advanced Air Quality Analysis,' State of California Department of Transportation [CALTRANS], Sacramento, California (1975).

83. A. H. Ranzieri, G. R. Bemis, and E. C. Shirley, "Air Pollution and Roadway Location, Design, and Operation--Preliminary Study of Distribution of Carbon Monoxide on and Adjacent to Freeways," CA-DOT-TL-7080-2-75-15. California Department of Transportation, Sacramento, California (1975).

84. D. H. Slade, ed., "Meteorology and Atomic Energy," U.S. Atomic Energy Commission, Office of Information Services, Oakridge, Tennessee (1968) (NTIS TID-24190).

85. A. J. Haagen-Smit, "Chemistry and Physiology of Los Angeles Smog," Ind. Eng. Chemistry, Vol. 44, p. 1423 (1952).

86. R. Scorer, Air Pollution (Pergamon Press, London, England, 1968).

87. G. Z. Whitten, M. J. Meldgin, and P. M. Roth, "A Preliminary Evaluation of the Potential Influence of Varying HC/NO_x Ratios on the Design of Oxidant Control Strategies," EF77-33R, Systems Applications, Incorporated, San Rafael, California (1977).

88. N. A. Fuchs, The Mechanics of Aerosols (Pergamon Press, New York, New York, 1964).

89. T. N. Jerskey and J. H. Seinfeld, "Continued Research in Mesoscale Air Pollution Simulation Modeling--Vol. IV: Examination of the Feasibility of Modeling Photochemical Aerosol Dynamics," EPA-600/4-76-016d, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

90. J. J. Huntzicker, S. K. Friedlander, and C. I. Davidson, "Material Balance for Automobile-Emitted Lead in Los Angeles Basin," Environ. Sci. Technol., Vol. 9, No. 5 (1975).

91. L. O. Myrup and D. L. Morgan, "Numerical Model of the Urban Atmosphere: Vol. 1, The City-Surface Interface," Contributions in Atmospheric Science, No. 4, Department of Agricultural Engineering, University of California, Davis, California (1972).

92. G. E. Anderson, "Mesoscale Influences on Wind Fields," J. Appl. Meteor., Vol. 10, No. 3 (1971).

93. A. G. Davenport, "The Relationship of Wind Structure to Wind Loading," National Physical Laboratory, Symposium No. 16, Wind Effects on Buildings and Structures, pp. 54-102 (Her Majesty's Stationary Office, London, 1965).

94. M. M. Orgill, J. E. Cermak, and L. O. Grant, "Laboratory Simulation and Field Estimates of Atmospheric Transport-Dispersion over Mountainous Terrain," CER70-71MMO-JEC-LOG40, Fluid Dynamics and Diffusion Laboratory, Department of Engineering, Colorado State University, Fort Collins, Colorado (1971).

95. R. I. Perla and M. Martinelli, Jr., "Avalanche Handbook," Agriculture Handbook 489, U.S. Department of Agriculture, Forest Service (1976).

96. J. Lin et al., "Laboratory and Numerical Simulation of Plume Dispersion in Stably Stratified Flow over Complex Terrain," EPA-650/4-74-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1974).

97. J. G. Edinger et al., "Penetration and Duration of Oxidant Air Pollution in the South Coast Basin of California," J. Air Poll. Contr. Assoc., Vol. 22, pp. 882-886 (1972).

98. W. A. Lyons and H. S. Cole, "Mesoscale Transport of Photochemical Oxidants Along the Western Shore of Lake Michigan," University of Wisconsin, Madison, Wisconsin (1975).

99. J. G. Edinger and R. H. Helvey, "The San Fernando Convergence Zone," Bull. Amer. Meteor. Soc., Vol. 42, No. 9 (1961).

100. T. W. Tesche et al., "Determination of the Feasibility of Ozone Formation in Power Plant Plumes," EA-307, Electric Power Research Institute, Palo Alto, California (1976).

101. H. W. Georgii, "Untersuchungen Uber Atmospharische Spurenstoffe und ihre Bedentung fur die Chemie der Niederschlage," Geofis. Puro e Appl., Vol. 47, pp. 155-171 (1960).

102. J. P. Killus and T. N. Jerskey, "Surface Sinks," in "Continued Research in Mesoscale Air Pollution Simulation Modeling: Volume V--Refinements in Numerical Analysis, Transport, Chemistry, and Pollutant Removal," S. D. Reynolds, ed., EF77-142, Systems Applications, Incorporated, San Rafael, California (1977).

103. W. H. White et al., "Formation and Transport of Secondary Air Pollutants: Ozone and Aerosols in the St. Louis Urban Plume," Science, Vol. 194, pp. 187-189 (1975).

104. C. W. Spicer, "Experimental Evidence of Long Distance Pollutant Transport," Proc. of the 83rd National AIChE Meeting, March 1977, Houston, Texas.

105. R. A. Willis and P. Williams, Jr., "A Study of the Low Level Jet Stream of the San Juan Valley (Project Lo-Jet)," NOAA Technical Memorandum NWS WR75, U.S. Department of Commerce, Salt Lake City, Utah (1972).

106. J. C. Kaimal and Y. Izumi, "Vertical Velocity Fluctuations in a Nocturnal Low-Level Jet," *J. Appl. Meteor.*, Vol. 4, pp. 576-584 (1965).

107. E. F. Danielson, *The Natural Stratosphere of 1974, CIAP Monograph 1*, DOT-TST-75-51, Chapter 6, pp. 115-122, A. J. Grobecker, editor-in-chief, Climatic Impact Assessment Program (U.S. Department of Transportation, Washington, D.C., 1975).

108. R. B. Husar et al., "A Study of Long Range Pollutant Transport from Visibility Observations, Trajectory Analysis and Local Air Pollution Monitoring Data," *Proc. of the Seventh International Technical Meeting on Air Pollution Modeling and Its Application*, NATO/CCMS, 7-10 September 1976, Airlie, Virginia.

109. L. N. Myrabo, K. R. Wilson, and J. C. Trijonis, "Survey of Statistical Models for Oxidant Air Quality Prediction," Conference on the State of the Art of Assessing Transportation Related Air Quality Impacts, October 1975, Washington, D.C.

110. T. Y. Chang and B. Weinstock, "Generalized Rollback Modeling for Urban Air Pollution Control," *J. Air Poll. Contr. Assoc.*, Vol. 25, pp. 1033-1037 (1975).

111. "Air Quality Criteria for Nitrogen Oxides," AP-84, Air Pollution Control Office, U.S. Environmental Protection Agency, Washington, D.C. (1971).

112. E. A. Schuck and R. A. Papetti, "Examination of the Photochemical Air Pollution Problem in the Southern California Area," Appendix D of "Technical Support Document for the Metropolitan Los Angeles Intrastate Air Quality Control Region Transportation Control Plan Final Promulgation," EPA Region IX, Environmental Protection Agency, San Francisco, California (1973).

113. J. C. Trijonis, "An Economic Air Pollution Control Model Application: Photochemical Smog in Los Angeles County in 1975," Ph.D. Thesis, California Institute of Technology, Pasadena, California (1972).

114. G. C. Tiao, M. S. Phadke, and G.E.P. Box, "Some Empirical Models for Los Angeles Smog Data," *J. Air Poll. Contr. Assoc.*, Vol. 26, p. 485 (1976).

115. "Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors," EPA-450/2-77-021a, U.S. Environmental Protection Agency, Office of Air and Waste Management and Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1977).

116. M. C. Dodge, "Combined Use of Modeling Techniques and Smog Chamber Data To Derive Ozone-Precursor Relationships," EPA-600/3-77-001b, *Proceedings of International Conference on Photochemical Oxidant Pollution and Its Control: Volume II*, Office of Research and Development, Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1977).

117. G. Z. Whitten and H. Hogo, "User's Manual for a Kinetic Model and Ozone Isopleth Plotting Package," Systems Applications, Incorporated, San Rafael, California (1977).

118. B. Dimitriades, "An Alternative to the Appendix J Method for Calculating Oxidant- and NO_2-Related Control Requirements," EPA-600/3-77-001b, Proceedings of International Conference on Photochemical Oxidant Pollution and Its Control: Volume II, Environmental Sciences Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1977).

119. G. Z. Whitten, M. J. Meldgin, and P. M. Roth, "A Preliminary Evaluation of the Potential Influence of Varying HC/NO_x Ratios on the Design of Oxidant Control Strategies," EF77-18R, Systems Applications, Incorporated, San Rafael, California (1977).

120. S. R. Hayes, S. D. Reynolds, and P. M. Roth, unpublished data, Systems Applications, Incorporated, San Rafael, California (1977).

121. G. Z. Whitten, private communication, Systems Applications, Incorporated, San Rafael, California (1978).

122. D. B. Turner, "Workbook of Atmospheric Dispersion Estimates," 999-AP-26, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1969).

123. J. J. Roberts, "Report to the U.S. EPA of the Specialists Conference on the EPA Modeling Guidelines," EPA-IAG-07-0013, U.S. Environmental Protection Agency, Chicago, Illinois (1977).

124. "User's Network for Applied Modeling of Air Pollution (UNAMAP)," (Computer Programs on Tape for Point Source Models, HIWAY, Climatological Dispersion Model and APRAC-1A), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1977) (NTIS PB 229 771).

125. D. B. Turner and J. H. Novak, "User's Guide for RAM," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1977).

126. J. H. Christiansen, "User's Guide to the Texas Episodic Model," Texas Air Control Board, Austin, Texas (1976).

127. A. D. Busse and J. R. Zimmerman, "User's Guide for the Climatological Dispersion Model," EPA-R4-73-024, National Environmental Research Center, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1973).

128. C. E. Ward and A. J. Ranzieri, "CALINE 2: An Improved Microscale Model for the Diffusion of Air Pollutants from a Line Source," in "Assessing Transportation-Related Air Quality Impacts," National Academy of Sciences, Transportation Research Board Special Report 167, Washington, D.C. (1976).

129. W. A. Carpenter and G. G. Clemena, "The Theory and Mathematical Development of Airpol-4," Virginia Highway and Transportation Research Council Report No. VHTRC75-R49, Charlottesville, Virginia (1975).

130. C. Maldonado and J. A. Bullin, "Modeling Carbon Monoxide Dispersion from Roadways," *Environ. Sci. Technol.*, Vol. 11, No. 12 (1977).

131. P. M. Roth et al., "An Examination of the Accuracy and Adequacy of Air Quality Models and Monitoring Data for Use in Assessing the Impact of EPA Significant Deterioration Regulations on Energy Developments," American Petroleum Institute, Washington, D.C. (1975).

132. M. K. Liu et al., unpublished data, Systems Applications, Incorporated, San Rafael, California (1976).

133. H. H. Lettau, "Physical and Meteorological Basis for Mathematical Models of Urban Diffusion Processes," *Proc. of Symposium of Multiple-Source Urban Diffusion Models*, Publ. No. AP-86, Air Pollution Control Office, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1970).

134. S. R. Hanna, "A Simple Method of Calculating Dispersion from Urban Source Areas," *J. Air Poll. Contr. Assoc.*, Vol. 21, pp. 774-777 (1971).

135. R. G. Lamb and J. H Seinfeld, "A Simple Dispersive Model for the Analysis of Chemically Reactive Pollutants," *Atmos. Environ.*, Vol. 8, pp. 527-529 (1974).

136. R. G. Lamb, "Continued Research in Mesoscale Air Pollution Simulation Modeling--Volume III: Modeling of Microscale Phenomena," EPA-600/4-76-016c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

137. J. P. Killus, private communication, Systems Applications, Incorporated, San Rafael, California (1978).

138. A. Q. Eschenroeder and J. R. Martinez, "Further Development of Photochemical Smog Model for the Los Angeles Basin," CR-1-191, General Research Corporation, Santa Barbara, California (1971).

139. J. H. Seinfeld, T. A. Hecht, and P. M. Roth, "Existing Needs in the Experimental and Observational Study of Atmospheric Chemical Reactions, A Recommendations Report," EPA-R4-73-031, U.S. Environmental Protection Agency, Washington, D.C. (1973).

140. L. G. Wayne, A. Kokin, and M. I. Weisburd, "Controlled Evaluation of the Reactive Environmental Simulation Model (REM)," EPA-R4-73-013a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1973).

141. A. Q. Eschenroeder, J. R. Martinez, and R. A. Nordsieck, "Evaluation of a Diffusion Model for Photochemcial Smog Simulation," EPA-R4-73-012a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1972).

142. M. K. Liu and J. H. Seinfeld, "On the Validity of the Grid and Trajectory Models of Urban Air Pollution," Atmos. Environ., Vol. 9, pp. 555-574 (1975).

143. B. Ackerman, "METROMEX: Wind Fields over St. Louis in Undisturbed Weather," Bull. Am. Met. Soc., Vol. 55, pp. 93-95 (1974).

144. A. Miller, "Wind Profiles in West Coast Temperature Inversions," Report No. 4, Department of Meteorology, San Jose State University, San Jose, California (1968).

145. A. J. Dyer, "Do GHOST Balloons Measure Eulerian Mean Velocities?" J. Atmos. Sci., Vol. 30, pp. 510-513 (1973).

146. J. K. Angell, C. R. Dickson, and W. H. Hoecker, Jr., "Relative Diffusion Within the Los Angeles Basin as Estimated from Tetroon Triads," J. Appl. Meteor., Vol. 14, pp. 1490-1498 (1975).

147. S. D. Reynolds et al., "Further Development and Validation of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants," R73-19, Systems Applications, Incorporated, San Rafael, California (1973).

148. R. C. Sklarew, A. J. Fabrick, and J. E. Prager, "A Particle-in-Cell Method for Numerical Solution of the Atmospheric Diffusion Equation, and Applications to Air Pollution Problems," 3SR-844, Systems, Science, and Software, Incorporated, La Jolla, California (1971).

149. M. C. MacCracken, "Initial Application of a Multi-box Air Pollution Model to the San Francisco Bay Area," Report UCRL-73994, Lawrence Livermore Laboratory, University of California, Livermore, California (1972).

150. M. C. MacCracken and G. D. Sauter, eds., "Development of an Air Pollution Model for the San Francsico Bay Area," UCRL-51920, Vol. 1, Lawrence Livermore Laboratory, University of California, Livermore, California (1975).

151. C. C. Shir and L. J. Shieh, "A Generalized Urban Air Pollution Model and Its Application to the Study of SO_2 Distributions in the St. Louis Metropolitan Area," RJ 1227 (19588), IBM Research Laboratory, San Jose, California (1973).

152. T. W. Tesche, "Evaluating Simple Oxidant Prediction Methods Using Complex Photochemical Models," EM78-14, Systems Applications, Incorporated, San Rafael, California (1978).

153. T. W. Tesche and C. S. Burton, "Simulated Impact of Alternative Emission Control Strategies on Photochemical Oxidants in Los Angeles," EF78-22R, Systems Applications, Incorporated, San Rafael, California (1978).

154. T. W. Tesche, unpublished data, Systems Applications, Incorporated, San Rafael, California (1978).

155. R. G. Lamb and H. Hogo, "Testing and Evaluating a Lagrangian Approach to Highway Modeling," Systems Applications, Incorporated, San Rafael, California (1978).

156. R. E. Eskridge and K. L. Demerjian, "A Highway Model for the Advection, Diffusion, and Chemical Reaction of Pollutants Released by Automobiles: Part I--Advection and Diffusion of SF_6 Tracer Gas," Joint Conference on Applications on Air Pollution Meteorology, 29 November-2 December 1977, Salt Lake City, Utah.

157. M. E. Danard, "Numerical Modeling of Carbon Monoxide Concentrations Near Highways," J. Appl. Meteor., Vol. 11, pp. 947-957 (1972).

158. M. I. Hoffert, "Laboratory Simulation of Photochemically Reacting Atmospheric Boundary Layers: A Feasibility Study," Atmos. Envir., Vol. 9, pp. 33-48 (1975).

159. A. H. Huber et al., "Stack Placement in the Lee of a Mountain Ridge: A Wind Tunnel Study," EPA-600/4-76-047, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

160. A. H. Huber and W. H. Snyder, "Building Wake Effects on Short Stack Effluents," Third Symposium on Atmospheric Turbulence, Diffusion, and Air Quality, 19-22 October 1976, Raleigh, North Carolina.

161. S. Sethuraman and J. E. Cermak, "Physical Modeling of Flow and Diffusion Over an Urban Heat Island," Proc. of Conf. on Turbulent Diffusion in Environmental Pollution, 8-14 April 1973, Charlottesville, Virginia.

162. R. S. Thompson and W. H. Snyder, "Environmental Modeling and Simulation: EPA Fluid Modeling Facility," EPA-600/9-76-016, Office of Research and Development and Office of Planning and Management, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

163. H. Jeffries, D. Fox, and R. Kamens, "Outdoor Smog Chamber Studies: Effect of Hydrocarbon Reduction on Nitrogen Dioxide," EPA-650/3-75-011, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1975).

164. B. Dimitriades, "Effects of Hydrocarbon and Nitrogen Oxides on Photochemical Smog Formation," Environ. Sci. Technol., Vol. 6, pp. 253-260 (1972).

165. W. E. Wilson, Jr. and A. Levy, "A Study of Sulfur Dioxide in Photochemical Smog. I: Effect of SO_2 and Water Vapor Concentration in the 1-Butene/NO_x/SO_2 System," J. Air Poll. Contr. Assoc., Vol. 20, p. 385, (1970).

166. K. E. Noll and T. Miller, "Highway Air Quality: Vol. I--Design of Air Monitoring Surveys," FHWA-RD-75-1, U.S. Department of Transportation, Washington, D.C. (1975).

167. "Quality Assurance Handbook for Air Pollution Measurement," EPA-600/9-76-005, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

168. K. E. Noll and T. Miller, "Highway Air Quality: Vol. II--Monitoring Manual," FHWA-RD-75-2, U.S. Department of Transportation, Washington, D.C. (1975).

169. Federal Register, Vol. 36, p. 8186 (1971).

170. A. B. O'Keefe and G. C. Ortman, "Primary Standards for Trace Gas Analysis," Anal. Chem., Vol. 38, p. 760 (1966).

171. F. P. Scaringelli, "Primary Standards for Trace Gas Analysis," Anal. Chem., Vol. 42, p. 871 (1970).

172. "Instrumentation for Environmental Monitoring," LBL-1, Lawrence Berkeley Laboratory, University of California, Berkeley, California (1976).

173. F. Pasquill, Atmospheric Diffusion (D. Van Nostrand Company, New York, New York, 1962).

174. "Objective Procedures for Optimum Location of Air Pollution Observation Stations," EPA-650/4-75-005, U.S. Environmental Protection Agency, Washington, D.C. (1975).

175. "Guidance for Air Quality Monitoring Network Design and Instrument Siting," (Revised), OAQPS No. 1.2-012, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1976).

176. "Report of the Air Monitoring Siting Workshop," U.S. Environmental Protection Agency, Las Vegas, Nevada (1976).

177. W. F. Dabberdt, F. L. Ludwig, and W. B. Johnson, Jr., "Validation and Applications of an Urban Diffusion Model for Vehicular Pollutants," Atmos. Environ., Vol. 1, p. 603 (1973).

178. G. E. Anderson et al., "Air Quality in the Denver Metropolitan Region: 1974-2000," EPA-908/1-77-002, U.S. Environmental Protection Agency, Region VIII, Denver, Colorado (1977).

179. T. C. Curran and N. H. Frank, "Assessing the Validity of the Lognormal Model When Predicting Maximum Air Pollution Concentrations," 68th Annual Meeting, Air Pollution Control Association, Boston, Massachusetts (1975).

180. W. S. Cleveland et al., "The Analysis of Ground Level Ozone Data from New Jersey, New York, Connecticut, and Massachusetts: Transport from the New York City Metropolitan Area," Fourth Symposium on Statistics and the Environment, Washington, D.C. (1976).

181. "Transportation Control Strategy Development for the Denver Metropolitan Area," APTD-1368, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1972).

182. G.E.P. Box and G. C. Tiao, "Intervention Analysis with Applications to Economic and Environmental Problems," J. Amer. Stat. Assoc., Vol. 70, p. 70 (1975).

183. G.E.P. Box and G. C. Tiao, "A Change in Level of a Non-stationary Time Series," Biometrika, Vol. 52, p. 181 (1965).

184. G. C. Tiao, G.E.P. Box, and W. J. Hamming, "Analysis of Los Angeles Photochemical Smog Data: A Statistical Overview," J. Air Poll. Contr. Assoc., Vol. 25, p. 261 (1973).

185. "Guidelines for Air Quality Maintenance Planning and Analysis: Vol. II--Air Quality Monitoring and Data Analysis," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1974).

186. T. C. Curran and W. F. Hunt, Jr., "Interpretation of Air Quality Data with Respect to the National Ambient Air Quality Standards," J. Air Poll. Contr. Assoc., Vol. 25, p. 711 (1975).

187. C. S. Burton et al., "Oxidant/Ozone Ambient Measurement Methods: An Assessment and Evaluation," EF76-111R, Systems Applications, Incorporated, San Rafael, California.

188. "Transportation and Traffic Engineering Handbook," Institute of Traffic Engineering (1976).

189. P. F. Everall, "Urban Freeway Surveillance and Control: The State of the Art," Federal Highway Administration, U.S. Department of Transportation, Washington, D.C. (1972).

190. "A Policy on Design of Urban Highways and Arterial Streets," American Association of State Highway Officials (1973).

INDEX

NOTE ADDED IN PROOF

On June 9, 1978 the Administrator of the EPA signed a proposed revision of the primary photochemical oxidant standard. At the time of this writing, the proposed standard had not been published in the Federal Register. Available information indicates that the proposal differs from the current standard in the following respects:

- > The proposal applies solely to ozone, not to the more general class of photochemical oxidants.
- > The concentration is specified as 0.10 rather than 0.08 ppm.
- > Only the maximum one-hour-average ozone concentration on each day is considered in evaluating compliance with the standard.
- > Compliance with the standard is to be determined by adding the number of exceedances during the past three years, dividing by three, and rounding the result to the nearest tenth. If that number is greater than one, the standard has been violated.

The proposed revision may also incorporate a change in wording from " . . . not to be exceeded . . . " to " . . . not expected to be exceeded . . . ." Such a change would permit the use of statistical procedures to extrapolate from less than a full year's data to determine the number of exceedances.

Following publication of the revision in the Federal Register, there will be a waiting period from public comment and, possibly, further revision by the EPA before promulgation of a new primary standard. Consequently, the above description may not accurately describe the standard that will be promulgated.

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FEDERALLY COORDINATED PROGRAM OF HIGHWAY RESEARCH AND DEVELOPMENT (FCP)

The Offices of Research and Development of the Federal Highway Administration are responsible for a broad program of research with resources including its own staff, contract programs, and a Federal-Aid program which is conducted by or through the State highway departments and which also finances the National Cooperative Highway Research Program managed by the Transportation Research Board. The Federally Coordinated Program of Highway Research and Development (FCP) is a carefully selected group of projects aimed at urgent, national problems, which concentrates these resources on these problems to obtain timely solutions. Virtually all of the available funds and staff resources are a part of the FCP, together with as much of the Federal-aid research funds of the States and the NCHRP resources as the States agree to devote to these projects.*

FCP Category Descriptions

1. Improved Highway Design and Operation for Safety

Safety R&D addresses problems connected with the responsibilities of the Federal Highway Administration under the Highway Safety Act and includes investigation of appropriate design standards, roadside hardware, signing, and physical and scientific data for the formulation of improved safety regulations.

2. Reduction of Traffic Congestion and Improved Operational Efficiency

Traffic R&D is concerned with increasing the operational efficiency of existing highways by advancing technology, by improving designs for existing as well as new facilities, and by keeping the demand-capacity relationship in better balance through traffic management techniques such as bus and carpool preferential treatment, motorist information, and rerouting of traffic.

3. Environmental Considerations in Highway Design, Location, Construction, and Operation

Environmental R&D is directed toward identifying and evaluating highway elements which affect the quality of the human environment. The ultimate goals are reduction of adverse highway and traffic impacts, and protection and enhancement of the environment.

4. Improved Materials Utilization and Durability

Materials R&D is concerned with expanding the knowledge of materials properties and technology to fully utilize available naturally occurring materials, to develop extender or substitute materials for materials in short supply, and to devise procedures for converting industrial and other wastes into useful highway products. These activities are all directed toward the common goals of lowering the cost of highway construction and extending the period of maintenance-free operation.

5. Improved Design to Reduce Costs, Extend Life Expectancy, and Insure Structural Safety

Structural R&D is concerned with furthering the latest technological advances in structural designs, fabrication processes, and construction techniques, to provide safe, efficient highways at reasonable cost.

6. Prototype Development and Implementation of Research

This category is concerned with developing and transferring research and technology into practice, or, as it has been commonly identified, "technology transfer."

7. Improved Technology for Highway Maintenance

Maintenance R&D objectives include the development and application of new technology to improve management, to augment the utilization of resources, and to increase operational efficiency and safety in the maintenance of highway facilities.

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* The complete 7-volume official statement of the FCP is available from the National Technical Information Service (NTIS), Springfield, Virginia 22161 (Order No. PB 242057, price $45 postpaid). Single copies of the introductory volume are obtainable without charge from Program Analysis (HRD-2), Offices of Research and Development, Federal Highway Administration, Washington, D.C. 20590.


FHWA
R&D