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CONTROLLING AIRBORNE PARTICLES

Committee on Particulate Control Technology
Environmental Studies Board
Commission on Natural Resources
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C. 1980

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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Acknowledgments

This report was prepared by the Committee on Particulate Control Technology, which was organized under the auspices of the Environmental Studies Board of the Commission on Natural Resources of the National Research Council. Although the initial drafts of various sections of this report were prepared by individuals, the document was extensively reviewed by the entire Committee. The report represents the collective views of the members.

The Committee was assisted in its work by a number of people who responded generously with their data, analyses, and views. Their names are listed in an Appendix. We gratefully acknowledge their help.

The staff officer for the Committee was Myron F. Uman; its administrative assistant was Nancy Fairfax. Editorial assistance was provided by Robert C. Rooney, Barbara Davies, and Judith Cummings, and the manuscript was prepared by the Manuscript Processing Unit under the capable leadership of Estelle Miller.

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Summary

In accordance with provisions of the Clean Air Act Amendments of 1977 (PL 95-95), the U.S. Environmental Protection Agency (EPA) asked the National Academy of Sciences to study (a) the relationships between characteristics of atmospheric particles and effects on public health and welfare and (b) the availability of technology for controlling airborne particles. Health and welfare effects were reviewed in *Airborne Particles* (NRC 1979) and potential effects of global climate have been described in *Energy and Climate* (NRC 1977).

This report describes current knowledge about ambient concentrations of particles in the air, their sources, and techniques for their control. Its purpose is to assess the availability of technology for protecting the population from potentially harmful exposures.

A growing body of evidence of the effects on health and welfare of particles of specific chemical composition and size has recently shifted the focus of public and scientific concern from total suspended particulate mass (TSP) to inhalable particles (those with diameters less than 15 micrometers [μm]) and to fine particles (those with diameters less than about 2 μm). Current standards, which establish maximum permissible levels of TSP, are under review by EPA, and revised standards may be promulgated for TSP, inhalable particles, and fine particles.

The origins, behavior, and natural removal processes for fine particles are different from those for particles larger than a few micrometers in diameter; recognition of these differences is essential to devising effective strategies for controlling atmospheric particles. Control of ambient concentrations of inhalable particles depends on control of fine particles, which comprise a substantial fraction of the inhalable particulate mass.

Despite dramatic reductions in national emissions of TSP over the past decade, current control strategies have been relatively ineffective in controlling atmospheric concentrations of fine particles and appear to be only moderately effective in controlling inhalable particles. One reason is that existing control techniques were designed to reduce emissions of TSP, which can be done most easily by removing the larger, more massive particles. Current control techniques, therefore, are less effective in removing fine particles from stack gas emissions than in removing coarse ones. A second reason is that control of atmospheric concentrations of fine particles depends on controlling emissions of certain gases—principally sulfur oxides, nitrogen oxides, and hydrocarbons—which are transformed into particles by physical and chemical processes that occur in the ambient atmosphere. Although reasonably effective controls for emissions of sulfur dioxide are currently available, they have only recently been applied and at that only on new sources. Similar controls are not now commercially available for oxides of nitrogen.

The problems of controlling fine particles will be exacerbated if projected trends in the use of fuels are realized. Forecasts indicate increases in the use of coal, synthetic liquid fuels derived from coal and oil shale, diesel fuel, fuels derived from refuse, and wood for residential space heating. As a result, emissions of both fine particles and gaseous precursors to fine particles are expected to increase even though projections suggest that national annual emissions of TSP will continue to decrease in the future. Emissions of sulfur dioxide are expected to remain almost constant over the next decade while those of the oxides of nitrogen are likely to increase, perhaps as much as 30 percent. The consequence of these trends will be a shift in the size distribution of the ambient aerosol from coarse to fine particles. Detailed studies of potential emissions and ambient concentrations of inhalable or fine particles, however, are not available.

Changes in the chemical composition and particle size distribution of emissions, improved control technologies, implementation of trade-off policies, and changes in operations (for example, use of alternative fuels or combustors) may alter the nature of the ambient aerosol. The hazards represented by airborne particles may increase even though the total mass—or even the mass of inhalable particles—emitted to the atmosphere may be reduced.

This report examines the elements of a national control strategy for atmospheric particles in light of the conditions and trends described above and assesses the availability of scientific knowledge about each element. The major issues, conclusions, and recommendations of the report are summarized below.

AMBIENT PARTICLES AND THEIR MEASUREMENT

The mass concentration of atmospheric particulate matter is generally bimodal; one mode consists of fine particles with diameters no greater than 2 μm and the other consists of coarse particles with diameters ranging between 2 and 100 μm. The fine particulate mode is composed primarily of sulfates and other secondary particles, but it also contains many of the more toxic elements that are emitted as fine primary particles. The coarse particulate mode is usually dominated by dusts.

Measurements of total suspended particulate mass tend to be dominated by relatively large dust particles which are probably less threatening to public health and welfare than fine particles. Measurements of inhalable particulate mass are also likely to contain substantial quantities of dust particles in sizes ranging from 2 to 15 μm.

To monitor airborne particles for purposes of protecting public health and welfare, it is necessary to obtain separate samples of particles in at least two size ranges: less than about 2 μm and between 2 and 15 μm. Dichotomous samplers, currently available, are suitable for this purpose. In addition to dichotomous samplers, monitoring networks should continue to maintain enough of the traditional high-volume TSP samplers to provide continuity in the historical record of such data.

We foresee the need for chemical elements and species present in aerosols to be routinely characterized as a function of particle size. To anticipate that need and to provide data for use in modern interpretive techniques, EPA should establish a small number of urban and rural sampling stations that incorporate advanced methods for determining particle size and composition, interactions with water vapor, light scattering and absorption, range of visibility, and other characteristics of the aerosol.

Current methods for collecting and analyzing nitrates and organics in aerosols need improvement. Methods for characterizing carbonaceous material in airborne particles should be improved, compared, and introduced into monitoring procedures. Well-characterized standard reference samples of organic materials should be developed and distributed for assuring the reliability of procedures used by analytical laboratories. If sources of carbon-bearing particles become more prominent, improved instruments for measuring the effects of both scattering and absorption of light on visibility should be developed and deployed.

SOURCES OF ATMOSPHERIC PARTICLES

Emissions from most sources—anthropogenic and natural—are not adequately characterized by particle size and composition. Ducted emissions of condensible vapors, unducted fugitive process emissions, and fugitive dusts are poorly characterized.

Emission factors, which relate emissions to the characteristics of processes such as fuel used or number of units produced, should be obtained under the normal range of operating conditions of facilities and should include consideration of particle size and composition. To obtain improved emission factors, field studies should include monitoring of operating conditions, sampling of stack gases and particles, and plume studies at the same time.

Conventional projections of future emissions do not distinguish between particles of different sizes and composition. Detailed studies are needed to estimate the effects on particulate air quality of perceived trends in the use of fuels. Research on emissions from sources using alternative fuels is essential.

Coal combustion, especially in electric utilities, is projected to be the single most important source of SO_x emissions through 1990. Effective controls for SO_x will be applied to new coal-fired power plants, but units built before 1976, most of which are essentially uncontrolled for SO_x, will account for the major fraction of national SO_x emissions through 1990. Increased use of coal by electric utilities and other industries will also account for the major part of the predicted increase in NO_x emissions.

The diesel engine, whether or not it replaces the gasoline engine in passenger cars, is likely to become a major source of urban particulate matter. The particles emitted from diesel engines are mostly in the submicrometer range, are readily inhaled, and contain many carcinogens. In addition, these particles may cause significant reductions in visibility.

CONTROL MEASURES

Engineering strategies for control have focused on end-of-pipe treatment of stationary and mobile ducted sources. End-of-pipe treatment may be an acceptable design strategy in many circumstances, such as when recognition of the need for controls comes after the process equipment has been designed and is operating, but a potentially more useful engineering strategy is to incorporate environmental considerations into every aspect of design, including selection of raw materials, processes, and products.

Conventional sources of ducted emissions can be controlled through use of electrostatic precipitators or fabric filters. The overall mass-removal efficiencies of these devices are generally greater than 95 percent. Current designs of these devices exhibit minima in collection efficiency for particles around 1 μm in diameter. Particle scrubbers are also effective control devices in some circumstances, but not for particles less than 1 μm in diameter. Modern designs of conventional stack gas scrubbers are about 90 percent efficient for removing sulfur oxides; effective controls for emissions of nitrogen oxides are not currently commercially available but improvements are anticipated. Emissions of condensible vapors and fugitive process emissions are poorly controlled.

Removal efficiencies of gas-cleaning devices should be determined as functions of particle size. Fractional efficiencies are, however, difficult to measure; further development of methods for measuring the size distributions of particles under process conditions should be supported. To improve control of emissions of fine primary particles, performance standards should be expressed in terms of particle size.

Because the efficiency of gas-cleaning devices depends on operating conditions, control strategies should be designed to insure proper maintenance of equipment.

Controlling emissions of SO_x and NO_x from coal combustion, especially in electric power generating facilities, is a major concern. If significant reductions in nationwide emissions of SO_x are to be achieved by 1990, control of coal-fired utilities and other industrial facilities built before 1976 will have to be addressed. Development of reliable, cost-effective controls for NO_x for coal-fired plants is of high priority.

Because atmospheric particles arise both from direct emissions of primary particles and from the transformation of gaseous pollutants in the atmosphere, it is important to consider synergisms and compromises in controlling emissions of particles and gaseous precursors. Control of gaseous precursors in some cases exacerbates the problem of controlling direct emissions of fine particles. Modification of production processes may be required to achieve improved, simultaneous control of particles and gaseous precursors. Potentially attractive alternatives for the long term are clean-burning fuels such as methanol, which produces few particles and gaseous precursors during combustion.

A major program for the development of controls of particulate and NO_x emissions from diesel engines is urgently needed.

RELATIONSHIPS BETWEEN EMISSIONS AND AIR QUALITY

Current understanding of the relationships between emissions of sulfur oxides and sulfate air quality indicates that sulfate problems can occur on large, regional scales, transcending state and national boundaries. Reasonably good empirical models of regional sulfate problems can be made. More empirical studies and fundamental research are needed, however, before these models can be used to predict severity of episodes or to devise optimal control strategies.

Even less complete than our understanding of the factors influencing the formation of sulfates is our understanding of the formation of nitrates, nitric acid, and organic particles by reactions of nitrogen oxides, hydrocarbons, and other species. The role of nitric acid in acid precipitation has not been adequately investigated. The reactions, transport, and deposition of organic materials need to be studied in detail.

Improving modeling capabilities will require, as a first step, expanding emission inventories to include the size distribution and chemical composition of conventional ducted emissions, fugitive process emissions, anthropogenic and natural fugitive dusts, and other natural sources. Eventually, inventories should also include information on the variations of emissions in time.

The application of modern methods—for example, chemical element balances—for assessing the contributions that categories of sources make to ambient concentrations should greatly benefit urban air quality management. Authorities should begin to make routine use of the chemical element balance model.

1 Introduction

National Ambient Air Quality Standards for the total mass of particulate matter suspended in the atmosphere were first promulgated in 1971. The primary standard, an annual geometric mean of 75 micrograms per cubic meter ($\mu g/m^3$), is intended to protect public health with an adequate margin of safety. The secondary standard, 60 $\mu g/m^3$, is intended to protect the public welfare from any known or anticipated adverse effects. The primary and secondary standards for maximum concentrations in a 24-hour period are 260 and 150 $\mu g/m^3$, respectively. The 24-hour standards may not be exceeded more than once a year.

The Clean Air Act Amendments of 1977 (PL 95-95) direct the Administrator of the U.S. Environmental Protection Agency (EPA) to undertake a thorough review of the criteria on which these and other air quality standards are based. The Act provides for studies to be conducted of the relationships between the presence and characteristics of airborne particles and public health and welfare, and of the availability of technology to protect the population against harmful exposures. This report describes current knowledge about ambient concentrations of particles in the air, their sources, and techniques for their control.

Among atmospheric contaminants, airborne particulate matter is unique in its complexity. Ambient concentrations of particulate matter result not only from emissions of particles as such, but also from emissions of certain gases that either condense as particles directly or undergo chemical transformation before condensing as particles. The relationships between emissions and air quality are complicated by the existence of interactions among gases, between gases and particles, and among particles as well as by the existence of several removal processes. Furthermore, an adequate description of particles in the atmosphere requires specification of not only density or concentration, but also size distribution, chemical composition, phase (i.e., liquid or solid), and morphology of the particles. Some particles, through a variety of mechanisms, can be significantly harmful to man and the environment, with effects on both health and welfare. Given these complexities, this report, rather than focusing only on control technology, addresses more broadly the state of scientific and technical information necessary for developing strategies for controlling atmospheric particles.

THE BASIS FOR CONCERN

Effects on health and welfare attributed to atmospheric particles in general and to sulfate aerosols in particular have been examined in detail in two recent reports (NRC 1979 and NRC 1978, respectively). A complete review of these effects is, therefore, not presented here. However, to lay the foundation for our discussion of control strategies, we highlight some of the most important health and welfare issues.

Health Effects

Current air quality standards for atmospheric particles specify limits on the concentration of the mass of total suspended particulate matter (TSP). However, the potential for adverse health effects depends not only on the mass concentrations to which people are exposed, but also on the physical and chemical properties of the particles in the aerosol. Two important properties are size and chemical composition. For example, natural mechanisms prevent larger inhaled particles from reaching the lower respiratory tract. Only particles smaller than about 15 micrometers (μm) reach the lower respiratory tract during mouth breathing, while the upper limit for nasal breathing is about 10 μm. Furthermore, only particles with diameters less than 2 or 3 μm penetrate to the deepest part of the lungs, the alveoli, where gases are exchanged with the circulatory system (Miller et al. 1979). The chemical nature of the particles, and in some cases their shape or morphology, determines their carcinogenicity, mutagenicity, and other toxic properties. Other important properties of aerosols include acidity (pH), solubility, and physical structure.

Both large particles retained in the nasal and ciliated portions of the upper airways and finer aerosols that reach the alveolar portion of the lungs may be potential hazards to health. Large particles can dissolve and enter the body as systemic poisons through the digestive or lymphatic systems. Small particles may, in themselves, be toxic to sensitive lung tissue or may transport toxic elements and compounds—such as lead, cadmium, antimony, arsenic, nickel, and benzo[a]pyrene—which are known to occur in higher concentrations in particles with diameters less than 2 μm than in larger particles.

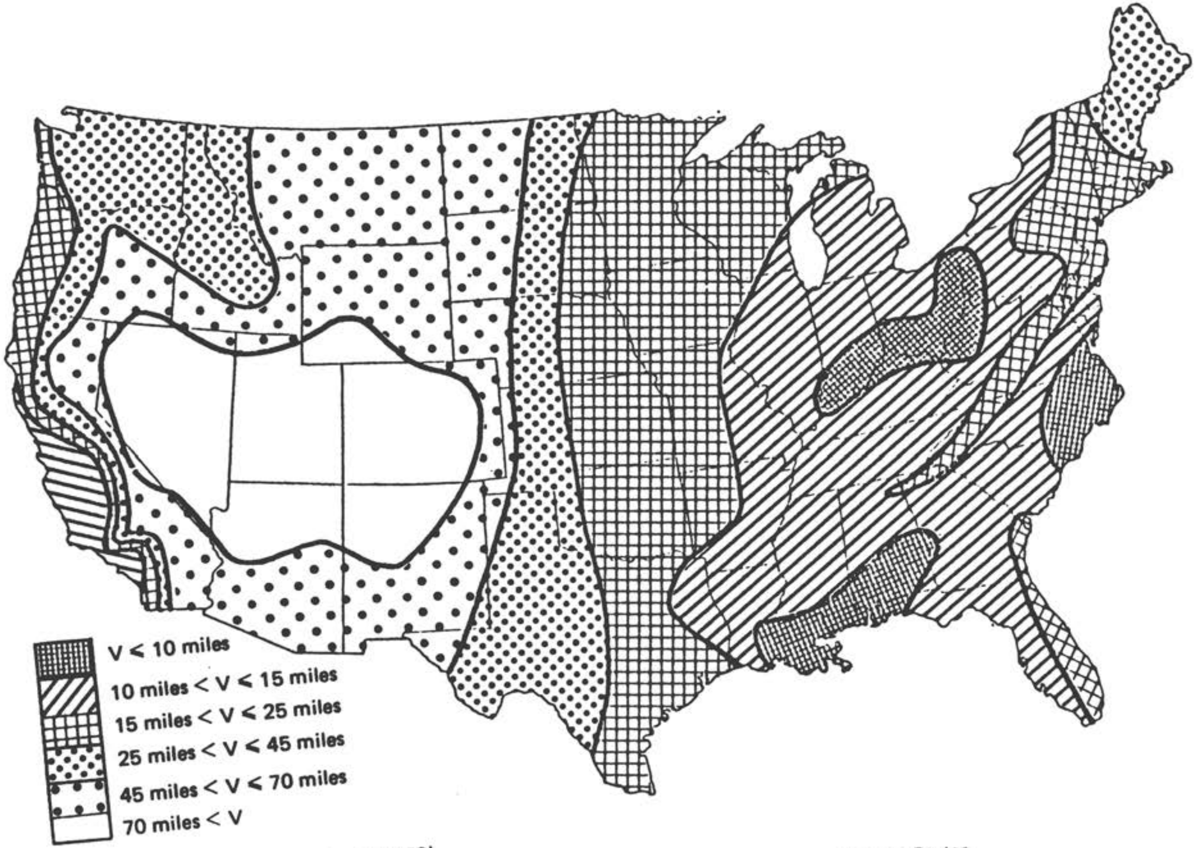
A thorough evaluation of the risks that airborne particles pose to public health should include not only analysis of the physical and chemical properties of the aerosol, but also assessment of the exposures to which populations are or will be subjected. Samples of airborne particles are collected at a large number of urban and rural sites throughout the United States and in other countries. However, sampling sites are located almost exclusively outdoors while most people spend the major portion of their time indoors. Hence, current air quality data may not be typical of the air breathed either by the general population or by particularly sensitive segments of the population.

Concentrations of airborne particles indoors are produced by both indoor and outdoor sources. Concentrations resulting from outside sources depend on penetration and ventilation rates; it is believed that penetration rates depend on particle size. Indoor exposures, however, are thought to be more influenced by indoor than by outdoor sources (Alzona et al. 1979, Moschandreas et al. 1979, Spengler et al. 1979). Potential problems associated with indoor sources will become increasingly important as ventilation and infiltration rates are reduced in response to increasing heating and cooling costs. To obtain more realistic estimates of actual exposures, relationships among outdoor sources, indoor sources, and the populations presumed to be at risk will have to be evaluated.

Welfare Effects

The presence of particles in ambient air may also have adverse effects on public welfare. These effects include degradation of visibility over wide regions; acidification of precipitation, which may adversely affect aquatic and terrestrial ecosystems, including the managed ecosystems of agriculture; and soiling and corrosion of buildings and other property.

The degradation of visibility due to regional haze (occurring across distances of 500 kilometers [km] or more) is caused by sulfates and other fine particles (Friedlander 1977, NRC 1979). The problem in the East differs greatly from that in the West as Figure 1.1 illustrates. In the Rocky Mountain West the rugged terrain and excellent visual range (averaging over 70 miles in many nonurban areas and exceeding 120 miles on the best days) produce many exceptional vistas. In areas of high visibility, the optical quality of the atmosphere is very susceptible to small changes in concentrations of pollutants. For example, in a uniform atmosphere with a visual range of 100 miles, adding only 1 $\mu g/m^3$ of sulfate particles of an appropriate size will reduce the visual range to approximately 80 miles. Recent



SOURCE: Trijonis and Shapland (1979).

FIGURE 1.1 Median yearly visual range at suburban and nonurban airports in the United States.

studies indicate that regional visibility in the Southwest has already been degraded by sulfates and other fine particles (Macias et al. 1979b, Trijonis 1979), and future energy development may lead to further deterioration of visibility.

East of the Mississippi and south of the Great Lakes, the median value of the visual range in nonurban areas tends to be between 10 and 15 miles as an annual average but 8 to 12 miles during the summer (Trijonis and Shapland 1979). There is growing evidence that much of the haze that limits visibility in the East is man-made and that it is caused, in large part, by relatively high concentrations of sulfate particles (NRC 1978, 1979; Trijonis and Yuan 1978; Leaderer and Stolwijk 1979). Concerns about haze in the East involve not only aesthetics, but also hindrance of aviation (Miller et al. 1972) and the possibility of significant climate modification on a regional scale (NRC 1979, Husar et al. 1979). Furthermore, sulfate (and possibly nitrate) aerosols, important components of the eastern haze, are also believed to be closely related to the ecological (and economic) problem of the increasing acidity of precipitation (Likens 1976, Likens et al. 1979).

CLASSIFYING AIRBORNE PARTICLES

In this report, the term *suspended particulate matter* refers to solid or liquid particles in the air. The particles and the gases in which they are suspended make up the *aerosol*. Because particulate pollution is a complex phenomenon, many terms are used to distinguish among various types of particulate matter.

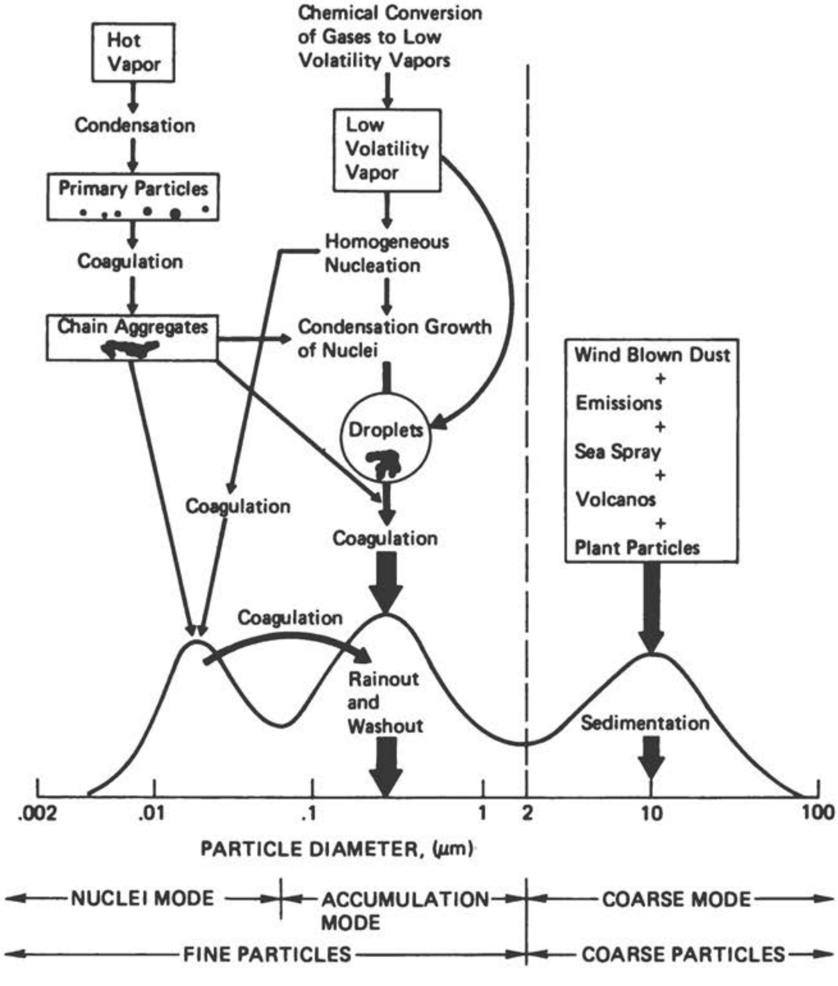
One way of distinguishing airborne particles is according to their origin. Two basic categories are *anthropogenic* (man-made) and *natural*. Among the anthropogenic and natural particles are both *primary particles*, which are emitted directly as particles, and *secondary particles*, which are formed in the atmosphere by gas-to-particle transformations. Examples of primary particles are fly ash, soot, and dust; examples of secondary particles are sulfates, formed from sulfur dioxide (SO_2); nitrates, formed from oxides of nitrogen (NO_x); and secondary organics, formed from hydrocarbon vapors. Man-made particles also include *condensibles*, particles that condense from vaporous emissions as a plume cools in the atmosphere.

It is often helpful to categorize atmospheric particles according to the type of source from which they are emitted. *Traditional* or *conventional* sources are those historically included in emission inventories, such as ducted exhausts from industrial or mobile sources. Among the *nontraditional* or *nonconventional* sources are *fugitive process* sources, i.e., nonducted emissions escaping from buildings or industrial sites; and *fugitive dust* sources, i.e., dust suspended by traffic, construction, agricultural practices, or other human activities, or by the wind from storage piles or exposed surfaces.

An important scheme for categorizing airborne particles is based on size. Figure 1.2 illustrates the three modes into which suspended particles are divided: the *nuclei mode, accumulation mode,* and *coarse mode*. The nuclei mode, from about 0.005 to 0.1 μm in diameter, accounts for the preponderance of particles by number, but because of their small size, these particles rarely account for more than a few percent of the total mass of suspended particles. Particles in the nuclei mode are formed from condensation of hot vapors during combustion processes and from gas-to-particle conversion in the atmosphere. The accumulation mode, from 0.1 to approximately 1 or 2 μm, usually accounts for most of the aerosol surface area and a substantial part of the aerosol mass. The accumulation mode originates from coagulation of particles in the nuclei mode and from heterogeneous nucleation (condensation of one material on another) of secondary aerosols. The coarse mode, from approximately 1 or 2 μm to 50 or 100 μm, is formed by mechanical processes such as grinding and usually consists primarily of man-made and natural dust particles. Because coagulation is very weak for particles in the accumulation mode, little of the mass in that mode is transferred into the coarse mode. The origins, behavior, and removal processes for the nuclei and accumulation modes are distinct from those for the coarse mode. To be effective, strategies for controlling atmospheric particles should recognize these differences.

An alternative method of classification according to size is based on the characteristics of instruments used in routine measurements. Most of the historical data base consists of measurements of *total suspended particulate* mass (TSP) obtained with the method specified by EPA, the high volume sampler (Hi-Vol). TSP essentially represents the mass of all particles smaller than about 50 μm in diameter, although the upper size cutoff of the sampler varies with wind speed and direction (see Chapter 2). Recently, EPA has begun acquiring extensive data with dichotomous samplers which collect the total mass of particles smaller than 15 μm in diameter, called the *inhalable particulate* mass (IP). The dichotomous sampler also separately determines particulate mass for diameters less than 2.5 μm; this fraction, called the *fine particulate* (FP) mass, consists primarily of particles in the nuclei and accumulation modes.

Particles should also be classified according to chemical composition. Chemical composition and size distribution are often interrelated. For example, in the ambient aerosol, sulfates are found predominantly in the accumulation mode, whereas soil particles and sea spray occur primarily in the coarse mode. In aerosols emitted from coal combustion, volatile elements such as cadmium and arsenic occur in higher concentrations in fine particles than in coarse particles. The chemical composition of the particles is important not only because it is a major factor in determining health and welfare effects, but also because it can be a helpful tool for determining the sources of the particles.



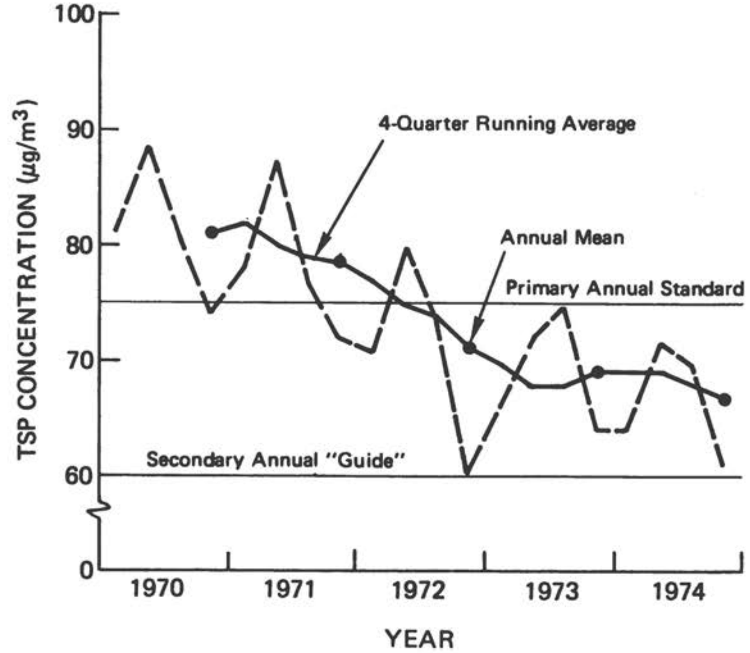
SOURCE: Whitby and Cantrell (1976) Fine particles. *In* International Conference on Environmental Sensing and Assessment. September 14-19, 1975, Las Vegas, Nevada. Institute of Electrical and Electronic Engineers.

FIGURE 1.2 Idealized schematic of the distribution of particle surface area of an atmospheric aerosol. (The principal modes, sources of mass, and formation and removal processes are indicated.)

CURRENT STATUS OF EMISSIONS AND CONTROLS

As a result of control strategies based on the air quality standard for total suspended particulate mass, emissions of TSP from conventional sources in the United States were estimated to have been reduced from 22.2 million metric tons per year in 1970 to 12.4 million metric tons per year in 1977 (U.S. EPA 1978). Data obtained at urban sites from 1970 to 1974 indicate a substantial reduction in TSP, from about 80 $\mu g/m^3$ in 1970 to about 66 $\mu g/m^3$ in 1974 (Figure 1.3). Data from 2,707 sampling sites in the National Aerometric Data Bank indicate that the national average concentration of particles in the atmosphere decreased by 8 percent between 1972 and 1977. More recent data indicate that the national average concentration of TSP remained relatively unchanged between 1975 and 1977 (U.S. EPA 1978).

Although the available data on TSP show an encouraging trend, concentrations of fine particles have been increasing. Concentrations of sulfates, a major portion of the fine particulate fraction, evidently increased in nonur-



SOURCE: Lynn et al. (1976).

FIGURE 1.3 Historical trends in the national average concentrations of TSP from 1,014 urban sites.

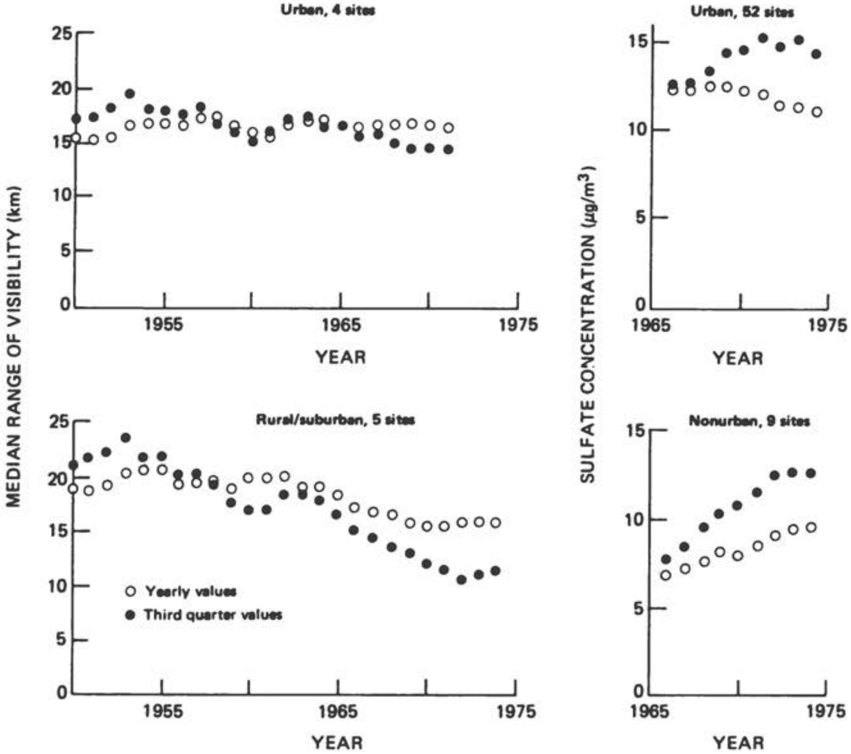


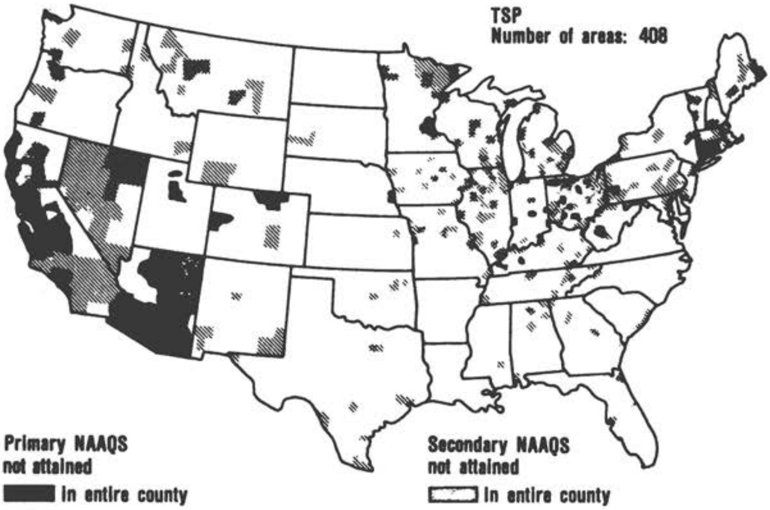
FIGURE 1.4 Three-year moving averages of concentrations of atmospheric sulfates and median range of visibility in the Northeast.

ban areas, especially in the summer, and remained approximately constant in urban areas during the late 1960s and early 1970s (Frank and Posseil 1976, NRC 1978). Data obtained at airports indicate that between the middle 1950s and the early 1970s visibility decreased substantially in suburban and nonurban areas of the East, especially in the summer (Miller et al. 1972, Trijonis and Yuan 1978, Husar et al. 1979), and in both urban and nonurban areas of the Southwest (Trijonis 1979). Our own analyses of available data to reveal trends in visibility and concentrations of sulfates for sites in the Northeast are illustrated in Figure 1.4. The sulfate data for this figure are from the EPA National Air Surveillance Network, while the visibility data are from Trijonis and Yuan (1978). Conditions in summer are represented by third quarter values. Although the sulfate and visibility data analyzed were not from the same sites, summertime and annual averages of visibility in nonurban areas are seen to be decreasing as sulfate concentrations increase. Similar trends in acidity of precipitation (Likens 1976, Likens et al. 1979) have also been reported.

Despite the decreases in emissions and ambient levels of TSP achieved in the early 1970s, many locations are not in compliance with either the primary or the secondary standards. Of 2,699 monitoring stations reporting a full year's valid data in 1977, 456 (17 percent) exceeded the primary annual standard, while 1,070 (40 percent) exceeded the secondary annual standard. Of 4,008 stations reporting at least three 24-hour values in 1977, 314 (8 percent) exceeded the 24-hour primary standard and 1,424 (36 percent) exceeded the short-term secondary standard (U.S. EPA 1978).

The geographic distribution of 408 areas in the contiguous 48 states that were not in compliance with TSP standards in August 1977 is shown in Figure 1.5. Violations of the TSP standards occur in areas that vary greatly in terms of terrain, meteorological conditions, and sources of emissions. They occur in states where coal is a major fuel (for example, Illinois, Ohio, Michigan, Pennsylvania), in states with petrochemical processing plants (Texas, Louisiana), in states with smelters (Washington, Montana, Arizona, New Mexico), and in agricultural states (Colorado, Kansas, Missouri).

As part of a comprehensive study of TSP data, Lynn et al. (1976) examined data collected in 1974 in and near 14 U.S. cities. Of 255 sampling



SOURCE: CEQ (1978).

FIGURE 1.5 Distribution of 408 areas in the contiguous 48 states that were in noncompliance with TSP standards in August 1977.

stations, 93 (36 percent) exceeded the primary annual standard, and 157 (62 percent) exceeded the secondary annual standard (Table 1.1). The cities studied ranged from lightly industrialized areas such as San Francisco to heavily industrialized areas such as Cleveland. From this study, a number of conclusions may be drawn about the contributions of various factors to observed levels of TSP: (1) Traditional sources such as power plants and industrial facilities contribute an average of about 25 $\mu g/m^3$ to urban TSP concentrations. These sources contribute from 20 to 30 $\mu g/m^3$ at monitoring sites in residential and commercial areas and as much as 50 $\mu g/m^3$ in industrial areas. (2) Nontraditional sources—fugitive process emissions and fugitive dusts—contribute roughly 25 $\mu g/m^3$ to urban TSP levels; contributions range from 20 $\mu g/m^3$ in residential areas to 30 $\mu g/m^3$ in industrial areas. (3) Nonurban concentrations of TSP consist mainly of natural particles and anthropogenic particles transported long distances from their sources. Only secondary particles or fine primary particles are transported over long distances. In the United States, the average concentration of TSP in nonurban areas is about 30 $\mu g/m^3$. The lowest levels, around 15 $\mu g/m^3$, generally occur on the West Coast, while the Northeast experiences the highest nonurban concentrations, about 35 $\mu g/m^3$. Concentrations in the mid-continent are on the order of 25 $\mu g/m^3$.

Available data suggest that control of nontraditional sources and secondary particles is at least as important as control of traditional sources for achieving compliance with current TSP standards.

FUTURE OF PARTICULATE AIR QUALITY

Insights into the future of ambient particulate concentrations in the United States can be gained from detailed projections of national emissions (for example, see MITRE 1979). Projections by MITRE suggest that total emissions of primary particles from conventional sources will decrease by 37 percent between 1975 and 1990. Their forecasts for anthropogenic emissions of gaseous precursors of secondary particles indicate that between 1975 and 1990 emissions of sulfur oxides will remain approximately constant, nitrogen oxide emissions will increase by 25 percent, and emissions of hydrocarbon vapors will decrease by 25 percent.

Projections of emissions and forecasts of future air quality are subject to considerable uncertainty. Potential regulatory action could have major effects on actual emissions; currently EPA is considering revisions of air quality standards and states are developing or revising implementation plans that may alter levels of control. It seems likely, however, that the national average concentrations of TSP will remain constant or even decrease somewhat by 1990 as a result of decreased emissions of primary particles from conventional sources and increased control of sources of fugitive dust.

TABLE 1.1 Summary of Sites in 14 Cities at Which TSP Standards Were Violated, 1974

		Annual Standard			24-Hour Standard				
		No. Sites Exceeding Standard			No. Sites Exceeding Standard		% Total Obs. > Standard		
City	Total No. of Sites with Complete 1974 Data	Primary, 75 $\mu g/m^3$	Secondary,[a] 60 $\mu g/m^3$	Highest Geometric Mean, $\mu g/m^3$	Primary, 260 $\mu g/m^3$	Secondary, 150 $\mu g/m^3$	Primary	Secondary	Highest Value, $\mu g/m^3$
Heavily Industrialized									
Cleveland	25	12	21	175	6	15	4.7	17.6	534
Birmingham	13	11	11	144	7	11	NA[b]	NA[b]	499
Philadelphia	10	7	9	122	4	8	NA[b]	~8	624
Baltimore	29	9	14	134	6	14	0.9	7.6	NA[b]
St. Louis	31	15	26	158	3	13	1.1	8.7	NA[b]
Cincinnati	25	8	21	130	0	7	0.1	4.2	296
Moderately Industrialized									
Chattanooga	12	5	5	101	1	7	0.9	6.9	434
Denver	22	14	21	131	13	22	NA[b]	NA[b]	565
Seattle	10	2	4	105	2	5	0.3	0.8	320
Providence[c]	21	1	5	88	0	1	0	0.8	173
Lightly Industrialized									
Washington, D.C.	9	2	5	102	9	9	2.2	NA[b]	527
Oklahoma City	14	5	6	107	5	13	0.7	5.5	NA[b]
Miami	17	2	7	86	0	3	0.2	1.8	NA[b]
San Francisco	17	0	2	74	3	10	0.2	1.3	286

SOURCE: Lynn et al. (1976).

[a] The secondary annual is a guide, not a standard.

[b] NA – Raw data not available.

[c] Totals are for statewide monitoring network.

Despite this conclusion, there are sobering reasons for concern over airborne particles and their effect on future air quality. First, as a result of the anticipated decrease in emissions of primary particles, the size distribution of airborne particles will continue to shift from coarse to fine. The shift in size distribution is considered likely because (1) most conventional control devices (for example, electrostatic precipitators) collect coarse particles more efficiently than fine particles; (2) some of the major categories of sources for which decreased emissions are projected (for example, production of structural materials and cement) contribute mostly coarse particles, whereas some categories of sources for which increased emissions are anticipated (for example, diesel engines) contribute mostly fine particles; and (3) the control of fugitive dust, which may become a significant element in state implementation plans, is more effective in reducing ambient concentrations of large particles than of small particles.

A second concern is about progress in controlling the precursors of secondary particles. Unfortunately, some of the most significant health and welfare effects of atmospheric particles are associated with secondary particles. Although progress is likely to be made in controlling gaseous precursors from a variety of sources, both emissions from existing uncontrolled sources and the rapid growth anticipated in new sources are likely to contribute to increased concentrations of secondary particles. Current control strategies, aimed at reducing TSP, therefore will not result in reduced exposures to fine particles, including secondary particles.

Trends in the chemical composition of ambient particulate matter are another source of concern. For example, the increased use of diesel-powered automobiles and the shift to synthetic, coal-derived fuels will probably result in increased emissions of polynuclear aromatic hydrocarbons. Furthermore, the toxic elements present in trace quantities in fuels such as coal tend to be emitted from stationary sources in the form of fine particles, which are the most difficult to control.

Concern has also been expressed about potential deterioration of air quality in particular regions of the country. Although emissions of sulfur oxides, precursors to sulfates, are expected to decrease in some regions, they are expected to increase in others. For example, national emissions of sulfur oxides are expected to remain unchanged, but these emissions are expected to increase by 70 percent in the Texas-Louisiana Gulf Coast region by 1990, owing to an increase in the number of sources and to changes in fuels used in that region. Because conditions in the Gulf Coast (for example, intense sunshine, high relative humidity, and the presence of hydrocarbon sources to promote photochemical reactions) are conducive to formation of sulfates and other secondary particles, a substantial increase in ambient concentrations of secondary particles may occur in that region and in states that are downwind (to the north and east).

All of these concerns are heightened by an examination of the reliability of emission forecasts. Projections tend to underestimate actual emissions because they do not take into account the inevitable deterioration in performance of control equipment, the introduction of unforeseen sources, and noncompliance. The problem of underestimating future emissions may be particularly severe in the MITRE study which assumes no unscheduled down-time for control equipment, no deterioration of control efficiency on stationary sources, and full compliance with control schedules.

ELEMENTS OF A CONTROL STRATEGY

We believe that an effective strategy for controlling air pollution due to particulate matter should take into account the following elements:

(1) evidence of the risks to public health and welfare of exposure to certain species of particles distinguished by size, composition, shape, and other characteristics;

(2) the extent to which sensitive populations are or will be exposed;

(3) the identification of anthropogenic and natural sources of harmful species;

(4) options for controlling anthropogenic sources or otherwise managing air quality to reduce harmful exposures;

(5) the differences in origin, behavior, control, effects, and removal processes among particles of differing sizes and composition; and

(6) the costs and benefits of alternative strategies, including assessments of how these costs and benefits are distributed in society.

It is not the purpose of this report to examine either the medical and biological evidence of risk or the costs and benefits of control strategies. The evidence of risk has been thoroughly reviewed by others (for example, NRC 1978, 1979). Assessing costs and benefits requires substantial investment of time and money, neither of which was available to us. Furthermore, under existing law, EPA may not take costs into account when establishing national air quality standards.

This report does, however, examine current scientific understanding with respect to each of the other considerations and describes what we believe to be the major problems. Chapter 2 describes our ability to measure particles in the air and current knowledge about existing ambient air quality. Chapter 3 describes sources of man-made atmospheric particles and attempts to predict how patterns of emissions may change in the future. Existing control technologies and needs for research and development are described in Chapter 4. Current understanding of the relationships between emissions and ambient concentrations of particles is treated in Chapter 5.

2 Ambient Particles and Their Measurement

Typically, the size distribution of airborne particles is bimodal. The fine and coarse particles in the atmosphere are formed by different mechanisms. Fine particles are usually formed by condensation; the condensing vapors are produced either directly by combustion or by photochemical processes that occur in the ambient atmosphere. The fine particle mode, therefore, generally consists of both primary and secondary particles. Coarse particles, on the other hand, generally result from mechanical processes, such as grinding, pulverizing, and resuspension. Windblown dust and dust generated by various human activities are important contributors to atmospheric concentrations of coarse particles.

Because of the differences in mechanisms of formation, fine and coarse particles generally have distinctly different chemical compositions. Many of the elements found in the soil, such as silicon, calcium, iron, and aluminum, generally appear in the coarse particle mode. Products of combustion such as sulfates, nitrates, organics, lead, and soot are generally associated with fine particles.

The characteristics of particles measured at any given place are strongly influenced by a number of factors, including meteorological conditions and the types of sources in the area. Usually, fine particles are rather uniformly distributed across an air basin or air shed while concentrations of coarse particles vary from place to place depending on the influence of localized sources. This fact should influence the design of sampling strategies and the interpretation of data on the atmospheric aerosol.

For more detailed discussion of the characteristics of atmospheric particles and their mechanisms of formation, see NRC (1979).

SAMPLING TECHNIQUES

Filter Samples

The air quality standards for particulate matter are based on TSP as measured by the high volume sampler (Federal Register 36, 8186, April 30, 1971). The high volume sampler is one of a class in which ambient air is drawn through a filtering medium that removes the particles in the air stream. The filter is later removed and weighed. The particles on the filter can also be analyzed using physical and chemical techniques. To collect a sample, the typical high volume sampler draws ambient air through the filter at a rate of 0.5 to 1 m^3/min. for a period of 24 hours. The design of the inlet sets an upper cutoff on the size of particles that may enter the sampler.

The high volume sampler has provided valuable historical data on TSP. Currently, TSP data are collected at approximately 4,000 federal, state, and local monitoring stations and then stored in the National Aerometric Data Bank. Of these stations, about 100 are maintained by EPA as the National Air Surveillance Network (NASN) while most of the rest are operated by state and local air quality agencies. The TSP data are used both for determining compliance with standards and for assessing trends in air quality.

Use of the high volume sampler as the standard device for measuring atmospheric particles has two major shortcomings. First, the upper cutoff in particle size is uncertain due to the aerodynamic characteristics of the inlet port; the cutoff depends strongly on wind speed and direction with respect to the orientation of the shelter housing the sampler (Wedding et al. 1977). Recent tests have shown that the aerodynamic particle diameter for which the sampling efficiency is 50 percent is probably on the order of 50 μm at a wind speed of 2 km/hr, decreasing to about 30 μm at 8 km/hr and 17 μm at 24 km/hr (McFarland et al. 1979). Because of this dependence, the device may not collect a representative sample of the larger particles, which are also the heavier ones, and may therefore underestimate TSP mass. Second, because the particles collected and the gases drawn through the filter may react chemically with one another or with the glass-fiber filter commonly used in samplers, chemical analyses of the samples may be flawed by artifacts. In particular, sulfur dioxide, nitric acid, and nitrogen dioxide react with some filter materials or deposited particles to form sulfate and nitrate when drawn through the filter (see section on Requirements for Sample Collection).

Measurement of TSP with any device suffers a more fundamental problem: the sample is strongly influenced by localized conditions, including local sources of coarse, massive particles. Larger, heavier particles are not transported far from their sources but, when present, dominate the total mass of typical samples. Consequently, fine particles, which pose the greater threat to public health and welfare, may not be accurately reflected in TSP data collected near significant sources of large particles.

The inlet of the high volume sampler can be modified to obtain different values of the upper cutoff size. For example, a 15 μm inlet may be used to collect only inhalable particles. Data obtained with such devices will be useful, but there is no reason to suspect that they will not suffer from some of the same shortcomings as TSP data. In particular, data on the mass of inhalable particulate matter will not provide information on the mass or chemical composition of the fine particle fraction.

Because of the limitations described above, research workers doing air pollution and air quality studies often use other devices to collect samples. These include the cascade impactor, the dichotomous sampler, and a variety of filter samplers, particularly those using inert Teflon filters. The cascade impactor provides a series of size-fractionated samples to a lower size limit of about 0.25 μm for impactors operating near the ambient pressure (Marple and Willeke 1976). For special low-pressure impactors the lower limit is about 0.03 μm (Hering et al. 1978, 1979). The dichotomous sampler provides two size-fractionated samples; particles with diameters less than about 2 μm are collected on one filter and larger particles (with diameters up to approximately 15 μm) are collected on another (Dzubay and Stevens 1975, Loo et al. 1976). When combined with analytical techniques such as x-ray fluorescence analysis, the cascade impactor and the dichotomous sampler are powerful tools for determining both the mass concentration and chemical composition of airborne particles as a function of particle size.

Automatic In-Situ Techniques

Existing knowledge of the size distribution of atmospheric particles has been based largely on data obtained by automatic, in-situ measuring instruments (Liu 1976). For example, the condensation nuclei counter is used for measuring the total number of particles per unit volume. Three instruments more commonly used for measuring size distribution are the optical particle counter for particles that range in size from 0.3 to 40 μm, the electrical aerosol analyzer for particles that range from 0.01 to 1.0 μm, and the diffusion battery for particles that range from 0.005 to 0.1 μm. Optical properties of the ambient aerosol can be measured with the nephelometer and attenuation devices, both of which respond predominantly to mass concentrations of particles that range in size from 0.1 to 1.0 μm.

The automatic, in-situ instruments listed here and in NRC (1979) are, in the main, research tools, but some can be operated reliably and at moderate cost for routine monitoring of air quality.

ANALYTICAL METHODS

Available Techniques

Advances in sampling methods during the 1970s have been paralleled by improvements in analytical methods for determining the elements and compounds present in collected samples. For example, x-ray fluorescence (XRF) can now be used routinely to measure concentrations of about 20 elements; it is used extensively for analyzing samples from dichotomous samplers (Jaklevic et al. 1978, Stevens et al. 1978). Instrumental neutron activation analysis (INAA) is especially useful for measuring a number of very rare elements that contribute little mass; the sources of particles can then be inferred from the presence of these elements, as described in Chapter 5 on Chemical Element Balances (Zoller and Gordon 1970, Kowalczyk et al. 1978). Because very few laboratories are equipped to do reliable INAA measurements, INAA has been used mainly for research and studies of source emissions (e.g., Greenberg et al. 1978a,b) rather than monitoring. Atomic absorption spectrometry (AAS) is widely available and can provide reliable analysis for many species. Unlike XRF and INAA, AAS is not a multi-element method. Samples must be dissolved, so great care is needed to insure complete dissolution and to avoid contamination. Ion chromatography is a new technique that is especially useful for important anions, but also requires dissolution of samples (Mulik et al. 1977). The species that can be measured with these techniques are listed in Table 2.1.

Through various combinations of these techniques, the concentrations of most elements of interest can be measured. However, other techniques must be used to measure the major light elements, especially carbon, hydrogen, nitrogen, and oxygen. Highly specialized methods have been developed using proton and neutron beams from accelerators to measure total carbon, sulfur, nitrogen, and other elements (Macias et al. 1978, 1979a; Failey et al. 1979). If proper filter materials are used, the carbon, hydrogen, nitrogen, and oxygen present in combustible materials can be measured with classical methods of combustion analysis.

Requirements for Sample Collection

The sensitivity of many multi-element methods permits accurate analysis of even small quantities of particulate matter, thereby eliminating the need for large samples. However, this sensitivity places more severe limitations on the techniques and materials that can be used in collecting samples. Filters and collectors that have not been exposed to the aerosol must, when tested for particular elements, yield readings low enough not to cause interference with measurements of ambient concentrations of those elements. In particular, the glass-fiber filters that are traditionally used in high volume samplers show enormous blank values (test readings without exposure) for many metals and therefore cannot be used with most of the new techniques. Fortunately, a wide range of organic-based filters made of materials such as cellulose acetate, polycarbonate, or Teflon exhibit low blank values for most metals. For applications involving carbonaceous materials organic-based filters may not be adequate; others of quartz or metal (for example, silver) may be needed.

Another sampling problem associated with both monitoring and research is the formation of artifacts. The most troublesome artifact, because of its relatively large magnitude and its inconsistency, is the formation of nitrates on filters exposed to NO_2 and nitric acid (Spicer and Schumacher 1979). Sulfates are also known to form on filters in air containing sulfur dioxide, especially in high relative humidity (Stevens et al. 1978). The sulfate artifact problem can be fairly serious for glass-fiber filters but is quite small for many of the newer filters such as those made of Teflon. Most of the sulfate artifacts associated with newer filter materials appear to form during the first few minutes of exposure to the aerosol. Therefore, the effect becomes unimportant if the sampling is continued for an hour or more.

Nitrate and sulfate formation from the collection of gases gives *positive* artifacts, i.e., apparent concentrations that are too high. There are also negative artifacts. For example, the vapor pressure of ammonium nitrate is sufficiently high that significant amounts that have been deposited on a filter may be revolatilized as more air is pumped through the sampler (Brosset 1979, Stelson et al. 1979). The same problem may exist for moderately volatile compounds or elements such as arsenic and selenium (Pupp et al. 1974). Currently, there is no completely satisfactory solution to the problem of negative artifacts and more research is needed. Placing a vapor-phase collector such as activated charcoal behind the filter would collect the full amount of a species in one way or another, but often separate knowledge of the amounts in the gas and particle phases of the ambient air is needed.

Recent Developments and Needed Improvements

Analytical techniques that would indicate not only the elements that are present, but also their ionic or molecular forms, are greatly needed for air quality monitoring and studies. Many of the potentially most pressing problems will entail detailed characterization of carbonaceous (organic) particulate matter (e.g., soot and polynuclear aromatic hydrocarbons). A number of methods for analyzing organic particles are currently available, but each reports a different category of carbonaceous material such as total carbon, benzene-soluble organics, noncarbonate carbon, volatilizable carbon, etc.

TABLE 2.1 Elements Measurable in the Urban Aerosol

Method	Type of Sample	Quality	Elements Measurable	Major Limitations
XRF	Dichot. sampler, >2.5 μm	Good:	Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Pb	No data on very light elements (e.g., C, N, H, O, Na) or on some very trace elements useful in source identification
		Marginal:	V, Ni, As, Se	
	<2.5 μm	Good:	Si, P, S, Cl, K, Ca, Fe, Cu, Zn, Se, Br, Pb	
		Marginal:	Al, Ti, V, Mn, Ni, As, Cd	
INAA	Filter or cascade impactor	Good:	Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Se, Br, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Hf, Ta, Th	No elements below Na; misses Si, Pb totally; marginal for Ni, Cd. Long turn-around time (2-3 weeks) for complete analysis
		Marginal:	S, Ni, Ga, Rb, Sr, Ag, Cd, In, Yb, Lu, W	
Atomic absorption	Filter or cascade impactor	Good:	Li, Be, Na, Mg, K, Ca, Cr, Mn, Co, Ni, Cu, Rb, Sr, Cd, Cs, Hg, Pb, Bi	Have to dissolve samples; some inter-element interferences, but difficult to detect. Special methods needed for some elements (e.g., Hg).
		Marginal:	Al, Si, Ti, V, Fe, Zn	
Ion chromatograph	Filter or cascade impactor	Good:	SO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^-, F^-, Br^-, Cl^-, NH_4^+, Na^+, K^+	Have to dissolve samples. Special care needed to preserve unstable oxidation states

SOURCE: Gordon et al. (1978).

The relationships among the various categories are not clear and should be thoroughly investigated.

Examples of more advanced and specialized techniques include laser transmission methods for soot (Rosen et al. 1978, Novakov 1979a), liquid chromatography (Fox and Staley 1976, Neher et al. 1979), and gas chromatography with mass spectroscopy (Hites et al. 1977) for polynuclear aromatic hydrocarbons.

Research is needed to determine optimum sampling methods for measurement of organic species. Polynuclear aromatic hydrocarbons in particles collected from as little as 1 m^3 of ambient urban air can be measured using high pressure liquid chromatography (hplc) and fluorescence detection (Fox and Staley 1976). This sample size is about equal to that used for trace element analysis. For complete analysis of a wide spectrum of organic compounds by gas chromatography and mass spectrometry, much larger samples are needed, perhaps requiring high volume collectors. Special care may also be needed to preserve the integrity of samples for analysis. In addition to problems of revolatilization, polynuclear aromatic hydrocarbons are subject to losses in the presence of light (Fox et al. 1976).

Some methods are available for determining the oxidation states of major elements in bulk particulate matter, but these methods have drawbacks that must be overcome. Electron spectroscopy for chemical analysis, for example, is only a surface technique (Novakov et al. 1974). Laser-Raman and infra-red methods for identifying complex species such as the ammonium ion (NH_4^+), the carbonate ion (CO_3^{2-}), and the sulfate ion (SO_4^{2-}), are confined to fairly major constituents (Novakov et al. 1977-1978, Cunningham and Johnson 1976).

At present, methods are not very reliable for measuring the acidity of particles, but such measurement is very important for assessing health effects and damage to materials. The interaction of aerosols with water vapor is important because of possible weather modification effects and the development of haze when the aerosol is subjected to high relative humidity. In this respect the "humidograph" of Charlson et al. (1974) is a helpful tool because it can be used to observe hygroscopic and deliquescent materials and to measure particle acidity by NH_3 titration.

Improvements are also needed in the methods used for identifying specific types of fibers, especially asbestos fragments.

Recently, an important advance has been reported for distinguishing between carbon derived from fossil fuels and that derived from organic matter such as wood that has been living recently (Cooper et al. 1979). The technique relies on measurement of the ratio of a radioactive isotope, ^{14}C, to the total carbon mass. Fossil fuels contain none of the isotope, whereas contemporary carbonaceous materials have a ratio that is about the same as that present in the atmosphere. Using this technique, Cooper et al. studied carbonaceous material in the atmosphere in Portland, Oregon. They found that, after accounting for carbonaceous particles from agricultural burning, the amount of this material that is of contemporary origin (attributed to wood burning) was surprisingly large. This technique should be further tested and applied to other urban areas.

Finally, methods need to be improved and developed for measuring the size, shape, and composition of individual particles. Much research is in progress on such methods. Electron microscopes are quite useful for determining particle morphology and micro-diffraction methods can identify crystal structures. Scanning electron microscopes with x-ray detectors can make qualitative or semiquantitative measurements of the major elements present on particles with diameters as small as 0.5 μm. Secondary-ion mass spectrometry has much promise for measuring elemental concentrations as a function of depth in individual particles, but many details must first be clarified. Micro-laser Raman spectroscopy can be used to identify major species such as $(NH_4)_2 SO_4$, $CaSO_4$, etc., on individual particles (Etz and Rosasco 1977), but its applicability is limited to particles that can withstand the enormous power density of the beam. (For example, most organic matter is partially converted to soot in the beam.) Because many of these methods require samples to be placed in vacuum, volatile materials may be lost. Recently, Chung et al. (1979) reported the development of a chamber that can be placed around samples in a transmission electron microscope, allowing for control of the atmosphere around the sample while observing growth or other interactions of individual particles.

PARTICLES IN THE AMBIENT AIR

Typical concentrations of a number of elements and species in the ambient air in several U.S. cities and nearby rural areas are listed in Table 2.2. Despite considerable differences in the types of activities that occur in different cities, there is a surprisingly high degree of uniformity among the various data sets. For example, the chemical compositions of the fine and coarse fractions are generally quite different. The fine fraction is dominated by secondary particles (especially sulfates, but also nitrates, ammonium, etc.) and volatile or moderately volatile elements from combustion sources (arsenic, zinc, vanadium, lead, bromine, etc.), whereas the coarse fraction is dominated by elements that mainly arise from soils and other crustal materials (aluminum, silicon, calcium, iron, etc.).

The concentrations of some elements give clues to activities in or near a city: concentrations of sodium and chlorine from sea salt spray are high in coastal cities (for example, Portland); concentrations of vanadium are high in areas where residual fuel oil is used (Washington, Portland); and concentrations of arsenic and selenium are high where large amounts of coal are burned (Charleston).

Secondary species are fairly uniformly distributed between urban and rural stations, presumably for two reasons: (a) some of these species are formed slowly as the precursor gases are transported over long distances, and (b) as fine particles, they are only slowly removed by settling and other processes. Nonetheless, sulfate levels are somewhat higher in cities than in the surrounding areas, suggesting that significant amounts of SO_2 are converted to sulfates within the metropolitan area or that primary emissions of sulfates may not be negligible.

Crustal dust accounts for most of the elements on large particles. Dust might be presumed to be rather uniformly distributed between urban and rural areas, but the data in Table 2.2 and elsewhere indicate that concentrations of crustal dust are usually two to four times greater in urban areas than in the surrounding countryside. (For Tucson, for example, see Moyers et al. 1977.) Crustal dust in the aerosol results from natural processes, as when dust is blown by the wind, and from human activities such as agricultural practices, construction, and the use of motor vehicles. Crustal dust is strongly entrained by human activities.

Carbonaceous particles of different sizes probably derive from different sources. Fine particulate carbon is probably a mixture of soot from combustion sources and secondary organic material. A portion of the carbon on large particles is present as inorganic carbonates that derive from limestone. Knowledge of the chemical composition of carbonaceous material in urban aerosols is, however, inadequate, although the subject is potentially of great importance for human health. As discussed earlier, there is much uncertainty regarding the relationships among the various types of measurements made on carbonaceous material. Based on the summary of available information by Novakov (1979b), we estimate that 30 to 40 percent of urban organic carbonaceous particulate matter (excluding crustal carbonates) is elemental carbon that is present as graphitic soot, and that the remainder is divided about equally between primary and secondary organic material. A great deal more information is needed on the molecular forms of carbon, especially compounds that are known or suspected to be carcinogenic.

IMPLICATIONS OF STANDARDS FOR MONITORING

The ability to monitor air quality is central to the application of any control strategy. Current strategies for controlling airborne particles are based on the TSP standard. Review of that standard, to be completed by December 1980 and periodically thereafter in accordance with provisions of the Clean Air Act Amendments of 1977 (PL 95-95, Sec. 106; 42 USC 7409), may result in one or more standards based on the sizes of particles and possibly even their chemical composition. A revised standard will require a revised monitoring strategy.

Available information on the size distribution of aerosol particles and on

TABLE 2.2 Typical Concentrations of Elements and Species in Selected Urban Aerosols (ng/m³)

	Charleston, W.Va.[a] 1976-Urban		St. Louis, Mo.[b] 1976-Urban		St. Louis, Mo.[b] 1976-Rural		Portland, Oreg.[d] 1977/78-Urban		Portland, Oreg.[d] 1977/78-Rural		Washington, D.C[f] 1976-Urban	
Species	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mass	33,400	27,100	23,100	23,100	17,000	16,200	25,000	39,000	14,300	16,300	–	–
C	5,200	3,200	–	–	–	–	6,800	6,900	4,100	3,000	–	–
N	3,300	460	–	–	–	–	350[e]	360[e]	250[e]	240[e]	1,200[g]	
SO_4^{2-}	9,900	1,020	8,500[e]	980[c]	7,400[c]	450[c]	2,500	1,300	1,830	710	8,900	
Na	190	34	–	–	–	–	280	750	250	400	120	290
Al	74	1,100	170	980	70	600	190	1,900	110	690	120	870
Si	410	2,800	250	3,400	170	2,400	200	6,000	180	2,200	–	–
Cl	40	80	165	320	20	100	840	810	390	320	190	340
K	100	290	180	300	110	240	150	320	120	155	90	220
Ca	100	960	130	2,600	100	1,800	120	1,270	65	410	60	580
Ti	11	77	–	190	–	55	9	160	4	48	11	75
V	<2[h]	<2[h]	–	–	–	–	12	12	4	3	31	13
Mn	7	10	24	27	5	14	32	55	8	16	9	12
Fe	150	590	240	1,000	110	515	200	1,800	60	430	150	610
Cu	20	4	45	11	10	3	26	58	17	52	14	7
Zn	32	10	140	110	60	24	62	70	19	12	98	18
As	26	–	–	–	–	–	4	1	3	–	1.8	1.0
Se	7	–	3	–	2	–	2	1	1	–	2.4	0.69
Br	150	39	145	30	25	5	240	95	38	–	260	95
Pb	660	120	630	190	170	30	645	410	100	40	440	

[a] Data from Lewis and Macias (1979). Fine fraction included particles with diam $< 3.5 \mu m$ and coarse fraction, $3.5 \mu m < \text{diam} < 20 \mu m$.

[b] Data from averages for 1976 computed by S. Rheingrover and G. Gordon (University of Maryland, unpublished) from data set obtained by Loo et al. (1978). Fine fraction has diam $< 2.4 \mu m$ and coarse, $2.4 \mu m < \text{diam} < 15 \mu m$. Urban values are for Station 105 and rural values for Station 122 of their network.

[c] Measured value was for S, assumed all to be SO_4^{2-}.

[d] Data from Watson (1979) for Central Air Monitoring Site for urban values and Sauvie Island Site for rural values. Fine particle data for $\text{diam} < 2 \mu m$. Coarse particle data obtained as difference between averages for whole-filter data and those for the fine fraction.

[e] Measured as NO_3^- only. This value misses a substantial quantity of N as NH_4^+.

[f] Data from Kowalczyk (1979), obtained with a Scientific Advances six-stage impactor. Fine fraction is summation of stages and backup filter that collected particles with diam $< 2 \mu m$ and coarse is for diam $> 2 \mu m$. Values for SO_4^{2-}, NO_3^- and Pb are for whole filters.

[g] Sum of N as NH_4^+ (710 ng/m³) and as NO_3^- (480 ng/m³).

[h] Stevens et al. (1978).

the implications of specific particles for public health and welfare supports the conclusion that size-specific standards are justified. Standards for specific chemical species may also be justified now or in the near future as understanding of effects and monitoring technology develop.

At this time, it appears as if the revised primary standard will specify maximum concentrations of the mass of particles smaller than a specific size such as inhalable particles (IP), defined as those with aerodynamic diameters less than 15 μm. We are concerned because an IP standard makes no distinction between the fine particle fraction and coarse particles with diameters up to 15 μm.

As noted earlier, the origins, behavior, chemical composition, removal processes, and potential effects on health and welfare of these two ranges of particles differ. Hence the effects of ambient aerosols can be significantly different depending on the relative proportions of the fine and coarse fractions. In Denver, for example, the fine particles constitute between 15 and 20 percent of TSP (Durham et al. 1975), while in Los Angeles the fine fraction is more nearly 40 to 60 percent of TSP (Friedlander 1973). Thus, particulate air quality is not adequately defined unless both the fine and coarse fractions are each defined.

Dichotomous samplers and other devices can be used in monitoring programs to obtain size-fractionated samples (Miller et al. 1979). These samples will provide data on which a standard for fine particles could be based.

We urgently recommend that air quality agencies use, at least at some monitoring sites, collection devices to monitor fine particulate mass as well as inhalable or total suspended particulate mass. These size-fractionated samples should be analyzed with reliable multi-element methods such as x-ray fluorescence and/or instrumental neutron activation analysis.

Monitoring for compliance with an IP standard, or a similar standard based on mass below a cutoff size, can be accomplished at minimum cost by modifying the inlet to existing high volume samplers. We believe, however, that compliance is not the only purpose of a national monitoring program. Monitoring should also provide data for assessing trends in air quality and for evaluating existing and proposed standards. Accordingly, we recommend that (1) a representative selection of unmodified high volume samplers be maintained at existing monitoring sites to assure the continuity of the historical record of TSP and (2) selected monitoring sites be equipped with reliable sophisticated equipment for measuring the size and chemical compositions of atmospheric particles.

A SUMMARY OF RESEARCH AND DEVELOPMENT NEEDS

To accomplish the multiple objectives of both monitoring and research, measurement and monitoring technologies must be refined, developed, and extended. The following is a summary of the important needs for research and development that have been identified throughout this chapter.

Reliability of Sampling Techniques

Monitoring devices such as the high volume sampler should be improved so that their performance will be less dependent on sampling conditions such as wind speed and direction. Filter media and sampling techniques must be developed to avoid or control artifacts, particularly for nitrates. Filters should also have low blank values for the elements or species to be measured. Standard methods must be developed for assaying the organic components of the aerosol and the degree of correspondence among alternative techniques must be determined.

Measuring Size Distributions and Chemical Speciation

Technology should continue to be developed for accurately sampling inhalable and fine particles to determine both mass and chemical composition. The design of sampling devices must be improved so that they collect a representative sample of particles both near the upper size cutoff and between the ranges. Significant advances are needed in sampling particles with diameters less than a few hundredths of micrometers in diameter—ultrafine particles—which are likely to become increasingly important for improving understanding of the behavior of the ambient aerosol.

Special attention should be directed to developing techniques for discriminating among the many species present in organic aerosols. To aid laboratories in developing and testing analytical methods for organic materials, a standard reference containing various compounds found in aerosols should be developed and distributed. In particular, methods must be refined and applied to the routine measurement of carbon soot. The technique of Cooper and coworkers (1979) for discriminating between carbon derived from fossil fuels and carbon derived from recently living matter should be extended and applied.

Measures of Visibility

Standard, reliable techniques for measuring visual range must be applied that respond to the effects of both scattering and absorption of light. Techniques for characterizing visibility should include instrumental methods that provide quantitative data, such as telephotometry and nephelometry, as well as subjective techniques that provide qualitative descriptions, such as human observations and color photographs.

Single-Particle Chemistry

Chemical composition varies from particle to particle in an aerosol as a result of differences in the sources from which the particles were derived and the conditions under which they were formed (Friedlander 1977). Lead and potassium in single particles have been measured on a continuous, real-time basis using mass spectrometry (Davis 1977). The development of methods for continuous, real-time chemical analysis of single particles should be continued. Such methods offer improved understanding of the mechanisms of aerosol formation and improved methods for identifying the sources that have contributed to the aerosol.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

1. The mass concentration of atmospheric particulate matter is generally bimodal; one mode consists of fine particles with diameters no greater than 2 μm and the other consists of coarse particles with diameters ranging between 2 and 100 μm. The fine particulate mode is comprised primarily of sulfates and other secondary particles, but it also contains many of the more toxic elements that are emitted as fine primary particles. The coarse particulate mode is usually dominated by dusts.

2. Measures of total suspended particulate mass may not be indicative of the presence of those airborne particles that are potentially of the greatest concern. TSP measurements tend to be dominated by fugitive dusts which, while difficult to control, are probably less threatening to public health and welfare than smaller particles. Measurements of inhalable particulate mass (less than 15 μm in diameter) also contain substantial contributions from dust particles in the size range from 2 to 15 μm. Fine particles are much more numerous in aerosols, yet because of their size they usually contribute half or less to the total mass measured.

3. The organic and nitrate components of the ambient aerosol are currently poorly characterized. Improvements are needed in both collection and analytical techniques. Research is needed to develop and compare methods for characterizing carbonaceous material on airborne particles and to introduce successful methods into monitoring procedures.

4. It is likely that future decisions on air quality standards for atmospheric particles will take into consideration particle size and composition. Therefore, to characterize airborne particles for purposes of protecting public health and welfare, it is necessary at a minimum to obtain size-fractionated samples. It would be even more useful to characterize the chemical elements and species present as a function of particular size.

5. We recommend that monitoring networks routinely employ dichotomous samplers to collect two separate size-fractionated samples—

one containing particles with diameters less than about 2 μm and the other containing particles with larger diameters. However, because assessment of air quality trends depends on the consistent collection of data over time, monitoring networks should also maintain a representative selection of unmodified high volume samplers at existing monitoring sites to measure TSP, providing continuity in the historical record.

6. The elemental composition of samples should be analyzed through use of reliable, highly automated methods such as x-ray fluorescence or instrumental neutron activation analysis. These methods will provide data of high quality that can be used in modern interpretive techniques such as factor analysis or chemical element balances (see Chapter 5).

7. EPA should establish sampling stations in several representative cities incorporating highly instrumented methods that have shown promise in research and development but that are not ready for widespread use in routine monitoring. Examples of the techniques currently available for use in such an installation include liquid chromatography and gas chromatography/mass spectrometry to measure various organic compounds, light transmission through filters to measure carbon soot, and laser methods for remote measurement of particle and gas concentrations. Concurrently, the optical properties of the atmosphere should be monitored so that visibility can be related to particulate air quality.

3 Sources of Atmospheric Particles

Airborne particles are derived from a number of sources. Primary particles are emitted directly into the atmosphere. These include particles of natural origin, ducted emissions from combustion sources and other industrial processes, and fugitive emissions. Particles are also formed in the atmosphere by condensation of vapors. Secondary particles are formed as a result of photochemical reactions of precursor gases in the atmosphere. The size and chemical composition of airborne particles are functions of the mechanisms by which they are formed.

SOURCES OF PRIMARY PARTICLES

Using methods described in Chapter 5, several investigators have estimated the contributions of various sources to atmospheric loadings in a number of cities (Table 3.1). The results of these and other analyses lead to the following understanding of the major sources of airborne particulate matter.

Natural Sources

The natural aerosol contains windblown soil and dust, biological particles such as spores and pollens, and sea spray and its evaporates. The types and quantities of natural particulate matter entrained in the air depend primarily on meteorological conditions, vegetation, soil or dust type, and moisture content. For example, very little crustal dust is entrained at wind speeds below 15 to 25 km/hr, but gusty conditions can entrain considerable quan-

TABLE 3.1 Origins of Ambient Urban Aerosols Based on Chemical Element Balances

	Estimated Contribution (% of TSP)						
	Washington, D.C.[a] 1976	St. Louis, Mo.[b] 1976		Portland, Oreg.[c] 1977/78		Pasadena, Calif.[d] 1970	Chicago, Ill.[e] 1971
Source	Total	Fine	Coarse	Fine	Total	Total	Total
Primary							
Crustal dust	24	9	56	–	–	11.4	18
Urban dust	–	–	–	4.7	46	–	–
Limestone (cement)	4.1	0.8	27	–	–	1.7	3.2
Sea salt	0.9	–	–	2.5	2.1	1.3	–
Coal	6.3	–	–	–	–	–	6.4
Residual oil	0.6	–	–	1.6	0.9	0.1	1.4
Refuse incineration	1.4	–	–	–	–	–	–
Motor vehicles	7.1	8	3	14[f]	7.8[f]	13.5[g]	2.8
Vegetative burning	–	–	–	15	9.3	–	–
Paint pigment	–	0.2	1	–	–	–	–
Steel processing	–	0.4	2	1.5	1.5	–	3.9
Trace elements	–	0.6	1	–	–	–	–
Other industry	–	–	–	1.8	3.8	7.3	–
Nonvolatile carbon	–	–	–	4.1	2.3	4.7	–
Secondary							
NH_4^+	1.4	59	6	–	–	–	–
SO_4^{2-}	14			10	5.1	>10	11.5
NO_3^-	3.2	–	–	7.5	3.8	~0.1	5.3
Volatile carbon	–	–	–	16	9.4	22	–
Fraction accounted for (%)	63[h]	78	96	79	92	>72.3	53

[a] Kowalczyk (1979).
[b] Dzubay (1979).
[c] Watson (1979).
[d] Friedlander (1973).
[e] Gatz (1975).
[f] Includes only emissions from leaded-fuel vehicles. Others presumably are included in volatile and nonvolatile carbon components.
[g] Includes auto exhaust (8.2%), tire dust (0.8%), diesel exhaust (1.8%), and aircraft exhaust (2.7%).
[h] Discrepancy may be rather large because the measured TSP was taken from District of Columbia monitoring data, which included only urban sites, whereas three of the ten stations for the chemical data were rural.

tities of soil and rock dust. Resuspended dust particles tend to be relatively large; for this reason they are less relevant to control strategies based on inhalable particles than a strategy for TSP. In sparsely vegetated, arid regions of the West, dust storms may create high levels of TSP. Natural emissions of hydrocarbon vapors that undergo photochemical transformation in the atmosphere to form secondary particles may contribute to the aerosol in heavily vegetated areas. Emission inventories for urban areas typically overlook many natural sources.

Anthropogenic Sources of Fugitive Dust

Man's activities also result in the suspension of dust and soil—activities such as transportation, agriculture, construction, and mining. An important component of fugitive dust in urban areas is surface dust that is entrained by motor vehicle activity. The wheels of the vehicle transfer kinetic energy to the particles, grind large particles into smaller ones, and break the cohesive bonds in the dust. The induced air flow carries dust well above the road where it can be entrained by the wind. Factors that influence the amount of dust entrained in this way include road surface characteristics, vehicle speed, and amount of traffic.

The chemical composition of anthropogenic fugitive dusts depends on the origins of the dusts. For example, the elements present in road dust are primarily elements, such as aluminum and silicon, that are found in the materials used in the road surface (and are also major elements in soil) and substances, such as lead, that are emitted in the exhausts of vehicular traffic. The origins of observed concentrations of calcium in urban air are not clear, but probably include construction activities (mixing and pouring concrete, removing forms, demolition, sandblasting), agricultural liming, erosion of streets and buildings, and cement and lime plants. The limestone component is strongly associated with large particles, as might be expected from the abrasional sources suggested. Anthropogenic fugitive dust particles are usually large.

Fugitive dusts contribute significantly to measured concentrations of TSP in both urban and rural areas. Evans and Cooper (1979) estimate that average annual emissions from open sources are approximately 400 million metric tons, about three-quarters of which is from unpaved roads. Most of the dust particles, however, are large and settle quickly near the source. Aside from the localized nuisance, the large total value of annual emissions of fugitive dust has little meaning for national air quality. In many urban areas, dust from open sources accounts for 30 to 60 percent of TSP mass. Although the size distributions of fugitive dusts are dominated by large particles, the contributions of open source emissions to ambient concentrations of inhalable particles are not negligible.

Unducted Process Emissions

Unducted process emissions are those that escape from unconfined industrial, commercial, or other activities such as grinding, pouring, blasting, open-air burning, and handling of materials. Leaks and evaporation may also contribute to particles in the atmosphere; a portion of this contribution consists of particles formed by condensation of vapors and a portion consists of gaseous precursors of secondary particles.

Fugitive process emissions contain both coarse and fine particles. Coarse particles are formed in processes involving comminution—grinding and pulverizing—of solids as well as in handling materials. Fine particles may be produced by the condensation of vapors such as those released from organic compounds. Fine particles may also result from the coalescence of vaporous metals emitted from smelting operations. Many of the vapors may be highly toxic; the tars that escape from coke ovens, for example, contain known mutagens and carcinogens (Mazumdar et al. 1975). Other processes, such as spraying, may produce particles in the intermediate size range.

The chemical composition and size distribution of unducted process emissions may differ significantly from those of the ducted emissions from the same facility.

Ducted Process Emissions

In many processes the effluent gases and particulate matter are ducted from the process equipment to their point of release into the atmosphere. These ducted air streams are amenable to control with end-of-pipe equipment, such as filters or chemical scrubbers (see Chapter 4). Many types of particulate removal equipment operate with overall mass-removal efficiencies that are greater than 95 percent. Still, about 12 million metric tons of particulate matter were emitted from ducted sources in the United States in 1977 (U.S. EPA 1978). Equipment is also available for removing or destroying many pollutant gases.

The nature of the pollutants depends on the processes that form them. Combustion products frequently contain a variety of particles, ash, char, soot, and tars. The relative concentrations of the various pollutants depend on the fuel burned, characteristics of the combustor, and operating conditions.

Numerous studies of the relationships between the chemical composition and size of particles emitted when fossil fuels are burned have shown that many toxic components of the aerosols are concentrated in the small particles. In a study of the Pasadena, California aerosol, Miguel and Friedlander (1978) showed that benzo[a]pyrene, a potent carcinogen, is present in a narrow range of diameters around 0.1 μm. This size is similar to that of the soot emitted by diesel engines (Kittelson et al. 1978) and other combustion sources thought to be major sources of benzo[a]pyrene and other polynuclear aromatic hydrocarbons (PAH).

In the effluent from coal combustion, many trace elements that are distributed in small inclusions in the bulk material (e.g., Se, As, Cd, Pb, Zn, Ni, Cr) are proportionally more abundant in small particles than in larger particles (Gladney et al. 1976, Davison et al. 1974, Ondov et al. 1979). The same is true of elements released from most high temperature combustion sources. The basic mechanism leading to this result has been suggested by Davison et al. (1974): In the combustion zone, volatile and moderately volatile elements are vaporized. After the gas stream leaves the combustion zone and cools, the moderately volatile elements condense on pre-existing particles in the gas stream, probably coating all particle surfaces uniformly. Since small particles have greater surface-to-volume ratios than large particles, the concentrations of volatile elements per unit mass of particulate matter will be greater on the small particles.

The suggested mechanism appears to be in agreement with all relevant experiments. The fraction of the mass of a moderately volatile element released on fine particles depends on (1) the size distribution of pre-existing particles of non-volatile material, (2) the efficiency of the pollution control device, if any, and (3) the temperature of the gas before it reaches the pollution control device and/or the stack. Size measurements of particles emitted from coal-fired power plants (e.g., Gladney et al. 1976, Ondov et al. 1979) suggest that the pre-existing particle distribution in a coal-fired plant is comprised predominantly of large particles, presumably because of the release and melting (but not vaporization) of small aluminosilicate fragments in the coal. As shown in Table 3.2, for virtually all of the elements emitted from a plant equipped with an electrostatic precipitator (ESP), Ondov et al. (1979) found less than 20 percent of the mass on particles of diameters less than 2 μm. By contrast, studies of an oil-fired power plant (Mroz 1976) and municipal incinerators (Greenberg et al. 1978a,b) reveal that the majority of the mass of many moderately volatile elements is on particles with diameters less than 2 μm (Table 3.2). Apparently there are fewer pre-existing large particles in the gas streams in these latter types of plants.

The size distribution of particles in the gas stream is often modified by pollution control devices, most of which have some variation of removal efficiency with particle size. The data of Gladney in Table 3.2 are for a different coal-fired plant, also equipped with an ESP, but the results are quite different from those of the plant studied by Ondov et al. (1979). Many electrostatic precipitators have a minimum in efficiency for particles about 1 μm in diameter. Particle scrubbers on coal-fired units investigated by Ondov et al. (1979) had rather flat efficiency curves down to about 1

TABLE 3.2 Fractions of Elements Released from Combustion Sources on Particles Less Than 2 μm in Diameter

Coal-Fired Power Plants with Electrostatic Precipitator				Refuse Incinerator with Water-Sprayed Baffle Greenberg et al. (1978a)	
Ondov et al. (1979)		Gladney (1974)			
Element	Percent Less Than 2 μm	Element	Percent Less Than 2 μm	Element	Percent Less Than 2 μm
Cr	0.58	Fe	8.8	Ca	14
Fe	4.5	Se[a]	17	Sc, Ti	<20
Al, Na	5.1	Co	25	Th	24
Th	5.8	V	27	Al	28
Ba	6.4	Na, Al	28	Mg	<30
K, Ca	7.5	K, Mg, Ca, Ba	29	Cr	32
Mn	7.9	Sc, Ti		Fe	38
V, Ga	9.6	Mn, Zn	30	Co	41
Se[a]	8.8	Ni	32	Se[a]	44
Zn	10	Cr	33	V	48
Co, Cl, W	11	I, Pb	49	Mn	55
As	13	Sb	57	Ba	58
Mo	16	Br	60	Au	72
Sb	17	As	63	Na	80
				Cl, W	83
				Cs	84
				Br	90
				Cu	91
				Zn, Ag	92
				As, Sb	94
				Cd, In	95
				Pb	96

[a] May be underestimated because of possible revolatilization of Se from small particles during sampling.

μm, followed by a sharp drop in efficiency for smaller particles. In that case, about 95 percent of the mass released was borne by particles with diameters less than 2 μm.

The combination of uniform deposition of moderately volatile elements on particle surfaces and decreased efficiency of pollution control devices for small diameters causes an enrichment of moderately volatile elements with respect to non-volatile elements on particles released from many combustion sources. The effect is described by an enrichment factor, *EF*, for each element normalized with respect to aluminum:

$$EF = \frac{(C_x/C_{\mathrm{Al}})_{\text{particles}}}{(C_x/C_{\mathrm{Al}})_{\text{fuel}}},$$

where *C* is the concentration of an element in the released particles or the input fuel. In Figure 3.1 the enrichment factors for a number of elements released from several coal-fired power plants equipped with electrostatic precipitators are shown. Although there are some differences depending on type of boiler, coal, or ESP, some general trends are evident: (1) a number of lithophile elements such as Sc, Ti, Fe, Th, and rare earths are little, if at all, enriched; (2) many moderately volatile elements, especially chalcophile elements such as Zn, As, Se, Mo, and Cd, are enriched with respect to nonvolatile elements; and (3) some highly volatile elements such as Cl and I are only slightly enriched or sometimes depleted. Major fractions of highly volatile elements are in the vapor phase at stack temperatures and, thus, are not collected with particles (see, for example, Andren et al. 1975, Gladney 1974, Billings and Matson 1972).

The study of enrichment of toxic elements on fine particles has concentrated on emissions from coal-fired power plants largely because these plants have been studied more extensively than other types of combustion sources. To gain perspective, the results of chemical element balance studies, described in Chapter 5, indicate that coal combustion is not the major source of a number of trace elements in most cities. For example, V and Ni come primarily from oil combustion; Pb, Br, Cl, and Ba from motor vehicles; and Zn, Sb, and Cd from refuse combustion. The trace elements that appear to arise predominantly from coal combustion are As, Se, I, and, possibly, Hg.

Fixed-bed (stoker) and fluidized-bed coal combustors are operated at low temperatures to prevent the fusion of ash. The resultant particles are irregular agglomerates that are easily broken into smaller fragments. Carpenter et al. (1978) report mean aerodynamic diameters of 1.8 to 4.7 μm for the particles leaving an experimental, coal-fired fluidized-bed coal combustor. Unlike the aerosols produced during combustion of pulverized coal, the fine particles from stoker and fluidized-bed combustion were not noticeably enriched with the volatile trace species. Presumably, little vaporization occurs at the lower temperatures of operation.

Char, partially burned and carbonized fuel particles, can be formed during combustion of both solid and heavy liquid fuels. Little char is emitted from pulverized coal combustors in conventional operating modes although much may be emitted from stoker-fired or fluidized-bed coal combustors. Char emissions are more common for units fired with heavy fuel oils. Char particles are generally large.

Condensible hydrocarbon vapors may be generated during combustion of any hydrocarbon fuel under sufficiently fuel-rich conditions, that is, when the air-to-fuel ratio is low. These vapors may polymerize to form compounds of high molecular weight that condense at relatively high tem-

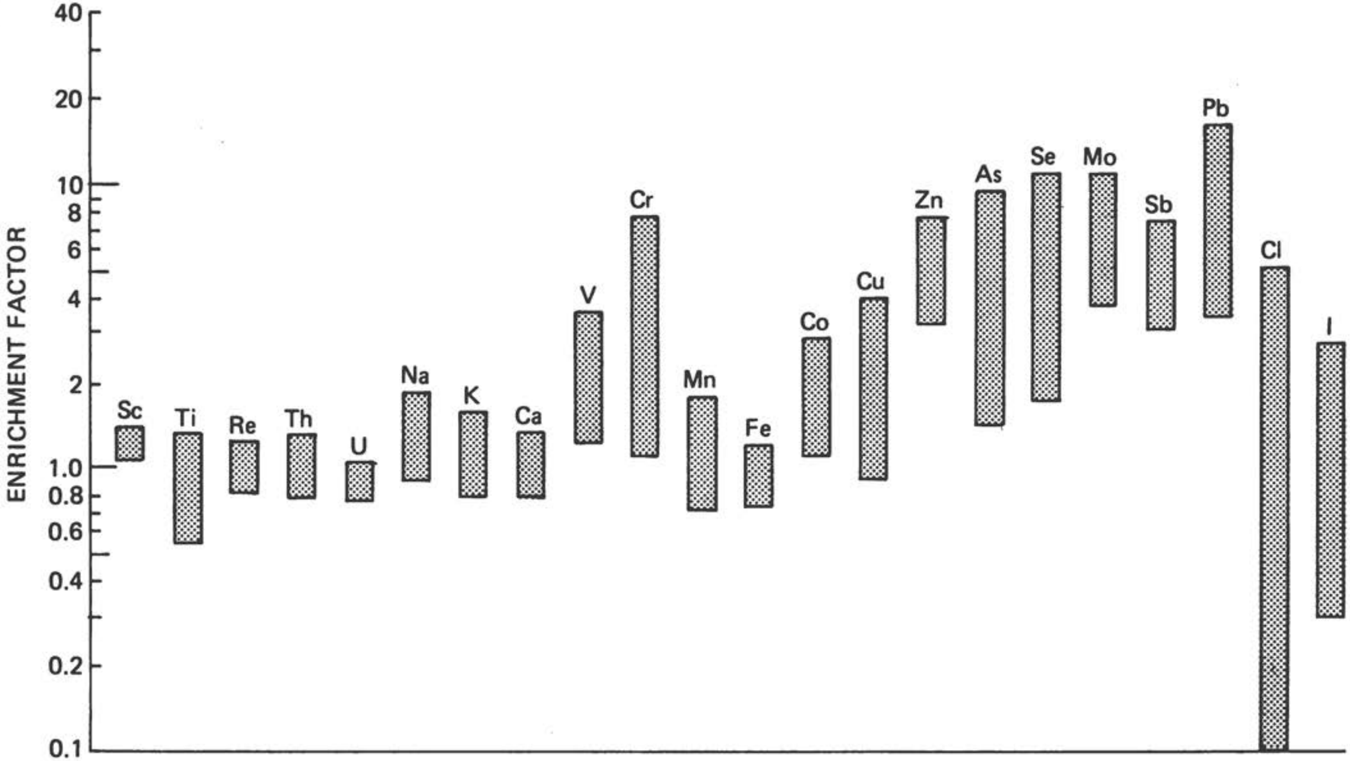


FIGURE 3.1 Enrichment factors (EF) for various elements on particles from coal-fired power plants with respect to input coal. Based on data from ten coal-fired power plants equipped with electrostatic precipitators.

peratures. The condensed liquids may then be pyrolyzed to form soot (Lahaye and Prado 1974). If the reactions of soot formation are quenched early by cooling, the aerosol will contain large quantities of PAH (Prado et al. 1977), many of which are carcinogenic. The aromatic concentrations decrease if the soot is allowed to age and pyrolyze at high temperatures. Appreciable quantities of aromatics may survive combustion conditions in which air and fuel are poorly mixed (Figure 3.2).

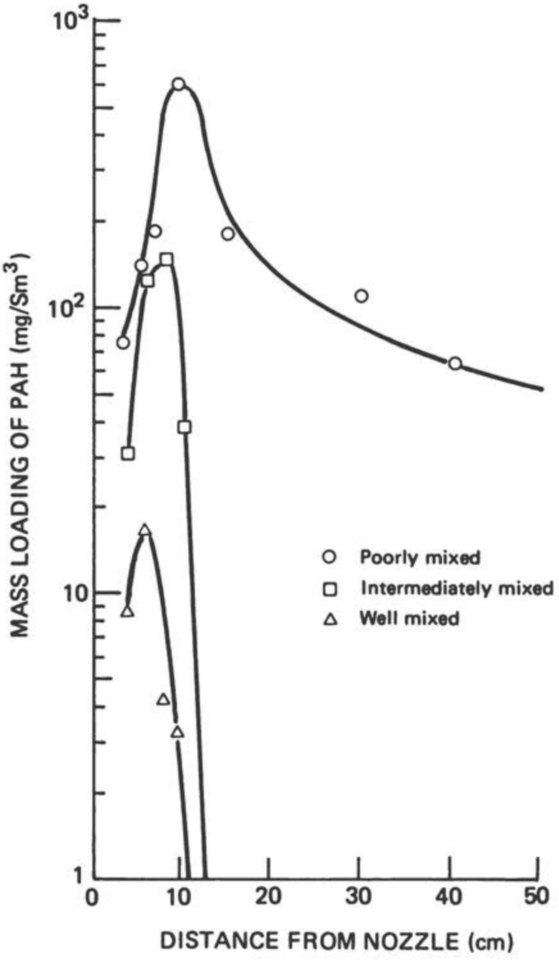
Large combustors often are characterized by sufficient residence time for the air-fuel mixture to burn out most of the soot and aromatics. However, even from the largest sources short-term deviations from normal operating conditions may result in substantial emissions of soot. Small combustors may produce very little soot if the fuel and air are well mixed, as is usually the case in the spark-ignition internal combustion engine. On the other hand, the poor mixing and rapid cooling typical of other small combustors, such as gas turbines and diesel engines, can generate large quantities of soot. Soot emissions are also dependent on fuel composition. Reducing the hydrogen content of a fuel increases its tendency to form soot.

There are, of course, ducted sources of airborne particles other than fuel combustion; one of these is the incineration of refuse. Particles released from incinerators are known to be rich in Zn, Pb, Cl, Cd, Sn, and other heavy metals (Greenberg et al. 1978a,b). A small contribution from this type of source probably accounts for the presence of major amounts of several trace metals in urban aerosols. However, chemical element balances sometimes indicate a contribution from incineration in cities in which there is little "official" incineration, so it is not clear whether those elements are coming from "unofficial" incineration (e.g., burning trash in fireplaces or in rural areas) or from other sources with similar emissions.

EMISSIONS OF CONDENSIBLE GASES

A variety of condensible vapors are emitted into the atmosphere. Sulfur trioxide, high molecular weight organics, nitric acid, and other species may be emitted depending on the source. When cooled by dilution with air, the vapors may condense. Condensation and re-evaporation depend on the degree and rate of dilution.

Dilution of a smokestack plume is relatively slow while exhaust gases entrained in the wake of a moving vehicle are diluted very rapidly, possibly below the saturation vapor pressure before significant condensation can occur. Condensible vapors may, therefore, contribute to the primary emissions under some circumstances but not under others. Sampling systems that simulate atmospheric dilution for particular sources will be required to measure the contributions of vapors to particle emissions.



SOURCE: Prado et al. (1977).

FIGURE 3.2 Effects of mixing rate on concentrations of polynuclear aromatic hydrocarbons (PAH) in a plug flow combustor burning a stoichiometric mixture of kerosene and air.

SOURCES OF GASEOUS EMISSIONS

A major fraction of the fine particulate mass in the aerosol is secondary material formed in photochemical reactions in the ambient air. The major gaseous precursors to secondary particles are sulfur oxides, nitrogen oxides, and hydrocarbons.

The oxides of sulfur (SO_x) are derived primarily from the sulfur present in coal and fuel oil. Approximately 27 million metric tons of SO_x were emitted in the United States in 1977 (U.S. EPA 1978), an average of about 130 kg for each person in the nation. Electric utilities accounted for about two-thirds of national emissions of sulfur oxides. Other combustion sources (industrial combustion of oil and coal, residential and commercial space heating) contributed another 20 percent. Although copper smelters were responsible for only about 8 percent of total SO_x emissions in 1975, they are dominant sources in a number of localities, especially in the West (MITRE 1979).

National emissions of nitrogen oxides (NO_x) were estimated to total 23 million metric tons in 1977 (U.S. EPA 1978). Roughly 40 percent of total NO_x emissions were from electric utilities and 10 percent were from other industrial combustion. Nitrogen oxides are formed from both atmospheric nitrogen (N_2) and organic nitrogen compounds present in fuels. NO_x is formed from N_2 by a series of chemical reactions known collectively as the Zel'dovich mechanism, which is highly dependent on temperature. In these reactions the rate of formation of NO_x is significant only at high temperatures (greater than 1800°K) and doubles for every increase in flame temperature of about 40°K. In contrast, the oxidation of nitrogen bound in fuels is only very weakly dependent on temperature. Typically, between 20 and 50 percent of fuel nitrogen is converted to NO (Sarofim and Flagan 1976).

Coals mined in the United States are about 1 percent nitrogen by weight. Fuel nitrogen accounts for most of the NO_x formed in coal combustion, limiting the degree of emission control attainable with conventional methods. In an experiment in which air was replaced by a mixture of oxygen, carbon dioxide, and argon, emissions of NO_x were reduced by only 20 percent (Pershing and Wendt 1977). Only limited progress has been made in controlling NO_x emissions from coal-fired utilities, because fuel nitrogen is the dominant origin in this case.

Natural gas and distillate oils contain little combustible nitrogen. Crude oils generally contain less than 1 percent nitrogen by weight. Thus, most of the NO_x from sources using natural gas or liquid petroleum fuels arises from reactions of N_2 and O_2 in the air drawn through the high temperature combustion zone.

Mobile sources, trucks and automobiles, accounted for about 40 percent of all NO_x emissions in the United States in 1977 (U.S. EPA 1978). About one-third of these mobile source emissions came from trucks, for which emission standards are less stringent than for cars.

The major anthropogenic source of hydrocarbon vapors is transportation. Trucks and passenger cars together emitted about 10 million metric tons of volatile organic compounds in 1977 (U.S. EPA 1978) or about 35 percent of total estimated emissions. Production and marketing of oil and gas contributed 11 percent, industrial solvents 10 percent, and the chemicals industry 10 percent. Emissions from carbureted engines result from incomplete combustion as the flame is quenched by the cold cylinder wall; poor mixing of fuel and air is probably the major source of hydrocarbons from diesels. Many of the hydrocarbons emitted are partially oxidized and for this reason are highly reactive. Hydrocarbons emitted during production and marketing of oil and gas, during refining operations or from storage tanks for example, are less reactive than engine exhausts and therefore have less of an impact on secondary aerosol production.

Little is known about the amounts and types of organic compounds emitted from natural sources, including vegetation, or about the relative importance of these emissions compared with those from anthropogenic sources. Air quality management should take into account natural emissions when developing strategies for abating anthropogenic emissions.

CHARACTERIZATION OF SOURCES

Measurements of emissions from sources are made for a number of purposes; the techniques used for sampling and analysis depend on these goals. One purpose is to assess the impact of specific sources. When impact assessment is performed to determine compliance with ambient standards and emission limitations, the predominant measurement is of TSP and regulated gases. When it is performed to estimate potential for affecting public health and welfare, more sophisticated techniques, such as measurement of size distribution and chemical composition, may be required. Thus, in characterizing emissions from sources, as in monitoring ambient air quality, a number of measurement techniques are required.

Measuring Emissions

Conventional ducted industrial sources, fugitive process emissions, fugitive dust sources, and mobile sources each emit one or more of the following classes of pollutants that affect the ambient aerosol: primary particles, condensible vapors, gaseous precursors of secondary particles, and evaporates from processes involving liquids. The types of sources and types of emissions determine the strategies and techniques used to characterize the sources.

Ducted Sources Standard methods for sampling emissions from ducted industrial and mobile sources have been developed and are in widespread use, particularly for monitoring compliance. The great majority of these measurements are made on the exhaust aerosol in the stack. Current methods emphasize measurement of TSP but with minor modifications of the sampling system could be extended to measure inhalable particles (Southern Research Institute 1979).

The size distributions of particles in stack gases are currently inferred from routine measurement of other properties of the particles. The collection instruments in widespread use do not provide for size-fractionated samples. However, particles could be separated by size in stack gas samplers through application of methods currently used in research: diffusion batteries and simple inertial separators such as cyclones, cascade impactors, and dichotomous samplers.

Several groups have used these research techniques to characterize emissions and to measure capture efficiencies of particulate control devices (see Chapter 4). These techniques also provide data from which emission factors can be developed. We regard these detailed measurements as highly useful and recommend that these efforts be extended with increased emphasis on particle size and composition.

Measuring the contributions of condensible vapors to primary aerosols is much more difficult than measuring primary particles in the stack. In-stack measurements for assessing these contributions will require development of systems for diluting stack gases to simulate the dilution and cooling of plumes in the atmosphere where the vapors condense. Care must be taken to condense neither too much nor too little of the vapor. Plume measurements should be undertaken both to characterize sources and to test the validity of dilution systems developed for routine in-stack monitoring.

Fugitive Emissions As control of traditional ducted industrial emissions increases, attention is turning to fugitive emissions, which make substantial contributions to the aerosol (Table 3.1). As defined in Chapter 1, fugitive emissions consist of unducted emissions from industrial processes and entrained dusts. It has been estimated that for a modern integrated iron and steel plant about 15 percent of total TSP emissions are from stacks, 25 percent are fugitive process emissions, and 60 percent are fugitive dusts from paved and unpaved roads inside the facility and from storage piles.

Measurements of fugitive emissions have been made for both interior and exterior sources: for outdoor sources, air is sampled upwind and downwind from the sources or on rooftops; for indoor sources, the air is sampled within the building. Ducting and sampling of air inside a building is a straightforward but expensive process. Great care must be taken in measuring open-air sources as emissions may depend strongly on wind conditions, humidity, the amount of time since precipitation, and other meteorological factors. The conditions of the source will also affect these measurements. Suitable sampling equipment, for example directional samplers with variable inlet configurations, and standards for sampling should be developed.

Emission Factors

The characteristics of emissions from sources of the same type are used to derive emission factors, relationships between inputs and outputs from a single type of source. An example of a typical emission factor is the number of pounds of sulfur dioxide emitted from an electric generating plant per ton of coal burned. In this example, the emission factor will depend on the coal used and on detailed specifications of the plant such as type and rating of the boiler and the pollution control equipment. Emission factors are used for estimating the potential impact on local air quality of proposed facilities and for predicting the effects on regional and national air quality of alternative control strategies. The accuracy of the emission factors and their appropriate application are therefore critically important.

Emissions from both ducted and unducted sources are rarely just simple functions of one or two factors (tons of coal, vehicles on the roadway, etc.). For example, the emissions of particles from an electric power plant depend not only on the quantities of coal burned, but also on the type of coal (for trace elements in the fine particles), operating conditions in the combustor (for NO_x, primary particles, and hydrocarbons), and performance of the pollution control equipment.

Emission factors that relate the important variables of the operation to the size distribution and composition of the emitted particles are likely to be required in the future. Oversimplified emission factors can be misleading. Detailed measurements of the aerosols in the stack and in the plume must be made while operating conditions are monitored so that accurate emission factors can be developed.

Measurement of emission factors for re-entrained dust is subject to similar difficulties. Source conditions are highly variable, and emissions are often intermittent. In most cases, the relationships between the source and its emissions involve many variables. Attempts to develop simple relationships in equations with only one variable have frequently produced unsatisfactory results. For example, emission rates for roadways depend not only on maintenance but also on surface materials, meteorological conditions, and level of service. Although the differences between unpaved roads, dirty and clean paved roads, and freeways are considerable, they are often ignored.

Deriving emission factors for large industrial facilities may be complicated when a single site includes a number of different types of sources—ducted and unducted. Under current practice for achieving air quality standards at minimum cost, operators may be allowed to select the degrees to which the various sources in a single facility are controlled, thereby trading emissions from one source for those from another that may be less costly to control. This system (the "bubble" concept) may be effective for reducing mass concentrations of TSP or IP. However, it may also result in a shift in the size distribution or composition of emissions. A specific component of particulate emissions from a source may remain unchanged, increase, or decrease while reductions in TSP are achieved. Similar shifts may arise in the application of EPA's offset policy in nonattainment areas.

The possible consequences of undifferentiated trade-off policies may not be in the interest of public health and welfare. We wish to stress that emission factors should be derived both for entire complexes and for individual sources within complex facilities. With this information, the bubble concept might be applied more selectively. A regulatory scheme based solely on mass measurements does not permit consideration of particle size or composition.

Characterization of Industrial Process Sources

In the past, most regulatory activities under the Clean Air Act and its Amendments have focused on emissions from automobiles and electrical utilities. Emissions from these sources, both gases and particles, have been reasonably well characterized although important work remains to be done. For example, emissions from coal-fired power plants should be more completely characterized in terms of chemical composition as a function of particle size. However, the sources themselves—stacks and tailpipes—are adequately defined and the dimensions of the problem are clear.

With the application of the Toxic Substances Control Act (PL 94-469; 15 USC 2601), process industries (including the petrochemical industry) are likely to be subject to greater regulatory activity. Emissions from process industries are probably more complex than those from automobiles, trucks, or power plants. For example, in each chemical manufacturing facility there are a variety of sources such as catalytic crackers, distillation and absorption columns, and combustion units using various fuels.

A satisfactory method for characterizing these sources has not yet been developed, and a significant effort is needed in this field. Efforts should be directed at methods for characterizing individual units (sources) within a complex and for characterizing the complex as a whole by measuring particles and gases in the total plant plume. Methods of source characterization for both particles and gaseous precursors should be developed. The primary and secondary particles should be characterized by size and distribution of chemical species as a function of size.

MAINTENANCE OF EMISSION CONTROL SYSTEMS

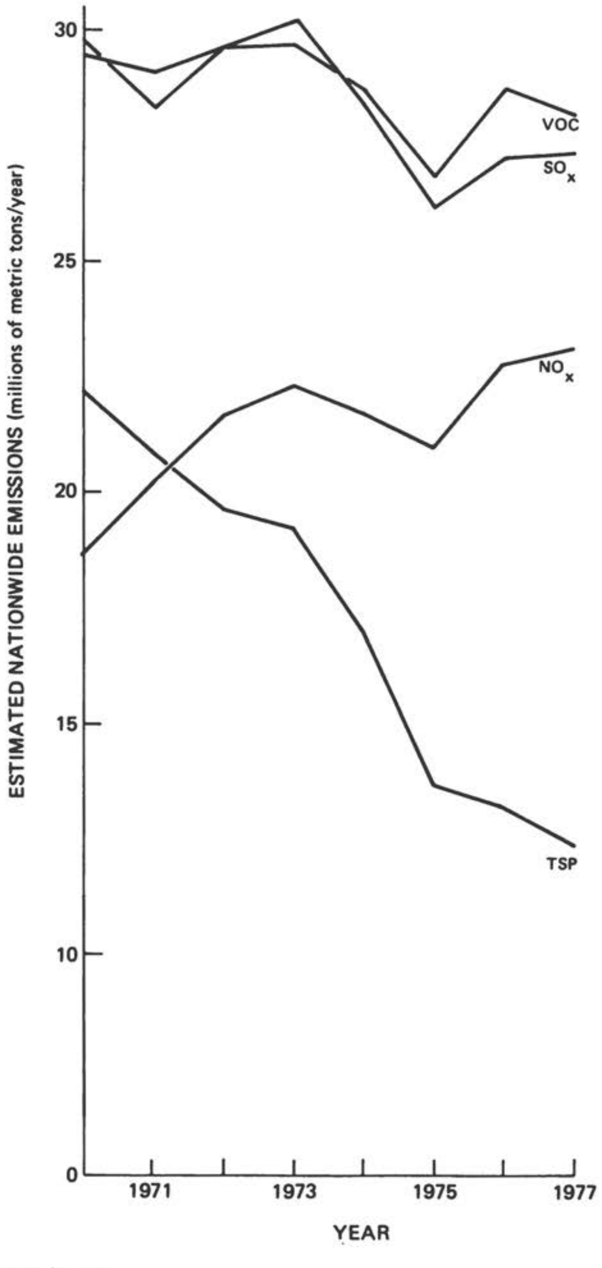
The performance of emission controls deteriorates with time unless devices are properly maintained. As performance deteriorates, emissions increase. This problem is clearly recognized for mobile sources; EPA has developed corrections for the loss of efficiency of automotive emission controls and projections of the effects of automotive emission controls on air quality usually take these losses into account (MITRE 1979). Potential losses in efficiency of stationary source controls should also be recognized and taken into account.

Control systems installed on large sources may be oversized by design so that emission standards will be met even though performance degrades during the intervals between scheduled inspections and maintenance. Although emission standards will be met in such cases, emissions will increase as performance deteriorates. Controls on smaller sources, which are subject to less frequent or less critical inspections, may be allowed to deteriorate significantly with time, leading to increased emissions. Some operators may have to rely on personnel of the equipment vendor to assess whether the controls are working according to specifications; these personnel may not be available to perform maintenance tasks very frequently. Some systems, such as residential furnaces, only rarely receive maintenance. To make realistic projections of emissions and to evaluate the effectiveness of regulatory activities, data on the deterioration of emission controls should be developed.

EMISSION TRENDS AND PROJECTIONS

Recent trends in nationwide emissions of TSP and gaseous precursors of secondary particles are shown in Figure 3.3 (U.S. EPA 1978). Between 1970 and 1977 estimated emissions of TSP declined sharply while estimated emissions of NO_x increased substantially. Emissions of SO_x and volatile organic compounds appear to have decreased slightly. Our concern, expressed earlier, that measurements of total mass may obscure the true nature of the particulate air quality problem is reinforced by the fact that total emissions of precursors of fine secondary particles increased while both the emissions and ambient concentrations of TSP decreased.

To assess whether existing particulate control strategies are adequate for the future, it is necessary to make projections of future emissions. The projections must of necessity be based on a number of assumptions about factors such as population growth, levels of economic activity, geographic dis-



SOURCE: U.S. EPA (1978).

FIGURE 3.3 EPA estimates of nationwide annual emissions for TSP, SO_X, NO_X, and VOC (volatile organic compounds) for 1970 through 1977.

TABLE 3.3 Projected Annual Emissions of TSP in 1975 and 1990 in Metric Tons (t) per Year

	1975			1990			
Rank	Category	t/yr	Percent of Total	Category	t/yr	Percent of Total	Percent of 1975
1	Other structural materials[a]	5.4	37	Other structural materials[a]	3.5	38	67
2	Coal electric utility pre-1976	3.2	22	Transportation	1.4	15	150
3	Iron and steel	1.2	8	Coal electric utility pre-1976	1.0	11	33
4	Coal industrial pre-1976	1.2	8	Coal transportation	0.4	4	175
5	Transportation	1.0	7	Oil–industrial combustion	0.4	4	290
6	Cement	0.6	4	Asphalt	0.4	4	140
7	Sewage	0.3	2	Residential and commercial heating	0.4	4	125
8	Residential and commercial heating	0.3	2	Nonferrous metals	0.4	4	200
9	Coal transportation	0.3	2	Coal industrial pre-1976	0.2	2	19
10	Asphalt	0.3	2	Oil refineries	0.2	2	120
	Other	0.9	6	Other	1.1	12	
		14.7			9.4		

SOURCE: After MITRE (1979).

[a] 90 percent crushed stone; 5 percent brick; 5 percent asbestos, lime, and sand.

tributions of growth in each sector of the economy, emission standards for all types of sources, levels of compliance, and changes in fuels or processes.

In our view, projections of future emissions generally tend to be optimistic because of the nature of the assumptions made. For example, projections rarely take into account failure to achieve compliance with emission limitations for stationary sources, whether due to recalcitrance or poor maintenance of control equipment. Furthermore, most forecasts do not include noncriteria pollutants, even though some of these pollutants may require regulation in the future.

Future emissions have been projected by the MITRE Corporation (1979) in a study prepared for the U.S. Department of Energy. The study, based on assumptions about future energy use developed by the Energy Information Agency, assumes full compliance with applicable emission standards. Some of the results, which are consistent with results of other studies, are summarized in Table 3.3. In this projection annual TSP emissions are expected to decrease from 14.7 million tons in 1975 to 9.4 million tons in 1990, despite a 98 percent increase in demand for coal. Emissions of TSP from most categories of sources are expected to increase; however, decreases in emissions are expected from those sources that currently make the largest contributions to the national inventory: structural materials other than cement, coal use by electric utility plants built before 1976, coal use by industrial sources built before 1976, and iron and steel manufacturing.

We recommend that estimates of future trends in emissions of primary particles distinguish among particles of different sizes—coarse, inhalable, and fine. In the absence of such a forecast we have made our own qualitative estimates of trends in future emissions of particles by size (Table 3.4). These estimates are based on the results of the MITRE study, current understanding of the size distributions of emissions from various sources, and current information on the differences in removal efficiencies of control equipment for particles of different sizes (Chapter 4).

While total particulate emissions are expected to continue to decrease in the future, emissions from several sectors are likely to increase substantially by 1990. According to the MITRE study, these sectors, which emit primarily small particles, include transportation, industrial oil combustion, and residential and commercial heating. Thus we expect that the decrease in emissions of primary fine particles will not be nearly so great as the decrease in TSP emissions. The MITRE projection assumes increased control of existing sources and even more stringent control of new sources. Unless emission standards include size-dependent removal efficiencies, further shifts toward the emission of fine and ultrafine particles could result from more stringent control.

The MITRE projection suggests that total emissions of sulfur oxides will remain almost constant between now and 1990, despite substantial im-

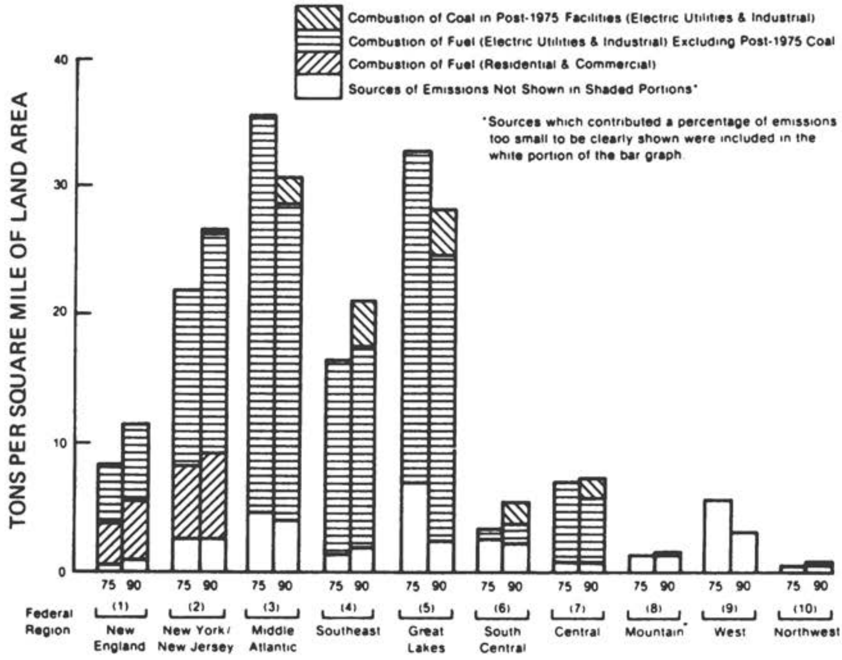
TABLE 3.4 Probable Trends in Future Emissions of Particles by Size

		Change in Emissions by Size Range (μm)		
Sources	Characteristics	<2.5	2.5–15	>15
Primary Particles				
Structural materials other than cement	Mostly coarse			-
Electric utility coal pre-1976	Fine particles enriched with volatile inorganics	-	?	-
Iron and steel		-	-	-
Industrial coal pre-1976	Fine particles enriched with volatile inorganics	-	-	-
Transportation:				
Automotive–gasoline	Lead	-	-	-
Automotive–diesel	Soot, tars, and PAH	+		
Truck–diesel	Soot, tars, and PAH	+		
Cement				-
Residential and commercial heating	Soot, tars, and PAH	+		
Transportation of coal:				
Coal dust re-entrainment				+
Railroad diesel	Soot, tars, and PAH	+		
Asphalt	Tars	+		
Industrial combustion	Soot, tars, PAH, and trace metals	+	+	+
Non-ferrous metals	Fine particles enriched with volatile inorganics	+	+	
Oil refineries	Organic, soot, tars, and PAH	+		
Secondary Particles				
Sulfates	Mostly fine	0		
Nitrates		+	+	

Symbols: + = increase, 0 = no change, – = decrease, ? = uncertain.

provements in controlling new source emissions. However, some dramatic shifts in the geographic distribution of these emissions are likely to occur. Substantial reductions are projected for the Middle Atlantic Region, the Great Lakes Region, and the West. The decrease in the West will result in large part from the control of emissions from existing electric utilities and smelters. SO_x emissions are predicted to increase in the Northeast, Southeast, South Central, Central Mountain, and Northwest Regions (Figure 3.4); much of the expected increase will be due to increased combustion of coal.

Because new power plants are subject to New Source Performance Standards for emissions, the dominant source of sulfur oxide emissions in 1990 is



SOURCE: MITRE (1979).

FIGURE 3.4 Net annual emissions of sulfur oxides in 1975 and 1990 by region and source.

expected to be fuel combustion in utilities that were operating prior to 1976. In many areas, emissions from these sources will actually increase as a result of the anticipated shift from oil to coal. Any strategy for reducing SO_x emissions by 1990 will probably have to incorporate controls for utilities and other industrial sources constructed before 1976.

Because most of the emissions of NO_x from coal combustion are due to inorganic nitrogen in the fuel, NO_x emissions will increase substantially in the future as a result of increased use of coal by electric utilities and industry. Increases in emissions will be concentrated in those areas where coal combustion is expected to increase.

Although the anticipated shifts in SO_x and NO_x emissions would result in improved air quality in some localities, large areas of the country may suffer further degradation. Since nitrates and sulfates apparently have long residence times in the air and are transported long distances, air quality problems associated with these particles—degradation of visibility and acidification of precipitation—tend to be regional problems.

The MITRE study expects hydrocarbon emissions to decrease substantially by 1990, largely as a result of automotive emission controls. Emissions from trucks are expected to decrease slightly, and other emissions are expected to remain about constant. Trucks and diesel automobiles are likely to be the sources of the most reactive hydrocarbons, so decreased emissions in these categories could result in some improvements in air quality (also see the section on Alternative Automotive Engines).

Trends in Fuel Use

Many forecasts predict that world demand for petroleum will exceed the supply in the near future, perhaps as early as 1985. Concern over the adequacy and reliability of petroleum imports is a strong driving force for the shift from oil to other energy sources, including nuclear fuels for electric power generation, coal for utilities and industrial combustion, and coal-derived fuels for use by industry. Use of heavy fuel oils, coal, wood, and refuse-derived fuel as substitutes for clean-burning fuels such as natural gas and distillate oils is likely to result in increased emissions of fine particles, toxic hydrocarbons, trace elements, and the gaseous precursors of secondary aerosols.

These shifts in fuel use—over and above increases in direct use of coal—should be of special concern because of their likely consequences for particulate air quality.

Transportation Fuels A shift in transportation fuels from gasoline toward middle distillates, such as diesel and jet fuels, is likely to result from increases in the number of diesel engines and a desire to obtain more energy per barrel of crude oil through refining. To supply a higher proportion of distillates, the aromatic content of fuels is increased while the hydrogen content is decreased. These changes result in increased production of soot when fuels are burned; such increases have already been observed in the case of jet fuels. Lower hydrogen content fuels are known, in some cases, to produce soots with higher contents of mutagenic PAH (Kraus and Coburn 1974). Even if soot emissions from the new fuels were equal in quantity to emissions from the fuels currently used, they might pose greater risks to health. Very little is known about the extent to which variations in the aromatic and hydrogen content of fuels affect emissions.

Synthetic Liquid Fuels A number of alternatives to petroleum liquids are being developed including liquids from coal, oil shale, and tar sands. Synthetic liquid fuels derived from coal have a high aromatic content; therefore they are well suited for the production of gasoline and heavy fuel oils, but are less suitable for the production of distillate fuel oils. Coal-derived liquids may be of optimal use in electric utilities. The high aromatic content of the fuel may, however, lead to substantial emissions of both primary particles and gaseous precursors of secondary particles. In contrast, shale oil and liquid fuels produced from carbon monoxide and hydrogen are well suited to the production of light distillate oils, but poorly suited to the production of gasolines (Longwell 1978).

Alcohol fuels can be produced from biomass (at high energy cost) or, more likely, from CO and H_2. Small amounts of methanol or other alcohols can be added to gasoline to reduce petroleum consumption. Methanol is well suited for direct use as a clean fuel for small stationary combustion sources, especially for gas turbine peaking units (Longwell 1978).

Synthetic liquid fuels that are rich in aromatic hydrocarbons or have high fuel-nitrogen content will necessitate the development of new emission controls to minimize nitrogen oxide emissions.

Other Changes in Patterns of Fuel Use Other changes in patterns of fuel use may also have pronounced effects on the ambient aerosol. Uncertainty about the availability of oil and natural gas has renewed interest in burning coal, wood, and refuse to meet residential and municipal energy needs.

Small coal-fired stokers, which might be used for residential and commercial heating, may have severe environmental impacts (Giammar et al. 1976, DeAngelis and Reznik 1978). Small stokers operate in an on-off cycle. When the stoker is "on," coal is fed at a constant rate. The stoker adapts to varying loads by adjusting the percentage of "on" time during each cycle. During the "on" time, fresh coal is fed beneath the hot coals and air is blown through the tuyeres. During the "off" portion of the cycle, both the screw feed and the fan are turned off. The bed continues to burn slowly with minimal amounts of air being supplied by natural draft. During this time the temperature decreases and unburned hydrocarbon emissions are likely to increase. Polynuclear aromatic hydrocarbons are emitted in substantial quantities throughout the cycle. Emissions of soot and aromatics from chemically cleaned coals are lower than those from unprocessed coals, but particulate emissions are high because the fuel breaks into a large number of fine particles during feeding.

Emissions from wood-burning stoves and fireplaces may be expected to increase dramatically in the future as residential burning of wood increases in response to tax incentives and higher costs of alternative forms of energy (Butcher 1978). Emissions from burning wood are primarily fine particles which contain benzo[a]pyrene, a known carcinogen, and other polynuclear aromatic hydrocarbons. These particles, because of their size, contribute to the degradation of visibility. Coal and refuse may also be burned in fireplaces, emitting characteristic particles and gases.

Refuse-derived fuels are another potentially important new source of energy that could have serious effects on air quality. Several studies have shown increased concentrations of toxic elements in the stack gases of power plants when refuse-derived fuels were mixed with coal (Gorman et al. 1979, Jackson and Ledbetter 1977, Shanks et al. 1978). Use of refuse-derived fuels on a wide scale could result in significant increases in particles of such species as Be, Cd, and Hg.

Alternative Automotive Engines Alternative types of internal combustion engines are being advocated for use in the passenger car fleet for purposes of reducing emissions and increasing fuel economy. Diesel engines are being marketed by General Motors, Volkswagen, and others; Ford is developing a programmed combustion stratified charge engine (PROCO) to meet the goals. In both types of engines, fuel is injected directly into the cylinder as a spray of droplets. Since the formation of soot is related to the combustion of droplets, particulate emissions from direct injection spark-ignition engines are similar to those of the diesel.

Diesels operate under fuel-lean conditions. Temperatures are lower and combustion reactions are more complete than in the spark-ignition engine. Diesels do not require throttling; they run at idle with very low fuel consumption. Despite low average temperatures, diesels produce high emissions of nitrogen oxides. Moreover, diesels emit large quantities of particles. These soot emissions are probably the result of poor mixing in the diffusion flame, a condition which causes soot formation in steady-flow combustors (Prado et al. 1977). Particulate emissions from light-duty diesels are about 10 times greater (about 300 mg/km vs. about 25 mg/km) than those from spark-ignition engines burning leaded fuels (Pierson 1979).

The particles in diesel exhausts have diameters in two size ranges. One mode consists of very fine particles with diameters in the order of 0.02 μm (Kittelson et al. 1978, Kittelson and Dolan 1979). These particles have carbon skeletons with hydrocarbons adsorbed on their surfaces. The material on the surface may account for 5 to 50 percent of the mass, depending on engine type, fuel, and emission control systems. A second mode, consisting of particles with diameters in the range of 0.1 μm, is made up of agglomerates of large numbers of very fine particles.

The particles generated by diesel engines contain many complicated aromatic compounds. Bioassays indicate that the emissions are highly mutagenic even though the fuels and lubricating oils from which they are formed are not (Kebely et al. 1978). The biological activity of the emissions may be enhanced by exposure to ultraviolet light (T.H. Risby, The Johns Hopkins University, private communication, May 18, 1979).

Diesel engines represent a major pollution source. Emissions of oxides of nitrogen, fine particles (principally soot), and hydrocarbon vapors from trucks are approaching the level of automotive emissions despite the much greater number of automobiles. The MITRE study projects that the mass of truck emissions will exceed the quantity of car emissions by 1990. Therefore, we conclude that research is needed to develop emission controls for diesel engines, whether or not the diesel engine displaces the gasoline engine for passenger cars.

Introduction of the diesel engine into the automobile fleet could lead to substantial increases in urban aerosol pollution. Our estimate of the impact of extensive use of diesels in passenger cars is based on the following rule-of-thumb assumptions: current diesels emit about 10 times as many particles as cars burning leaded fuel; about 40 percent of the particulate emissions by weight of cars burning leaded fuel is lead; and when most cars used leaded fuel, lead concentrations in cities were about 1.5 $\mu g/m^3$. Using these assumptions, we conclude that if 25 percent of the passenger car fleet were converted to unimproved diesel engines, these cars would contribute about 10 $\mu g/m^3$ of fine soot to the urban aerosol.

Adding 10 $\mu g/m^3$ of diesel soot to the urban aerosol would have different effects in the East and in the West. The range of visibility in eastern cities is typically about 15 km. Conversion of 25 percent of the passenger car fleet to diesels in this circumstance would lower this range to about 12 km; if all cars used diesel engines, the range would be only about 8 km. The range of visibility in western urban centers is typically 75 km. Converting one-quarter of the fleet to diesels would reduce that range to about 35 km whereas if all cars used diesel engines in the West, the range would be about 13 km. These estimates assume that the added particulate matter is uniformly distributed across distances on the order of the range of visibility and represent upper bounds on the effects on visibility in each case.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

1. For the most part, emissions of primary particles and gaseous precursors of secondary particles have been characterized by total mass. Except in certain cases emissions have not been adequately characterized by particle size and composition. Only in isolated cases have condensible vapors, fugitive process emissions, and fugitive dusts been characterized. New methods for sampling sources should be developed to characterize particles in specified size ranges, to collect condensible species, and to measure fugitive emissions. Standard methods for stack gas sampling should be revised. In addition, newer methods, such as airborne sampling of plumes and remote sensing methods, should be considered. Samples should be analyzed with advanced techniques such as those described in Chapter 2.

2. Emission factors—the relationships between emissions from a process and the equipment, operating conditions, feedstock, and fuels used in the process—are complex. Over-simplification can be misleading. Improved

emission factors should include consideration of particle size and composition of both ducted and fugitive emissions. To obtain better emission factors, field tests that include simultaneous measurement of operating conditions, sampling of stack gases and particles, and plume studies are recommended.

3. Projections suggest that national emissions of TSP will continue to decline over the next decade, those of SO_x will remain approximately constant, and those of NO_x will increase. Coal-fired utilities are the most important source of SO_x emissions. Through 1990 coal-fired power plants constructed before 1976 will still account for the majority of SO_x emissions in the United States. The utility sector also accounts for the major part of the anticipated increase in NO_x emissions.

4. Shifts in the use of fuels from clean-burning ones such as natural gas and distillate oils to coal, heavy fuel oils, diesel fuels, wood, refuse-derived fuels, and synthetic fuels are likely to result in increased emissions of fine particles, trace elements, polynuclear aromatic hydrocarbons, and gaseous precursors of secondary particles. Diesel engines, synthetic fuel processing and use, the petrochemical industry, and wood fires emit carbonaceous particles that tend to be small, bear carcinogenic compounds, and cause disproportionate degradation of visibility by absorption of light. Improved knowledge of the emissions resulting from the use of new fuels is vitally needed to assess the implications of perceived trends on public health and welfare.

5. We recommend that projections of future emissions incorporate consideration of particle size and composition. To make these projections, improved emission inventories will be needed; these inventories should be based on better characterization of anthropogenic and natural sources, improved emission factors, and new techniques for estimating source emissions (described in Chapter 5).

6. In the case of particulate control, indiscriminate application of tradeoff policies may have adverse consequences for health and welfare if emissions of fine and toxic particles are substituted for emissions of coarse and benign particles.

4 Control Measures

Controlling exposures to potentially harmful airborne particles entails controlling emissions of particles and gases from both ducted and unducted sources. Engineering approaches to controlling emissions have been applied to a wide variety of sources. Examples of devices used to control emissions of primary particles from ducted sources are electrostatic precipitators and fabric filters; scrubbers may be used to remove both particles and gaseous precursors of secondary particles.

In the main, engineering strategies for control have focused on end-of-pipe treatment of stationary and mobile ducted sources, in which devices are installed in the ducting after the process equipment to treat the waste stream before it enters the atmosphere. End-of-pipe treatment may be an acceptable design strategy in many circumstances, such as when recognition of the need for controls comes after the process equipment has been designed and is operating, but in our view this approach to designing controls for some types of new installations represents a failure in engineering practice. We believe that a potentially more useful engineering strategy, which is now being practiced in more and more cases, is to incorporate environmental considerations into every aspect of design, including selection of raw materials, processes, and products. Often this type of integrated design can avoid the need for end-of-pipe treatment. Adopting this philosophy will require changes in engineering educational programs which we believe are urgently needed.

End-of-pipe controls always entail costs to the operators while alternative process designs might in some cases prove less costly than controlled but unimproved processes. Operators of facilities may be reluctant to incur additional costs that are attributable to pollution control even though these costs will eventually be passed on to the consuming public.

In the absence of legislative constraints to the contrary, an economically reasonable approach to setting air quality standards would incorporate some type of balance between costs of control, which the public ultimately bears, and benefits to public health and welfare. Estimating the costs of control is, relatively, an easy task, especially when end-of-pipe treatment is used so that the capital and operating costs arising exclusively from control are readily identified. Other costs associated with control—for example, energy penalties and waste disposal costs—are more difficult to estimate but should be accounted for.

Estimating the benefits to public health and welfare that would accrue from more stringent standards is inherently difficult for three reasons. First, as discussed in Chapter 5, the relationships between anthropogenic emissions and population exposures are uncertain; moreover, some anthropogenic emissions are supplemented by natural sources. Second, the relationships between the concentrations of most pollutants in ambient air and deleterious health effects are complex and inadequately understood. Individual exposures and responses are highly variable and many pollutants may act simultaneously. Furthermore, a number of years may elapse after exposure to some pollutants before serious health effects are manifested. Third, agreement is lacking on the costs to be assigned to various degrees of deterioration of health, degradation of visibility, agricultural losses, degradation of materials, and other effects of air pollution—and even about whether it is possible to assign such costs.

Because the costs and benefits of control are difficult to assess, it may not be possible to strike an accurate balance between them. We believe that reducing pollution control costs is a desirable public goal, provided that doing so does not create environmental hazards or costs elsewhere. Public agencies should support research and development, including the search for alternative processes, to make pollution control less costly as well as more reliable.

In this chapter we address some current and anticipated problems in controlling emissions of particulate matter. As indicated above, we interpret the term "pollution control" broadly to include separation processes for the removal of primary particles, condensible vapors, and gaseous precursors to secondary particles; the development of new technologies and processes that substitute more amenable pollution problems for current or anticipated ones; and the maintenance of process and control equipment so that it can operate at peak efficiency.

The progress toward reducing atmospheric concentrations of TSP that has been achieved to date has been the result of the imposition of controls on stationary and, to a lesser extent, mobile sources. The particulate control devices that are currently employed have been designed in response to standards and emission limitations for TSP and by themselves may not be satisfactory for controlling fine particle exposures or ambient concentrations of specific species.

To promote the development of technology for controlling emissions of fine particles, performance standards should be expressed in terms of particle size and, where feasible, composition. In addition, control strategies should include consideration of siting and dynamic control of sources (so that emissions result in less damage) and conservation of energy and materials (so that smaller quantities of pollution are generated). Effective application of siting and dynamic controls requires improved understanding of the relationships between emissions of ambient air quality (see Chapter 5).

MEASURING REMOVAL EFFICIENCIES

The report on the *Abatement of Particulate Emissions from Stationary Sources* (NRC 1972) stressed the need for data on the fractional efficiencies of gas cleaning devices. Until that time, no information had been available on the efficiencies of such devices as a function of particle size for submicron aerosols. Following the recommendations of that report, EPA initiated a program to measure fractional removal efficiencies of electrostatic precipitators, fabric filters, and scrubbers. To determine fractional efficiencies, it is necessary to measure particle size distributions as gas streams enter and exit gas-cleaning devices. These measurements are difficult to make because of problems associated with sampling at high gas temperatures and aerosol concentrations.

The ability to measure fractional removal efficiencies is potentially of great importance to the development of improved gas-cleaning systems since removal efficiencies provide sensitive tests of the effects of varying the parameters that influence the performance of control equipment (such as gas velocity and temperature, geometric factors, and so on). Fractional removal efficiencies are also necessary for predicting the size distribution of particles emitted from new sources, and should be coordinated with studies of the aerosol characteristics of plumes to provide data for understanding the relationships between emissions and air quality (see Chapter 5).

In addition, measurement of fractional removal efficiencies will be required to determine compliance with emission standards or limitations if these are expressed as functions of particle size as recommended. Requirements for measurements to determine compliance must be tailored to regulations (Smith 1979) but may not be adequate for assessing the effects of emissions on environmental quality and public health or the changes likely to result from changes in control technology. For example, sampling to determine compliance with an emission standard for inhalable particulate matter would likely occur only downstream of gas-collection devices and include all mass in particles with aerodynamic diameters less than 15 μm. The consequences of emissions for environmental quality and public health depend on factors other than total mass, for example, chemical composition, transport properties, and patterns of exposure and deposition. The characteristics of emissions measured for compliance are not likely to include these factors unless standards or regulations require it.

Further development of sampling methods capable of measuring particle size distributions under process gas conditions should be supported. Measurements of size-fractionated removal efficiencies should be made under field conditions to guide the improvement of the performance of gas-cleaning devices.

Many methods are available for the measurement of aerosol characteristics as a function of particle size (see Chapter 2). For example, single particle counters, electrical mobility analyzers, cyclone separators, and cascade impactors can provide data on particle size distribution while information on the chemical composition of particles of different sizes can be obtained by analysis of individual particles or of size-fractionated samples. If single particles are studied, large numbers must be analyzed to provide statistically significant data on the distributions of size and composition.

Cyclone separators can collect large size-fractionated samples for analysis, but the size resolution of these devices is limited, especially for particles smaller than a few micrometers in diameter. Cascade impactors can classify particles as small as a few tenths of a micrometer in diameter if operated at atmospheric pressure. Size resolution has been extended to several hundredths of a micrometer by operating at reduced pressure (Hering et al. 1978). Only a very small mass of particles can be collected in the small size ranges by low pressure impactors unless very large and bulky vacuum pumps are used. The size resolution that can be achieved with properly designed and operated cascade impactors is good. However, there are many problems that can severely limit the resolution. Large particles may bounce off the impaction stages or be reentrained after deposition, thereby contaminating the samples of small particles with large particles (Ondov et al. 1978, Cushing et al. 1979).

Additional research is required on methods for determining particle size distributions and chemical composition of particles smaller than 0.1 μm. Few such measurements have been made to date, and most of those were obtained at ambient temperature and pressure with very small samples necessitating sensitive micro-analytical analysis. Systems that can collect larger size-fractionated samples of fine particles and are calibrated for operation at the elevated temperatures and pressures of process gas streams and stack gases are badly needed to characterize the aerosols in those systems and the removal efficiencies of gas-cleaning devices.

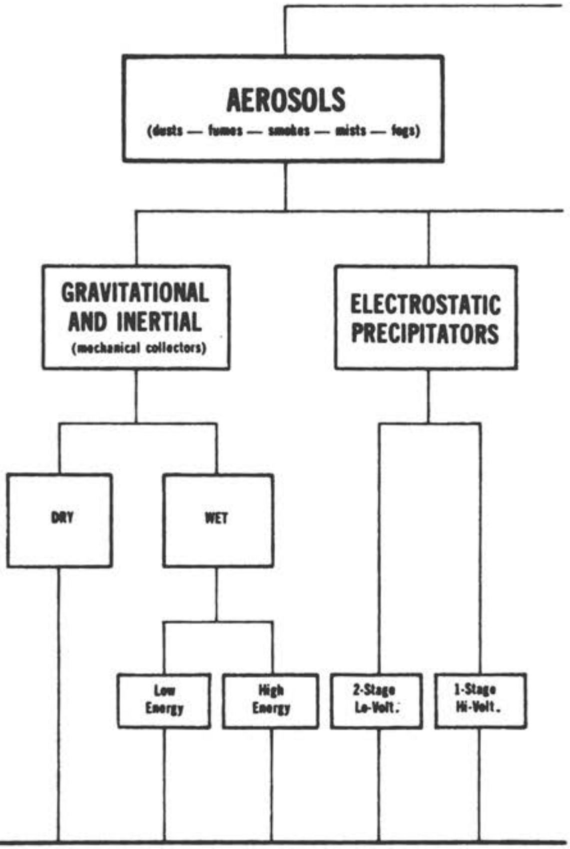
CONTROLLING EMISSIONS FROM DUCTED SOURCES

Primary particles in ducted sources are usually controlled by filtration, precipitation, or flue-gas scrubbing, while gaseous emissions are controlled by adsorption, absorption, or chemical conversion to less harmful species (U.S. HEW 1969, Strauss 1971, Stern 1977, Szobo and Gerstle 1977). The standard techniques are currently under review for EPA in connection with the Agency's review of the TSP and SO_2 standards. Figure 4.1 lists the more common methods of control and characteristics of gas-cleaning devices using these processes.

Filtration

Fabric filters have become an important class of particulate control device, especially for coal-fired power plants. In these devices the dusty gas stream is passed through a fabric, usually made of glass fibers, and particles are collected in a built-up cake of dust by impaction, diffusion, sieving, and sedimentation. As the cake of deposited particles builds up on the fabric, the efficiency of collection increases, but so does the pressure drop across the filter and, consequently, the energy costs of operating the device. The filters are cleaned periodically, usually by shaking or by reversed air flows, to remove the accumulated cake. The frequency of shaking is determined by the need to balance capture efficiency with operating costs and the lifetime of the fabric, which decreases as the frequency of shaking increases (Dennis and Wilder 1975, Venditti et al. 1979).

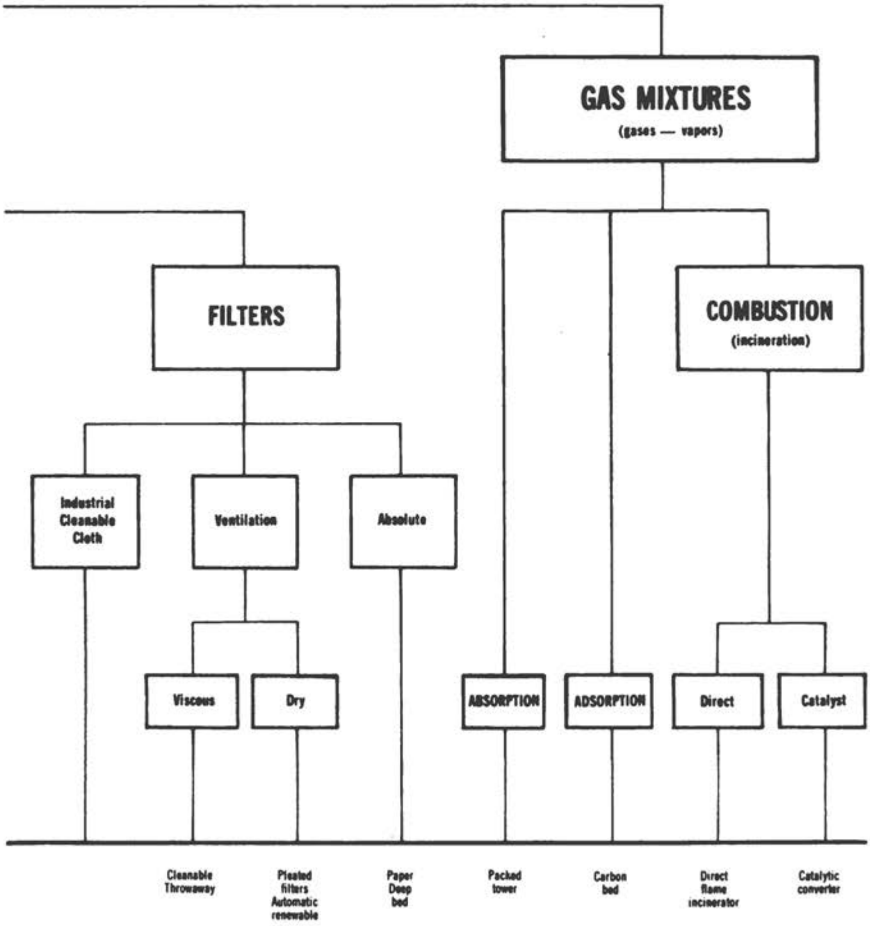
Removal Efficiency Fabric filters operate at overall mass-removal efficiencies on the order of 99 percent. The efficiency of capture, however, depends on the size of the particles. The removal process is dominated by diffusion for smaller particles and by impaction, sieving, and sedimentation for larger particles; the result is that fabric filters often show a minimum in removal efficiency for particles with diameters in the range between 0.1 and 1 μm (Figure 4.2). However, some studies have indicated removal efficiencies that are almost independent of particle size. Pinholes or tears in the fabric are thought to be responsible for this result; a fraction of the dusty gas may pass virtually untreated through these pinholes. In such cases the area of the pinholes obviously limits removal efficiency.



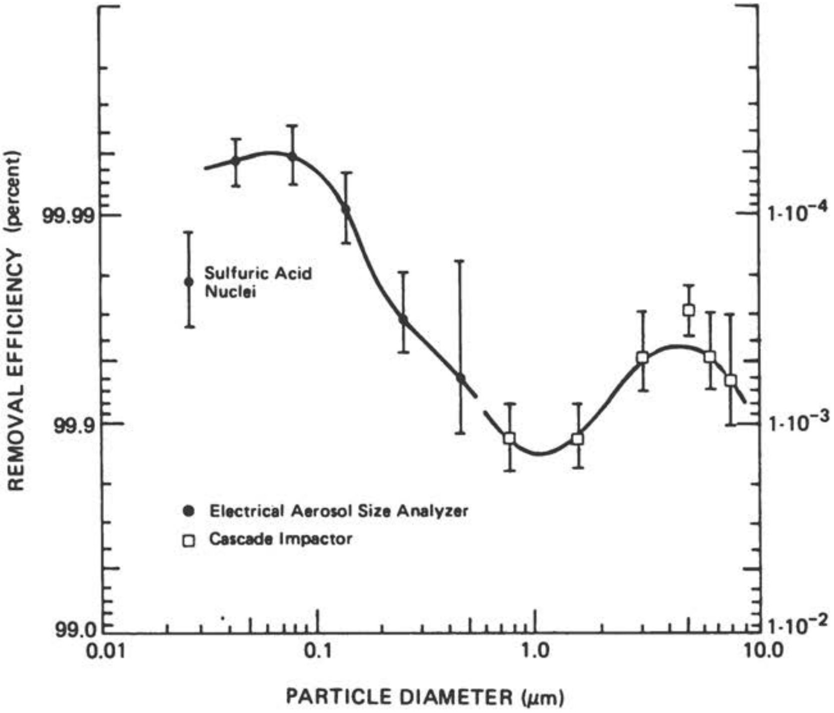
	Settling chambers. Inertial separators. Cyclones Dynamic (Fan & Sep.)	Wetted baffles Wetted cyclone Wetted dynamic Ejector	Venturi scrubber Fog tower	Furnace air cleaner	Plate and wire Tube and wire
TYPES OF CONTAMINANTS	Crushing Grinding Machining	Same as dry	Chemical & Metallurgical fumes	atm. air oil mist	flyash tar H_2SO_4
LOADINGS..................	.1-100 g/m^3	.1-100 g/m^3	.1-100 g/m^3	<0.1 g/m^3	.1-2 g/m^3
COLLECTION EFFICIENCY	high for >10 μm	high for >2 μm	high for $>.25$ μm	high for $>.25$ μm	high for $>.1$ μm
SERVICEABILITY DURABILITY.....	good (erosion)	good (corrosion)	good (corrosion)	poor	fair

SOURCE: Unpublished figure by D. Leith and M.W. First, Harvard University School of Public Health.

FIGURE 4.1 Characteristics of gas-cleaning methods and equipment.



all dry powders	atm. air	atm. air	pre-cleaned atm. air	inorganic gases(HCl, HF, SO_2, Cl_2)	organic gases & vapors (odors)	organic gases & vapors (odors)	organic gases & vapors (odors)
.1-20 g/m^3	<.01 g/m^3	<.01 g/m^3	<.001 g/m^3	ppm to %	ppb to %	ppb to %	ppb to %
high for >.1 μm	high for >.1 μm	high for >.5 μm	high for all sizes		95-99+	90-99	90-99
	good	poor	fair to poor	poor	fair	good	poor



SOURCE: After Ensor et al. (1976).

FIGURE 4.2 Removal efficiency as a function of particle size for a fabric filter installed on a coal-fired power plant.

Research and Development Needs Perhaps the most important research and development need for improving the performance of filters is for fabrics that withstand shaking without fatigue and the formation of pinholes and tears. Another important need is for finding methods of producing more open cake structures so that the pressure drop across the filter is reduced, thereby increasing intervals between cleaning and extending the life of the fabric. Alternatively, the cleaning cycle might be avoided by using a moving-bed granular filter that operates continuously.

Research is under way for use of electric and magnetic forces to augment the deposition of particles on filters but these forces are not yet commercially used in air filtration.

Mathematical models that can predict the performance of fabric filters in specific applications are not well developed. Further theoretical understanding of the fundamental mechanisms is required before modeling of filtration becomes a reliable tool in engineering design.

Precipitation

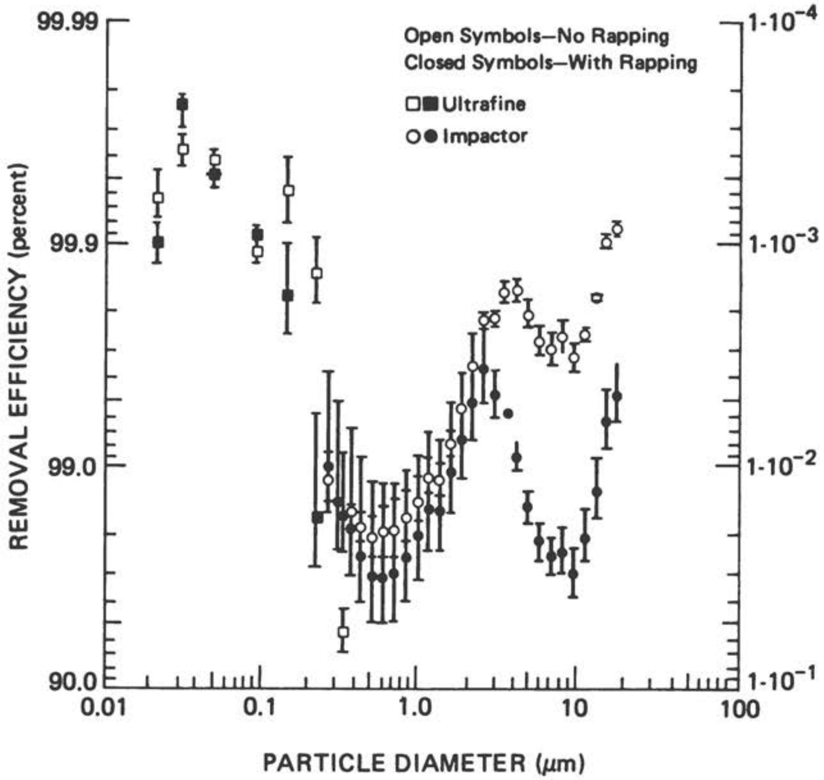
In electrostatic precipitators, the primary particles are electrically charged in a corona discharge and collected in the electric field near a grounded electrode. Two charging mechanisms predominate: diffusional charging by capture of gaseous ions for small particles and field charging for larger particles. As with fabric filters, the cake of particles that builds up on the collection electrode must be cleaned periodically, in this case to prevent back corona. Cleaning is accomplished by mechanically rapping the electrode (Oglesby and Nichols 1977, 1978).

Removal Efficiency Although precipitators designed before around 1970 generally performed poorly, more recent designs operate reliably with overall removal efficiencies of 99 percent or higher (Nichols 1978). The performance of units on coal-fired facilities depends on the resistivity of the coal, with low-sulfur, high-resistivity coals yielding lower precipitation rates. Two avenues of approach are being taken to improve removal efficiencies for the high-resistivity fly ash of low-sulfur coal: chemical additives and novel configurations of electric fields. The additives are used to lower the resistivity of the particles while the objective of developing alternative electric field patterns is to enhance the charging of the particles.

Because both the charging mechanisms and the viscous force resisting the motions of particles toward the collection plate depend on particle size, capture efficiency is size dependent. Figure 4.3 shows a minimum in collection efficiency for particles with diameters in the range from about 0.2 to 1 μm (Gooch 1978).

Figure 4.3 also demonstrates typical decreases in collection efficiency due to rapping. The air flow in precipitators is usually highly turbulent, tending to mix particles migrating near the collector. On rapping, some of the collected particles are entrained in this turbulent flow and are carried through the unit. Rapping losses can be controlled by placing several units in series or by conditioning the cake with a substance that enhances agglomeration and prevents the cake from disintegrating when the collector plate is cleaned.

Research and Development Needs Configurations of electrodes that enhance charging and reduce sparking and flue gas conditioning to decrease the resistivity of the fly ash of low-sulfur coal are perhaps the two most important developments needed to improve performance of electrostatic precipitators. Care must be taken in selecting additives used to condition the gas stream to ensure that one emission problem—primary particles—is not replaced with another, perhaps more serious one. For example, one scheme currently under development uses SO_3 as a conditioner to enhance



SOURCE: After Gooch (1978).

FIGURE 4.3 Removal efficiency as a function of particle size for an electrostatic precipitator on a coal-fired power plant.

removal of particles from the waste stream. The quantities of SO_3 added are small compared with SO_2 concentrations. Care should be taken to assure that sulfur oxide emissions from such a unit are not increased by the use of SO_3 as a conditioner, leading to increased concentrations of fine sulfate particles in the aerosol.

Theoretical understanding of the mechanisms of charging and collection are required to improve mathematical models of the performance of electrostatic precipitators. Current models underestimate collection efficiencies for particles at either end of the range of sizes.

Particle Scrubbing

Particle scrubbing employs a liquid, usually water, to capture particles; the particle-laden liquid must then be separated from the cleaned gas (Calvert 1977a). The most common forms of wet scrubbers spray the liquid into the gas stream. The efficiency of capture depends on the total surface area of the liquid so smaller drops are preferred. However, more energy is required to produce smaller drops and separation of the liquid from the cleaned gas is made more difficult. Entrainment of small particle-laden liquid droplets with the cleaned gas has been identified as one of the major factors limiting overall performance of scrubbers. Consequently, most scrubbers are equipped with mist eliminators.

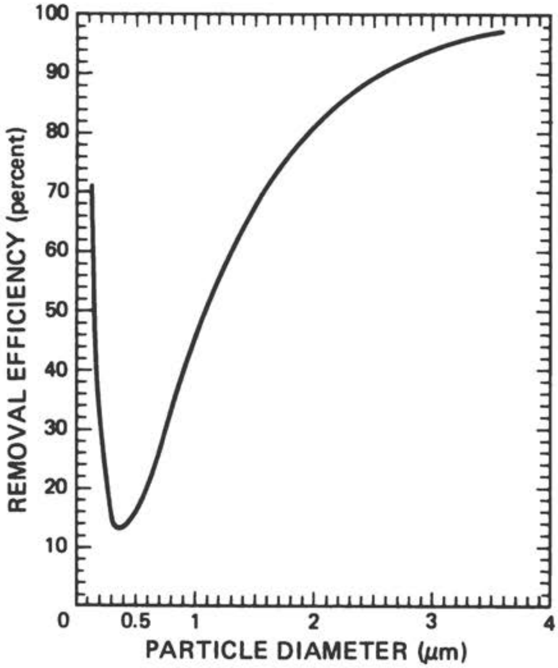
Particle scrubbers have been widely employed in many types of industrial facilities with the exception of electric utilities where the costs of such units are higher and efficiencies lower than those of filters or precipitators.

Removal Efficiency Properly designed and maintained particle scrubbers can typically be operated reliably with removal efficiencies greater than 90 percent for particles larger than 1 μm in diameter. Figure 4.4 shows typical data on removal efficiency as a function of particle size. The efficiencies of particle scrubbers are greatly reduced for particles less than about 2 μm in diameter but may be increased for particles less than about 0.01 μm in diameter. As a consequence, these devices are not as effective for controlling emissions of primary fine particles as filters and precipitators.

Research and Development Needs Problems with the performance of particle scrubbers that are amenable to research and development include corrosive scaling, mist elimination, and regeneration of the particle-laden liquid. Two promising techniques are under study to improve performance by using larger drops or less liquid: electrical charging of the spray and/or the dust and introducing some of the liquid as a vapor that condenses on the dust thereby increasing the effective size of the dust particles.

Gaseous Emissions

Particulate control, especially of fine particles, also includes removal of both condensible vapors and gaseous precursors of secondary particles. The chemical species that have received most attention to date are sulfur oxides, nitrogen oxides, and hydrocarbons. Very little attention has been paid to controlling condensible vapors, a deficiency that must be corrected. Of the precursor gases, much is known about controlling SO_x because the importance of sulfates in the aerosol has been recognized for some time. Control of NO_x emissions is more difficult, but will be of increasing importance as



SOURCE: Calvert (1977b). How to choose a particulate scrubber. *Chemical Engineering* 29:54-68.

FIGURE 4.4 Removal efficiency as a function of particle size for a typical particle scrubber.

emissions increase in the future. Greater attention should be paid to the range of organic pollutants classified as hydrocarbons since shifts to coal, diesel fuel, and synthetic liquid fuels derived from coal or oil shale are likely to produce pollutants more deleterious to health than does the burning of more common petroleum products (Longwell 1978).

Flue Gas Desulfurization The most common means for removing oxides of sulfur from a gas stream is the conventional lime-limestone wet scrubber (NRC 1975). In the reactive zone of the scrubber, the flue gas is washed by a lime or limestone reagent that adsorbs the SO_2, producing a slurry. The slurry is treated to remove the solid wastes in the form of a sludge. The lime-limestone scrubber removes SO_2 with an efficiency of about 90 percent in short-term tests.

Developments needed to improve performance of wet gas scrubbers include means to prevent corrosive scaling, to eliminate mist problems, and to permit operation in closed-loop cycles. Dry gas scrubbing, in which the gas to be removed is adsorbed on the surfaces of fine particles injected into the gas stream, may be an area for fruitful development. Several dry scrubbers have been designed or are being installed, but there is disagreement about whether these systems are ready for commercial use.

The major source of emissions of SO_2 through 1990 is projected to be coal-fired electric utilities built before 1976 (MITRE 1979). These facilities are expected to emit 50 percent of the national total in 1990. Controlling these sources will require the design and installation of retrofitted gas-cleaning equipment, load shifting to more modern facilities, or use of alternative fuels.

Controlling NO_x Emissions Substantial improvements in controlling emissions of NO_x formed from atmospheric nitrogen can be achieved through small reductions in peak combustion temperatures. Exhaust gas recycle is an effective control for most systems. Fuel-lean combustion reduces emissions from some combustors such as the gasoline engine, but is not as effective on combustors that do not premix the fuel and air, such as the diesel engine. Incomplete mixing allows much of the combustion to take place under stoichiometric conditions where the formation of NO_x is favored.

Fuel nitrogen is readily oxidized as long as the temperature is high enough for complete combustion. The strategies developed for controlling thermal fixation of N_2 have little effect on NO_x emissions from the combustion of high nitrogen fuels such as coal, residual fuel oil, and liquids derived from oil shale (Sarofim and Flagan 1976). Under reducing conditions, however, fuel nitrogen can react to produce N_2. A number of control strategies have been based on this observation. Staged combustion, where the fuel is first burned under fuel-rich conditions and later diluted with air to complete the combustion, has achieved modest emission control. An alternative approach is to reduce the effectiveness of mixing in the combustor to increase the time the fuel is in a reducing environment (Flagan and Appleton 1974). New burner designs, based on this principle, are under development (Michelfelder et al. 1976); substantial improvements in NO_x controls are anticipated.

Because most NO_x emission controls involve changes in combustor operation, they have secondary effects. Automotive NO_x controls may decrease fuel economy. Controls suitable for fuels that contain nitrogen may increase the generation of fine particles. Schmidt et al. (1976) show that fine particle emissions may increase during low-NO_x combustion. With further development, low-NO_x burners are likely to reduce NO_x emissions significantly below those attainable with current burner designs. Moreover, low-NO_x burners may be used as retrofitted controls on existing boilers, thereby reducing emissions from these sources.

An alternative method of NO_x control is to introduce combustible nitrogen compounds, such as ammonia, into the cooled combustion products. Over a narrow range of temperatures, an additive will reduce NO to N_2. If the temperature is too high the additive may be oxidized to form additional NO. If the temperature is too low, the reactions may not go to completion. At intermediate temperatures, NO_x concentrations can be reduced by as much as 90 percent (Muzio and Arand 1976). The quantity of ammonia required is comparable to, but somewhat greater than, the amount of NO to be reduced. The narrow range of temperatures over which NO reduction is efficient makes this process difficult to control. The temperature range can, however, be extended by the injection of hydrogen or the use of a catalyst. This approach offers the possibility of obtaining very low levels of NO_x emissions, although the costs may be high.

Use of Alternative Fuels An important strategy for reducing gaseous emissions is the use of alternative fuels, for example low-sulfur or desulfurized coal, fuel oils, and gasoline. Removal of sulfur from coal is complicated by the fact that organic sulfur, which may constitute half of the total sulfur present, is much more difficult to remove than the inorganic sulfur. An advantage of coal cleaning is the simultaneous removal of heavy metals that are associated with the inorganic sulfur in small amounts. The removal of organic nitrogen from coal and oil is even more difficult. The conversion of coal to clean-burning synthetic gas or methanol is also feasible. Hydrogen can be produced from organic fuels or from water with an external energy source (nuclear or solar). While fuel substitution appears attractive, the effects of pollutants generated in producing and using new fuels must be balanced against the pollution generated with conventional fuels and controls.

Integrated Control of Particles and Gases

Integrated control of both primary particles and gaseous precursors to secondary particles would appear to be a highly desirable goal. Wet scrubbers may have an advantage for end-of-pipe treatment if the gases can be made sufficiently soluble in the liquid used. Dry scrubbers may be used in conjunction with fabric filters or electrostatic precipitators to remove both the primary particles and gas-laden adsorbant. The latter method, of course, requires two steps and therefore is not truly an integrated system.

Given the apparent difficulty of simultaneously reducing both NO_x and particulate emissions from coal combustors, considerable ingenuity will be required to devise alternative processes and gas-cleaning methods that will achieve simultaneous reductions in emissions of particles and precursor gases.

An alternative strategy for simultaneous control of particle and gas emissions is the use of clean-burning fuels such as hydrogen, methanol, desulfurized fuel oil, and chemically treated coal. These fuels are more expensive than conventional ones, but the extra fuel costs could be offset at least partially by reduced expenditures for control equipment. Methanol derived from coal appears to be an especially attractive alternative because it can be burned producing essentially no particles, SO_x, or hydrocarbon vapors and little NO_x (Reed and Lerner 1973, Trijonis et al. 1975). Detailed studies of the total costs and benefits of using such fuels should be conducted.

Maintenance

Maintenance of both process and gas-cleaning equipment can result in improved performance and reduced emissions. Maintenance of gas-cleaning equipment is required by most states as a condition of permits and by the federal New Source Performance Standards. However, gas-cleaning equipment is not always properly maintained. As indicated earlier, deterioration of performance in automobile emission controls due to lack of maintenance is acknowledged in most projections of air quality. Maintenance is a serious problem for commercial and residential space heaters, which have evidenced substantial discrepancies between emissions under test conditions in the laboratory and those under operating conditions in typical installations. Maintenance of process equipment affects operating conditions, which, in turn, affect emissions.

Maintenance is normally performed during scheduled downtimes. Most firms have to depend on outside personnel for testing and maintenance and, as a result, performance can deteriorate substantially between scheduled visits of maintenance personnel before being detected by on-site personnel.

It appears to us important to develop improved methods—perhaps incentives—for assuring that process and gas-cleaning equipment is in proper operating condition.

CONTROLLING FUGITIVE EMISSIONS

Control of fugitive emissions may take many forms, depending on the source of the emissions. Fugitive process emissions in confined areas often represent a greater hazard for occupational exposure than for exposure of the general population. Occupational exposures are easier in principle to control. Leaks and spills, for example, can be controlled by good housekeeping practices and maintenance. Other fugitive process emissions can be captured by enclosing the operation, ventilating the air, and collecting emissions with filters, precipitators, etc.

Fugitive dust sources are normally controlled by stabilizing the exposed surfaces from which the dust is raised by the wind. Sweeping, wetting, oiling, and paving are common practices for roads and at construction sites. Alternative agricultural practices exist for preventing erosion of soils by the wind.

The first step in controlling fugitive emissions must be to characterize the emissions from the source. As indicated in Chapter 3, fugitive sources are, on the whole, poorly characterized. Much work needs to be done in this regard.

CONTROLLING MOBILE SOURCE EMISSIONS

The problem of controlling emissions from cars and trucks is an important one because these sources make a substantial contribution to urban loadings, especially in the fine particle range (U.S. EPA 1978; Table 3.1). Emissions of carbon monoxide and unburned hydrocarbons from spark-ignition engines using unleaded fuel can be effectively controlled with catalytic converters if the engines and converters are properly maintained. A three-way converter has also been demonstrated to control NO_x emissions as well. Spark-ignition engines using leaded gasoline without converters account for most of the lead in the urban aerosol except near smelters or other facilities processing that element (see Table 5.1).

Controlling emissions from diesel engines will require ingenuity. As described in the section on Controlling NO_x Emissions, incomplete mixing of the fuel and air in the combustion chamber of the diesel allows much of the combustion to take place under conditions that favor production of NO_x. Engine modifications to reduce NO_x tend to increase emissions of primary particles.

Alternatives to modifying the diesel engine itself are modifying the fuel and after-treatment. Fuels with lower cetane numbers produce fewer particles, presumably because ignition is slower and the mixing time longer. Additives may be used to reduce the visibility of diesel exhausts, but the additives may introduce new, fine particles into the emissions. In some cases, the use of smoke-suppressing additives may actually increase the total mass emissions of fine particles even though the opacity of the exhaust is reduced. As in the application of other control techniques, the benefits of reduced emissions of one type should be weighed against the potential environmental impacts of the control activity itself.

Most of the research and development on gas-cleaning devices for end-of-pipe treatment of diesel engine exhausts has been for use on stationary engines. Filters, electrostatic precipitators, and particle scrubbers have been tried, so far apparently with only limited success. Filters appear to be the most promising, although periodic cleaning of the filter and disposing of the collected aerosol are problems.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

1. Engineering strategies for control have focused on end-of-pipe treatment of stationary and mobile ducted sources. End-of-pipe treatment may be an acceptable design strategy in many circumstances, such as when recognition of the need for controls comes after the process equipment has been designed and is operating, but a potentially more useful engineering strategy is to incorporate environmental considerations into every aspect of design, including selection of raw materials, processes, and products.

2. Conventional ducted sources of particles can be controlled with efficiencies of mass removal of greater than 95 percent using electrostatic precipitators or fabric filters. Current designs of these devices exhibit minima in collection efficiency for particles around 1 μm in diameter. Particle scrubbers are not effective at removing particles smaller than about 1 μm. Modern designs of conventional SO_x scrubbers have removal efficiencies of the order of 90 percent. Effective controls for NO_x emissions that do not enhance emissions of particles or entail other penalties (especially in fuel efficiency) are not now commercially available, but injection of ammonia and improvements in the designs of burners should lead to more effective NO_x control. The problems of controlling fugitive process emissions and condensible vapors are poorly characterized.

3. Data on the removal efficiencies of gas-cleaning devices as functions of particle size are potentially of great importance to the development of improved control technologies. These data are also necessary for predicting the size distributions of particulate emissions from new sources, and should be coordinated with plume studies to improve understanding of the relationships between emissions and air quality. Fractional removal efficiencies are difficult to measure because of problems associated with sampling at high gas temperatures and high particle concentrations; further development of methods capable of measuring particle size distributions under process gas conditions should be supported.

4. To promote the development of technology for controlling emissions of fine particles, performance standards should be expressed in terms of particle size and, where feasible, composition.

5. The performance of both process and control equipment deteriorates if the equipment is not properly maintained. One component of an air quality control strategy should be to insure that industrial, commercial, residential, and automotive sources and associated control devices are properly maintained.

6. Controlling emissions of SO_x and NO_x from coal combustion, especially in electric power generating facilities, is a major concern. If significant reductions in nationwide emissions of SO_x are to be achieved by 1990, control of coal-fired utilities and other industrial facilities built before 1976 will have to be addressed. Development of reliable, cost-effective controls for NO_x for coal-fired plants is of high priority.

7. Because atmospheric particles arise from direct emissions of primary particles and from the transformation of gaseous pollutants in the atmosphere, it is important to consider synergisms and compromises in controlling emissions of particles and gaseous precursors. Control of gaseous precursors in some cases aggravates the problem of controlling emissions of fine primary particles. Modification of production processes may be required to achieve simultaneous control of both particles and gases. Continued research and development is needed to improve alternative combustion techniques, such as fluidized-bed combustion and advanced burners, and to design alternative processes and products. Potentially attractive in the long term are alternative clean-burning fuels, such as methanol derived from coal, which produce neither particles nor significant quantities of gaseous precursors during combustion.

8. Continued research and development to refine the operation of conventional gas-cleaning equipment is recommended. A number of potentially promising avenues of approach have been identified and are currently being pursued. A major program for the development of controls of particulate and NO_x emissions from diesel engines is urgently needed.

5 Relationships Between Emissions and Air Quality

Assessing the quantitative relationships between anthropogenic and natural emissions and air quality is fundamental to sound air quality management. Methods of assessment have developed along two distinct lines: the design of dispersion models that simulate the transportation and dilution of emissions in the atmosphere; and the development of statistical models based on empirical relationships between source characteristics and measured ambient conditions. Given changes in emissions, both types of models can be used to predict changes in ambient air quality.

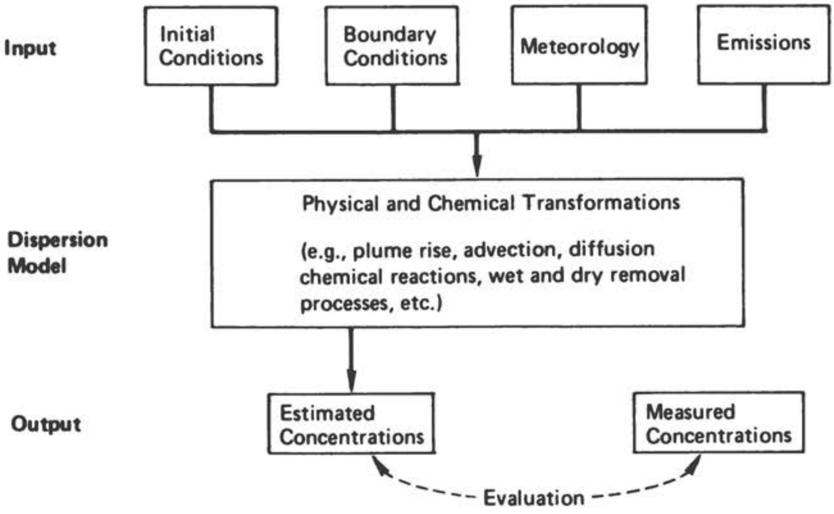
These models have important applications in air quality management. First, predictive models may be used to estimate the impact of an individual source; this information can then be used to determine the need for controls or to assist in site selection. Second, models may be used to identify sources or categories of sources that contribute significantly to ambient concentrations; regional strategies for air quality control can then be based on this information. The latter application is likely to become more important in the future as attention turns to chemical species as well as mass and to dynamic management of air quality. Third, models may be used to estimate regional and national changes in the exposures of populations to aerosols that would result from potential changes in energy development, conversion technologies, and control measures.

DISPERSION MODELS

Development of dispersion models for urban air pollution began in the 1950s. Since that time several types of dispersion models have been developed: urban models of point, area, and highway sources; models of single and multiple point sources in flat and complex terrain; and urban and regional scale models of atmospheric photochemical reactions. Currently simulation of long-distance transport and conversion of gases to particles is under development. Numerical simulation models of the advection and diffusion processes are also areas of ongoing research.

Dispersion models are mathematical expressions of the effects of the atmosphere on air pollutants. These effects include "advection (transport) and dispersion (including dilution by the wind and dispersal due to turbulence) and may also include considerations of plume rise, wind shear, and chemical and physical transformations (including removal mechanisms)" (Turner 1979). Figure 5.1 illustrates the elements common to all dispersion models.

The primary inputs to these models are the meteorological and emission data. For most models, uncertainties in emissions and meteorology are serious limitations to accuracy. The needs for detail in these data vary from model to model. Background concentrations of a single species may be used with less sophisticated models while a complicated array of initial boundary conditions (both for meteorological and air pollution variables) is needed for other models. Some photochemical models may require knowledge of initial concentrations and chemical reaction rates for as many as 25 pollu-



SOURCE: After Turner (1979). Reproduced with permission from *Journal of the Air Pollution Control Association* 29(5):502-519.

FIGURE 5.1 Elements of dispersion models.

tants. The most sophisticated treatments include a chain of reactions that may be comprised of as many as 150 steps, many involving highly reactive intermediate species.

Dispersion models generally are used to predict air quality. Their output is the pollution concentration over an area for various periods of time. The accuracy of these models is normally tested through trial runs on cases where meteorology, emissions, and concentrations are known. However, analyses of the sensitivity of the results to the input parameters are not routinely available, a serious deficiency. In the absence of such information, dispersion models have been widely applied without effective evaluation of their accuracy for specific situations.

We believe that descriptions of models should specify clearly the sensitivity of results to the uncertainties in the input parameters. One method of accounting for uncertainties is to express the input parameters in terms of ranges of values; probabilistic methods may then be used in the analysis to obtain results expressed in terms of a confidence interval around a most likely value (Hammersley and Handscomb 1964, Morgan et al. 1977). Having results expressed as confidence intervals has advantages to users and decision makers. The value in resolving uncertainty can be assessed. The impacts of alternative choices (for example, in sites, controls, equipment, or fuel use) can be expressed by the level of statistical significance. The relative risks of violating standards or changing population exposures can be incorporated into the decision-making framework.

State of the Art of Dispersion Modeling

Local Models The most accurate models are those that simulate local dispersion of unreactive pollutants from an isolated point source. If a source is located in relatively flat terrain and data on emissions and meteorology are known, then the predicted concentrations averaged over time periods from a day to a year can be expected to be within a factor of two of actual values within a few kilometers of the source. As terrain becomes more hilly or as the atmospheric mixing becomes complicated by small-scale influences, the predictions become less certain. For transport over longer distances the errors associated with chemical conversion and other processes become more important. If long-term seasonal or yearly average concentrations are acceptable, then less precision in emissions, meteorological conditions, and rates of conversion and removal can be tolerated due to averaging.

Our ability to predict the aggregated impact of a number of point, area, and line sources in urban areas needs improvement. Improving multisource dispersion models may come about through use of statistical receptor models to extrapolate from actual ambient concentrations to the contributions of classes of sources (see section on Statistical Models).

Urban models are limited primarily by the accuracy of emission inventories. Most inventories do not include information about emissions by particle size, emissions from natural sources, or the variations of emissions over time. Data on the parameters affecting fugitive emissions from industrial sources, resuspension of road dust, or wind erosion of open areas are also not included in most inventories despite the fact that fugitive urban, crustal, and limestone dusts account for a substantial fraction of TSP mass in many locales (see Table 3.1).

Modeling urban concentrations of inhalable particles or fine particles with conventional models and existing source inventories will present additional difficulties. Fine particles comprise from 10 to 90 percent of inhalable particles, depending on the relative strengths of different sources. The fine fraction may be dominated by secondary particles, especially sulfates, that have been transported from one region to another. These particles will be difficult to include in dynamic models.

Regional Models Models may be used to estimate whether projected emissions will cause an area to be in noncompliance with ambient standards. Although this application has, for purposes of regional planning, been expanded to include the impact of many sources in a region, models are still site-specific and scales of motion are small (less than 50 km) because treatment of meteorological phenomena must be greatly simplified.

In some regional models, transport mechanisms conserve mass and diffusion is assumed to be statistically stationary and homogeneous over discrete time intervals so that it can be treated as Gaussian. These assumptions are invalid for time periods of more than a few hours and for distances more than a few tens of kilometers. Instead, the trajectory of the pollutants over longer time periods and greater distances is determined by the changing synoptic meteorology and by processes of transformation, decay, and removal.

Four state-of-the-art regional transport models are currently being developed: the Stanford Research Institute model (Mills and Hirata 1978), the Sulfate Regional Experiment (SURE) model (Lavery 1978), the Brookhaven National Laboratory model (Meyers et al. 1978), and the Teknekron multiscale model (Niemann 1977). These models, which focus on sulfate concentrations, use different methods of computation to estimate transport, dilution, conversion, and removal of SO_2 and sulfates. Moderate success has been obtained in estimating the long-term concentration averaged over large geographic areas.

Improvements in long-distance transport models await refinements of emission inventories and improved scientific understanding of chemical conversion, particle and gas removal, and atmospheric dispersion processes. Several promising efforts are now underway: the SURE study (Lavery 1978), EPA's Multi-State Atmospheric Power Production Pollution Study (MAP3S) being conducted in cooperation with the Department of Energy (MacCracken 1979), and EPA's VISTTA program (Visibility Impairment due to Sulfur Transformation and Transport through the Atmosphere) (Macias et al. 1979b,c).

Sulfates have dominated recent modeling efforts because of historical health and ecological concerns. More is known about emissions of SO_2 than about emissions of NO_x, organics, or fine primary particles. The data base for sulfates, though limited, is available for model evaluation. The concentrations of other secondary particles will be more difficult to model. Efforts should be made to expand our capabilities to model fine primary particles and chemical species such as nitrates and organics, which increasingly appear to be important.

Emissions The strengths of sources are very important input data for determining ambient concentrations. In the classical Gaussian model, downwind concentration is directly proportional to source strength and the spatial distribution of ambient concentrations over a local region is principally determined by the spatial distribution of sources (Hanna 1971). Given good emissions data, the predictions of the Gaussian model compare well with observations of yearly mean concentration.

In addition to deficiencies in characterization of particle size and chemical composition, the lack of specification of temporal variations is a weakness with the emissions data base. Gaussian models are frequently used in regulatory decisions to calculate annual mean concentrations based on annual mean meteorological data and annual mean emission rates. While there is some value in using annual mean values as inputs, emission rates and meteorology are not independent. For example, emissions from space heating increase as the ambient temperature decreases. Such dependencies may be significant when peak short-term averages or episodic meteorological conditions are of interest.

Emissions, however, are specified as annual average rates in most inventories. Even simple diurnal and seasonal cycles in emissions are not included in the data base. The use of simple annual average emissions may lead to large errors in calculations for any given day. Over a large number of days these errors may cancel each other out so that predictions of long-term averages are not unreasonable. Nevertheless, because of time variations of emissions and meteorological conditions, modeling for short-term meteorological episodes and the 24-hour standard produces uncertain results. Perhaps the best approach to this problem would be use of distributions to describe the range of input conditions and their relative probabilities and use of statistical techniques to obtain a distribution of outcomes.

It might be inferred from the discussion above that annual average emission rates are well known. In fact, the task of gathering the data is extremely tedious and difficult, and errors are frequently made. States are required by EPA to update their inventory of sources annually, but this task appears to be beyond the capabilities of many state programs. Higher quality emission data are available from specialized intensive studies such as the SURE study (Lavery 1978) and EPA's RAMS/RAP project in St. Louis (Littman 1978). However, the data that are most readily available are in EPA's National Emissions Data Systems (NEDS). NEDS is most representative of emissions in 1973 and is known to contain significant errors. These data have been used in various modeling efforts but have required major review and updating in each case.

Emissions inventories suffer from several other deficiencies. They are subject to errors because of variations in the performance of gas-cleaning equipment. They normally quote only the total mass released with no indication of size distributions or chemical compositions. They frequently do not include either fugitive dust or fugitive process emissions. All of these deficiencies can be rectified. We strongly recommend that, as a first step, emission inventories be improved to specify particle size and chemical composition of emissions from conventional ducted sources, from fugitive process sources, and from fugitive dust sources. Eventually, consideration of time variations in emissions due to variations in performance of process and gas-cleaning equipment should be incorporated into emission inventories.

Transport Physical advection of pollution downwind is another important determinant of atmospheric concentrations. Because the volume of the diluting air is directly proportional to wind speed, concentrations of pollutants are inversely proportional to wind speed. In the Gaussian model used for local studies, the transport wind is treated as a constant across the region. This assumption is less valid for transport over greater distances and longer time periods because of changes in mesoscale and synoptic wind fields. Topographic features produce large local changes in the flow field. Realistic representation of transport over long distances, therefore, requires a more detailed specification of the flow field than that used in the Gaussian model.

Treating topography in detail increases the complexity of models; compromises must be made between describing the complexity of reality and building practical models. Simple approximations usually do not compromise predictions of long-term mean values, but may not be adequate for estimating peak concentrations or for averaging over short periods of time.

Dispersion In local models, pollutants are assumed to be dispersed by random processes and distributions of concentrations are described by a normal (Gaussian) curve. The rate of dispersion is a function of the stability of the air mass and of downwind distance. Observations of spreading plumes have been made for distances up to 50 km; little is known about dispersion parameters at greater distances (Husar et al. 1978).

As with transport processes, the modeling of dispersion processes requires that compromises be made between describing reality in all its complexity and building practical models. For example, the calculation of horizontal dispersion by diffusion must be greatly simplified because the number of computations for each source at each time interval is prohibitive. A full range of simplifying assumptions about horizontal dispersion can be made, including that horizontal dispersion is negligible compared with advection and vertical dispersion. Improved computational techniques would permit more detailed treatment.

Vertical dispersion over long time periods is physically limited by the earth's surface and by elevated stable layers in the atmosphere. Gaussian models predict complete vertical mixing of pollutants beyond distances of the order of 10 km from the source for mixing heights as large as several kilometers; therefore the rate of vertical dispersion classically would not be expected to be critical to long-range modeling. The concept of complete mixing in the boundary layer is used in some models, called flooded boundary layer models. For urban models with ground-level sources in the local area, the assumption of complete mixing in the boundary layer is invalid.

In regional models the concept of uniform vertical mixing is inconsistent with natural removal processes that depend on vertical gradients in concentrations, surface characteristics, and meteorological conditions. Removal processes result in mass flux to the surface. In flooded boundary layer models, this flux is approximated by a "deposition velocity," assumed to be constant throughout the mixing layer.

In fact, the rate at which pollutants move toward the ground depends on both height in the mixing layer and time of day. Pollutants from elevated sources are generally trapped above stable air layers in the atmosphere. Mixing to the ground occurs during the day as solar heating of the surface overturns the atmosphere, but is strongly suppressed at night. In addition, the assumption of a constant deposition velocity omits the effects of vertical concentration gradients and variable surface characteristics.

In simplified models that incorporate vertical diffusion, an average diffusion coefficient is assumed for the mixing layer. An average diffusion coefficient should produce a reasonable estimate of long-term mean concentrations but estimates of daily values using this simplification are of limited accuracy and will deviate significantly from observations. Other more realistic models of vertical dispersion are based on diffusion in a vertical concentration gradient (Lavery 1978). The dependence of diffusivity on height may be treated by dividing the mixing zone into layers, each with its own diffusion constant and meteorological conditions. Diurnal variations may also be treated.

Transformation The transformation of gases such as SO_2, NO_x, and hydrocarbon vapors to particles is affected by a variety of mechanisms including photochemical and catalytic oxidation (Graedel 1979, Crutzen 1979). These mechanisms are of two types: homogeneous, involving gas phase reactions, and heterogeneous, in which the reactions occur at the surfaces of particles or droplets.

Of all the gas-to-particle conversion processes, the most heavily studied are those that transform SO_2 to sulfates. Most urban and long-range models that include transformation processes incorporate empirical, first-order conversion rates. The empirical rates are adjusted to obtain agreement with available data; for example, the rate of conversion from SO_2 to sulfates typically may be between 0.5 and 2 percent per hour but may range up to 10 percent under extreme photochemical conditions. In other circumstances, the conversion rate may be below 0.5 percent per hour. There is a continuing need for research on fundamental reaction rates to understand atmospheric conversion processes (Hegg and Hobbs 1978, Wilson 1978, Middleton et al. 1979).

In one study of transformation processes, calculations of the production of sulfates in the atmosphere were made under a variety of conditions; appropriate assumptions were made about the initial distributions of particle size and concentrations of some of the more important reactive gases such as SO_2, ammonia, ozone, and hydrogen peroxide (Middleton et al. 1979). The results of Middleton's calculations of sulfate concentrations produced under different atmospheric conditions after five minutes of reaction time are shown in Figures 5.2 and 5.3. The following conclusions can be drawn based on the results of this study:

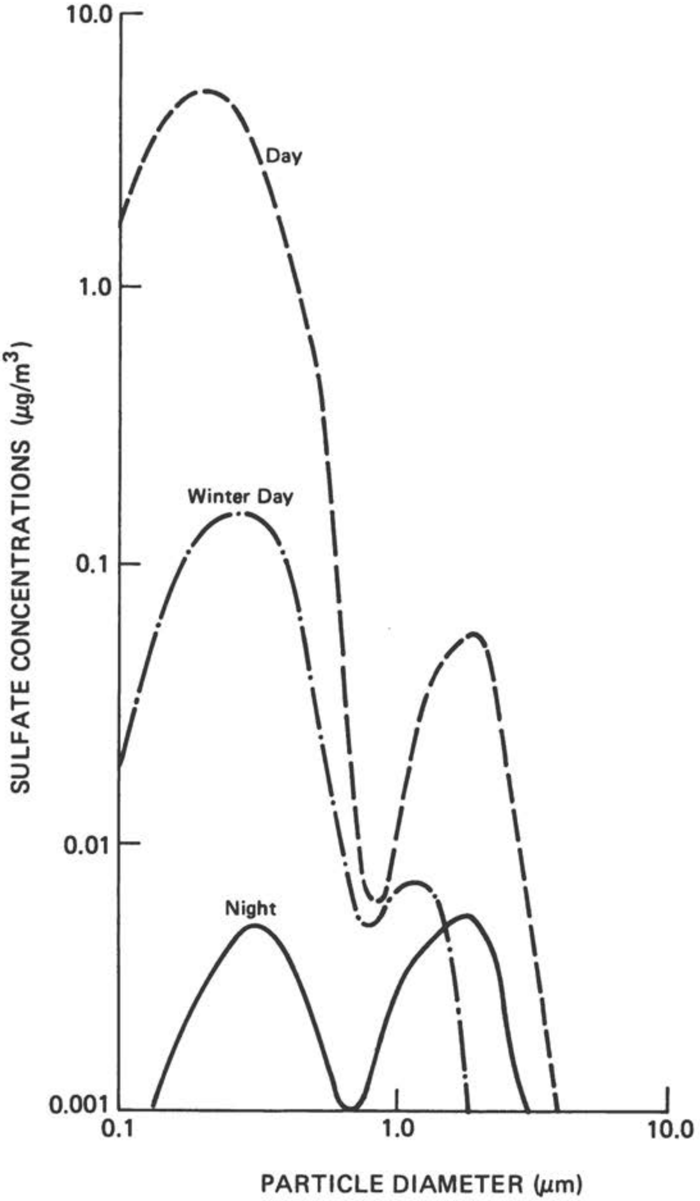
(1) conversion rates are much higher on average days than during the night or on winter days;

(2) homogeneous oxidation is by far the dominant mechanism under daytime conditions;

(3) when homogeneous mechanisms dominate, the particles formed are predominantly submicron sulfates, but there is a shift toward larger particles when heterogeneous mechanisms are more important; and

(4) oxidation by hydrogen peroxide is the predominant heterogeneous mechanism during the day, but oxidation catalyzed by carbon soot and iron becomes more important at night.

Many of the experimental data support the conclusions that sulfates are predominantly present in the fine particle mode and that sulfate levels are distinctly higher in summer than in winter (Figures 5.4 and 5.5). However, the differences between winter and summer production of sulfate do not appear to be as great as those predicted by the Middleton study. Some mecha-



SOURCE: Middleton et al. (1979). Reproduced with permission from the American Chemical Society, Division of Environmental Chemistry.

FIGURE 5.2 Sulfate concentrations as a function of particle size produced from transformation processes under different atmospheric conditions after five minutes.

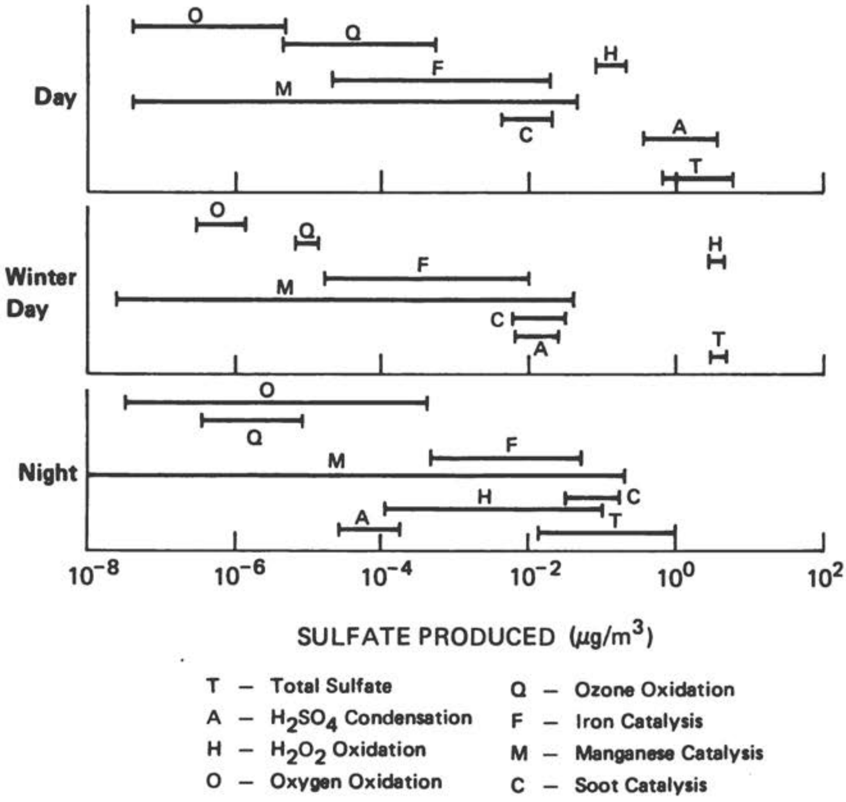


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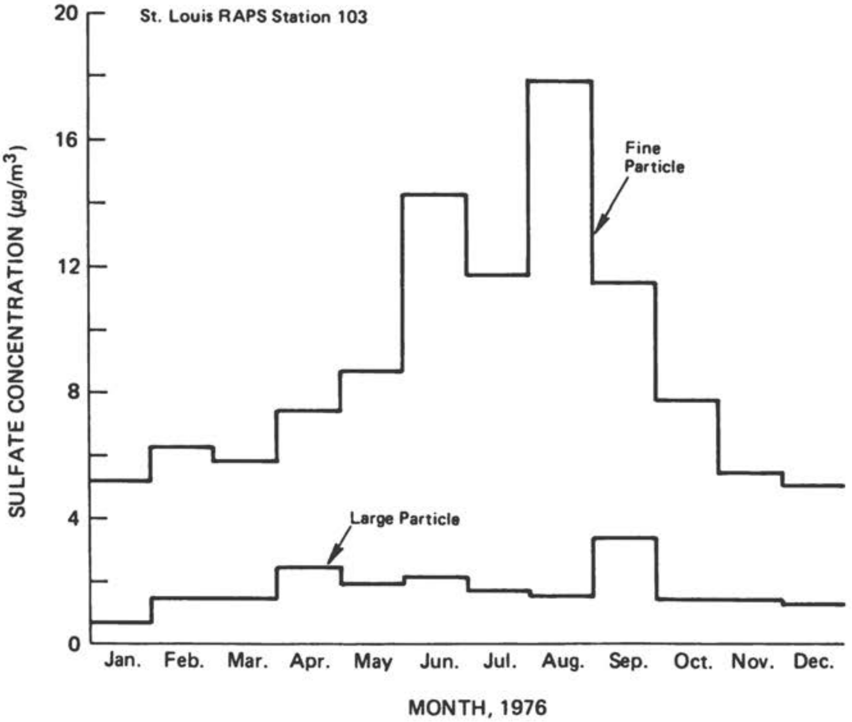
FIGURE 5.3 Contribution of different mechanisms of formation of sulfates under different atmospheric conditions after five minutes.

nism that is less dependent on photochemistry is probably more important than indicated by the calculations of Middleton et al. (1979). Much of the conversion may occur when air containing SO_2 passes through clouds and some SO_2 dissolves in cloud water (Hegg and Hobbs 1978). If the cloud evaporates, as most do, any sulfate formed would be left as aerosol.

The suggested importance of in-cloud processes for sulfate formation is supported by calculations showing that there is not enough sulfate aerosol present in the United States to account for the sulfuric acid in rainfall (Newman 1979). The implication is that much of the acid of rainfall must be made by in-cloud processes. Newman makes a similar case for the nitric acid in rainfall.

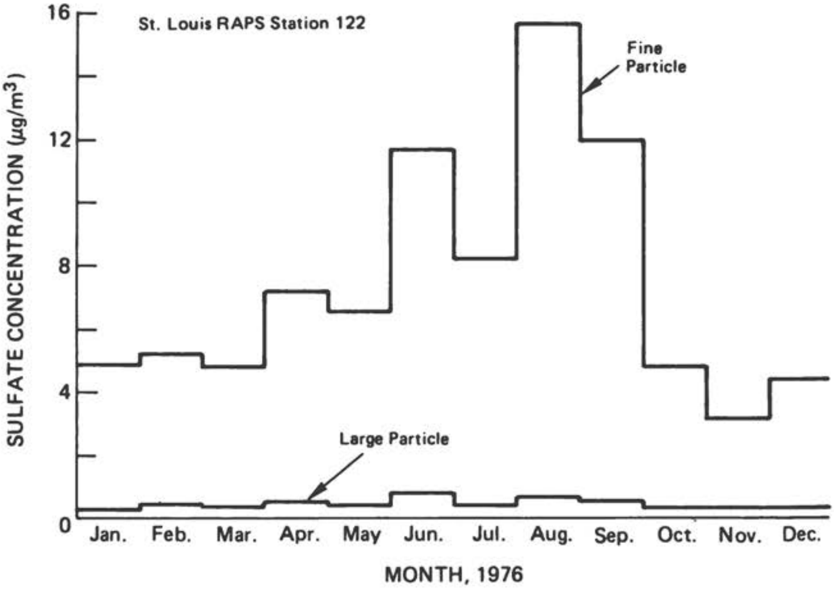
Current understanding of the mechanisms by which nitrates and organic particles are formed in the atmosphere is not as well developed as that for sulfates. With increased control of SO_2 emissions, increased emissions of NO_x, and increased emissions of hydrocarbons that will result from changes in the patterns of fuel use, research will be needed to understand and predict nitrate and organic concentrations.

Removal Particles and gases are removed from the atmosphere by interactions with the surface or through precipitation. Dry deposition, including absorption of gases by vegetation, is a function of surface roughness and meteorological conditions. Wet deposition includes rainout (the removal of pollutants by condensation and the growth of raindrops) and washout (the removal of pollutants by precipitation falling through a polluted layer). Both dry and wet removal processes may be described in terms of deposition



SOURCE: Drawn from the data of Loo et al. (1978).

FIGURE 5.4 Average monthly sulfate concentrations in fine and coarse particles at an urban sampling site in St. Louis, 1976. (Measurements were of sulfur, all of which was assumed to be present as sulfates.)



SOURCE: Drawn from the data of Loo et al. (1978).

FIGURE 5.5 Average monthly sulfate concentrations in fine and coarse particles at a rural sampling site in St. Louis, 1976. (Measurements were of sulfur, all of which was assumed to be present as sulfates.)

velocities, which are considerably different for gases and particles (Slinn et al. 1978, Davidson and Friedlander 1978).

Dry deposition of particles in the atmosphere is governed by sedimentation and inertial impaction for particles with diameters greater than 1 μm and Brownian diffusion for particles with diameters less than 0.1 μm. As a result, the deposition velocity is lowest for particles between 0.1 μm and 1 μm for which the physical processes leading to dry deposition act weakly. Therefore, atmospheric residence times are greater for particles in this size range.

While wet deposition has been described in terms of a constant deposition velocity, it has also been treated in more detail. For example, the Stanford and Brookhaven models, using daily observations of precipitation, calculate deposition as the product of pollutant concentration, precipitation rate, and washout coefficients for specific pollutants (Meyers et al. 1978, Mills and Hirata 1978).

In-cloud removal processes are not well understood. As described earlier, scavenging of fine and ultrafine particles by cloud droplets may be the dominant removal mechanism for particles of these sizes. Clouds are also receiving increased attention from their potential role in the conversion of gases to aerosols. These processes are not likely to be adequately described by a constant conversion rate or deposition velocity.

STATISTICAL MODELS

In traditional models, source emissions have been used to project ambient concentrations; these projections are then used to predict impacts and to design controls. However, it is also possible to use empirical data on the composition of ambient particles to gain insight into the influences of various sources on the ambient aerosol. The techniques used are often described as statistical models because they are based on statistical methods rather than numerical simulation of physical and chemical processes.

Statistical models have been used almost exclusively for research purposes, but these techniques could—and should—be applied to problems in air quality management.

Receptor Models

There are two major classes of receptor models: chemical element balances and multivariate techniques (also called "pattern recognition") (Gordon 1979). The older and simpler of these methods is that of the chemical element balances (CEB) (Hidy and Friedlander 1971, Winchester and Nifong 1971, Miller et al. 1972, Friedlander 1973).

Chemical Element Balances The CEB method assumes that the composition of ambient particulate matter is a linear combination of the compositions of the particulate matter originating from various sources. In theory, accurate knowledge of the composition of the ambient aerosol and of the emissions of all important sources permits solution of a set of simultaneous equations for the contributions of each source to the aerosol.

In practice, the information is never as complete or reliable as desired, so simplifying assumptions must be made. Typically, rather than use all the emissions from each source, a set of "marker" elements is used to characterize a few prominent sources. The marker elements are normally those that are strongly associated with specific sources; examples are lead with motor vehicles, sodium with sea salt, and vanadium or nickel with combustion of residual fuel oil.

An example of the results of a CEB for the Washington, D.C. area is shown in Tables 5.1 and 5.2 (Kowalczyk 1979). A set of 130 air-filter samples from a network of 10 stations was analyzed for about 40 elements. It was assumed that the total composition of aerosols could be represented as the sum of contributions from seven sources: soil, coal, residual oil, refuse

TABLE 5.1 Average Fits to the Concentrations of Nine Marker Elements in 130 Whole Filter Samples in a Chemical Element Balance for the Washington, D.C. Aerosol

	Contributions from Components (ng/m^3)							Total Concentration (ng/m^3)	
Element	Soil	Coal	Limestone	Oil	Refuse	Motor Vehicle	Sea Salt	Predicted	Observed[a]
Na	40	8	1	12	50	–	189	300	300±20
Al	750	490	10	0.4	9	–	–	1,250	1,350±110
Ca	61	44	700	8	10	21	7	853	860±40
V	1.0	1.5	0.05	22.7	0.02	–	–	25	25±2
Mn	12	1.5	2.5	0.1	0.5	–	–	16.5	17±2[b]
Fe	470	340	9	3	4	19	–	850	1,000±60
Zn	1.0	2.4	0.05	1.6	74	6	–	85	85±6
As	0.056	2.9	0.002	0.027	0.15	–	–	3.2	3.2±0.2
Pb	0.1	2	0.02	0.4	50	388	–	440	440±20

SOURCE: Kowalczyk (1979).

[a] Uncertainty is the standard deviation of the mean value.

[b] Experimental value reduced by factor of 0.69 as explained in the reference. Actual average concentration is 25±ng/m^3.

TABLE 5.2 Predicted and Observed Concentrations for Elements Not Used in Fitting in a Chemical Element Balance for the Washington, D.C. Aerosol

Element	Concentration (ng/m^3)		Observed/ Predicted	Major Source(s)
	Predicted	Observed[a]		
K	227	400±20	1.7	Soil
Rb	1.7	2.2±0.2	1.3	Soil
Cs	0.07	0.17±0.03	2.5	Coal, soil
Mg	270	440±30	1.6	Limestone
Sr	8.2	10±1	1.2	Soil, coal
Ba	18	19±2	1.02	Soil, motor vehicle, coal
Br	151	136±9	0.90[b]	Motor vehicle
I	3.1	1.9±0.1	0.65[b]	Coal, sea salt
Sc	0.31	0.33±0.03	1.07	Coal, soil
Ti	80	110±10	1.4	Soil
Cr	1.9	15±2	7.3	Coal, soil
Co	0.60	0.83±0.08	1.4	Coal, soil, oil
Ni	5.7	17±2	3.0	Oil
Cu	6.0	17±2	2.9	Coal
Ga	0.78	1.29±0.17	1.7	Coal, soil
Se	0.79	2.4±0.2	3.1[b]	Coal
Ag	0.35	0.20±0.01	0.57	Refuse
Cd	2.0	2.4±0.2	1.2	Refuse, motor vehicle
In	0.007	0.020±0.001	2.9	Refuse
Sb	1.75	2.1±0.2	1.2	Refuse
La	1.0	1.5±0.1	1.5	Soil
Ce	1.5	2.0±0.2	1.3	Soil
Sm	0.12	0.20±0.02	1.6	Soil, coal
Eu	0.028	0.029±0.003	1.0	Soil, coal
Yb	0.065	0.034±0.003	0.52	Soil, coal
Lu	0.015	0.006±0.001	0.38	Coal, soil
Hf	0.051	0.10±0.01	1.9	Soil, coal
Ta	0.049	0.035±0.004	0.69	Soil
W	0.061	0.24±0.02	4	Coal
Th	0.21	0.25±0.02	1.2	Soil, coal

SOURCE: Kowalczyk (1979).

[a] Uncertainty is standard deviation of the mean value.

[b] Because of volatility, perfect agreement not expected.

incineration, motor vehicles, limestone, and sea salt. Nine marker elements were used to characterize these sources: sodium was used for sea salt, vanadium for residual oil, lead for motor vehicles, zinc for refuse incineration, calcium for limestone, aluminum and iron for the sum of coal and soil, manganese for soil, and arsenic for coal (Table 5.1). The source contributions determined by analyzing these nine elements were used to predict the concentrations of 27 nonvolatile elements as a test of the results of the analysis (Table 5.2). On the average, all the elements not used in the analysis are predicted to within a factor of two with the worse case, chromium, being underestimated by a factor of seven.

The CEB of Kowalczyk (1979) was used to estimate the source contributions listed in Table 3.1 for primary aerosols. The source strengths for secondary particles in Table 3.1 are, however, based on other analyses because the CEB technique does not handle secondary material well. As shown in Table 3.1, the primary particles and NH_4^+, SO_4^{2-}, and $NO_3^=$ account for only 63 percent of the total measured TSP mass in the data for Washington, D.C. However, some contributions to TSP mass would not have been included in the CEB, for example absorbed water and some carbonaceous material.

The CEB of Tables 5.1 and 5.2 assumes that material from a particular type of source retains the same composition as long as it remains airborne. However, fine and coarse particles, even from the same source, often have different chemical compositions; hence the composition of the emissions from a source may change with time as coarse particles preferentially settle out. Separate CEBs can be performed on the fine and coarse fractions (Dzubay 1979) or on the fine and total particulate masses (Watson 1979). The results of Dzubay's CEB for St. Louis and Watson's CEB for Portland, Oregon are shown in Table 3.1; both studies achieved a better accounting for TSP than that of Kowalczyk (1979).

The application of CEB is still in the testing phase; various groups apply it in different ways, for example by analyzing for different components and elements. Component selection depends on the various activities in the cities studied and on the focus of the study. For example, different components would be selected if the study were accounting for sources of elements, sources of TSP, or sources of different size fractions.

Although the CEB method is reasonably effective for accounting for TSP and elemental sources, further refinements are needed and are under investigation. Currently, the greatest weakness of the method is its inability to handle secondary aerosols and carbonaceous material. The latter could be incorporated effectively with analytical tools now available. For example, there are series of organic compounds, such as the PAH compounds, which are released in patterns unique to their sources. A chemical species balance has been performed by using patterns of distributions of PAH to identify sources (Gether and Seip 1979). The ratio of carbon-14 to total carbon has been used to differentiate between fossil and contemporary sources of carbon (Cooper et al. 1979).

Factor Analysis Factor analysis is another technique for analyzing data on the chemical composition of aerosols to infer the contributions of various sources. In the usual factor analysis approach (e.g., Hopke et al. 1976), data on the concentrations of each element in each sample are manipulated to find groupings of variables (i.e., common factors) that best explain the variations of concentrations from their average values. The objective is to determine the fewest common factors that account for the major fraction of the variations.

Factor analysis has been applied to a set of 18 elements in 90 samples from the Boston area (Hopke et al. 1976). Of the total variance in the Boston data, 77.5 percent could be accounted for by six common factors, with little improvement when more factors were permitted. From factor strengths or "loadings," primary airborne particles could be attributed to several sources: soil (mixed with coal), sea salt, oil, auto emissions, and incineration of refuse. A sixth factor, with large loadings for only manganese and selenium, could not be identified with a particular source.

Factor analysis has several advantages over CEB in that no a priori assumptions need be made about either the number or composition of sources. Thus, secondary particles that become associated with primary particles between their release and collection can be incorporated in the analysis. For example, NH_4^+, SO_4^{2-}, NO_3^-, and TSP were included along with 20 metals in a factor analysis of data on the Tucson, Arizona aerosol (Gaarenstroom et al. 1977). The analysis showed that ammonium and sulfate ions were the strongest members of one of the factors; this factor also contained major amounts of copper and minor amounts of other chalcophile metals. Most of the variation in nitrates in the Tucson aerosol was explained by a different factor that contained little else.

The data sets for factor analysis can include not only particle concentrations, but also particle size group, meteorological data, concentrations of gaseous pollutants measured simultaneously with sample collections, measures of visibility, and so forth. Although this feature of factor analysis has not been exploited in aerosol studies, Hopke (1976) used many variables in addition to elemental concentration in his interpretation of lake sediment data.

Factor analysis also has weaknesses. Because it is based on variations rather than absolute concentrations, it works best with data in which there are large variations from sample to sample. It is not effective for data in which little variation occurs. In an unpublished study in 1978, Gladney and coworkers applied factor analysis and CEB to data from a network of stations in a rural area of Prince George's County, Maryland (G.E. Gordon, University of Maryland, private communication, July 6, 1979). Using six components, Gladney's CEB obtained fits to the data that were slightly better than those obtained by Kowalczyk et al. (1978) for the Washington, D.C. aerosol. However, for most of the data, Gladney's factor analyses yielded only two or, at most, three factors. Because the data are from a rural network, most of the particles, excluding those from soil, were transported from some distance and, hence, were sufficiently well mixed that elemental concentrations were rather uniform throughout the network.

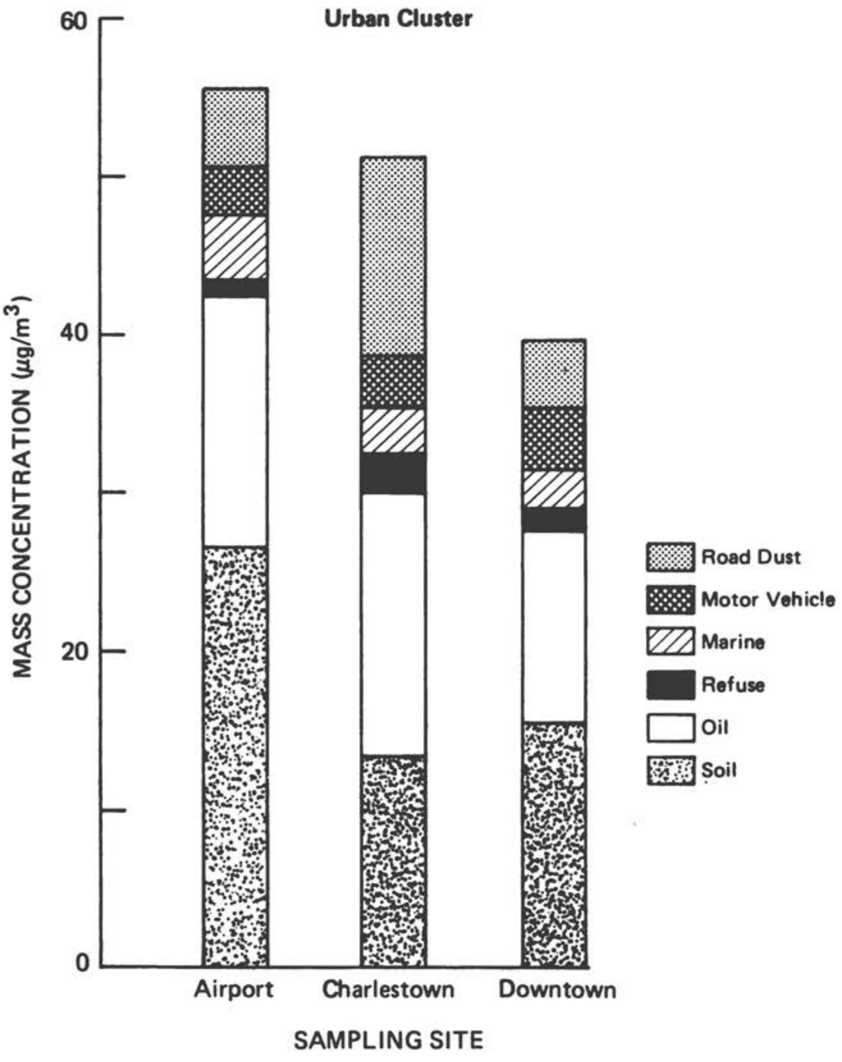
Another weakness of factor analysis is that it cannot currently resolve components that have very similar compositions (e.g., soil and coal emissions). Overcoming this weakness could prove to be impossible. In its usual form, factor analysis suffers from another problem: the relative contributions of sources within the factors cannot be obtained. The output indicates only that part of the variation of the concentrations that is explained by the sum of the sources in each factor.

Progress has been made in rectifying this deficiency by bringing the treatment more into agreement with CEB (Alpert and Hopke 1979). By employing an alternative factor model and with foreknowledge of the probable compositions of the factors from the CEB approach, the analysis can obtain more physically understandable results. It is possible in this procedure to adjust the factors to achieve maximum overlap with test factors that are similar to the components used in CEB. The results are more reliable patterns of concentrations for poorly characterized sources or detection of modifications of the compositions of emissions after release into the atmosphere.

Alpert and Hopke (1979) applied this new approach to the same Boston data that were treated in the earlier application of the usual factor analysis (Hopke et al. 1976). Six factors were needed to account for most of the observed concentrations and variations of primary particles: soil, residual oil, refuse, marine aerosols, motor vehicle emissions, and road dust. With these six sources the average fitting error for the 16 elements used was 27 percent for urban samples and 20 percent for suburban samples. The resulting contributions of those sources to TSP at the urban sites are shown in Figure 5.6. It was not possible to resolve a coal component (which would not be large in Boston, as there were no data in the set for some of the better indicators of coal combustion such as arsenic and selenium.

Empirical Models

In addition to chemical element balances and factor analysis, other empirical methods have been used to investigate the types of sources affecting the ambient aerosol and to explain site-to-site variations in particle concentrations. For example, the variations in TSP in urban areas have been explained rather well by a statistical model involving five factors: nonurban background primary particles, urban sulfates and nitrates, general urban activity influence, local scale influence, and industrial influence (Pace 1978). Contributions from the first two factors were estimated from data from high volume samplers at various urban and nonurban locations; contributions from the last three factors were estimated from statistically derived equa-



SOURCE: Reprinted with permission from *Atmospheric Environment,* Alpert and Hopke (1979). A quantitative determination of the sources of Boston urban aerosol. Pergamon Press, Ltd.

FIGURE 5.6 Mass concentrations by source in the urban Boston aerosol from modified factor analysis.

tions related to land use (rural, residential, general industrial, or steel mill industrial) and distance between the monitoring site and local sources of fugitive dust (major arterial highways). This analysis was later refined (Pace 1979) by deriving statistical relationships between TSP concentrations and data on sources. The relationships were derived for area sources located within 1 mile of the monitoring site and for point sources located within 5 miles of the monitoring site. These analyses considered fugitive dust sources and secondary aerosols as well as conventional sources of particles.

Several other techniques have also been used to identify the sources affecting ambient air quality: microscopic examination of filters from high volume samplers (Record et al. 1976; Price et al. 1977; Draftz 1975, 1977; Graf et al. 1977), analysis of the relationships between TSP levels and meteorology (Record et al. 1976, Price et al. 1977, Trijonis et al. 1979, Richard and Tan 1977, U.S. EPA 1977, PEDCo 1976, Samson et al. 1976), and studies of the spatial and temporal patterns in TSP data (Record et al. 1976, Price et al. 1977, Record and Bradway 1978, PEDCo 1976, Spertas and Levin 1971, Throgmorton and Axetell 1978). Several comprehensive studies have combined the results of various analytical techniques to assess causes of high particulate concentrations in the country as a whole (Record et al. 1976) as well as in individual air basins (Price et al. 1977, PEDCo 1976, Record and Bradway 1978, Hidy et al. 1975, Richard and Tan 1977, Watson et al. 1979). The results of these empirical studies indicate that contributions to total particulate mass from fugitive dust sources and secondary particles generally tend to be larger than contributions from primary particles emitted by conventional industrial sources.

EVALUATION OF MODELS

To be of use in air quality management, models must be evaluated. As indicated earlier, models have been evaluated against test data, but this method of evaluation may give misleading results because the test data may not be representative of the actual conditions for which the models will be used.

The ability to predict existing concentrations from existing emissions is the usual test of validity of models. However, the principal use of models is to predict the results of changes in emissions. This is particularly troublesome for dispersion models with reactive components (e.g., sulfates). Proper evaluation of dispersion models requires extensive field studies; these studies are also expensive. Fortunately, several field studies are underway or are being planned. Among these are the Sulfate Regional Experiment (SURE) (Lavery 1978), the Midwest Interstate Sulfate Transformation and Transport (MISTT) study (Wilson et al. 1977), and the Multi-State Atmospheric Power Production Pollution Study (MAP3S) (MacCracken 1979). These projects rely heavily on data collected for the purposes of the respective studies. It should be possible to evaluate some models by analyzing existing data in detail (Mills et al. 1979).

Although major advances have been made in the application of statistical methods, the methods have not been widely tested. The tests that have been applied have attempted to determine how well the models predict the concentrations of elements not included in the analytical process and how well the models account for measured concentrations of TSP. These evaluation procedures should suffice for proof of validity. Deficiencies in data on sources and emissions limit the ability to evaluate statistical models.

Unless more accurate source emissions data become available, the best test may come from measurements of additional chemical species, especially of the spectra of closely related members of families of organic compounds, for example the PAH compounds. As discussed in Chapter 2, new methods now exist for performing measurements on many classes of organic compounds. Unless the "fingerprint" of a class of compounds is strongly fractionated by reactions or by deposition after release, organic data could provide important tests of the statistical approach. Other chemical parameters such as carbon soot and concentrations of trace gases could also be useful in this context.

APPLICATION OF MODELS TO AIR QUALITY MANAGEMENT

Air pollution dispersion models play a central role in the management of air pollution at the local, state, and national levels. To fulfill regulatory responsibilities mandated by federal laws, local and state governments use models to review proposals for new or modified stationary sources and to predict the effectiveness of air quality maintenance plans. In both applications, decisions must be made—permits granted or plans revised—prior to the initiation of potentially polluting activities. In such cases, air quality management agencies must rely on a priori assessments; hence a modeling capability is required.

Modeling is also required to estimate the effects on ambient concentrations of pollutants of proposed emission standards or other federal policies, such as fuel switching, that may affect air quality.

Applications of modeling can, however, be expanded to serve purposes other than assisting governments to meet current regulatory requirements.

Use of modeling to estimate population exposures can assist in development of national siting policies. The conversion of existing sources to coal or other fuels should incorporate considerations of population exposures to particles and of important welfare effects. New Source Performance Standards, regulations to prevent significant deterioration of air quality, and National Ambient Air Quality Standards are useful for controlling particulate concentrations on a local scale. However, exposure to secondary aerosols for populations beyond 30 km must also be considered because 90 percent of the particulate mass from new sources with tall stacks is transported beyond this distance.

More accurate estimates of exposures of populations to respirable particles would improve assessments of the effects of air pollution on health. Concentrations of indoor air are the most important determinants of human exposure for some pollutants. Contributions of outdoor sources to indoor concentrations depend on building ventilation and penetration rates. To arrive at better estimates of the effects of outdoor sources on actual exposures, penetration and filtration must be evaluated and included in model calculations. This information would be important to test the adequacy of any standards that might be promulgated for inhalable particles or particulate sulfates.

Even if such standards are not promulgated, estimates of the effects of controlling ventilation and filtration could serve as a foundation for pollution control strategies based on intervention at the receptor. These estimates would necessitate quantification of the effects of remaining indoors under varying ventilation rates and filtration efficiencies, and with different types of air cleaning equipment. Air pollution may represent a health threat only during infrequent episodes of specific meteorological conditions. Protecting the population, and in particular the most sensitive segment of the population, during these times may be the most cost-effective control strategy, but this approach is less desirable from the point of view of welfare effects and aesthetics.

If regional transport and conversion models were used in combination with predictive weather models, a system of dynamic controls for episodic events might be devised. Peak exposures might thus be prevented. Regional studies have provided a body of information from which systems for predicting episodes could be developed (Tong and Batchelder 1978, Niemann 1979). Examples of dynamic control strategies for periods of adverse meteorological conditions include use of alternative fuels, use of more highly controlled or distant plants to generate power, and reduction in levels of operation.

Progress toward meeting and maintaining ambient air standards will increasingly involve trade-offs among emissions of different sources. The management and banking of emissions eligible for trading will, in part, be determined by modeling.

The CEB and multivariate methods for identifying sources of particular chemical species could be used effectively in devising emission trade-offs and site-specific control strategies. For example, the application of these models may result in a list of the relative contributions of various classes of sources to TSP at sampling sites. If a standard is frequently violated at a particular site, the analysis would indicate the reductions of ambient levels that could be achieved by control of these classes of sources. Note that these methods differ from dispersion modeling in that they indicate contributions by class of source, not by specific sources in a class. For most classes of sources, emissions of individual sources are similar and separate contributions of each currently cannot be determined unless they are quite unique or isolated, such as pigment plants (Dzubay 1979) and copper smelters (Small et al. 1979, Germani 1979). If distinguishing among sources in a class is not essential for implementing a control strategy, CEB and multivariate methods would be very useful.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

1. Current understanding of the relationships between emissions of sulfur oxides and sulfate air quality indicates that sulfate problems can occur on large, regional scales, transcending state and national boundaries. From results of large-scale projects now in progress, it appears that reasonably good empirical models of these relationships can be made. However, these models cannot be used to predict sulfate levels in air pollution episodes or to estimate the impact of alternative fuels or controls on acid precipitation. They also cannot be used to devise optimal strategies for controlling sulfates. Both empirical studies and fundamental research are required to develop a modeling capability for use in predicting and controlling sulfate episodes in the East.

2. Although our knowledge of the relationships between emissions of SO_x and ambient concentrations of sulfates is incomplete, it is far greater than our knowledge about the formation of nitrates, nitric acid, and organic particles by reactions of nitrogen oxides, hydrocarbons, and other species. The role of nitric acid in acid precipitation has not been adequately investigated. The reactions, transport, and deposition of airborne organic materials need to be studied in detail.

3. Modern methods of assessing the contributions of sources to ambient concentrations of particles, such as chemical element balances, can potentially be of great benefit to urban air quality management. As statistical techniques are developed and refined, we believe that air quality management authorities should begin to make routine use of these models. Research should be undertaken to determine if approaches similar to chemical element balance and factor analysis, but based on the characteristic signatures of classes of organic compounds, can be used to identify emissions from certain types of sources; a capability to use such approaches would greatly increase the usefulness of this type of analysis.

4. Improving modeling capabilities will require, as a first step, expanding

emission inventories to include the size distribution and chemical composition of conventional ducted emissions, fugitive process emissions, anthropogenic and natural fugitive dusts, and other natural sources. Eventually, inventories should also include information on the variations of emissions in time due, for example, to changes in operations or variations in the performance of process and gas-cleaning equipment.

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Appendix

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