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HEALTH AND SAFETY IMPACTS OF
NUCLEAR, GEOTHERMAL, AND FOSSIL-FUEL
ELECTRIC GENERATION IN CALIFORNIA

A project performed for the
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Title

Energy and Environment Division

Health Effects and Related Standards for Fossil-Fuel and Geothermal Power Plants

G.D. Case, T.A. Bertolli, J.C. Bodington, T.A. Choy and A.V. Nero

January, 1977

Lawrence Berkeley Laboratory University of California/Berkeley

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Volume 6

of

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ELECTRIC GENERATION IN CALIFORNIA

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

January 1977

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This is one of a series of reports prepared as part of the Lawrence Berkeley Laboratory project, "Health and Safety Impacts of Nuclear, Geothermal, and Fossil-Fuel Electric Generation in California." This project was performed for the State of California Energy Resources Conservation and Development Commission as its "Health and Safety Methodology" project, funded under contract number 4-0123. The reports resulting from this work are listed below. Their relationship to one another is described fully in volume 1, the Overview Report.

Vol. 1: "Health and Safety Impacts of Nuclear, Geothermal, and Fossil-Fuel Electric Generation in California: Overview Report," by the entire staff, Lawrence Berkeley Laboratory Report LBL-5924. Includes "Executive Summary" for the project.

Vol. 2: "Radiological Health and Related Standards for Nuclear Power Plants," by A.V. Nero and Y.C. Wong, Lawrence Berkeley Laboratory Report LBL-5285.

Vol. 3: "A Review of Light-Water Reactor Safety Studies," by A.V. Nero and M.R.K. Farnaam, Lawrence Berkeley Laboratory Report LBL-5286.

Vol. 4: "Radiological Emergency Response Planning for Nuclear Power Plants in California," by W.W.S. Yen, Lawrence Berkeley Laboratory Report LBL-5920.

Vol. 5: "Control of Population Densities Surrounding Nuclear Power Plants," by A.V. Nero, C.H. Schroeder, and W.W.S. Yen, Lawrence Berkeley Laboratory Report LBL-5921.

Vol. 6: "Health Effects and Related Standards for Fossil-Fuel and Geothermal Power Plants," by G.D. Case, T.A. Bertolli, J.C. Bodington, T.A. Choy, and A.V. Nero, Lawrence Berkeley Report LBL-5287.

Vol. 7: "Power Plant Reliability-Availability and State Regulation," by A.V. Nero and I.N.M.N. Bouromand, Lawrence Berkeley Laboratory Report LBL-5922.

Vol. 8: "A Review of Air Quality Modeling Techniques," by L.C. Rosen, Lawrence Berkeley Laboratory Report LBL-5998.

Vol. 9: "Methodologies for Review of the Health and Safety Aspects of Proposed Nuclear, Geothermal, and Fossil-Fuel Sites and Facilities," by A.V. Nero, M.S. Quinby-Hunt, *et al.*, Lawrence Berkeley Laboratory Report LBL-5923.

HEALTH EFFECTS AND RELATED STANDARDS FOR FOSSIL-FUEL AND GEOTHERMAL POWER PLANTS

ABSTRACT

This report reviews health effects and related standards for fossil-fuel and geothermal power plants, emphasizing impacts which may occur through emissions into the atmosphere, and treating other impacts briefly. Federal regulations, as well as California State and local regulations are reviewed. Emissions are characterized by power plant type, including: coal-fired, oil-fired, gas-fired, combined cycle, and advanced fossil-fuel plants; and liquid and vapor geothermal systems. Dispersion and transformation of emissions are treated. The state of knowledge of health effects, based on epidemiological, physiological, and biomedical studies, is reviewed.

Foreword

This report is the largest of nine volumes constituting the final report of a project performed by the Lawrence Berkeley Laboratory for the California Energy Resources Conservation and Development Commission. A list of these volumes follows the title page of this report. This sixth volume assembles into one report information on the emissions from fossil-fuel and geothermal power plants, on the possible health impacts of these emissions and their products, and on the regulations pertaining to these emissions. Because of the diverse topics covered and the large amount of research that has been performed on emission and their health effects, this volume is necessarily large.

The diversity of topics has also required participation of several investigators in the collection and analysis of information and in the writing of this report. Sections, subsections, and even smaller segments were written by individuals, and the pieces have been melded together into a single volume. This has led, for example, to the fact that references are grouped by section for sections 2 and 5 and by subsection for sections 3 and 4. (Section 1, the introduction and summary, is not referenced, but refers to the more complete discussions of sections 2 through 5.)

The participation of several scientists in this work has also made it difficult to maintain a consistent level of treatment throughout. Moreover, the variety of topics has made review of this report a difficult process. We thank the several individuals who generously commented on this report. Any errors which remain are, of course, solely the responsibility of the authors. We would, in fact, appreciate communications about any such errors.

In spite of the difficulties inherent in producing a report such as this, the need for a single volume treating the health effects (and related standards) of fossil-fuel and geothermal emissions justifies the effort involved. We hope that this volume serves as a useful reference document, both for the California Energy Commission and for a larger scientific and regulatory community.

A. V. Nero
Project Manager

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SELECTED ABBREVIATIONS

ACA - Air Conservation Area (California)
ACP - Air Conservation Program (California)
APCD - Air Pollution Control District
APEP - Air Pollution Emergency Plan (California)
AQMA - Air Quality Maintenance Area
AQMP - Air Quality Maintenance Plan
AQS - Air Quality Standards
ARB - Air Resources Board (California)
Btu - British thermal unit
Cal - Calorie
cfm - cubic feet per minute
CFR - Code of Federal Regulations
CHESS - Community Health and Environmental Surveillance System
Ci - Curies
dBA - decibels
EPA - Environmental Protection Agency
ERCDC - Energy Resources Conservation and Development Commission (California)
g - gram
gal - gallon
hr - hour
Hz - Hertz (cycles per second)
kwh - kilowatt - hour
l - liter
lb - pound
m - meter
mg - milligram
Mg - Megagram
MHD - magnetohydrodynamic
MMD - mass median diameter
MWe - megawatts (electric)
NAAQS - National Ambient Air Quality Standards
NSPS - New Source Performance Standard
NSR - New Source Review
OSHA - Occupational Safety and Health Administration
PAH - Polynuclear Aromatic Hydrocarbon
PAN - Peroxyocetyl Nitrate
ppm - parts per million
ppb - parts per billion
ppt - parts per trillion
pCi - Picocurie
PSD - Prevention of Significant Deterioration
SCF - Standard Cubic Foot
SIP - State Implementation Plan
SNG - Synthetic Natural Gas
T - Ton
Te - Metric-ton
TDS - Total Dissolved Solids
TSP - Total Suspended Particulate (mass)
WRB - Water Resources Board (California)
μg - microgram
μm - micron (micrometer)

1. INTRODUCTION AND SUMMARY

1.1 The Purpose and Scope of this Report

The potential for conventional power plants to affect the health of individuals in the community and workers in the plant is determined largely by their emissions of chemical agents into the air and water. Amounts of these pollutants discharged into the environment depends on such factors as the size of the power plant and the type of fossil-fuel firing or geothermal harnessing employed. This report discusses critically the types of standards and regulations relating to public and occupational health which apply to the siting and operation of power plants, the specific class of pollutants emitted by the various types of fossil-fuel and geothermal power plants, and the known and suspected effects that these agents have on human health. Finally, we emphasize areas in which essential information is lacking and to which future research ought to be directed, closing with a comment on the presently limited capabilities for assessing the projected health consequences of hypothetical new power plants.

The prinicpal health impacts from fossil-fuel and geothermal power plants may occur through the emission of "conventional" pollutants, primarily those that are emitted into the atmosphere. These are primarily chemical pollutants, although radioactivity, water, and heat may also be emitted into the air. Pollution of water resources is of somewhat less concern than air emissions, largely because potentially significant impacts may be avoided by incorporation of available control technology; the one possible exception is materials which may be leached from waste disposal sites into water supplies. In addition to such emissions, power plants may produce significant noise levels.

The two major categories of air emissions from fossil-fuel and geothermal plants are gases and particulates. In general, the important gases are compounds of sulfur, nitrogen, and carbon. The particulate matter may contain important amounts of all of these elements, usually in compounds, and in addition may contain significant amounts of heavy metals. Certain of these metals, such as mercury and selenium, may be emitted in vapor form. The relative and absolute importance of various emissions is highly dependent upon the specific technology. The basic types of fossil fuel systems to be considered are conventional coal, oil, and gas fired plants, although advanced systems may assume increasing importance. The only significant geothermal power plants are based on vapor-dominated fluids, but liquid-based plants are under rapid development. Not only do the fossil-fuel and geothermal technologies differ from one another, but the variants of each differ significantly among themselves. However, the general classes of emissions and their effects are similar, so that it has been useful to consider them together. These power plants can significantly alter the ambient levels of these substances in regions around the plants. Because of competing sources of comparable importance, the effects of a specific power plant cannot usually be treated independently. This is especially true because the emissions undergo extremely important alterations in the atmosphere.

To complicate analysis further, the information available on the effects of the emissions (and their products) on human health is imprecise concerning both what the effects are and what the relationship between exposures and such effects might be. Several investigatory approaches may be employed to yield such information. Broadly speaking, these are epidemiological and physiological studies of workers and the general public and more fundamental studies of basic physical and biochemical interactions of pollutants, either alone or in combination, with human or animal organisms. For each of the pollutants of concern, some or all of these approaches may yield information which warrants regulatory attention. Pollutants may harm individuals, from high-level acute exposures or from low-level chronic exposures, through the induction of diseases (particularly respiratory illness, cardiovascular disease, and cancer), through the impairment of bodily functions (such as difficulty with breathing), or through biochemical alterations (such as carbon monoxide blockage of the oxygen-carbon dioxide mechanism). Research on effects is conducted on a wide scale and funded by a number of agencies. In spite of this, no comprehensive picture of these health effects can presently be drawn. Although in some cases specific effects can be quantified, this is normally not possible. At sufficiently high levels, these substances can cause serious illness and death among the general population. It is not clear to what extent power plants have caused such effects.

Although these overall impacts cannot presently be assessed numerically, the available evidence from various types of studies, considered together, may serve as the basis on which standards for public (or occupational) protection may be formulated. Such standards may be established at the Federal, State, or local level. Standards may apply to either air or water, and may specify limits on both ambient concentrations and emissions. To a large extent, Federal agencies rely on agencies in the states for implementation of Federal standards and for development of other (possibly more stringent) standards. As much as possible, the review of new stationary sources, such as power plants, is left to the states.

Section 2 of this report discusses standards and regulations pertaining to emissions from fossil-fuel and geothermal power plants; these considerations are summarized in Section 1.2 immediately below. Section 3 treats the various types of pollutants, the extent to which various plant types emit these substances, and the manner in which they are dispersed and transformed in the atmosphere; these matters are summarized in Section 1.3. Section 4 reviews the epidemiological, physiological, and biochemical evidence of health impacts of pollutants arising from fossil fuel and geothermal plants and is summarized in Section 1.4. Finally, Section 5 summarizes the gaps in current information, new studies which might be initiated, deficiencies in current standards, and the difficulties of assessing the health impacts of fossil-fuel power plants. A summary of these areas is given in Section 1.5.

1.2 Standards Applicable to Power Plant Emissions

Protection of the public health from the hazards of air and water pollutants is the responsibility of Federal, State, and local agencies. The Federal agencies of direct concern for power plants are the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA). The State of California has delegated parallel regulatory and enforcement responsibilities to the Air Resources Board (ARB) and the Water Resources Board (WRB), together with regional districts, and to the Occupational Safety and Health Administration.

Ambient air quality standards (AQS) are established by the EPA and ARB to ensure that community air is sufficiently free of pollutants to safeguard the public health and welfare. They stipulate a maximum allowable pollutant concentration, the time over which concentrations are averaged, and the means by which concentrations are measured. Frequently, two standards may be specified for the same pollutant, with a higher concentration permitted for a shorter time period. These control both acute and chronic exposures. For some pollutants such as particulates, oxidants, and oxides of nitrogen, the form of AQS depends heavily upon the available analytical monitoring methods. As presently formulated, the responsibility for meeting national (or stricter) AQS rests with State and ultimately local agencies, with certain provisions for intervention by higher authorities when necessary. While the onus for compliance with ambient air standards does not fall directly on the utilities, their enforcement via emission limitations applied during new source review affects power plants directly.

Emission standards represent a major mechanism for meeting air quality standards within a given air basin. Emission standards depend on the available pollution control technology and on local air quality goals. Hence, emission standards may vary from one Air Pollution Control district (APCD) to another. However, the EPA has promulgated New Source Performance Standards (NSPS) for new and modified fossil-fuel fired power plants. These standards are expressed as pollutant emissions per unit heat input and include provision for plant inspections and performance tests, as well as for maintenance and breakdown of pollution control devices. In addition, each APDC has established applicable emission standards that are similar to the EPA limitations, except that some are more stringent or use different criteria for defining emissions. Among these criteria are (added) ground level pollutant concentrations, visibility reduction in opacity units, and fuel sulfur content.

New source review represents a procedure instituted by the EPA through the local APCDs to prevent the deterioration of community air quality by review of proposed emission sources for compliance with EPA and (stricter) ARB requirements. This review includes consideration of the impact of new sources on ambient air quality.

Air quality maintenance areas are those regions in which air pollution levels presently exceed or are projected to exceed the ambient air quality standards on a regular basis. These include eight California air basins. Long-range ARB air quality maintenance plans for bringing these regions into compliance will undoubtedly affect the siting and operation of power plants in these basins. Regulations for prevention of significant air quality deterioration apply to areas in which the existing air quality is superior to that required under the standards. The principal purpose of these regulations is to control the harm which new emission sources might cause to relatively unspoiled areas.

Air pollution emergency plans provide for action during periods of unusually severe pollution. In order to alleviate the immediate threat of a pollution-induced medical disaster, the APCDs are empowered to recommend or order restrictions on the production, distribution, and consumption of electric power, including limits on the amounts and types of fuels burned, among other measures.

Other standards which have been given lesser attention here due to smaller potential impacts on the public include occupational,water, and noise standards. Occupational air quality standards, established by OSHA, represent the maximum allowable concentrations of a given pollutant to which employees inside the plant may be exposed during an 8-hour day. Water quality standards exist to protect the public from harm due to biological and chemical contamination of water. Noise limitations are set by OSHA and, in addition, the EPA has suggested community noise limitations; in the community, such limitations often take the form of nuisance regulations.

See Section 2 for further discussion and references.

1.3 Power Plant Emissions

Fossil-fuel-fired power plant emissions characteristically arise from high temperature combustion and are, to some extent, qualitatively independent of the fuel or boiler type. Typically, these plants emit sulfur dioxide, nitrogen oxides, and fly ash particulates as major by-products; carbon monoxide, mercury, selenium, and other trace elements are relatively minor emissions. Geothermal emissions, on the other hand, are typically rich in hydrogen sulfide and ammonia, as well as mineral salts and lesser amounts of mercury.

The impact of these emissions on ambient air quality may be analyzed by atmospheric dispersion modeling of varying type and sophistication. Realistic modeling must include the secondary chemical reactions in the atmosphere, since reaction products may be more important than the primary emissions themselves. Important secondary reactions include the formation of photochemical oxidants, sulfates, NO_2, nitrates, ammonia, and organic products. Furthermore, the apparent anti-coincidence, in some cases, of maxima in emissions and ambient air concentrations points out the importance of meteorological conditions and chemistry in air pollution. A particularly important, and not well understood, consideration is the role of particulate matter in atmospheric transformations.

For further discussion of (and references on) the emissions treated briefly below, see the corresponding parts of Section 3.1.1, as well as the discussion of specific plant types (Sections 3.1.2 and following and Section 3.2) and of dispersion (Section 3.3).

1.3.1 Sulfur Oxides

Sulfur oxides (SO_x) result from the combustion of reduced sulfur compounds present in coal and oil. Most of the sulfur is emitted as sulfur dioxide (SO_2), with lesser amounts as sulfur trioxide (SO_3), sulfuric acid (H_2SO_4) and other sulfates (SO). It is thought that, once in the atmosphere, SO_2 can be oxidized to sulfates. However, there is no consensus on where or at what rate such oxidation may occur. There is also considerable disagreement on the oxidation mechanism - whether sunlight, metal oxides, or carbon is the responsible catalyst. Many investigators now favor a photochemical oxidation mechanism; however, a large body of work supports the heterogeneous catalysis by either metal oxides or soot. (See Section 3.3.3.2). The implication of this would be that sulfate formation may be controlled by reducing the emissions of SO_2 or the correct class of particulates. However, considering that there is no consensus on the amount of SO_2 that is converted to sulfates (or on the rate at which this occurs), it is not clear what is the most effective method to control sulfates.

While man-made SO_x pollution accounts for only 10-35 per cent of the total global emissions, most of that is concentrated in industrialized urban areas, so that concentrations in urban air may be several orders of magnitude above natural background. Electric power generating plants are responsible for some 54 per cent of the total man-made SO_x emissions in the U. S. Much of this contribution is due to old uncontrolled coal-fired plants in the eastern U. S. However, in California, where coal-firing is not yet prevalent, power plants account for only 13.5 per cent of the total SO_x emissions.

The principal methods to limit SO_x emissions are: a) use of low-sulfur fuels; b) fuel desulfurization prior to combustion; c) flue gas desulfurization after combustion; d) modification of combustion conditions; and e) increasing stack height, of which b) and c) are the ones to be given primary consideration. However, although fuel desulfurization to remove hydrogen sulfide (H_2S) is routinely used in the treatment of natural gas, effective and economical methods for removing sulfur from coal and oil before it is burned have yet to be developed.

On the other hand, several methods for flue gas desulfurization in coal-fired and oil-fired power plants are now available commercially. Most of these involve scrubbers, either solid or liquid suspensions of metal oxides or carbonates or catalytic oxidation devices. Flue gas desulfurization processes are now capable of removing some 90 per cent of the SO_x produced during combustion. Higher removal rates can be achieved in some instances, at the expense of power plant operating efficiency. 90 per cent SO_x removal requires about 2-6 per cent of the total energy output. Invariably, these systems accumulate large quantities of sulfite or sulfate sludges. In some cases, the sulfates can be recycled into the original scrubber, and the resulting sulfur or sulfuric acid sold for commercial use. With some types of scrubbers, however, reclamation is not feasible, and a solid waste disposal problem appears with the sludge. Usually, the scrubber sludge is mixed with collected fly ash and bottom ash and buried or stored. If the sludge is not stored properly, sulfates and sulfites, as well as other mineral salts and trace elements, can be leached or eroded into community water supplies where they may interfere with local water treatment processes or harm individuals directly. Consequently, most temporary and/or permanent fill areas are lined on the bottom to prevent contamination of nearby water sources.

With the construction of new power plants in California, SO_x emissions are expected to increase since most new facilities will be fired with either coal or oil. Relative to other SO_x sources, the contribution of power plants to total emissions may rise slightly. However, with appropriate control devices, the impact of new coal-fired power plants and new oil-fired plants on atmospheric SO_x levels should not be very different from one another.

1.3.2 Nitrogen Oxides

Nitrogen oxides (NO_x) are formed during combustion of any substance in air, from nitrogen compounds in the fuel and/or nitrogen gas (N_2) in the atmosphere. At the very hot flame temperatures used in all fossil-fuel-fired power plants, nearly all of the NO_x emissions occur as nitric oxide (NO). While NO is poisonous in its own right, the principal threat posed by NO emissions is due to the ease with which it is converted to NO_2 and higher oxides of nitrogen which are even more toxic. NO and NO_2 also participate in the photochemical cycle which produces ozone (O_3) and other noxious oxidants in urban atmospheres. In most of the U. S., including large areas of California, the limiting reagent for this cycle appears to be NO/NO_2, so that increased NO_x emissions from new power plants could increase ambient oxidant levels. (However, there is evidence that in some situations the converse may be true.) Additional nitrogen compounds which occur in the atmosphere as a result of NO emissions include nitrates, ammonia (NH_3), nitrosamines, and other organic forms of nitrogen.

While man-made NO_x pollution accounts for only about 10 per cent of the total global emissions, most of that is concentrated in urban areas, so that NO and NO_2 concentrations may lie far above natural background. Electric power generating plants are responsible for about 25 per cent of the total NO_x emissions in the U. S. In California, power plants account for only 11 per cent of the total NO and NO_2 released into the atmosphere. The lower value observed for California is due to the relatively greater reliance on hydroelectric power, and also to the fact that gas-fired and oil-fired power plants emissions are up to 30-40 per cent lower than those from coal-fired power plants. If recent plume dispersion data are indicative, the impact of one large power plant in the South Coast Air Basin on the NO_x concentration is at least 8 parts per billion (ppb) over a 300 km^2 area. Locally, contributions up to 120 ppb can be expected over a much smaller area for a 1-hour averaging time.

The principal methods to limit NO_x emissions fall into three classes: a) conversion to a lower NO_x - producing fuel such as natural gas; b) modification of the combustion process; and c) flue gas treatment. Since natural gas is in short supply, its use in power plants, if any, will probably be limited to periods of severe air pollution episodes. Flue gas treatment to remove NO involves the use of liquid or solid suspensions of metal oxides as scrubbers. These can be used in tandem with SO_2 removal systems, but are not now as effective since NO is not as soluble nor as reactive as SO_2, but improvements are occurring. Solid waste disposal problems resulting from flue gas denitrogenation would be similar to those encountered with SO_2 removal systems.

Combustion modification techniques include low-excess-air operation, staged or off-stoichiometric combustion, flue gas recirculation, reduced air preheat, steam or water injection, or a combination of these methods. All of these methods serve to reduce NO_x emissions by lowering the flame temperature below the N_2 oxidation threshold or by cutting the supply of N_2 to the combustion mixture. NO_x emission control up to 90% can be achieved, and is limited by the contribution of fuel nitrogen to the total NO_x emissions.

An attractive alternative method which might be encouraged for controlling NO_x emissions is catalytic decomposition. Its principal advantages include the potential for better than 90 per cent NO_x removal efficiency without the need for scrubbers or combustion modification methods,which lower the energy output of the power plant.

With the construction of new power plants in California, NO_x emissions are expected to increase, especially if coal-firing is introduced into the state. Great care should be exercised in the siting of these plants, unless NO_x emissions control can be maintained at a level that is satisfactory for California air basins in which high NO_2 or oxidant concentrations are already encountered.

1.3.3 Particulates

Particulates occur in the emissions from fossil-fired power plants because of the presence of mineral (ash) components in coal and fuel-oil and the formation of "soot" as a minor by-product of the combustion of all fossil fuels. These plants may contribute to the ambient particulate burden either through these direct emissions, which may contain carbonaceous compounds, as well as trace metals, or through the results of secondary reactions, such as sulfates and nitrates. Geothermal plants may contribute also, but not as significantly. Urban ambient air contains particulates which can be characterized as mixtures of "soot", fly ash, hydrocarbon condensates, sulfuric acid mist, soil dust, sea sprays, etc. Particles in the atmosphere differ from one another in their aerodynamic size, their chemical composition, their surface properties, and their reactivity and volatility, all depending on how they were originally formed. Current ambient air standards for particulates are defined solely on the basis of total suspended mass (TSP), neglecting the influences of particle size or chemical compositon, which are important for their health effects.

The size distribution of particulates from man-made sources is very different from that of naturally-occurring particles. Combustion-generated particles are initially very tiny--with number median diameter on the order of 0.01 μm--but coagulate rapidly into particles whose mass median diameter (MMD) approaches 0.1-0.5 μm. Most continental dust particles and marine aerosols are quite large by comparison, with average diameters in the 5-20 μm range and larger. Understanding the size distribution of atmospheric particulates is important for the proper assessment of their health effect.

The chemical composition of particulate matter is also of importance to the attendant health risks. Compounds of major interest are those of sulfur (such as sulfates), nitrogen (such as nitrates), and carbon. Sulfates may arise from the oxidation of SO_2, and subsequent reactions with water or metal oxides, and include ammonium sulfates ($(NH_4)_2SO_4$ and NH_4HSO_4), sulfuric acid mist (H_2SO_4), sodium sulfate (Na_2SO_4), and other salts of sulfur species. While natural background sulfates, harmless to humans, are present in concentrations on the order of 5 $\mu g/m^3$, man-made sulfates, which are more acidic and much more irritating, achieve urban levels of 5-20 $\mu g/m^3$ on the average, and occasionally surpass 40 $\mu g/m^3$, in California. Sulfate aerosols are generally small, with MMD about 0.4 μm. It is not safe to generalize on the form in which they occur in cities. In the South Coast Air Basin, 10-15 per cent of TSP is sulfate; however, the percentage is generally much lower in other parts of California. The ARB now has an ambient air standard for total sulfate of 25 $\mu g/m^3$. Nitrates are derived from the oxidation of NO and NO_2 to nitric acid (HNO_3) and its salts such as ammonium nitrate (NH_4NO_3). Natural background levels of nitrates are on the order of 0.85 $\mu g/m^3$, but urban concentrations range between 2-36 $\mu g/m^3$ in California. During oxidant smog episodes, particulate nitrate levels may reach 60 $\mu g/m^3$, and gaseous HNO_3 concentrations of 25 ppb (63 $\mu g/m^3$) may be detected. Whether nitrates exist primarily as NH_4NO_3 most other times remains to be settled. Nitrates typically constitute about 5-20 per cent of TSP in urban California air samples and may rival sulfates as a threat to human health. No ambient air standard presently exists for nitrates, although one is being considered for California.

Carbon compounds in particulate matter may occur directly as the result of incomplete combustion of fossil fuels or secondarily through chemical reactions in the atmosphere. Particulates below 0.1 μm (MMD) are tremendously enriched in carbon; essentially all of the carbon found in particulate matter exists in particles smaller than 1 μm. Most of the carbon mass in ambient aerosols or in power plant emissions has never been characterized completely. However, very crude, operational, or limited analyses have been carried out.

Carbon in all forms typically accounts for 9-20 per cent of TSP mass in ambient air from U. S. or California cities. Of that, somewhat less than half is extractable as organic substance. Quantitatively, only a few per cent or less of the organic mass in particulates has ever been identified. Most analytical efforts have been devoted to characterizing the poly-nuclear aromatic hydrocarbon (PAH) compounds present, perhaps because they are easier to measure in the atmosphere than other organics. Electric power generating plants, for example, are an insignificant source of the PAH compound benzo(a)-pyrene (BaP) nationwide and in California. However, more work needs to be devoted to characterizing carbon compounds in airborne particulates and power plant emissions. As the number of fossil-fuel power plants increases, and their type changes, their organic emissions may assume greater importance.

Of the 50% of particulate matter in urban ambient air that arises from man-made emissions, half appears due to secondary particulate products such as sulfates and nitrates. The remainder is probably direct combustion products, mostly carbon, but still containing substantial amounts of other elements, many of which may be found in the fly ash from power plants. Trace elements of obvious and suspected man-made origin have been detected in California air.

We have summarized the composition of anthropogenic particulate matter, but indicated only briefly the direct power-plant contribution to this burden. Such direct emissions from coal-fired and oil-fired plants, emphasized in the discussion below, are referred to as fly ash and consist of a host of common minerals and trace elements. Geothermal particulate emissions consist primarily of the last two categories. Particulate emissions from gas-fired plants are almost totally carbonaceous "soot," rather than "ash."

The chemical composition of fly ash depends quantitatively on the origin of the fuel, but has some qualitative uniformity. Major elements from both coal-fired and oil-fired power plants include carbon, silicon, aluminum, sodium, potassium, magnesium, calcium, and often lead. Fly ash from coal-fired plants contains substantial amounts of iron, titanium, and phosphorus, while fly ash from oil-fired power plants is heavy in nickel, vanadium and iron. Besides these elements, coal fly ash may contain substantial amounts of alkali earth elements, while oil fly ash may be enriched in other transition metals such as chromium, manganese, and copper.

Fly ash particle sizes from both coal-fired and oil-fired power plants extend over a wide range. Most of the mass in coal fly ash is concentrated in particles larger than 20 μm in diameter if no control devices are used. On the other hand, fly ash from oil-fired power plants is found in generally smaller particles, MMD equal to or less than 1 μm. As a rule, the less volatile elements such as silicon, aluminum, etc. accumulate preferentially in the larger particle fractions, while the more volatile elements such as lead, nickel, vanadium, chromium, cadmium and zinc occur preferentially in the smaller size ranges (2 μm MMD and smaller). More importantly, the more volatile elements also preferentially aggregate on the particle surfaces, where they are in a position to inflict the greatest health insult.

Bottom ash is the non-combustible mineral ash product from coal-fired power plants which does not enter the atmosphere, but is deposited in the bottom of the boiler. Bottom ash is most prevalent in coal-fired power plants, and while it does not contribute to atmospheric pollution, it does add substantially to the solid waste which must be disposed, representing a potential for leaching into water resources. The elemental composition is similar to that for fly ash from coal-fired power plants. Both bottom ash and collected fly ashare expected to be mixed with used SO_2 scrubber suspensions in order to reduce the water content to a level acceptable for disposal. The substantial bulk of ash-sludge mixture must be isolated from public drinking water supplies.

Control of airborne particulate emissions from power plants is presently accomplished by one or more of the following methods: a) inertial separators (cyclones); b) (baghouse) filtration; c) electrostatic precipitation; d) gravity settling; and d) wet (venturi) scrubbing. The effectiveness of these fly ash removal methods depends heavily on particle size, and is sometimes sensitive to chemical composition. Inertial separators, including single and multiple cyclones, are suitable for removing particles of diameter 5-40 μm (with efficiency around 85 per cent) from flue gas streams, but efficiency declines rapidly as the particle diameter decreases. Cyclone collectors are presently used alone as a particulate control device on most currently operating oil-fired power plants, and are also used in conjunction with other devices on some coal-fired power plants. Electrostatic precipitators, the most prevalent particulate control device for coal-fired plants, have collection efficiencies for particles larger than 10 μm diameter on the order of 99-99.9 per cent, but are likely to collect only about 50 per cent of submicron range particles. Ninety per cent of the particulate mass which escapes an electrostatic precipitator occurs in particles smaller than 5 μm MMD. Fabric filtration is receiving acceptance for coal-fired power plants in the form of a baghouse, a chamber in which the flue gas flows through filters consisting of fabric tubes or envelopes. Provided that the filters are precoated with coarse dust, particle collection efficiencies for a coal-fired power plant are 99.7 per cent overall, 99.5 per cent for particles with 0.5 μm MMD, and greater than 90 per cent for smaller particles. Hence fabric filtration appears to offer a promising method for small particle removal.

1.3.4 Other emissions

Hazardous metal vapors from coal-fired or oil-fired power plants include primarily mercury and selenium, and to a lesser extent, fluorides and arsenic. Electric power generation accounts for about 30 per cent of the total man-made emissions of mercury; corresponding percentages for selenium and arsenic are not known. Mercury is also emitted by geothermal steam plants, and amounts in sludge are 100 times those found in fly ash. There are currently no reliable methods for controlling power plant emissions of these hazardous metal vapors, but they are not expected to cause air quality standards to be exceeded in most California air basins.

Hydrocarbons and carbon monoxide are common gaseous organic pollutants in urban air. Since fossil-fuel-fired power plants are responsible for no more than 1 per cent of the total emissions, these pollutants are not controlled, and do not represent a significant problem. Methane, emitted from geothermal plants, is relatively inert and does not appear to require control.

Hydrogen sulfide (H_2S) is a common constituent of the non-condensible gases from geothermal power plants. Concentrations of H_2S in the vicinity of the plant frequently reach 10 parts-per-million (ppm), which is the occupational standard, and levels in nearby counties often exceed the 30 ppb ARB standard for H_2S. Because of variations in geothermal steam areas in California, emission rates may vary by up to a factor of 5 from power plant to power plant. Because H_2S oxidizes to SO_2, it usually cannot reach substantial concentration throughout an air basin. In some conditions, though, the 30 ppb level may be exceeded. H_2S abatement procedures used in some California geothermal plants include the use of an iron-catalytic scrubber, whose effectiveness remains to be determined.

Radioactive emissions have also been detected from coal-fired power plants, oil-fired power plants, and geothermal steam plants. Uncontrolled emission factors for radium and thorium from a typical coal-fired power plant are typically about 1 curie/GW-year; liquid fossil fuels typically yield less. These emissions constitute a long-term, low-level hazard, primarily through their radon decay daughters. Geothermal plants, on the other hand, have been observed to emit directly 1500 curies/GW-year of radon (at the Geysers) with potentially greater emissions associated with geothermal resources in the Imperial Valley. The 1500 curies is less than the amount that would result from the decay of the curie amounts of radium and thorium in the millenia after their emission from fossil fuel plants. But the relative effects are difficult to compare, in view of the effects of controls, population densities, and other factors. In any case, applicable standards are never approached.

Waste water effluents are generated by all types of fossil-fuel and geothermal power plants. Principal contaminants in waste water from fossil-fuel plants include alkali, metal and calcium salts. In addition, iron, manganese, and copper salts are present in significant concentrations in all waste waters. Other elements are present in trace amounts. Waste waters from fossil-fuel power plants may also contain organic chemicals, used to prevent corrosion of the plumbing, and antioxidants.

Noise is generated at fossil-fuel power plants, as at any industrial facility. Perhaps the highest levels arise from turbogenerator operation; these, however, are enclosed in buildings. At a geothermal plant, higher noise levels may be associated with the geothermal wells themselves, unless abatement techniques are employed.

1.4 Health Effects

Ambient air quality standards, water quality standards, and emissions standards and associated regulations have been established to protect the public from the known or suspected effects of pollutants on human health. Information from epidemiological, physiological, biochemical, and carcinogenesis studies together has been used to assemble a picture of what these health effects are, or at least what they might be. However, many of the pieces of information are so fragmentary, results so tenuous, or the exposure conditions so totally unrelatable among studies, that identification (let alone assessment) of health effects which are supported by evidence at every level of biomedical investigation cannot be made.

Much of the research into the health effects of air pollution was sparked by the "classic" episodes which resulted in unusually high numbers of reported illnesses and deaths. The first of these to be thoroughly documented occurred in the Meuse Valley of Belgium in December 1930, where for five days an inversion caused pollutants accumulation such that the SO_2 concentration was estimated to be as high as 8 ppm (20,800 $\mu g/m^3$) and an abnormally large number of deaths was observed. A similar incident occurred in Donora, Pennsylvania, in October 1948, resulting in twenty deaths instead of the predicted average of two deaths, and a very highly elevated number of illnesses. Of documented disasters, the worst occurred in London, England during December 1952, when an inversion caused the ambient concentration of SO_2 to reach 1.5 ppm (4000 $\mu g/m^3$) and suspended particulate matter to reach almost 4500 $\mu g/m^3$, resulting in some 4000 more deaths than would ordinarily have been expected. Application for hospital bed service in London were also some 2.5 times the normal average for the period. Similarly, high (SO_2 and particulate) pollution was blamed for the 400-800 excess deaths reported in New York City during January and February 1963, and 168 excess deaths there during Thanksgiving weekend of 1966. In all of these episodes, health effects were noted as cardio-respiratory diseases and were attributed to SO_2 and particulate matter. The most vulnerable people were generally the very young, very old, and those with pre-existing conditions, although others were also affected.

A brief summary of possible health effects of specific pollutant types constitutes the remainder of this section. For references and a fuller discussion, see the corresponding parts of Sections 4.1 (epidemiology), 4.2 (laboratory studies of physiological and cellular effects), and 4.3 (biochemical and genetic interactions).

1.4.1 Sulfur oxides and other sulfur compounds

Sulfur oxides and sulfates have received a considerable amount of attention with regard to their interactions with biological systems, as a direct result of their presence in acute smog episodes. Sulfur dioxide (as SO_2 or as sulfites) is a biochemically reactive compound. In living cells enzyme-bound thiamine is destroyed at relatively low concentrations. Other potentially damaging reactions are less important because of the higher doses of SO_2 required. However, the most important biochemical reaction of SO_2 in the body is probably its detoxification by the sulfite oxidase system. This highly efficient system is found in many organs, including the lung, and various cells of the respiratory tract. Hence, the toxicity of SO_2 is governed by the competition between the dose received and the rate at which sulfite oxidase removes the pollutant, and at ordinary urban levels SO_2 should have no metabolic health effects whatever.

Physiological investigations have shown that SO_2 can affect the mechanical properties of the lung, and alter the populations of certain types of cells in the respiratory tract, typical physiological responses to general irritants. SO_2 increases airway resistance in humans and animals at concentrations above 1-10 ppm (2,600- 26,000 $\mu g/m^3$). Mucous secretions in the respiratory tract are stimulated, and the rate at which foreign particulate bodies are removed decreases upon exposure. The ability of SO_2 exposure to increase susceptibility to respiratory infections may originate from interactions with alveolar macrophages. Because of its high solubility in water, the ability of SO_2 to elicit these effects depends on whether the subjects breathe through the nose or through the mouth, and increases with relative humidity. Typically, the doses needed to generate measurable phsiological responses are 3-4 orders of magnitude higher than concentrations of SO_2 ordinarily found in urban air.

Many of the same irritant responses attributed to SO_2 exposure are also observed with sulfates, especially sulfuric acid (H_2SO_4) mist. Increased airway resistance is evident following brief exposure to H_2SO_4 concentrations above 700-5000 $\mu g/m^3$, depending on aerosol size as well as relative humidity. Other sulfates have also been reported as irritants.

However, sulfates, unlike SO_2, do not react biochemically with cell constituents; when waterborne, their toxicity is negligible. The ability of most airborne sulfates to elicit pathological changes in respiratory function may arise from the local acidity or salinity of these aerosols, since no active mechanism for detoxifying strong acids has been detected in the body. If this is the case, similar effects would result from exposures to other acidic particulates. It should be noted that when sulfates have been present in sufficient concentration to elicit changes in morbidity and mortality, (acid) nitrate levels were probably also high.

Several epidemiological investigations have suggested a link between the occurrence of respiratory infections and the presence of SO_2 or sulfates in community air. Differences in the methodologies and the variables controlled, however, are extremely important since other types of pollutants generally coexist with sulfur oxides and since study populations are often heterogeneous with respect to age, socio-economic status, smoking history, etc.

The best known studies of the effects of sulfur oxides are the Community Health and Environmental Surveillance System (CHESS) programs sponsored by the EPA. In this program, health indicators of long-term effects of air pollution include: a) prevalence of chronic bronchitis in adults; b) increased lower respiratory infections in children; c) increased acute respiratory illnesses in families; d) changes in ventilatory function in children, and e) aggravation of cardiopulmonary symptoms and asthma attacks. The CHESS results showed no relation between asthma attacks and measured SO_2 levels, but did find an inverse correlation with temperature. In one instance, however, an association between asthma and sulfates was observed. Similar results were obtained regarding cardiopulmonary diseases. Again, SO_2 and total particulate levels were not associated with aggravation of symptoms, but elevated sulfates consistently correlated with cardiopulmonary dysfunction. Chronic bronchitis was found to vary according to the severity of air pollution in several localities; however, the individual contributions of SO_2, particulates, or sulfates could not be determined. Studies failed to establish a clear connection between the incidence of lower respiratory infections in children and sulfur oxide in the air; however, the investigators suggested a connection with combined SO_2 and sulfates, despite considerable criticism of the experimental methodology and data. Studies of acute respiratory diseases in families reported an excess disease rate of 5-20 per cent for 80 ppb (210 $\mu g/m^3$) SO_2 with 104 $\mu g/m^3$ total particulates and 16 $\mu g/m^3$ sulfates, but the credibility of these data has been questioned on the grounds of uncontrolled confounding variables. Parallel studies of the effects of SO_x on pulmonary function gave inconclusive results, since no dramatic changes were observed, and any (small) effects due to sulfates may have been confounded by nitrates and other variables. It is important to note, however, that the validity of CHESS results has been heavily criticized by many observers, largely because of methodological problems.

Other investigations of community morbidity not related to the CHESS program have suggested an increase in the frequency and duration of respiratory diseases due to <u>sulfates</u>. On the other hand, direct examinations of cardio-respiratory function in adults by several groups have shown no consistent relationship to any observable air pollutant.

Numerous investigations of the influence of SO_x on <u>death rates</u> have also been reported. In the New York City area, for example, mortality correlated positively with extremes in SO_2 concentrations; however, "coefficient of haze" gave the same correlation. Other studies have shown positive associations between sulfate levels and infant mortality, but only occasionally a relation with SO_2. Socioeconomic variables, however, were not controlled in these investigations.

Current ambient air standards for SO_2 (EPA: 30 ppb, ARB: 40 ppb) are based on results from pulmonary function studies and old epidemiological evidence linking respiratory disease and mortality to SO_2 exposure. Biochemical evidence presently does not support these standards. Physiological function data support the standards if one assumes a margin of safety factor of at least 100. Epidemiological studies, as originally cited by the EPA, suggested a threshold between 30-100 ppb for increases in morbidity and mortality. However, recent reassessments of the epidemiological information now suggest that most of the health effects originally attributed to SO_2 actually correlate better with sulfates. However, even this conclusion is now open to question.

The current ambient air standard for sulfates (ARB: 25 $\mu g/m^3$) is based principally on the threshold for measurable changes in respiratory function (minimum concentration: 350 $\mu g/m^3$), incorporating a stated margin of safety factor of ten. Epidemiological evidence is also used to support the ARB standard qualitatively, especially the CHESS program results, which are, however, questionable. No biochemical criteria are considered.

Hydrogen sulfide (H_2S) reacts with a number of heme proteins in the body, including hemoglobin and cytochrome oxidase, to give the sulfoderivatives. However, H_2S in the body is detoxified much as SO_2, including oxidation via sulfite oxidase to sulfate. Physiological effects of actue H_2S toxicity include eye irritation and sensitivity to light, followed by lung irritation and symptoms of cardiovascular stress at higher levels, and are said to occur at concentrations above 5-20 ppm. However H_2S is rarely encountered in community air in significant quantity, so that epidemiological assessment of its health effects is limited largely to accidents. An accident near Terre Haute, Indiana in 1964, causing average concentrations between 22 and 300 ppb, resulted in public complaints of nausea, shortness of breath, headaches, and insomnia, even at these sub-ppm concentrations. An episode at Poza Rica, Mexico, in 1950, during which ambient levels were not measured, resulted in 22 deaths and over 300 hospitalizations for acute H_2S poisoning.

The California ARB ambient air standard (30 ppb) is based largely on the odor and nuisance threshold for H_2S. It could also be justified on the basis of the health effects reported during the Terre Haute episode, incorporating a factor of 2-10 as the margin of safety. It would be desirable to incorporate epidemiological information on the health effects of H_2S exposure from populations in the vicinity of natural or geothermal induced H_2S emissions.

1.4.2 Nitrogen oxides and other nitrogen compounds

Nitrogen oxides (NO_x) can inflict a wide variety of adverse health effects, resulting from the separate actions of nitric oxide (NO), nitrogen dioxide (NO_2), nitrates, and nitrosamines. NO and NO_2 can both oxidize hemoglobin in blood to methemoglobin, which is an inactive form, a reaction that is similar to that generated by nitrites and nitrates in food and water. The physiologicalmanifestations are expected to be identical to those observed for carbon monoxide toxicity, reflecting the increased cardiovascular stress due to oxygen deficiency. Although NO_x has been implicated in methemoglobin burdens in humans and animals it is not clear that any of the physiological and epidemiological effects are realized.

In addition, nitrogen dioxide (NO_2) is known to be a strong respiratory irritant and pulmonary toxin. Ill effects seem to reach their worst extent during the first 24 hours, after which general repair and recovery takes place even during continued exposure. For this reason, it is difficult to fix the concentration and exposure range in which certain physiological changes take place, although relatively few effects are observed at levels below 0.5 ppm. NO_2 can alter pulmonary function by increasing airway resistance in humans at levels on the order of 1.5-5ppm (2,900-9,400 $\mu g/m^3$). Considerable tissue damage is visible in the lung, and the populations of various types of cells in the lung and respiratory tract are altered. Exposure to NO_2 destroys ciliary activity in the respiratory trace, decreases the capacity for removal of foreign objects,and causes an increased frequency of respiratory infections. On the basis of animal experiments, symptoms of emphysema have been postulated to result from NO_x exposure, but evidence proving the relationship is tenuous and other studies, including those on humans, have not confirmed this hypothesis.

The evidence above suggest the following as possible (not necessarilty probable)results of NO_2 exposure: respiratory infections, emphysema, difficulty with breathing, and risk of cardiovascular problems. The only systematic epidemiological appraisal of NO_2 health effects has been a Chattanooga, Tennessee study (now a CHESS program). Significant impairment of ventilatory function was reported for school children living in an area with typical NO_2 concentrations of 0.10 ppm, with illness incidence rates 18.3 per cent higher in the high NO_2 area than the norm. Subsequent follow-up studies also suggest a higher incidence of acute bronchitis among infants and school children. However, other pollutants such as ozone, sulfates, other oxidants, metal fumes, and particulates are confounding variables which have made interpretation of these data less than certain. While neither NO nor NO_2 is throught to cause cancer, biochemical and secondary atmospheric derivatives of these oxides of nitrogen may pose a significant cancer risk. Nitrous acid (HNO_2) may be one such derivative. In addition, reactions of NO and NO_2 with organic amines gives rise to nitrosamines, which are extremely carcinogenic.

Existing EPA air quality standards for NO_2 are based on epidemiological data (however controversial) which suggest that 60 ppb is the threshold for increased risk of respiratory diseases (EPA: 50 ppb annual average), and on studies of pulmonary function impairment (EPA: 350 ppb, 1-hour), with no safety margins stipulated. The ARB standard (ARB: 250 ppb, 1-hour average) is based on acute pulmonary function studies, and stipulates a factor of 2 margin of safety. No standards presently exist for NO or for nitrosamines in ambient air, although it is likely they will be promulgated in the near future.

1.4.3 Oxidants

Oxidants are primarily products of secondary reactions of pollutants. The major constituent of oxidants is ozone (O_3). Ozone reacts vigorously and specifically with unsaturated lipids in lung surfactant and cell membranes. Other reactions of ozone and its hydrolysis products may occur with proteins and other cell constituents. Such effects can be observed at O_3 levels between 0.1-1.0 ppm.

Predictably, the physiological effects of O_3 exposure include changes in cell populatoins, leading to impairment of foreign body removal from the respiratory tract and lung and, perhaps, temporary impairment of the metabolism of other pollutants, drugs, and chemical species in the lung. (See Section 4.2.3.) Interaction of ozone with other metabolic systems can induce physiological symptoms. An important effect of oxidants is hindrance of the exchange of gases between air and blood. Since the threshold lethal dose of ozone can be as low as 0.5 ppm, a level which is periodically reached in parts of California, the danger of acute poisoning from oxidant pollution cannot be neglected.

Acute and chronic diseases which might be triggered or aggravated by ozone include respiratory infections, acute and chronic bronchitis, and emphysema. These diseases are suggested on the basis that O_3 impairs foreign body clearance from the lung, and causes digestive enzymes to appear in the alveolar spaces. Ozone has been shown to be mutagenic as well. On the other hand, its potential to cause cancer is not known. No concrete epidemiological evidence now exists to establish that any of these health effects (respiratory disease, emphysema, or cancer) is actually being felt in urban (California) population.

Existing air quality standards for oxidants (EPA: 80 ppb; ARB: 100 ppb) are based on biocehmical and physiological criteria regarding pulmonary function and cellular/metabolic integrity, with the margin of safety not greater than 1.25. However, revising these standards to lower concentrations is difficult, considering the high levels of ozone believed to occur naturally.

1.4.4 Particulates

Particulates can impart adverse health effects due to physical interactions, independent of chemical composition, or due to the biochemical interactions of some of the constituents. Physical interactions of particulates in air depend heavily on the deposition characteristics of particles, which are in turn a function of particle size. As a rule, particles larger than 0.5-2 μm diameter are trapped in the upper respiratory tract, while those smaller than this range lodge in the deep lung spaces. (Any obstructive respiratory condition will, however, change this distribution.) Clearance of particles from the upper tract is rapid, requiring only a few minutes. On the other hand, small particles which reach the alveoli may remain there for months or years, or else may reside in the lymphatic system for a similar time period. Particulates, including those which are biologically active, often elicit an inflammatory response which results in the entrapment of the particle within a fibrotic network. Sulfates, nitrates, and ammonium species, which often occur in sub-micron particles, are generally sufficiently soluble to enter the bloodstream cells for metabolism. Lead and (insoluble) carbon, on the other hand, typically accumulate in the lymph following engulfment by the alveolar macrophages. The principal clinical manifestation of the physical interactions of particulates with the respiratory-pulmonary system might be expected to be a change in the incidence of respiratory infections. However, epidemiological research indicates that incidence of respiratory disease correlates better with sulfate than with total particulates.

Individual chemical constituents in particulate matter may also affect the health of exposed individuals by their specific chemical interactions. For example lead (derived mostly from motor vehicles, but also from fly ash from both coal-and oil-fired power plants) blocks the synthesis of hemoglobin and damages other proteins; the California standard (ARB: 1.5 $\mu g/m^3$ over 30 days) is predicated on a body burden analysis of not more than 5 per cent depression of hemoglobin synthesis. Respiratory irritation arises from (very high doses of) manganese, iron, and vanadium. Nickel is a known carcinogen at high doses. Health effects of carbon compounds in particulate matter are largely unknown, except for the ability of some to cause cancer; these are principally certain polynuclear aromatic hydrocarbon (PAH) compounds. Finally, the impacts of sulfates and nitrates have been noted above.

Existing ambient air quality standards for particulates (EPA: 60 μg/m^3, annual average, and 260 μg/m^3, 24-hours; ARB: 60 μg/m^3, annual average, and 100 μg/m^3, 24-hours) define particulate matter in terms of total mass only. Both sets of standards are predicated on the respiratory effects resulting from the physical interactions of particles with the physiological clearance mechanisms. Except for the ARB sulfate standard, they ignore the importance of particle size (and deposition characteristics) and neglect the chemical interactions of individual constituents, in spite of a growing body of aerosol characterization data.

As a result of the failure of standards to consider particulate size, emission control measures may not always produce optimum results. For example, although uncontrolled emissions of fly ash from coal-fired plants may exceed those from oil-fired plants by a factor of 20, if emissions from an oil-fired plant are controlled by cyclones and those from a coal plant by filtration, then emissions from the oil plant in the respirable size range may exceed those from the coal plant by a large factor (say 20), even though both plants meet applicable standards.

1.4.5 Other substances

Carbon monoxide (CO) toxicity, like that due to nitric oxide (NO), is the result of inactivation of hemoglobin, which generates an increased cardiovascular stress. Symptoms of tissue hypoxia resulting from CO-induced cardiovascular burdens include impaired visual response, impaired judgment, and at higher exposure levels headaches, dim vision, and nausea. Similar symptoms are expected for prolonged NO (NO_x) exposure.

Hazardous metal vapors of greatest potential concern for power plant emissions are mercury and selemium. Mercury is absorbed with high efficiency by inhalation, and is deposited in brain, nervous tissue, and salivary glands. Its principal toxic reaction occurs with sulfur groups of proteins, leading to anemia, hypothyroidism, hyperexcitability, and loss of appetite. The present mercury standard (EPA: 1 μg/m^3) assumes that a daily uptake of 20 μg is the maximum safe level. Selenium in trace amounts is an essential nutrient, but at higher concentrations is extremely toxic. It is known to interfere with reactions of sulfur groups in the body, but the health implications are totally unknown. Accordingly, the maximum selenium concentration allowed in the atmosphere has been tentatively set at 100 μg/m^3, based on 2000 μg/day safe intake.

1.5 The State of Information

The existing data on the emission, dispersion, and health effects of air and water pollutants from fossil fuel and geothermal power plants are incomplete, tenuous, and in some cases, contradictory. Much of the research employed methods too crude for the precision and accuracy required. Many crucial questions have also gone unanswered because of deficiencies in the investigative tools or errors in experimental logic. Although the data have provided some guidance for establishment of air and water quality standards and supporting emission standards, they are not a sufficient basis for accurately estimating the human health impacts of additional sources.

Epidemiological studies have traditionally accepted the available data on community air quality, and have attempted to ferret out health effects due to specific pollutants in the face of confounding variables such as smoking history, socio-economic class, age, and mobility. Frequently, the health effects studied are some gross phenomenon such as pulmonary-respiratory disease or cancer, for which tens or hundreds of varieties of each may exist. More specific clinical diagnoses may allow epidemiologists to establish correlations with pollution more clearly.

Air pollution monitoring information is presently supplied in most cases by central station monitors which are often poorly placed. Better human exposure data for use in epidemiological appraisals could be obtained by more adequate monitoring networks, by personal dosimetry measurements, or by body burden analysis. Analytical methods used in most regulatory monitoring are not the most accurate or sensitive techniques available. In some cases, they are insufficient even for standards enforcement purposes. Interferences from other pollutants are not always controlled, and the level of discrimination among classes of pollutants may be poor, particularly for sulfates, nitrate, and particulates.

The sensitivity and accuracy of biomedical measurements frequently determine the exposure concentrations of pollutant used in many laboratory health effects studies, particularly for sulfur oxides (where doses 100-10,000 times ambient concentrations have been used for respiratory function tests). In other cases, effects (such as those on morphology) may be difficult to interpret in terms of a concrete impairment of function. Biochemical studies often focus on metabolic activities which are easy to measure, rather than ones which are most likely to be affected by exposure. Hence, interpretation may again be difficult.

Important objectives for future research endeavors are: 1) providing more reliable exposure data for epidemiological study populations; 2) characterizing the metabolic reactions of pollutants, including their detoxification in the body; 3) correlating the different types of biomedically observable effects in terms of a single root cause; and 4) improving characterization of pollutant levels. This is especially true for particulate monitoring.

Future regulatory endeavors should include: 1) monitoring and enforcement of particulates according to their size and chemical constituents; 2) clarification of the standards and criteria for sulfates; 3) re-examination of the SO_2 standards; 4) preparation of standards and criteria for nitric oxide (NO) and nitrates; 5) re-examination of reference and equivalent methods for monitoring all pollutants.

These proposed research and regulatory activities would improve, respectively, the state of information on health effects of pollutants and the detailed regulatory response to this improved information. Moreover, actual assessment of human health impacts due to introduction of new sources would be more feasible and could, in fact, more directly serve as a basis for formation of standards and for new source review. Presently, some tentative estimates for the health impact of new sources have been advanced, often solely on the basis of elevated sulfate levels. Such estimates naturally depend on specific emission controls and on local population distributions, but very large uncertainties arise from modeling atmospheric transport and transformation and especially from formulating dose-response relationships on the basis of imcomplete health-effects evidence. For this reason, these estimates, which typically range from 1 to 100 premature deaths (and vastly more illnesses) among the public per year of 1000 MWe coal or oil-fired plant operation, cannot be relied upon. Even presuming that more reliable estimates become possible in the future, these penalties must be considered in the light both of benefits received from plant operation and of competing risks from other sources. For the present, decisions on individual plants cannot be made on the basis of such assessments. On the other hand, they may rely partially on predictions of the extent to which a plant would expose populations to specified levels of pollutants. Such predictions could involve analysis somewhat more refined than a simple policy to site plants away from urban areas and would provide a framework for actual health impact assessment when more complete dose-response data become available.

2. EXISTING STANDARDS AND REGULATIONS

The basic mechanism through which the operation of an electric generating plant has the potential for harm to the public is by the emission of materials from the power plant site. Although effects can occur through other mechanisms, such as the transportation of materials to and from the site or the production of fuels and disposal of waste materials, the emissions mechanism is subject to the most attention during any review of compliance of a proposed facility with standards designed to protect the public health and safety.

Such standards are formulated to maintain adequate air quality, to protect water quality, and to place limits on noise levels in the public domain. It is generally perceived, moreover, that this is the ranking in which electric generating plants can have their most substantial effects: air, water, and noise emissions. Accordingly, the primary attention in this report is devoted to health effects related to air pollution and to standards formulated for maintenance of air quality. Water and noise are discussed more briefly.

Of standards related to air quality, those specifying the quality of ambient air (that in the public domain) are most directly related to protection of the public health and welfare, the stated object of standards for air quality. These ambient air quality standards are formulated and administered by agencies at the federal, state, regional, and even local levels. Such standards and the responsible agencies are discussed below in section 2.1.

Control of emissions is the basic tool for limitation of the effect of power plants on ambient air quality. Section 2.2 treats generally applicable emissions standards, including new source performance standards. In addition to the application of such emission standards, detailed consideration is given to the actual effect that a proposed plant would have on the ambient air quality in the region on which the plant would be located. This examination takes place during the new source review discussed in section 2.3.

Two general programs have been formulated with respect to national ambient air quality standards. The first is the definition of maintenance areas in which it is predicted that national standards will not be met at some specified time. The second program, applicable to areas where air is better than that required by the national standards, has as its goal the prevention of unwarranted deterioration of air quality in these areas.

Air quality maintenance areas and the prevention of significant deterioration are discussed, respectively, in sections 2.4 and 2.5.

Finally, plans have been formulated for dealing with episodes during which excessive pollutant levels occur, posing substantial dangers to the public health. The "air pollution emergency plan" for California is discussed in section 2.6.

As a part of new source review, emergency planning, or overall assessment of air pollution impacts, models simulating or predicting meteorological behavior and pollutant concentrations are often employed. These models utilize a variety of methods and are implemented with varying degrees of sophistication. They are discussed in a separate report(1) and, more briefly, in section 3.3 of this report. Although they will not be discussed in this section, it is appropriate to note that the type of model employed depends strongly on the application at hand. For example, predictions of episodal levels of pollutants often depend on statistical models, which calculate future pollutant levels or durations purely on the basis of analysis of historical data. On the other hand, the long term effects of new sources introduced into an air basin could employ a deterministic model which actually simulates the physical processes of dispersion, again yielding concentrations and durations.

Several sources, referred to below, served as the primary basis for the information on standards relating to air quality; reference 2 among them also served as a useful overall guide. It is important to note that such standards are still in a process of rapid change, so that details of direct significance should be reviewed when they are needed. For example, the appendix on emission standards includes many changes compared with the compilation on which it is based (Ref. 2).

2.1 Air Quality Standards

Purpose, basis, and form of air quality standards

Although standards related to air quality may take a variety of forms, those most directly related to the public health and welfare are ambient "Air Quality Standards" (AQS). These AQS are usually stated in terms of maximum concentrations ($\mu g/m^3$ or ppm) of pollutants for a specified time. Occasionally other bases, such as visibility reduction, may be used for specifying air quality.

AQS protecting the public health are formulated on the basis of epidemiological and toxicological studies. Were epidemiological information comprehensive enough, it could serve directly as the sole basis for AQS. Since this is not the case, laboratory studies also serve as a substantial information base. In using the latter information for formulating a standard, a safety factor is incorporated to take account of the difference between short-term laboratory measurements and long-term community exposures, as well as the differences involved in translating observed effects on animals into predicted effects on humans.

Historically, a significant factor in the formulation of AQS has been the assumed existence of "threshold" levels (concentrations) below which there is no adverse effect. Based on this concept, the specification of an AQS at a particular pollutant concentration assumes that health consequences from pollutant levels below the AQS are insignificant, at least as compared with other factors. Although this concept of a threshold level is convenient from a regulatory viewpoint, an alternative view argues that at any pollutant concentration, no matter how low, some portion of the population will be sensitive enough to suffer some adverse effects. If the latter concept is correct, selection of an AQS necessarily includes consideration of the trade-offs between the level of protection provided and the feasibility, including cost, of control. The AQS then serves to protect most, though not all, of the public.*

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*We have not distinguished between several different possible types of effects at levels below the selected concentration. These include: 1) the fact that the more sensitive members of the population may still be affected, 2) the possibility that at low levels, random individuals, without any particular sensitivity, may be affected, 3) the fact that less adverse, but still significant, effects may be caused by the lower levels. Since the AQS is, in any case, formulated considering some ill-defined mix of these possibilities, it is not useful to distinguish them in the above discussion.

For the threshold concept, a "margin of safety" may be defined as the difference between the AQS and the threshold level. If it is supposed that there are always some adverse effects, the safety margin may be regarded in terms of the fraction of the population protected by the specified AQS. As the AQS becomes more and more stringent, a larger portion of the population is protected, thereby offering, in some sense, a greater margin of safety.*

For some AQS, substantial margins of safety exist; for others there is little margin. Where the threshold level is surrounded with uncertainty, conflicting evidence, or controversy, public health officials will likely argue for a large safety margin to protect the public against possible, but as yet undetermined, hazards. Individual or corporate sources of the pollutant, on the other hand, will argue for smaller margins to avoid costs incurred with pollution control equipment and strategies necessary to meet a perhaps unnecessarily stringent standard. Since purely scientific considerations cannot settle such questions, final decisions on these matters are necessarily and appropriately political in nature.

Although an attempt is made to formulate an AQS for each pollutant that can be applied independently of local circumstances or other pollutants, this approach cannot be followed uncritically. For example, local circumstances <u>can</u> lead to increased hazards to members of an exposed population unless the AQS is formulated to take account of these circumstances. A specific case is the more severe impact of a specified concentration of carbon monoxide (CO) at higher altitudes, such as the Lake Tahoe region. Because the concentration of oxygen at these elevations is <u>lower</u> than at sea level, the reduction in blood oxygen caused by CO would have greater adverse effects. (Standards for CO at Lake Tahoe are therefore more stringent than for the rest of the State.) Similarly, although AQS are typically stated independently for each pollutant, this approach should be altered when the significance of a particular pollutant can be increased by the presence of another. For example, the AQS for SO_2 in the presence of small aerosols, which penetrate deep into the lungs, should be more stringent than the AQS for SO_2 with very low concentrations of these aerosols if, as the available evidence suggests, there is a synergism between these pollutants.

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*See footnote, previous page.

Although the protection of public health is the primary purpose of air quality standards, we should emphasize that they are also designed to protect other values under the general category, the "public welfare". They therefore serve to prevent significant curtailment of major activities of the public or the sacrifice of important economic or personal values. Possible examples are damages to crops from even lower pollutant concentrations than are thought to harm man directly, destruction of aesthetic values by reducing visibility, or causing odors at levels below limits imposed for protection of the public health.

Since the air quality sought usually cannot be maintained at all times, AQS often permit freedom appropriate to particular circumstances. For example, many standards allow higher concentrations averaged over short periods, while specifying a lower concentration when averaged over long periods. Such differences are based on the fact that tolerance to a specified pollutant concentration may depend on the time of exposure to that concentration. On a broader time scale, unusually high concentrations may be permitted on rare occasions; thus Environmental Protection Agency AQS are not to be exceeded more than once a year.(3) These provisions allow for extreme or unusual conditions and are analogous to flood designs based on expectations for the "hundred year flood," a very rare case, but not the worst possible.

Present status of air quality standards

The federal Clean Air Act of 1963 and the amendments of 1970 give the federal government the responsibility and authority to establish National Ambient Air Quality Standards (NAAQS) and to set new source and hazardous emissions standards (see section 2.2). Beyond this, the Act requires that actions be taken to meet the NAAQS on a specified time schedule. The federal government has the power to enforce pollution controls and even to assume the duties of state or local control agencies, should they fail in their responsibilities.(3)

The federal agency with primary responsibility for implementation of the Clear Air Act is the Environmental Protection Agency (EPA). The EPA has established NAAQS of two types, primary and secondary (see below), and requires that states submit "State Implementation Plans" (SIPs) within nine months of the issuance of NAAQS. These SIPs provide for "implementation, maintenance, and enforcement" of the primary NAAQS. The EPA also administers, as necessary, specific programs for implementation of the NAAQS. These include the Standards of Performance of New Stationary Sources and the Prevention of Significant Deterioration Programs (see sections 2.2 and 2.5). The EPA may also directly administer programs, such as the New Source Review (see section 2.3), when state and local agencies fail to act.

As noted above, NAAQS are divided into primary and secondary standards. Primary standards are designed to protect public health "with an adequate margin of safety". Secondary AQS are established to protect more general aspects of the public welfare. Secondary standards are generally more stringent, and therefore harder to meet, than primary standards.

In 1969, the year before the 1970 Clean Air Act Amendments gave the federal government authority to establish the NAAQS, California began setting air quality standards under the provisions of the Mulford-Carrell Act.(4) Unlike the primary NAAQS, which are required to be met by 1977, California's AQS have no deadline for compliance. (Nor are primary and secondary standards distinguished among California AQS.) These AQS are therefore goals to be used in establishing air pollution control policies, rather than requirements to be attained by some date. Federal and state air quality standards are given in Table 2-1. Wherever there is a difference between federal and state AQS, the stricter one shall apply.

Also under the provisions of the Mulford-Carrell Act, the State Air Resources Board (ARB) was established in 1967 to administer the state's air pollution programs.(4) The ARB has primary responsibility over motor vehicle pollution control, but it also oversees the activities of the local "air pollution control districts" (APCDs), whose primary responsibility is to police stationary sources of air pollution. The ARB can intervene in stationary source control if the APCDs fail in their responsibilities. Since the APCDs exercise authority more in the area of actual emission control than in the establishment of air quality standards, APCDs are discussed in more detail in succeeding sections.

Current regulatory actions are considered adequate to provide for meeting some, but no all, of <u>present</u> AQS. However, it is anticipated that AQS will be established for <u>additional</u> species, with more activity expected at the state than federal level. Several possible areas for new or modified standards are identifiable.

Figure 2. Ambient air quality standards (from Ref.(5)).

Pollutant	Averaging Time	California Standards[1]		National Standards[2]			Objectives of the standard (ref. (6)).
		Concentration[3]	Method[4]	Primary[3, 5]	Secondary[3, 6]	Method[7]	
Oxidant (Ozone)	1 hour	0.10 ppm (200 ug/m^3)	Ultraviolet Photometry	160 ug/m^3 (0.08 ppm)	Same as Primary Std.	Chemiluminescent Method	To prevent eye irritation and possible impairment of lung function in persons with chronic pulmonary disease. Also to prevent damage to vegetation
Carbon Monoxide	12 hour	10 ppm (11 mg/m^3)	Non-Dispersive Infrared Spectroscopy	—	Same as Primary Standards	Non-Dispersive Infrared Spectroscopy	To prevent interference with oxygen transport by the blood based on carboxyhemoglobin levels greater than 2%.
	8 hour	—		10 mg/m^3 (9 ppm)			
	1 hour	40 ppm (46 mg/m^3)		40 mg/m^3 (35 ppm)			
Nitrogen Dioxide	Annual Average	—	Saltzman Method	100 ug/m^3 (0.05 ppm)	Same as Primary Standards	Proposed: Modified J-H Saltzman (O_3 corr.) Chemiluminescent	To prevent possible risk to public health, and atmospheric discoloration
	1 hour	0.25 ppm (470 ug/m^3)		—			
Sulfur Dioxide	Annual Average	—	Conductimetric Method	80 ug/m^3 (0.03 ppm)	—	Pararosaniline Method	To prevent possible increase in chronic respiratory disease and damage to vegetation
	24 hour	0.04 ppm (105 ug/m^3)		365 ug/m^3 (0.14 ppm)	—		
	3 hour	—		—	1300 ug/m^3 (0.5 ppm)		
	1 hour	0.5 ppm (1310 ug/m^3)		—	—		To prevent possible alteration in lung function, and irritating odor
Suspended Particulate Matter	Annual Geometric Mean	60 ug/m^3	High Volume Sampling	75 ug/m^3	60 ug/m^3	High Volume Sampling	To improve visibility and prevent acute illness when present with about 0.05 ppm sulfur dioxide
	24 hour	100 ug/m^3		260 ug/m^3	150 ug/m^3		
Sulfates	24 hour	25 ug/m^3	AIHL Method No. 61	—	—	—	To prevent possible increase in chronic respiratory disease
Lead	30 Day Average	1.5 ug/m^3	AIHL Method No. 54	—	—	—	To protect health
Hydrogen Sulfide	1 hour	0.03 ppm (42 ug/m^3)	Cadmium Hydroxide Stractan Method	—	—	—	To prevent offensive odor
Hydrocarbons (Corrected for Methane)	3 hour (6-9 a.m.)	—	—	160 ug/m^3 (0.24 ppm)	Same as Primary Standards	Flame Ionization Detection Using Gas Chromatography	To prevent the formation of photochemical smog
Ethylene	8 hour	0.1 ppm	—	—	—	—	To prevent damage to vegetation
	1 hour	0.5 ppm					
Visibility Reducing Particles	1 observation	In sufficient amount to reduce the prevailing visibility to less than 10 miles when the relative humidity is less than 70% (8)		—	—	—	To improve visibility
APPLICABLE ONLY IN THE LAKE TAHOE AIR BASIN:							
Carbon Monoxide	8 hour	6 ppm (7 mg/m^3)	NDIR	—	—	—	To prevent interference with oxygen transport by the blood based on carboxyhemoglobin levels greater than 2%.
Visibility Reducing Particles	1 observation	In sufficient amount to reduce the prevailing visibility to less than 30 miles when the relative humidity is less than 70% (8)		—	—	—	To improve visibility

NOTES:

1. California standards are values that are not to be equaled or exceeded
2. National standards, other than those based on annual averages or annual geometric means, are not to be exceeded more than once per year.
3. Concentration expressed first in units in which it was promulgated. Equivalent units given in parentheses are based upon a reference temperature of 25°C and a reference pressure of 760 mm of mercury. All measurements of air quality are to be corrected to a reference temperature of 25°C and a reference pressure of 760 mm of Hg (1,013.2 millibar); ppm in this table refers to ppm by volume, or micromoles of pollutant per mole of gas.
4. Any equivalent procedure which can be shown to the satisfaction of the Air Resources Board to give equivalent results at or near the level of the air quality standard may be used.
5. National Primary Standards: The levels of air quality necessary, with an adequate margin of safety, to protect the public health. Each state must attain the primary standards no later than three years after that state's implementation plan is approved by the Environmental Protection Agency (EPA).
6. National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant. Each state must attain the secondary standards within a "reasonable time" after implementation plan is approved by the EPA.
7. Reference method as described by the EPA. An "equivalent method" of measurement may be used but must have a "consistent relationship to the reference method" and must be approved by the EPA.
8. Prevailing visibility is defined as the greatest visibility which is attained or surpassed around at least half of the horizon circle, but not necessarily in continuous sectors.

Standards presently exist for particulate matter; however, such matter may vary in both composition and size, and federal AQS address neither of these parameters, but consider only the total mass concentration or the reduction in visibility. California AQS for particulates are likewise stated in terms of total mass, but California has recently established a sulfate AQS, recognizing that sulfate particles are considered to be more harmful than other types. This sulfate standard and one for lead are the only AQS which reflect the fact that particles with different chemical compositions have different effects. Other particulate constituents which may be specifically regulated in the near future are nitrates and polycyclic aromatic hydrocarbons.

AQS specifying particle size are also being considered. A standard for "fine" or "respirable" particles may be established to protect the population from inhaled particles after methods for measuring ambient concentrations of small particles have been accepted by the regulatory community.

The limited availability of measurement methods is a significant obstacle to development of more comprehensive AQS. This obstacle is to some extent related to the fundamental difficulty caused by the manner in which pollutants may interact in the atmosphere, so that ambient pollutant concentrations do not depend in any simple way on actual emissions. Such conversions may make it difficult to identify what pollutants are responsible for observed health effects. Further, even when the harmful substances are identifiable, interactions in the atmosphere may obscure the origin of these particular substances. Understanding of these processes must be comprehensive enough for formulation of standards which take account of the chemistry of pollutants in the atmosphere. Enforcement of standards for reactive pollutants will be complicated by the need to monitor groups of pollutants, rather than single, independent pollutants. Measurements will have to be made rapidly enough, often at low concentrations, to avoid losing information essential to understanding the chemical conversions occurring. At present, no AQS take explicit account of interacting pollutants, although certain standards (such as that limiting oxidants) may apply to the results of atmospheric chemistry.

2.2 Emission Standards

Ambient air quality depends substantially on the emission rates of the various pollutant sources. The only tool which society currently possesses to exert even partial control over ambient air quality is the implementation of emission standards. Such standards are the means to attain air quality goals as expressed by air quality standards (AQS) and therefore should be tailored to meet prevailing AQS.

The air quality standards can be set at much lower concentrations than the concentrations that are prevalent at the time of formulation, with the lower values to be met at some future date. However, emissions standards, the means to attaining the AQS, are generally written so that enforcement is currently possible, i.e., the limitations can realistically be met with existing technology. For this reason, the emission standards are strongly influenced by the state-of-the-art and the cost of pollution control technology. In addition, they include specific provisions for temporary increases in emissions caused by certain equipment failures and by scheduled maintenance.

The Environmental Protection Agency (EPA) has established New Source Performance Standards (NSPS)(7) for new and modified sources of air pollutants. A portion of these standards apply to fossil-fuel power plants with a heat input rate of more than 250 million Btu per hour; emission limits are given in terms of pounds per million Btu. The stated NSPS reflect "the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated," thus acknowledging the limits imposed by technology. The standards depend on fuel type (gaseous, liquid, or solid), reflecting the varying difficulties of control. Table 2-2 lists the applicable NSPS for fossil-fuel steam generators.

NSPS also provide for enforcement coordination between state and local agencies and the EPA (40 CFR 60) and for plant inspection procedures for performance tests and field surveillance. Performance tests are required of all new or modified sources and must follow specified testing methods and procedures. The instrumentation required for emission monitoring and recording is also specified.

Table 2-2. New Source Performance Standards for Fossil Fuel Fired Steam Generators with a Capacity over 250 Million Btu per hour.[a]

Pollutant	Standard	Fuel
Particulates	0.10 lb/MM* But Input	Gas, oil, coal
SO_2	0.8 lb/MM Btu Input	Oil
SO_2	1.2 lb/MM Btu Input	Coal
SO_2	Prorated according to total heat input derived from each fuel	Combination of Oil and Coal
NO_x	0.20 lb/MM Btu Input	Gas
NO_x	0.30 lb/MM Btu Input	Oil
NO_x	0.70 lb/MM Btu Input	Coal
NO_x	Prorated according to total heat input derived from each fuel	Combination of gas, oil, and/or coal
Opacity	20%	Gas, oil, coal

*MM = million.

[a] Reproduced from ref. (2).

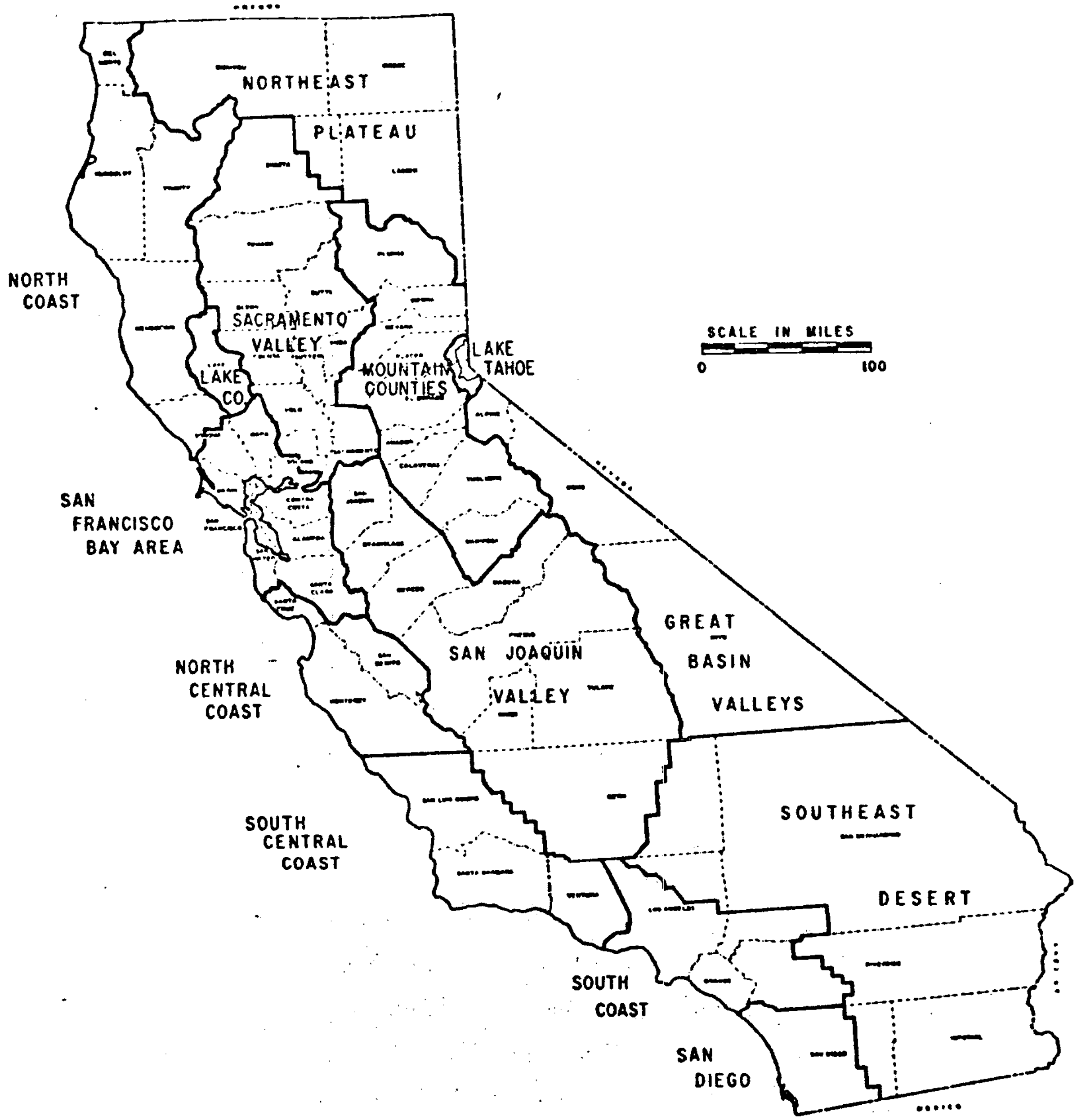

Figure 2-1. California Air Basins (supplied by the Air Resources Board).

The Air Resources Board (ARB) has divided California into 14 air basins, with boundaries determined by geographical and meteorological conditions, considering political boundary lines wherever possible (See figure 2-1). Each air basin contains one or more air pollution control districts (APCDs), which were established by the Mulford-Carrell Act.(4) An APCD may consist of a portion of a county, single county, or part or all of several counties. When one air basin contains several APCDs, a basin coordinating council, made up of representatives from each APCD, provides the guidance necessary for a coordinated air quality program to be carried out throughout the basin. APCDs have jurisdiction over stationary sources such as industries and open burning. (Mobile sources in California are the responsibility of the state and the federal government: the ARB for motor vehicles, except where Federal standards are more stringent; the EPA for aircraft.)(3) APCDs also have the power to establish AQS, but none have any standards that are stricter than the federal or state standards.

A number of APCDs have adopted the federal NSPS for fossil-fuel steam generators and have been granted EPA approval for their enforcement. These districts are given below.* In addition to adopting the federal NSPS, the APCDs have established emission standards tailored to their own needs. They also control emissions indirectly by curtailing open burning, by requiring process changes to meet direct controls, or by denying construction permits.

These local emission standards are expressed as absolute limits (stated in pounds per hour), as stack concentration limits [stated in either percent by volume, parts per million (ppm), or grams per standard cubic foot (grams/scf)], and as ambient concentration limits (sometimes stated as a maximum ground-level concentration during some averaging time). Emission limits are also based on effects, including visibility (expressed as opacity limits, usually in terms of a Ringlemann number and time limit), and nuisances, including odor and large-particle fallout. These limits are applicable not only to combustion processes, but also to geothermal power generation and to fuel storage

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[*] They are: Monterey, Del Norte, Humboldt, Mendicino, Northern Sonoma, Trinity, Bay Area, Fresno, Kern, Madera, San Joaquin, Stanislaus, Santa Barbara.(8)

(especially for liquid fuels). APCDs can also specify fuel concentrations for particular pollutants. (As an example, the Bay Area APCD imposed limitations on the sulfur content of fuel oil.) Such fuel regulations, as presently written, are generally expressed as percent sulfur by weight of fuel, for example, rather than as pounds of pollutant precursors per million Btu or KW-hr.

The APCD rules and regulations pertaining to fossil-fuel and geothermal power generation are given in the appendix to this report. (Wherever federal, state, or local standards overlap, the most stringent shall apply.) Emission standards are only applied to the largest stationary sources, thereby avoiding control programs for large numbers of relatively small sources. Several APCD emission standards apply only to equipment with heat inputs of over 1.775×10^9 Btu/hr (about 180 MWe, if a power plant boiler). The NSPS apply to units of more than 250×10^6 Btu/hr heat input (about 26 MWe).(6) Almost all of the districts use a graduated scale for determining the maximum emission rate of solid particulate matter, based on the process weight per hour. However, above a certain maximum process weight per hour, there is a fixed maximum for particulate emissions, which effectively places more stringent limitations on very large sources. As more and more large sources are brought into compliance with the existing emission standards, smaller and smaller sources will be regulated.

Existing standards may be rewritten so that they are expressed as pounds of pollutant per output instead of per unit input. For example, instead of a pounds-per-million Btu-input emission limit, as the NSPS are currently stated, standards could be given as pounds emission per megawatt-hour of electricity generated. This would add an incentive to employ more energy-efficient processes. (NSPS for nitric acid and sulfuric acid plants are currently expressed this way, i.e., on a pounds per ton of acid produced.)

The Clean Air Act and Amendments explicitly provide for the limitations on the emission of hazardous air pollutants. Once a substance has been declared hazardous, an emission standard may be imposed without first demonstrating that the substance poses any health hazard as an air pollutant and without establishing appropriate AQS. Substances for which hazardous emission standards have so far been established are asbestos, beryllium, and mercury (40 CFR 61).

2.3 New Source Review

Air quality depends not only on individual emission rates, but also on the number and location of emission sources. The commitment to attain a certain level of air quality therefore requires attention to the introduction of new sources and may effectively restrict the amount or character of industrial development that can take place in an air basin. Review of projects that may constitute new sources has been introduced in the form of "New Source Review" (NSR) procedures aimed at helping to meet air quality standards.

Such procedures are implicitly authorized by the Clean Air Act, recognizing that emission limitations alone are not sufficient to attain and maintain NAAQS in some areas. In section 110, the Act requires that State Implementation Plans (SIPs) contain:

> "emission limitations...and such other measures as may be necessary to insure attainment and maintenance of such...(ambient) standard(s), including but not limited to, land use and transportation controls."[4] (our emphasis added)

The EPA has interpreted (40 CFR 51.18) these "other measures" to include procedures to review the air quality impact of all new or modified sources. Section 24301(a) of the California Health and Safety Code requires that APCD permit systems ensure that a pollutant source "...for which the permit was issued shall not prevent or interfere with the attainment or maintenance of any applicable air quality standard."

When California first submitted its SIP to the EPA (1972), the New Source Review Section was disapproved because no APCD rules and regulations contained any NSR provisions. As required by Section 110(c) of the Clean Air Act, the EPA therefore promulgated and implemented, in 1973, NSR regulations for California [40 CRF 52.233(f)]. All the APCDs have subsequently adopted NSR rules to supplement their permit processes. However, the EPA only approved NSR rules from ten of the APCDs in 1973, while the ARB maintained that none of these APCD NSR rules satisfied the California Public Health and Safety Code.[2]

On October 28, 1975, the ARB drafted suggested NSR regulations as guidelines for the APCDs. The EPA stated that, if and when all the APCDs adopt and implement rules similar to those suggested by the ARB, the EPA will consider discontinuing its program, leaving NSR to the State.[12] A number of APCDs now have NSR rules approved by the ARB.*

The ARB guidelines include requirements for an air quality impact analysis performed on any proposed new or modified source which would emit more than 25 pounds per hour or 250 pounds per day of any pollutant for which there is an air quality standard, except carbon monoxide (CO), for which the limits are 250 lb/hr and 2500 lb/day. The permits for any new or modified source which would, by the results of such an analysis, prevent or interfere with the attainment or maintenance of any AQS should be denied. The guidelines also require the use of the best available emission control technology by most new or modified sources which would have emissions greater than 15 lb/hr or 150 lb/day (150 lb/hr and 1500 lb/day for CO).[9]

The guidelines also contain a "trade-off" provision, which permits the approval of a proposed (new) source if it is coupled with the cleanup of existing (old) sources, so that net effect is beneficial. This may become a technique of great importance in areas where new development would otherwise be prevented in the light of mandatory air quality goals.

2.4 Air Quality Maintenance Areas

EPA regulations (40 CFR 51.12) require that SIPs provide for the identification of potential air quality maintenance areas (AQMAs): regions where the NAAQS are not predicted to be met or maintained by 1977 and/or where growth and development between 1975 and 1985 may cause deterioration of air quality to levels below the NAAQS. The EPA has designated eight of the State proposed areas as AQMAs** (see Fig. 2-2).

State agencies are to perform a detailed analysis of the future air quality of each AQMA, with specific attention to each pollutant which prompted designation of the AQMA. If the results of these analyses confirm

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*These APCDs are: Great Basin, Unified, Lake County, Monterey Bay, Del Norte, Humboldt, Mendocino, Trinity, Sacramento, San Diego, San Francisco Bay Area, Southern California (not necessarily approved by the EPA).[8]

**They are the South Coast Air Basin, the San Francisco Bay Area Basin, the San Diego Air Basin, The Sacramento Metropolitan Area, San Joaquin and Stanislaus counties, Fresno county, the valley portion of Kern county and the Riverside-San Bernadino Area.

that a primary or secondary NAAQS will not be maintained through 1985 or achieved by 1980, the State is required to develop and submit to the EPA a long-range plan to bring about and maintain compliance with that NAAQS as soon as is feasible. In California, the ARB is responsible for developing these long-range Air Quality Maintenance Plans (AQMPs). They may involve technological control of both mobile and stationary sources, as well as transportation and land use controls.[2,10]

2.5 Prevention of Significant Air Quality Deterioration

The Federal Program

The air in some areas of the United States is of higher quality than mandated by the NAAQS. To prevent potential exploitation of such areas, in 1974, the EPA promulgated regulations (40 CRF 52.2) providing for the protection of air with higher quality than the limits specified by secondary NAAQS for concentrations of sulfur dioxide (SO_2) and suspended particulate matter. These Prevention of Significant Air Quality Deterioration (PSD) regulations provide for the classification of all areas of each state as Class I, II, III, or exempt, each reflecting different societal, economic and environmental goals.

Class I and II areas are limited to certain additional increases in ambient pollutant concentrations over baseline air quality levels. Table 2-3 shows these allowable increases. The baseline levels are the SO_2 and particulate concentrations existing during 1974 plus the additional concentrations estimated to result from sources granted approval for construction but not operating prior to January 1, 1975.[11] Air quality in Class III areas is allowed to deteriorate to the level of the secondary NAAQS for SO_2 and particulate matter. Areas where air quality exceeds the SO_2 or particulate NAAQS are exempt from the PSD regulation for that particular pollutant. In the initial PSD regulations, the EPA designated all areas of California as Class II.

The PSD regulations require review of proposed power plants and other stationary sources to determine compliance with the prevailing PSD standards for the area (or adjacent areas) in which the power plant would be built.[11] Any state or local agency can be delegated the responsibility for such review, but none in California has requested this authority.

Fig. 2-2. Air Quality Maintenance Areas (reproduced from ref. 2).

Table 2-3. Allowable Increases in Pollutant Concentrations over the Baseline Air Quality Concentrations as described in the Significant Deterioration Regulations.[a]

Pollutant	Class I* ($\mu g/m^3$)	Class II* ($\mu g/m^3$)	Class III ($\mu g/m^3$)
Particulate matter:			
Annual geometric mean	5	10	*
24-hour maximum	10	30	*
Sulfur dioxide:			
Annual arithmetic mean	2	15	*
24-hour maximum	5	100	*
3-hour maximum	25	700	*

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*Class I applies to areas in which practically any change in air quality would be considered significant. Class II applied to areas in which deterioration normally accompanying moderate, well-controlled growth would be considered insignificant. All values are allowable increases in pollutant concentrations over the baseline air quality concentration. Areas designated as Class III shall be limited to concentrations of particulate matter and sulfur dioxide no greater than national ambient air quality standards which are shown in Table 2-1.

[a] Reproduced from ref. 11.

the initial PSD regulations, the EPA designated all areas of California as Class II.

The PSD regulations require review of proposed power plants and other stationary sources to determine compliance with the prevailing PSD standards for the area (or adjacent areas) in which the power plant would be built.[11] Any state or local agency can be delegated the responsibility of such review, but none in California has requested this authority.

California Air Conservation Program

States may develop their own plans to prevent significant deterioration of air quality, but they must be at least as stringent as the federal program and be approved by the EPA. The ARB is currently developing an Air Conservation Program (ACP) to protect present superior air quality in certain areas, while permitting necessary, planned development in other areas. Although the ACP is being developed with the same goal as the PSD regulations, California's special requirements for maintaining air quality make it necessary to have a much broader program than the present PSD regulations.[2,5]

The EPA's PSD regulations only address two pollutants, sulfur dioxide and particulate matter. Sulfur dioxide is currently not one of the more significant pollutants in most of California. However, higher levels could occur if shortages of natural gas and low-sulfur oil result in greater use of higher-sulfur fuels. Such fuel switching is specifically exempted under the PSD regulations. Much of the particulate matter in California air comes from agricultural activities and wind-blown dust rather than from sources listed in the PSD regulations.

The pollutants of critical importance in California, photochemical smog and its precursors, are not covered in the federal regulations. Many of the 19 specific large industrial source categories covered in the PSD regulations are not now located in California. Many of the sources in California that are covered are located in urban areas which are exempted from PSD regulations. A significant exception to this exemption would be large, remotely-sited power plants.

The proposed ACP, in addition to fulfilling the specific requirements of the PSD regulations, will include all pollutants for which state and national standards exist and will cover all geographic areas of the state. The EPA has indicated that such a program would be acceptable, and therefore could supersede the federal PSD regulation.

The ACP will classify all areas of California into one of four categories, Class A, B, C, or D. Class A Air Conservation Areas (no significant deterioration areas) will be those areas where natural resource values clearly warrant the protection and preservation of existing superior air quality. Class A areas will probably be composed of national parks and monuments, national forest wilderness and primitive areas, and selected coastal areas and state parks, with the exception of those federal and state lands in the heavily polluted South Coast and Southeast Desert AQMAs. A list of potential Class A areas is given in Table 2-4.

Class B Air Conservation Areas (minimum deterioration areas) will be areas where some deterioration will be allowed, but where air quality better than existing standards will still be maintained. All the national forests within California, except those in Orange, Los Angeles, Riverside, and San Bernardino Counties, will probably be designated Class B areas. Other areas will be considered as additional criteria for Class B areas are established.

Class C Air Conservation Areas (agricultural areas) are regions where agriculture is a principal activity. In these areas, air quality sufficient to protect agricultural productivity will be maintained. Such regions as the Central and Imperial Valleys will probably be designated Class C areas.(9)

Class D Air Conservation Areas (urban/industrial areas) will be those areas of California where current State and National Ambient Air Quality Standards provide an adequate measure of protection and are consistent with the areas' present and anticipated use. In addition to urban and industrialized areas, all of the State's AQMAs are probable Class D areas. This could create a sizable amount of overlap between Class C and D areas since many agricultural areas are within designated AQMAs. Resolving the air quality needs in places where agricultural and air quality maintenance areas overlap is a major issue to be worked out during the development of the ACP.

The ARB will take the lead role in classifying the various areas of the State and implementing measures to ensure that ambient air quality in the different areas is maintained according to the ACP. Figure 2-3 shows a potential classification scheme for California under the criteria of the ACP.

Table 2-4. Partial List of National Parks, National Monuments, Wilderness Areas, Primitive Areas, and Large State Parks in California.[a]

AREA NAME		COUNTIES
Kings Canyon	National Park	Fresno, Tulare
Lassen Volcanic	National Park	Shasta, Lassen, Plumas
Redwoods	National Park	Del Norte, Mendocino
Sequoia	National Park	Tulare
Yosemite	National Park	Mariposa, Madera, Toulumne
Joshua Tree	National Monument	San Bernardino, Riverside
Lava Beds	National Monument	Siskiyou, Modoc
Death Valley	National Monument	Inyo, San Bernardino
Agua Tibia	Primitive Area	Riverside, San Diego
Caribou	Wilderness Area	Shasta
Desolation	Wilderness Area	El Dorado
Dome Lake	Wilderness Area	Tulare, Kern
Emigrant Basin	Primitive Area	Toulumne
High Sierra	Primitive Area	Fresno
Hoover	Wilderness Area	Amador, Calaveras
John Muir	Wilderness Area	Mono, Inyo, Madera, Fresno
Marble Mountains	Wilderness Area	Siskiyou
Minarets	Wilderness Area	Mono, Madera
Mokelumne	Wilderness Area	Amador, Calaveras
Salmon-Trinity Alps	Primitive Area	Siskiyou, Trinity
San Rafael	Wilderness Area	San Bernardino
South Warner	Wilderness Area	Modoc
Thousand Lakes	Wilderness Area	Lassen, Plumas
Ventana	Wilderness Area	Monterey
Yolla Bolly-Middle Eel	Wilderness Area	Trinity, Tehama
Anza Borrego	State Park	San Diego, Imperial
Cuyamaca Rancho	State Park	San Diego
Del Norte Coast Redwoods	State Park	Del Norte
Humboldt Redwoods	State Park	Humbolt
Jedediah Smith	State Park	Del Norte

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[a] Reproduced from ref. (5).

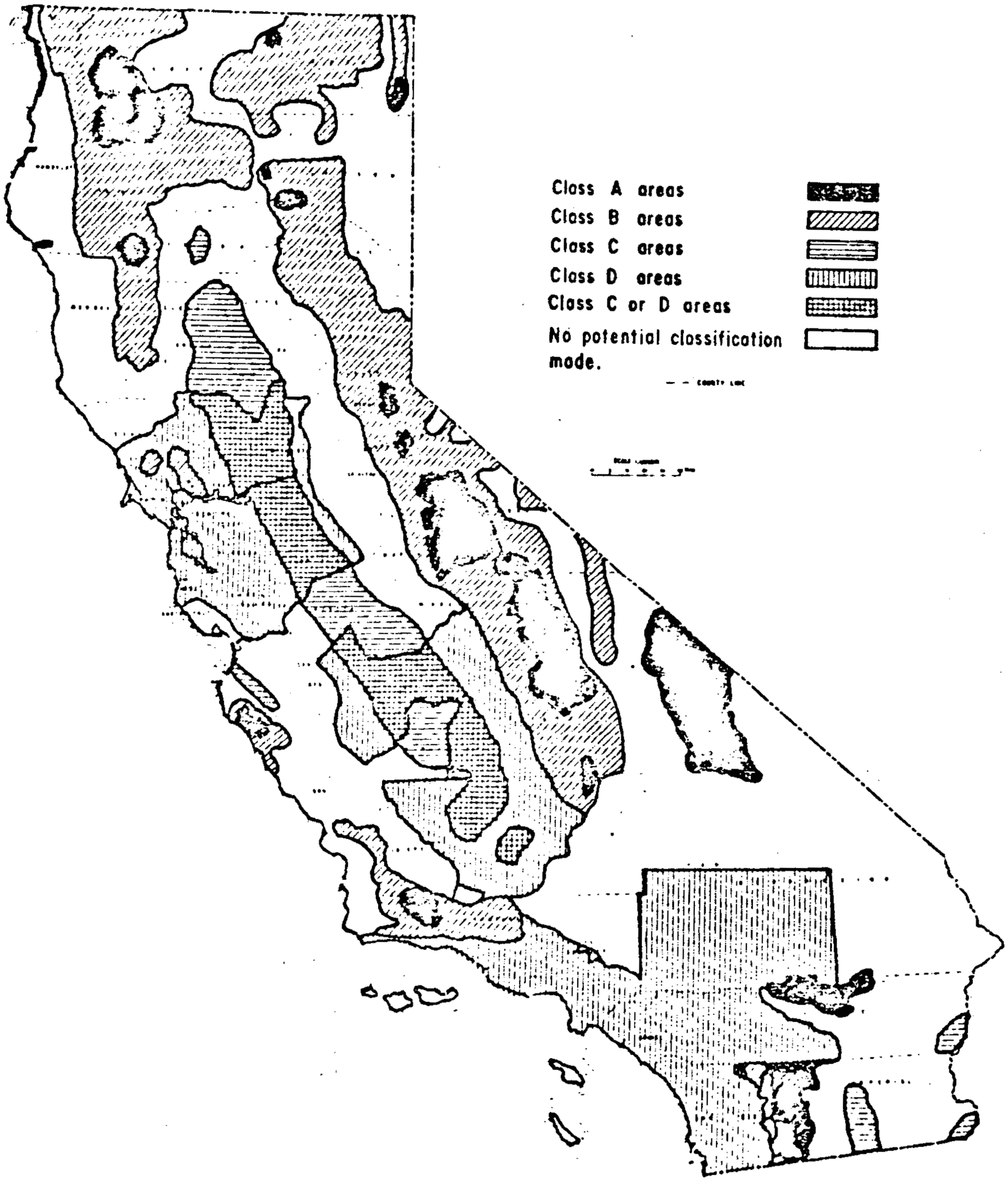

Figure 2-3. A Potential Classification of California for the Air Conservation Program (reproduced from ref. [5]). (This map does not indicate ARB policy nor is it proposed for consideration by the ARB. Rather it is an illustration prepared by the ARB staff to indicate how various areas could eventually be classified based on current land use and the four class scheme.)

2.6 Air Pollution Emergency Plan

Some urban areas of California frequently exceed the applicable AQS and have the potential for air pollution levels high enough to endanger public health. The California Air Pollution Emergency Plan(12) (APEP) sets forth the legal basis for dealing with such episodes of high pollution.

The local APCDs have the main responsibility for developing and implementing detailed plans to prevent air pollutant concentrations from reaching dangerous levels or to abate such concentrations should they occur. If an episode is so severe as to be beyond the capacity of the APCD to prevent or abate it, the state (ARB) shall take appropriate actions to alleviate the condition.

Table 2-5 shows the areas and the pollutants for which the APEP is applicable. Definitions of the various episodal stages are given on Table 2-6, and the pollutant concentrations at which the various episode stages are declared are given in Table 2-7. Actual instances of such episodes in California are given in Section 3.3.1.

The APEP spells out in detail the required responses of the ARB and the local APCDs. Abatement actions for each pollutant covered and for each episode stage are outlined. For example, sulfur dioxide related abatement actions include several which pertain to power plants*:

- requesting power plants to import additional power from outside the air basin,
- requiring electric utilities in the affected air basin to reduce the use of fuel oil for power generation by specified amounts, plus requesting electricity users to reduce their consumption,
- requiring all combustion sources to use natural gas, 0.1% sulfur fuel oil, or 0.25% sulfur fuel oil.

Additional actions include controlling other stationary sources, curtailing automobile travel, and restricting any energy-intensive or polluting activities.

Administrative actions required by the APEP include:

- issuing health warnings for sensitive persons in receptor areas,

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* Other types of episodes have associated actions which pertain, less specifically, to power plants.

Table 2-5. Areas in which the Air Pollution Emergency Plan is applicable.[a]

Area	Carbon Monoxide	Oxidant	Sulfur Dioxide	Sulfates
Bay Area APCD	X	X	X	X
Monterey Bay Unified APCD		X		
Ventura County APCD, the Southern California APCD and the South Coast Air Basin portion of the Santa Barbara County APCD	X	X	X	X
San Diego County APCD	X	X		X
Sacramento County and Yolo-Solano APCDs	X	X		
Fresno, Kern, Tulare, San Joaquin, Kings, Madera, Merced, and Stanislaus County APCDs	X	X		

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[a] Reproduced from ref. (12).

Table 2-6. Definitions of Air Pollution Episode Stages and Required Responses.[a]

Listed below in order of increasing air pollution severity are the episode stages at which specific actions are required.

A. Stage 1 Episode

A Stage 1 episode is declared when the concentration of pollutants specified for this stage is predicted or reached. Persons with respiratory or coronary artery disease should be notified to take precautions against exposure. Schools should be notified so they can curtail students' participation in strenuous activities. First steps in abatement action plans shall be undertaken.

B. Stage 2 Episode

A Stage 2 episode is declared when the concentration of pollutants specified for this stage is predicted or reached. Abatement actions shall be taken with a minimum of delay to reduce the concentration of the pollutant at issue.

This is an intermediate stage. Abatement actions needed will vary depending on circumstances; e.g., maximum concentrations and duration.

C. Stage 3 Episode

A Stage 3 episode is declared when the conditions specified for this stage are predicted or reached. Extensive actions shall be taken to prevent exposure of people to pollutant concentrations of the indicated levels.

D. Air Pollution Disaster (State of Emergency)

When it is determined by medical authorities or local officials that a substantial number of persons are suffering or are to suffer incapacitating effects from air pollution, regardless of measured pollutant concentrations, and analysis of meteorological and air quality data by the ARB or an APCD indicates that the condition is likely to continue, or recur, the Chairman of the ARB (the Secretary of the Environmental Quality Agency if and when established) shall confer with the Director of the Office of Emergency Services (OES) and they shall jointly recommend to the Governor that an air pollution disaster (State of Emergency) be declared.

E. Episode Termination

An episode is terminated whenever the concentration of the pollutant(s) which causes the declaration of such episode has been verified to have fallen below the criteria level for the declaration of the episode, and analysis of meteorological and air quality data indicates that the pollutant concentration is expected to decrease.

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[a] Reproduced from ref. (12).

Table 2-7. The Air Pollution Concentration Criteria for Various Episode Stages.[a]

	Averaging Time	Stage 1	Stage 2	Stage 3
Oxidant, as Ozone	1 Hour	0.20 ppm	0.35 ppm	0.50 ppm
Oxidant, in Combination with Sulfur Dioxide	1 Hour	0.20 ppm*	0.35 ppm*	0.50 ppm*
Carbon Monoxide	1 Hour	40 ppm	75 ppm	100 ppm for one hour and predicted to persist for one additional hour
	12 Hours	20 ppm	35 ppm	50 ppm
Sulfur Dioxide	1 Hour	0.5 ppm	1.0 ppm	2.0 ppm
	24 Hours	0.2 ppm	0.7 ppm	0.9 ppm

Sulfate, in Combination with Oxidant	24 Hours (Sulfate)	$25\ \mu g/m^3$
	1 Hour (Oxidant)	0.20 ppm

[*] These levels shall apply when the oxidant concentration and the sulfur dioxide concentration each exceeds 0.10 ppm, one-hour average, and shall be determined by adding the oxidant and sulfur dioxide concentrations.

If excessive concentrations of pollutants for which criteria have not been established occur or are predicted to occur, appropriate abatement actions shall be taken by the affected APCD after consultation with the ARB.

(Underlined portions indicate the latest revision, November 24, 1976.)

[a] Reproduced from ref. (12).

- advising schools that strenuous activities by students must be discontinued,
- notifying various officials and organizations, and the news media
- monitoring meteorological and air quality data
- suspending programs which involve physical exertion by participants using public parks or public recreational facilities. Professional sports activities are excepted.
- inspecting pollutant sources.

Under normal circumstances, emission standards applying to power plants remain at constant levels. But under emergency situations it may be necessary to reduce emissions substantially from the levels specified in these standards. Episode control strategies implementing such emergency emission reductions could have a major impact on power generation.

One response to mandated reductions would be to decrease the amount of electricity generated inside the affected air basin, while increasing the amount generated outside. This requires an integrated generating system spanning several air basins, a possibility with a large utility or with several utilities in a "power pool." A second possible response would be the installation of intermittent controls, to be used under emergency conditions. The feasibility of this option depends on the cost of installation and maintenance of such equipment. A third solution would be to have the capability of burning clean fuels such as natural gas or very low sulfur fuel oil. Fuel oil, if chosen, would have to be stockpiled in storage tanks at the plant.

Power plants built in areas that are prone to episodes of high pollution might be required to participate in a power pool to have intermittent controls, or to be able to burn natural gas or 0.1% sulfur fuel oil.

2.7 Water Quality Standards

Although water is one of man's most valuable resources and, throughout much of recorded history, these resources have deteriorated through his use, it is only in the industrial age that much attention has been given to safeguarding water quality. It was not until the nineteenth century that western man has seriously considered purifying it. The first municipal water filtration plant was built in Paisley, Scotland in 1800. The U. S. Federal government first expressed its interest with the Harbor Act of 1899.[13] Today there is a proliferation of water standards.

Standards are established on three levels: federal, state, and local. In California, the strictest regulation has precedence. The standard-setting agency for the federal government is the Environmental Protection Agency (EPA), although the U. S. Geological Survey may also suggest methods for identifying and measuring pollutants. The Federal enabling legislation is the Federal Water Pollution Control Act as amended in P.L. 92-500 (conventional pollutants) and the Atomic Energy Act of 1954 (radioactive pollutants). The regulations for conventional pollutants are contained in 40 CFR, parts 423 (Effluent Guidelines and Standards), 122 (Thermal Discharges - possible variances), 401, 402 (Cooling Water Structures, 146 (Underground Injection Systems - proposed), and 128 (Pretreatment Standards). The standards for radioactive pollutants, administered by the Nuclear Regulatory Commission (NRC), are found in 10 CFR Part 20, sections 20.106, 20.303, 20.304, and Appendices B and C.

California State standards are administered by the State Water Resources Control Board (WRCB), jurisdictions being set by the Porter-Cologne Water Quality Control Act and the Health and Safety Code. The standards are defined in the California Administrative Code, Title 23, Subchapter 15, and the Water Quality Control Plans (WQCPs). Three of the WQCPs which are pertinent to electrical power generation are:

1. WQCP Policy on the Use and Disposal of Inland Water Used for Powerplant Cooling, June 1975.
2. WQCP-Ocean Waters of California, July 1972.
3. WQCP for Control of Temperature in the Coastal and Interstate Waters and Enclosed Bays and Estuaries of California.

In addition, there are 16 major hydrologic basins in the state, each with a control plan.

Under direction of Assembly Bill 1575, section 25216.5, the ERCDC has compiled this multitude of regulations in Piekarz et al., Compilation of Water Quality Standards Applicable in California.[14]

The numerous pollutants which are governed by the regulations and standards may be categorized as:

- Physical and Chemical (including pH-hydrogen ion concentration measure, metal ion concentrations, turbidity, alkalinity, concentrations of phosphorus, sulfur, etc.).
- Bacteriological Characteristics- i.e., fecal coliform and coliform count primarily.
- Biological Characteristics - concerning biota and ecosystems.
- Thermal.
- Toxicological.
- Radioactive.

Water quality standards govern both ambient water quality and effluent streams. Regulations regarding ambient water quality are termed "water quality objectives" or "receiving water" standards. Those which govern the adulterants in a waste water stream are called "effluent" or "discharge" regulations. Concurrent with the regulations concerning the pollutants in the water are suggested methods for determining the amounts of those pollutants.

The water governed by these standards may be categorized in several ways. The federal regulations initially make a distinction between industrial and municipal waste water and drinking water. The criteria documents[15-18] which establish recommended limits for receiving waters divide the various waters by usage: recreational or beneficial uses, public water supplies, water for use by freshwater or marine life and wild life, agricultural uses, and industrial uses.[15] The receiving waters may also be described as fresh water (ground and surface) or saline (including ocean waters, bays, and estuaries). These last categories help to determine the background levels necessary for monitoring, to establish compliance or non-compliance with the standards.

Initially, compliance was determined by tedious sampling and chemical tests performed on the samples. Today, sophisticated systems exist for continuous analysis or sampling followed by instrumental analysis. The methods of analysis commonly used are described in Standard Methods for the Examination of Water and Waste Water.[19] Instrumental techniques and monitoring equipment are described in Instrumentation for Environmental Monitoring, Vol. 2, Water.[13]

The problem of water pollution as applied to electrical power generation is discussed in the Development Document for Effluent Limitations Guidelines and New Sources Performance Standards for the Steam Electric Power Generating Point Source Category.[20] It describes fully the sources of pollution throughout a facility, the chemicals involved throughout the process of power generation and the control equipment that can be used to meet the standards, and serves as the basis for the discussion of section 3.1.1.6.

While the regulations and standards may be costly in some cases, their requirements appear to be achievable, particularly in the case of electric generating facilities. Furthermore, they seem to be serving their purpose, at least to some extent; in many cases, substantial improvements in water quality have been noted.

2.8 Noise Standards

Noise is commonly defined as unwanted sound. At an electrical power generating facility noise can be generated by the basic generation unit, along with all the peripheral aspects of the plant, particularly the transmission lines. In regulating the noise associated with a power plant one must consider both the occupational noise (that experienced by the workers, governed by OSHA standards) and community noise (experienced by the surrounding population and legally starting at the property line).

The Walsh-Healy Act, which regulates noise levels in industries with federal contracts, sets maximum noise exposure limits. These OSHA standards are included in Table 2-8. They were initially established to prevent permanent hearing damage. Currently, there is some attempt to prevent the other physiological or psychological conditions which can result from excess noise, such as stress and loss of work function, by establishing a stricter guideline.[21]

Table 2.8. Federal Occupational Safety and Health Administration Maximum Permissible Noise Levels.

PERMISSIBLE NOISE EXPOSURES[b]

Duration Per Day (hr)	Sound Level Slow Response (dBA)
8	90
6	92
4	95
3	97
2	100
1-1/2	102
1	105
1/2	110
1/4	115

b. When the daily noise exposure is composed of two or more periods of noise exposure of different levels, their combined effect should be considered, rather than the individual effect of each. If the sum C1/T1 + C2/T2 = Cn/Tn exceeds unity, then the mixed exposure should be considered to exceed the limit value. Cn indicates the total time of exposure at a specified noise level, and Tn indicates the total time of exposure permitted at that level.

b. From Ref. 22.

The EPA has established community noise limitation standards in EPA Document No. 550/9-74-004 (March 1974), and recommended that noise levels at the property line should not exceed 55 decibels (dBA) from the onset of construction and station operation activities.[22]

In addition, there are a multitude of community standards. They may be found at the State Office of Noise Pollution or at the local community agencies. Establishing community noise regulations differs from establishing occupational standards in two important respects. First, in considering health impact, one must consider a possible 24 hr. exposure, including time sleeping. The worker who can listen to 90 dBA all day may not be able to sleep with sound levels as low as 35 dBA. The ear appears to be able to recover from an 8 hr. exposure to 90 dBA but the ears of the person living next to a power plant may not have a chance to recover. Secondly, a community can choose not to permit a noisy environment - no matter what the physiological impact. In this case, they may enact the important catch-all, the nuisance regulation. (A typical regulation is given in Table 2-9.)

Methods for monitoring noise and the problems involved are discussed in the Air volume of LBL's Survey of Instrumentation for Environmental Monitoring.[23]

See section 3.1.1.2 for a very brief discussion of noise generated by power plants. The potential health impacts of noise are not treated in this report.

Table 2-9. An Example of a Public Nuisance Noise Ordinance.[a]

SEC. 3-1.01 UNNECESSARY NOISES. Every person using any mechanical instrument or device for the intensification of any sound or noise into the public streets; or who attaches any cans, bells, pans, iron or other metal or noise producing attachment to any vehicle for the purpose of producing unnecessary noise; or who blows any bugle, horn, whistle, or beats any drums, or rings any bells, or makes any other loud, unusual or unnecessary noise for the purpose of advertising, announcing or otherwise calling attention to any goods, wares or merchandise, or for the purpose of advertising, announcing, or calling attention to any show, entertainment or event; or who makes any unnecessary noise which disturbs the peace, and the producing of such noise is alone the object to be attained, is guilty of a misdemeanor.

SEC. 3-1.02 PERSISTENT NOISES A NUISANCE. The persistent maintenance or emission of any noise or sound produced by human, animal or mechanical means, between the hours of 9 p.m. and 7 a.m. next ensuing, which, by reason of its raucous or nerve-racking nature, shall disturb the peace or comfort, or be injurious to the health, of any person shall constitute a nuisance.

Whenever the existence of any such nuisance shall come to the attention of the Health Officer, it shall be his duty to notify in writing the occupant of the premises upon which such nuisance exists, specifying the measures necessary to abate such nuisance, and unless the same is abated within forty-eight (48) hours thereafter, the occupant so notified shall be guilty of a misdemeanor, and the Health Officer shall summarily abate such nuisance.

SEC. 3-1.03 NOISES. EXCEPTIONS. Nothing in Sections 3-1.0. and 3-1.02 of this Article shall apply to the playing of music by a band or the blowing of a bugle, or the announcing of any show, entertainment, or event upon the public streets for which band music, bugle blowing or privilege of announcing, the Chief of Police of the City of Oakland has granted a special permit specifying the time and place when and where such music may be played or such bugle blown, or shall apply to the blowing of any whistle or horn or the ringing of any bell or other noise necessary as a vehicular traffic warning or signal; or to any regularly licensed peddler calling his wares in an ordinary tone of voice, or ringing a bell or blowing a horn of moderate size in front of the residence of any customer of such peddler for the purpose of announcing the presence of such peddler; or to any public celebration or public function on a public holiday or other public occasion generally celebrated.

[a] Reproduced from the Oakland Municipal Code: Chapter 3, Public Welfare, Morals and Policy, Article 1 Public Nuisances.

References for Section 2

1. L. C. Rosen, "A Review of Air Quality Modeling Techniques," Lawrence Berkeley Laboratory Report LBL-5998, 1977.

2. "Compilation of Air Pollution Control Regulations and Standards," staff draft report, California Energy Resources Conservation and Development Commission, Facility Siting Division, June 8, 1976.

3. Clean Air Act (CAA) (42 U.S.C. 1857 et seq.), which includes the Clean Air Act of 1963 (P.L. 88-206), and amendments made by the Motor Vehicles Air Pollution Control Act (P.L. 89-272, October 20, 1965), The CAA Amendments of 1966 (P.L. 89-675, October 15, 1966), the Air Quality Act of 1967 (P.L. 90-148, November 21, 1967), the CAA Amendments of 1970 (P.L. 91-604, December 31, 1970), the Comprehensive Health Manpower Training Act of 1971 (P.L. 92-157, November 18, 1971), and the Energy Supply and Environmental Coordination Act of 1974 (P.L. 93-819, June 22, 1974).

4. Mulford-Carrell Act, Division 26, Health and Safety Code (added by Stats. 1967, Ch. 1.545 and amended 1970, 1972, and 1974), State of California

5. Plan Development Program for an Air Conservation Program for California, Air Resources Board, September 1976.

6. Samuel J. Williamson, Fundamentals of Air Pollution, Addison-Wesley Publishing Co., Menlo Park, 1973.

7 Environmental Protection Agency, New Source Performance Standards, 40 CFR, part 60, December 23, 1971.

8. Information supplied by the staff of the California Air Resources Board.

9. Public Hearing to Review and Consider Amendment or Adoption of New Source Review Rules for the Southern California Air Pollution Control District.

10. The State of California Implementation Plan for Achieving and Maintaining the National Ambient Air Quality Standards, Revision 5: Identification of Air Quality Maintenance Areas, Air Resources Board, June 13, 1974.

11. Environmental Protection Agency, Prevention of Significant Deterioration, Regulations, 40 CFR, part 52.2, December 5, 1974.

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12. *Air Pollution Emergency Plan*, Air Resources Board, adopted November 13, 1973.

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14. E. Piekarz, S. Leung, F. Hahn, *Compilation of Water Quality Standards Applicable in California*, Staff Draft, Facility Siting Division, Energy Resources Conservation and Development Commission, June 15, 1976.

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16. *Water Quality Criteria*, Report of the National Technical Advisory Committee to the Secretary of the Interior, Federal Water Pollution Control Administration (1968), available from U.S. Government Printing Office, Washington, D.C. 20402.

17. National Academy of Sciences, National Academy of Engineering for the Environmental Protection Agency, *Water Quality Criteria*, EPA-R3-73-033-March 1973, Environmental Protection Agency.

18. U. S. Environmental Protection Agency, *Quality Criteria for Water*, EPA-440/9-76-023, Environmental Protection Agency, Washington, D. C., 20460.

19. American Public Health Association, *Standard Methods for the Examination of Water and Waste Water*, 14th Ed., Washington, D.C. 20036, 1976.

20. United States Environmental Protection Agency, *Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Steam Electric Power Generating Point Source Category*, EPA 440/1-74 029-a, Group I, October 1974.

21. U.S. Environmental Protection Agency, *Public Health and Welfare Criteria for Noise*, EPA Document No. 550/9-73-002, July 27, 1973.

22. Allen-Warner Valley Energy System, (Preliminary Environmental Assessment Document, Vol. IV), Harry Allen Station, (Proposed by the Los Angeles Department of Water and Power and others), September 1975.

23. Environmental Instrumentation Group, *Survey of Instrumentation for Environmental Monitoring*, *Publication LBL-1*, Vol. 1, AIR, Lawrence Berkeley Laboratory, June 1976.

3. POWER PLANT EMISSIONS AND DISPERSION

The bulk of non-nuclear electric generation in California is accomplished by the combustion of oil and gas in fossil-fuel fired power plants, with lesser output from hydroelectric and a few geothermal steam plants. The emission of pollutants from these plants into the surrounding air and water supplies poses the most direct threat to public health and welfare from such power generation. To a great extent, these emissions are an unavoidable aspect of combustion or of geothermal energy utilization. Only the quantities of the pollutants emitted are subject to control.

Fossil fuels consist of varieties of carbonaceous-organic decayed matter that have accumulated over several geological eons and exist today in the form of either natural gas, petroleum, coal or coal precursers. Natural gas consists primarily of methane (CH_4) with lesser amounts of higher alkanes such as ethane (C_2H_6), propane (C_3H_8), etc. In addition, natural gas out of the well may contain up to 50% hydrogen sulfide (H_2S) and ammonia (NH_3); however, these gases are generally removed prior to distribution and combustion.

Crude petroleum is a suspension of alkanes, tars, and minerals. It is usable as commercial-grade fuel only after fractional distillation. The distillation products commonly include gasoline, petroleum ether, kerosene, paraffins, fuel oil, other distillates (used generally as solvents), and asphalt tars. Only the fuel oil fraction is used as a fuel in steam electric generators. Fuel oil contains a mixture of hydrocarbons (alkanes: C_nH_{2n+2}, where $n \geqslant 30$), as well as heteroatomic organic compounds such that the total nitrogen content may reach 5% weight, and organic sulfur content between 0.1% and 8% of the total weight. Fuel oil also contains trace amounts of many other elements and minerals. Many of these inorganic constituents exist in sufficiently volatile form to pass over in significant amounts into the fuel oil distillate fraction, and are invariably present in residual fuel oil (residue).

Coal is a class of solid carbonaceous materials. It can exist in several mineralogical grades including anthracite (the hardest form), bituminous (soft coal), lignite, and sub-lignite forms such as peat. Like fuel oil, coal contains fixed nitrogen and sulfur species in concentrations ranging from 0.1-8% weight, as well as variable levels of minerals. Unlike fuel oil, however, these inorganic elements do not necessarily exist in a volatile organic form. The carbon in coal also differs from fuel oil in that very little hydrogen is associated. In fact, most of the carbon in coal exists as combinations of polynuclear aromatic hydrocarbons (PAH), asphaltenes, and graphite. The softer grades of coal generally tend to contain less elemental carbon and more carbon as organic compounds.

The type of fuel used governs the combustion conditions that can be employed. These conditions have a major impact on how much and what types of pollutants are emitted into the surrounding air and water. Fuel oil combustion, for example, usually occurs at higher temperatures than does the burning of (powdered) bituminous coal. Higher combustion temperatures, as a rule, mean higher levels of nitrogen oxides (NO_x) emitted, but lower emissions of carbon monoxide (CO) and particulates. Methane in natural gas can burn with the hottest flame temperature of any fossil fuel. In general, however, all fossil-fuel combustion processes will generate technology-characteristic levels of sulfur oxides (SO_x, mostly sulfur dioxide SO_2), NO_x, CO, metal vapors such as mercury (Hg) and selenium (Se), and particulate matter. General characteristics of these emissions are discussed in section 3.1.1, while the degree to which they are emitted from particular types of plants is treated in section 3.1.2 and following.

Sulfur dioxide is an important emission product of coal-fired and oil-fired steam generating plants largely because of the organic sulfur found in the initial fuel. While other sulfur compounds such as sulfates may occur in air and water, the primary sulfur emissions are almost exclusively SO_2. In the absence of effective emission control procedures, coal and oil-fired power plants can account for as much as 70% of the SO_2 emissions in a community. Fuel gas desulfurization by means of either wet or dry scrubbing can remove up to 97% of the SO_2; however, unless care is taken to prevent leaching of the resultant sludge, these measures may merely transfer the discharge of sulfurous species from the air to the water supplies. Natural gas-fired power plants do not emit significant quantities of SO_2 because nearly all of the gaseous sulfur (as hydrogen sulfide, H_2S) is removed from the fuel prior to combustion.

Nitrogen oxides (NO_x) result from nearly all known types of combustion processes. At temperatures above 800°C, a significant portion of the fixed nitrogen in the fuel is converted to nitric oxide (NO). In addition, NO_x emissions from power plants and other high-temperature (> 1100–1500°C) combustion processes can arise from the oxidation of nitrogen gas (N_2) in air to give NO. In California, electric power generation accounts for about 11% of total NO_x

emissions, and only about 20% of the NO_x emissions from all stationary sources. Aside from regulating conditions in the combustion zone, there is presently no technology available for curbing NO_x emissions by more than about 30%, although some promising methods are under development.

Carbon compounds, when burned completely, exit the combustion zone in the form of carbon dioxide (CO_2). However, there is invariably a fraction of the exhaust gas in which the carbon was not completely oxidized, so that the exhaust contains some carbon monoxide (CO). Because of the very efficient combustion conditions associated with most fossil-fuel fired electric power generation, very little CO is produced. In general, power plants account for barely 1% of the total CO emissions in California. However, if any low temperature combustion processes are incorporated into electric power plants, the rate of CO emissions will increase. In addition to CO, incompletely burned carbon can also exit in the form of carbonaceous particulates or soot. Relatively little is now known about soot particles from power plants, as discussed below.

Particulates from fossil-fuel fired power plants have historically been studied in two categories - mineral ashes and soot. Mineral ashes occur in both the bottom ash fraction, which is removed with water in a slurry, and fly ash, which escapes into the air. Coal ashes frequently contain silicates, aluminates, and alkali metal oxides and carbonates which, because of the high temperature of combustion, have fused into glasses. The occurrence of trace metals such as vanadium, iron, chromium, lead, manganese, nickel, etc. in the ash fractions has been extensively documented. However, very little is known about either the physical or chemical form in which these elements exist. Carbonaceous particulates (soot) have been analyzed primarily for total carbon or for polynuclear aromatic hydrocarbons (PAH), without much regard for their relationship to the minerals in the ash fractions.

Particulates generated from combustion processes are not homogeneous. Consequently total particulate mass (TSP) is a poor indicator of the pollution potential or the community health risk from fossil-fuel fired boilers. Typically, particulates from boilers show a biomodal size distribution spectrum with mass modes at 0.2-1.0 μm and >10 μm. Obviously the physiological effects of 0.2-1.0 μm particles are very different from those of the 10 μm particles, especially since the smaller sized particles penetrate into the deep lung spaces whereas the larger particles do not. In addition, the chemical compositions of the two size modes of particles differ, as do their surface properties.

If one considers particulates on a total mass (TSP) basis, then the total particulate emissions from coal-fired power plants, if uncontrolled, would be approximately ten times those from oil-fired plants with the same generating capacity. However, most of the particulate mass from coal-fired plants lies in the 10μm size range, while most of the total mass from an oil-fired plant is in the 1.0μm size range. Therefore, if one considers the emissions of respirable particulates, both coal-fired and oil-fired power plants emit similar quantities; nearly all of these respirable particulates are in the fine size fractions (< 1μm).

Particulate control devices are of several types; their particle removal efficiencies cover a wide range and depend heavily on particle size. The most commonly used method for particulate control today is the electrostatic precipitator, which is reported to be capable of removing some 98-99% of the total suspended particulate mass from a flue gas stream. Electrostatic precipitators, as well as nearly all other methods, are particularly effective in removing very large particles. Since these contain the bulk of the mass, efficiencies will be high even if nearly all of the smaller particles escape into the atmosphere. Collection efficiencies for electrostatic precipitators and most other devices fall off drastically for particles which are smaller than 1 μm in diameter, the respirable range. One notable exception to this behavior is the fabric filter or "baghouse." When properly conditioned, baghouse filters can remove particles smaller than 1 μm with 95% efficiency. Larger sized particles are also removed by the fabric filter, with efficiencies close to those for the electrostatic precipitator. Consequently, although very little is known about the physical and chemical properties of combustion-generated particulates, it is possible with existing technologies to control the particulate emissions of even the "dirtiest" fossil-fuel combustion processes.

Metal vapors are also emitted from certain types of electric power plants. Coal-fired plants characteristically generate significant amounts of airborne mercury (Hg) vapor, for which no control measures have yet been devised. Information on the impact of Hg from power plants is obscured by the uncertainties in the analysis of emissions from other natural and man-made sources. Selenium vapor, like Hg vapor, is also emitted from coal-fired plants, again with no available method for control. Oil-fired power plants also release these two elements. However, much more information is also needed to assess their impact realistically.

Possible fouling of local water supplies and aquifers by fossil-fuel and geothermal power plants may also constitute a significant problem. Prohibitions against the direct discharge of heat into lakes, rivers, and bays have forced the use of cooling towers or evaporation ponds. These procedures tend to result in accumulations of salts and sludges which have to be disposed without damaging the quality of local water sources. In addition, sulfur removal devices in power plants generate copious quantities of sludges which must, likewise, be safely disposed. Organic compounds are not presently a major source of concern in effluent water discharges from power plants as long as all wet scrubbing processes occur after combustion.

Geothermal power plants use underground heat reservoirs as a source of energy. Pollution problems can result from the transfer of heat from the reservoir to the surface, a transfer that utilizes either water or steam. Geothermal liquids generally contain high concentrations of mineral salts; geothermal steam is frequently rich in hydrogen sulfide (H_2S) and ammonia (NH_3). The amounts of these emissions depend heavily on the geothermal field. The pollutants associated with geothermal power production are discussed in section 3.2.

Dispersion of pollutants emitted from the stacks of power plants throughout the community presents a rather complex series of problems, discussed in section 3.3. Foremost of these are the chemical transformations of pollutants which occur in the atmosphere (section 3.3).

SO_2, for example, is converted into sulfuric acid mist (H_2SO_4) in the presence of water vapor at a rate which may range as high as 13% of the original SO_2 per hour, depending on meteorological conditions. H_2SO_4 aerosols are believed to be much more irritating and toxic than SO_2 alone, so that SO_2 emissions can have an even more serious impact on public health if the conditions favor conversion to H_2SO_4.

Likewise NO, which is itself only mildly toxic, can be oxidized in the atmosphere to the more dangerous nitrogen dioxide (NO_2). Further, during periods of intense solar radiation, as in the summer months, both NO and NO_2 interact with other pollutants in the photolytic cycle to generate atmospheric ozone (O_3), nitric acid (HNO_3), and other noxious oxidants. Of all air pollutants, ozone and oxidants have posed the most serious threat to public health in California, and several air pollution episodes have occurred in California in which public health and welfare were clearly endangered.

Gas-particle reactions are probably involved in many of these secondary conversion reactions of air pollutants. The ability of metal oxides or soot to catalyze the conversion of SO_2 to H_2SO_4, and the conversion of NO to HNO_3 or NH_3 and other nitrogenous species have all been demonstrated. Particulates are also thought to be involved in the photolytic cycle which produce O_3. Consequently, the control of particulates may be important for controlling oxidants. Particulate control may also be an effective means of slowing the oxidation of SO_2 to H_2SO_4. These questions are, however, controversial.

The effects of airborne and waterborne emissions from electric power plants should be considered in the context of what the people actually inhale or ingest as well as in terms of emissions from other sources. For example, while power plants may account for over half of the sulfur oxide emissions in California, it is doubtful that power plants contribute more than 1/9 to the atmospheric loading of NO_x. Furthermore, individuals in their own houses are frequently exposed to NO_x levels from ranges and furnaces that are much higher than those attributable to all outdoor community sources combined. Health risk assessments must therefore account for confined-space air quality as well as community emissions.

3.1 Fossil-Fuel Emissions

3.1.1 General Characteristics

The fossil fuels (coal, oil, and gas) are so named because of their origin from prehistoric organic matter. In order for the decayed fossil organisms to become coal, oil, or natural gas, the material must be sedimented rapidly - effectively removing carbon, hydrogen, oxygen, nitrogen, phosphorous, and sulfur from the elemental cycles in the biosphere. In addition to these major constituents, trace elements accumulated by the prehistoric organisms, as well as the elements present in the prehistoric sediments, find their way into coal and oil. The fates of these elements when coal, oil, and natural gas are burned represent the major portion of this discussion. We also note that additives to the fuel or to the treatment processes can contribute to emissions.

Because reduced carbon is the primary element in fossil fuels, the principal combustion product common to all is carbon dioxide (CO_2). CO_2 is not toxic to humans and animals in typical atmospheric concentrations, and is therefore not usually considered a pollutant. The only threat which might occur from global CO_2 accumulation is the possibility of weather modification due to a "greenhouse effect." In addition, combustion of fuel oil and natural gas releases copious quantities of water vapor (H_2O), as does coal combustion to a lesser extent. Water itself is non-toxic; however, it may affect weather and perhaps more importantly interact with other emissions. Large fossil-fuel power plant boilers employ high flame temperatures, resulting in highly efficient combustion of the fuel, and therefore in low carbon monoxide and hydrocarbon emissions since almost all of the carbon and hydrogen is oxidized to CO_2 and water.

Aside from this CO_2 and water, every other combustion product associated with fossil fuel-fired steam electric generation poses a potential hazard of one kind or another to human health. These typical products are discussed in the sections below. Primary pollutants, those which are formed directly in the flame, are discussed first, as the emissions from fossil fuel power plants. Secondary pollutants, which are products that form in the atmosphere from the original combustion emissions, are discussed in a subsequent section (3.3.3).

3.1.1.1 Sulfur Oxides (SO_x)

Sulfur is an essential element for all living organisms, utilized primarily in the form of sulfur-containing amino acids. Biological degradation of organic matter converts most of this sulfur to hydrogen sulfide (H_2S) and mercaptans. During the formation of coal and oil, the breakdown of amino acids is incomplete, and the pyrolysis which follows sedimentation converts the breakdown products into a host of reduced sulfur compounds, including H_2S. In natural gas, the prevailing form of sulfur is specifically H_2S. Typical concentrations of sulfur in coal and oil range from 0.1 - 5% or more. Natural gas from the well may contain as much as 50% H_2S (sour gas); however, the refined gas which is used for most purposes contains no more than 15.3 ppm (parts per million) by volume H_2S.[1]

Combustion of sulfur-containing fuels generates a mixture of H_2S,[1] sulfur dioxide (SO_2), and sulfur trioxide.[2-5] H_2S emissions generally occur during low-temperature combustion processes; at higher temperatures most of the H_2S is oxidized to SO_2.[1]

Ordinary combustion of fossil fuels forms SO_2 and SO_3 in a ratio of 30 to 1,[2] but in a ratio of 60 to 1 in power plants with controlled reaction conditions.[4] Sulfur dioxide oxidizes slowly in air to form SO_3 or, in the presence of water vapor, sulfuric acid (H_2SO_4) mist. Other forms of sulfates may ensue if ammonia (NH_3) or alkali metals are present. H_2SO_4 in the atmosphere assumes an aerosol form and can account for as much as 30% of the total particulate mass.[2] The sulfur oxides (SO_x) also react with the oxides of various metals to form the metal sulfites ($SO_3^=$) or sulfates ($SO_4^=$).[2,6] All of these substances in the atmosphere can be irritating, noxious, and toxic. Sulfates are now suspected to be particularly dangerous.[5] Atmospheric reactions of SO_2 are described in greater detail in section (3.3.3.2) below. The properties of sulfates and H_2SO_4 mists are discussed in greater detail in section (3.1.1.3.2) on particulates.

Several investigators have attempted to estimate the annual global emission and removal rates of sulfur oxides in the atmosphere (see Ref. 7 for a review). Man-made sulfur pollution (as SO_2) accounts for no more than 10% - 35% of the total world-wide SO_2 emissions. While anthropogenic sources have had no large impact on the global SO_2 level, which is on the order of 2 ppb (parts per billion) volume, local concentrations of SO_2 in urban atmospheres may be orders of magnitude higher.[2,7] In fact, nearly half of the SO_x emitted from man-made sources between 1968 and 1972 originated in the United States, and most of that in heavily populated areas.[7,8] Figure 3.1-1 shows annual emissions of conventional pollutants according to source as reported by the National Emissions Data System (NEDS) for 1972.[8] Fossil fuel-fired electric power plants accounted for 54% of the total SO_x emissions in the U.S. (Fig. 3.1-1A). Most of these emissions arise from uncontrolled or poorly controlled coal-fired plants in the Eastern U.S. Industrial processes and fuel combustion for heating purposes accounted for most of the balance of nationwide SO_x emissions. In contrast, controlled oil-fired and natural gas fired electric power plants emitted only 13.5% of the SO_x total in California (Fig. 3.1-1B). This difference is notable in view of the fact that the total per capita emissions of SO_x in California are only about 1/7 of the national average. On the other hand, Drivas and Shair[9a] have presented evidence that one power plant in the South Coast Air Basin increases the atmospheric concentration of SO_2 by 10 ppb over an area of 300 km^2. Their contention that the maximum 1-hour equivalent SO_2 concentration is no more than 130 ppb is possible, provided that prevailing winds can prevent a net accumulation of pollutants. Thus, even in California, individual power plants can have a significant impact on air quality.

Introduction of coal-fired power plants in California could certainly increase SO_x emissions, although this need not significantly decrease California air quality (see Fig. 3.1-2, or Ref. 9): with installation of appropriate SO_2 control devices, the impact of new coal-fired power plants on the atmospheric SO_x levels should not be significantly worse than for controlled oil-fired plants (Fig. 3.1-2).

The principal methods used to limit sulfur oxides emission are: a) use of low-sulfur fuels, b) fuel desulfurization prior to combustion, c) removal of sulfur oxides from gases after combustion, d) modification of the combustion process, e) (really a dispersion method) increasing stack height. Debate over which control technology offers the best promise of success has been heated during the past six years. The principal problem with either fuel desulfurization or stack gas desulfurization is the disposition of the solid or slurry waste products. Leaching of sulfites, sulfates, or other salts from the sludges into local water supplies is a possible hazard. Hence, measures which either isolate accumulated sludges from contaminating the environment or which recycle the sulfurous product must be incorporated into the design and operation of all coal-fired and oil-fired power plants. For further discussion of control measures, see sections (3.1.2) through (3.1.6).

3.1.1.2 Oxides of Nitrogen (NO_x)

Fossil fuels contain significant quantities of nitrogen, primarily as ammonia (NH_3) or reduced organic compounds (NR_3 = amines) formed from the incomplete denitrification of decayed organic matter. Typical concentrations of fixed nitrogen in fossil fuels range from 0.07% to 1.4% by weight in fuel oil, and 0.7% to 1.9% by weight in coal.[21] The emissions of nitrogen oxides from fossil fuel combustion arise not only from the nitrogen in the fuel, but also from nitrogen gas present in the air.

The nitrogenous products of fuel combustion depend heavily on the flame temperature, air pressure, and the flow rates of material through the flame. The products are primarily nitric oxide (NO), nitrogen dioxide (NO_2), or gaseous nitrogen (N_2), and typical reactions are given in Table 3.1-1. Since steam electric power generation utilizes very high flame temperatures ($>1700^\circ C$) in order to maximize the thermodynamic efficiency,[20] copious quantities of NO can be produced by oxidation of atmospheric nitrogen. It has been estimated[22] that in power plants at least 30-60% of the nitrogen in fuel oil and at least 18-25% of the nitrogen in coal becomes NO during combustion.

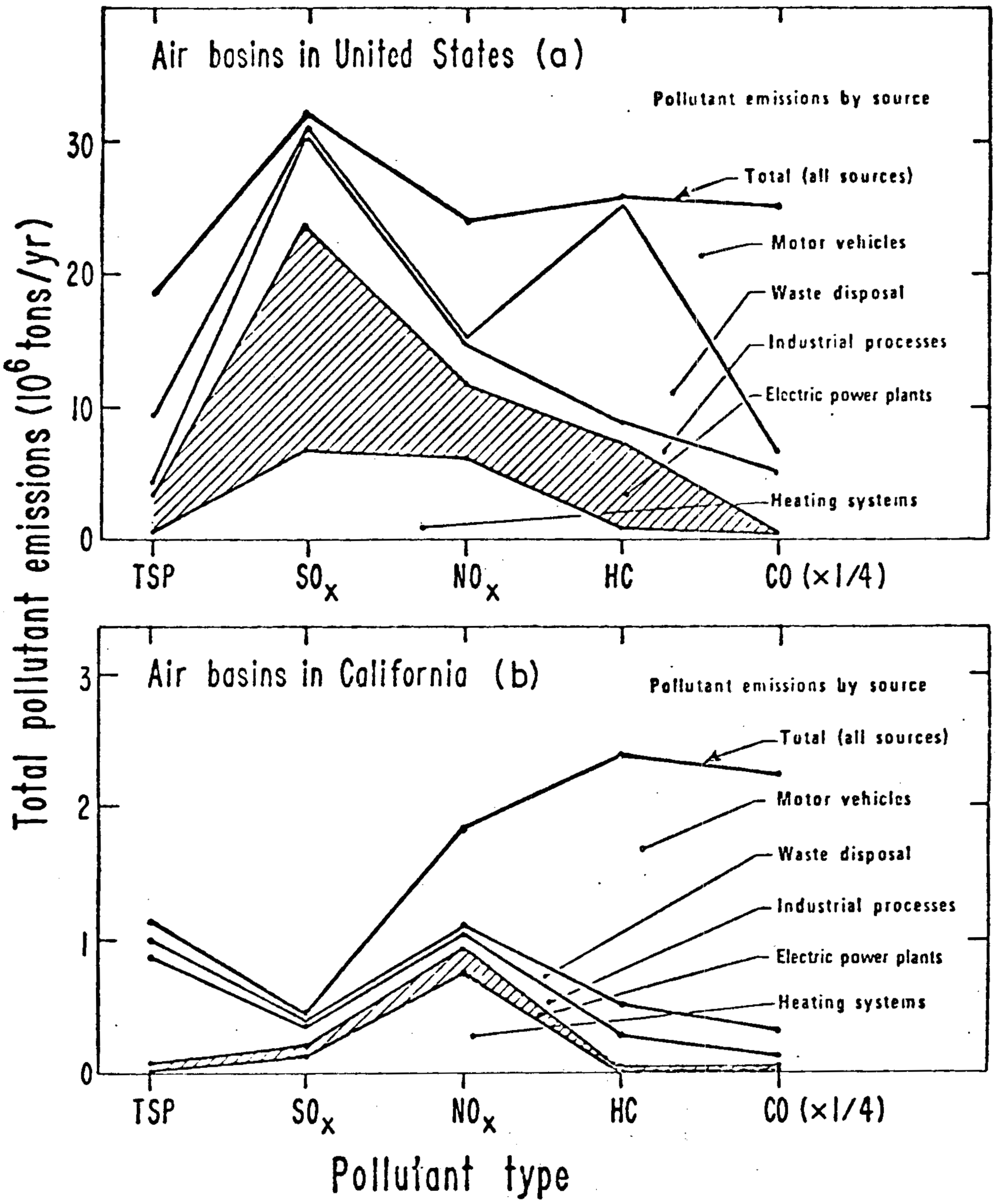

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Figure 3.1-1. Pollutant emissions (million tons/year) by source in 1972 (contributions from power plants are shaded): (a) Air basins in the United States; (b) Air basins in California; (c) South Coast Air Quality Control Region (AQCR); (d) San Francisco Bay Area AQCR; (e) Southeast Desert AQCR; (f) San Joaquin AQCR; (g) Great Basin Valley AQCR; (h) Northeast Plateau AQCR; (i) North Central Coast AQCR, (j) South Central Coast AQCR; (k) San Diego AQCR; (l) North Coast AQCR; and (m) Sacramento Valley AQCR. These emissions are based upon ref. 8.) TSP is the total suspended particles (mass), SO_x is all oxides of sulfur, NO_x is all oxides of nitrogen, HC is all hydrocarbons, and CO is carbon monoxide.

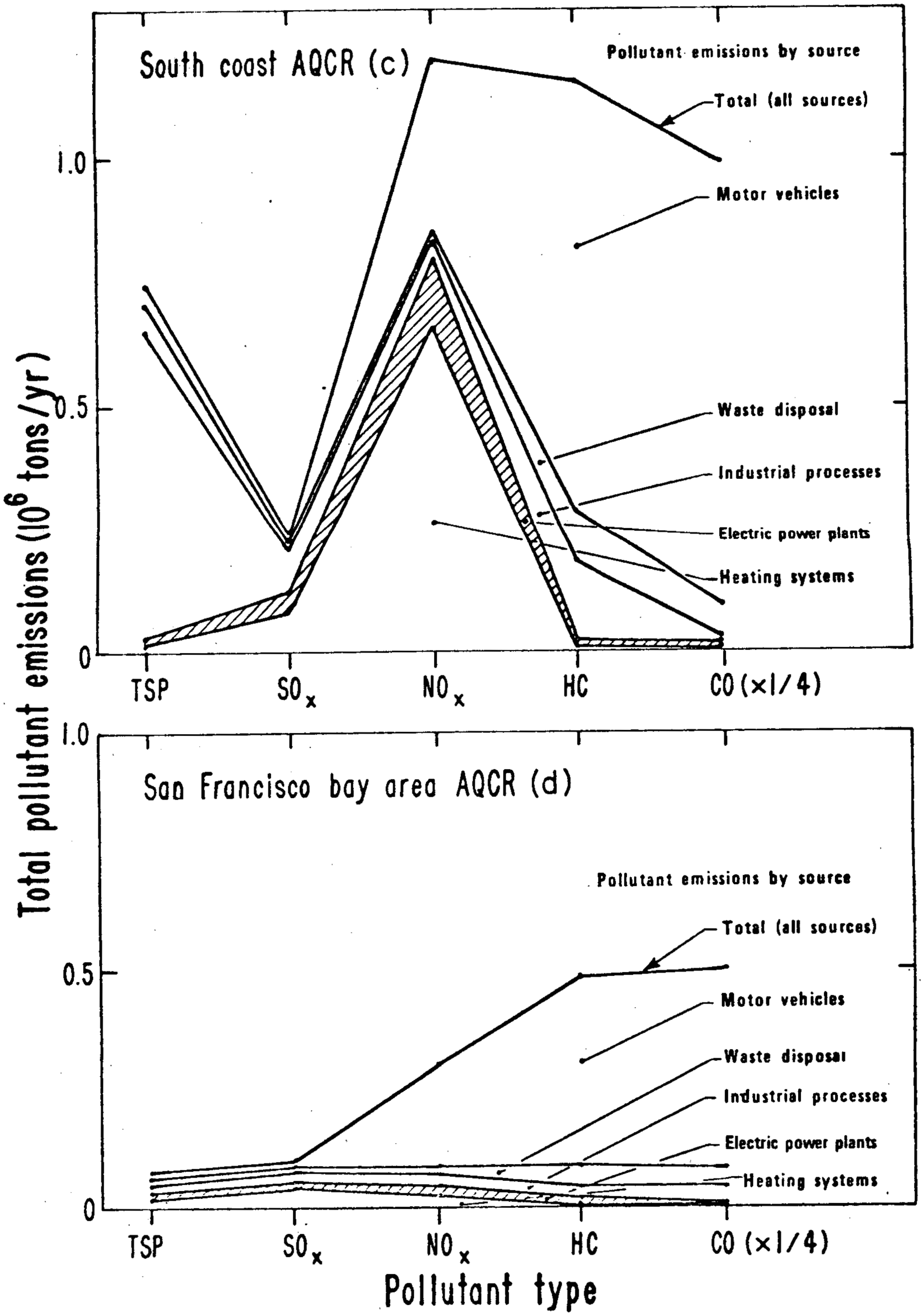

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Figure 3.1-1 (continued). (c) South Coast Air Quality Control Region AQCR; (d) San Francisco Bay Area AQCR;

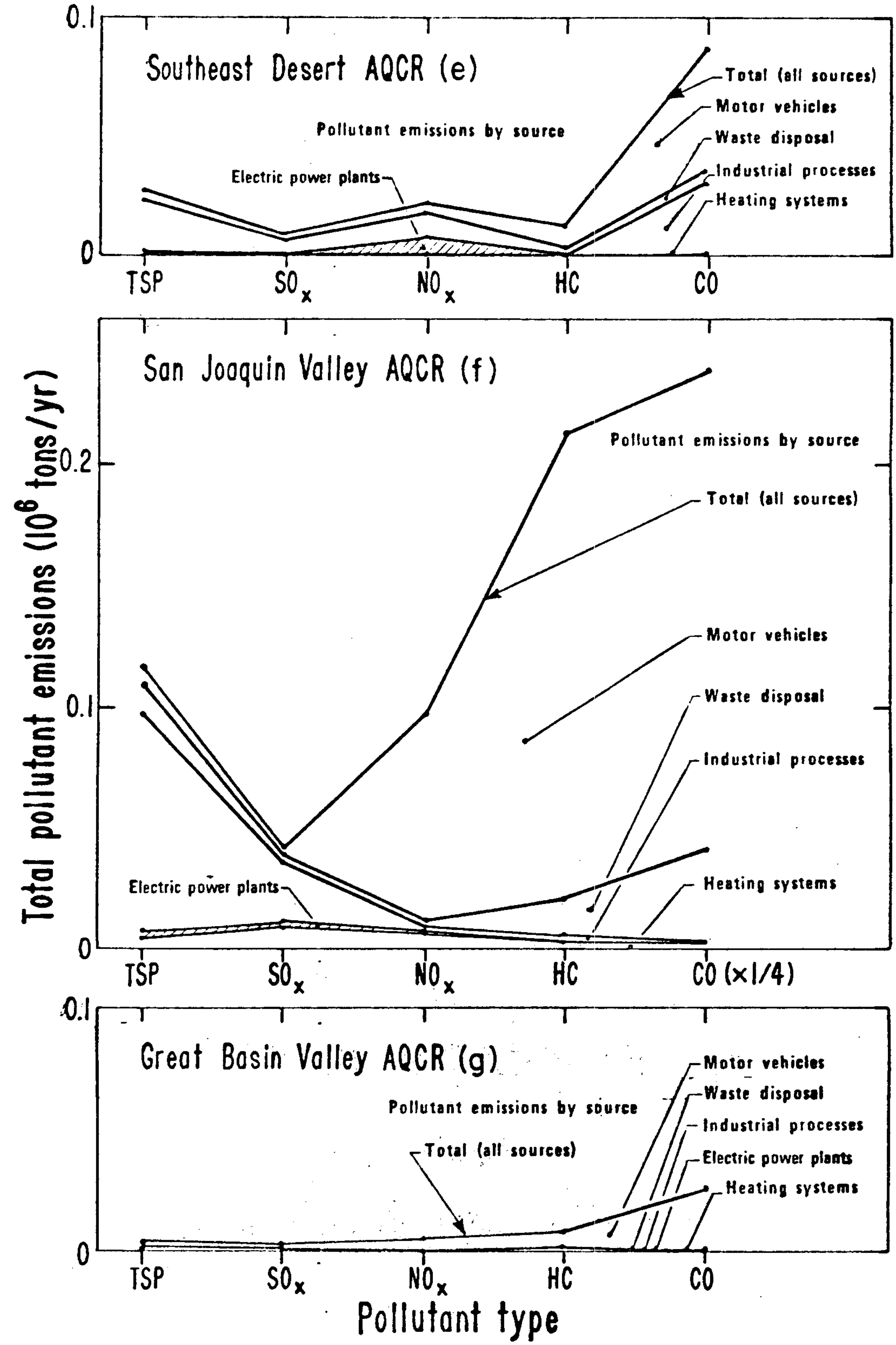

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Figure 3.1-1 (continued). (e) Southeast Desert AQCR; (f) San Joaquin AQCR; (g) Great Basin Valley AQCR;

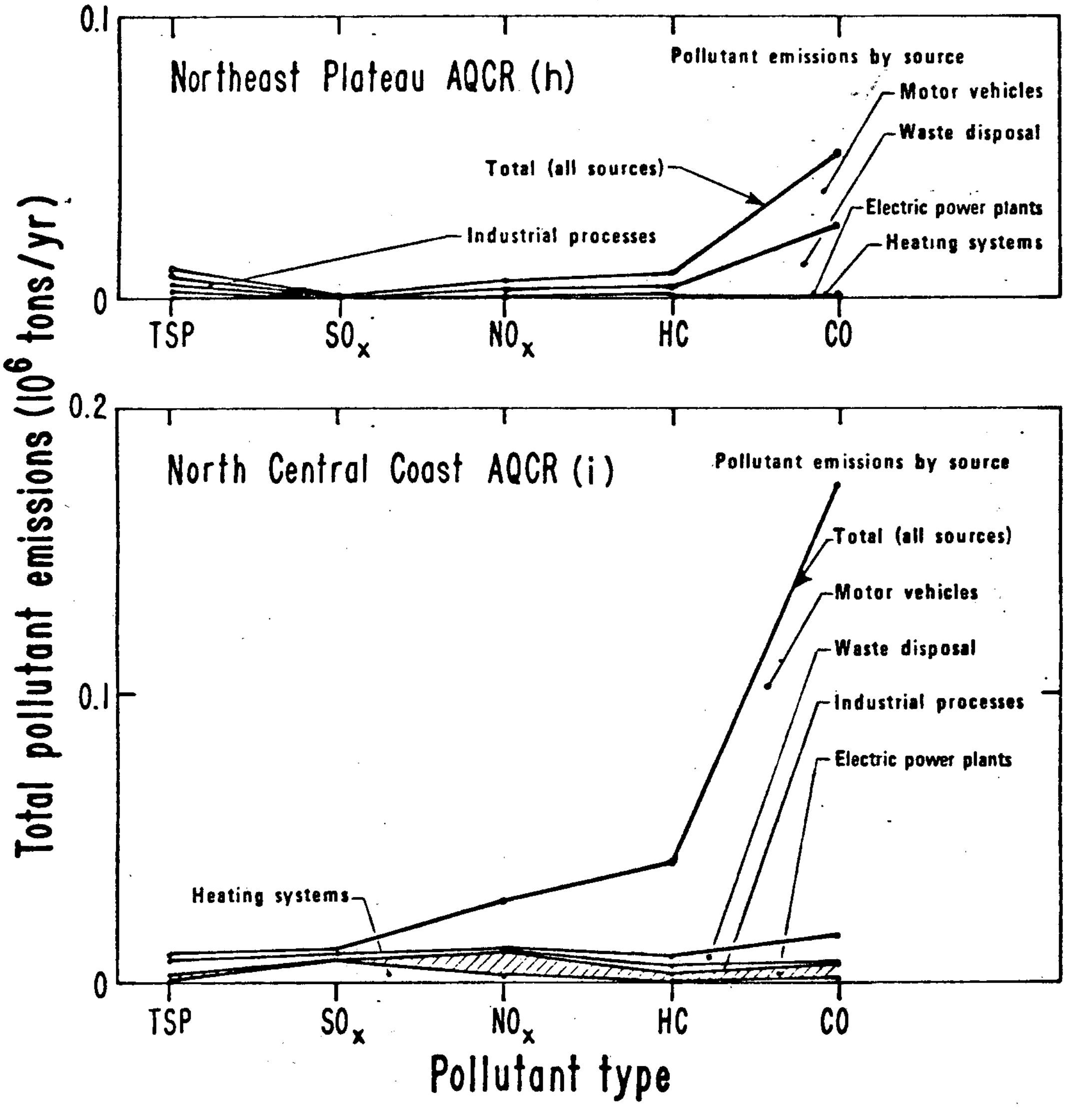

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Figure 3.1-1 (continued). (h) Northeast Plateau AQCR; (i) North Central Coast AQCR;

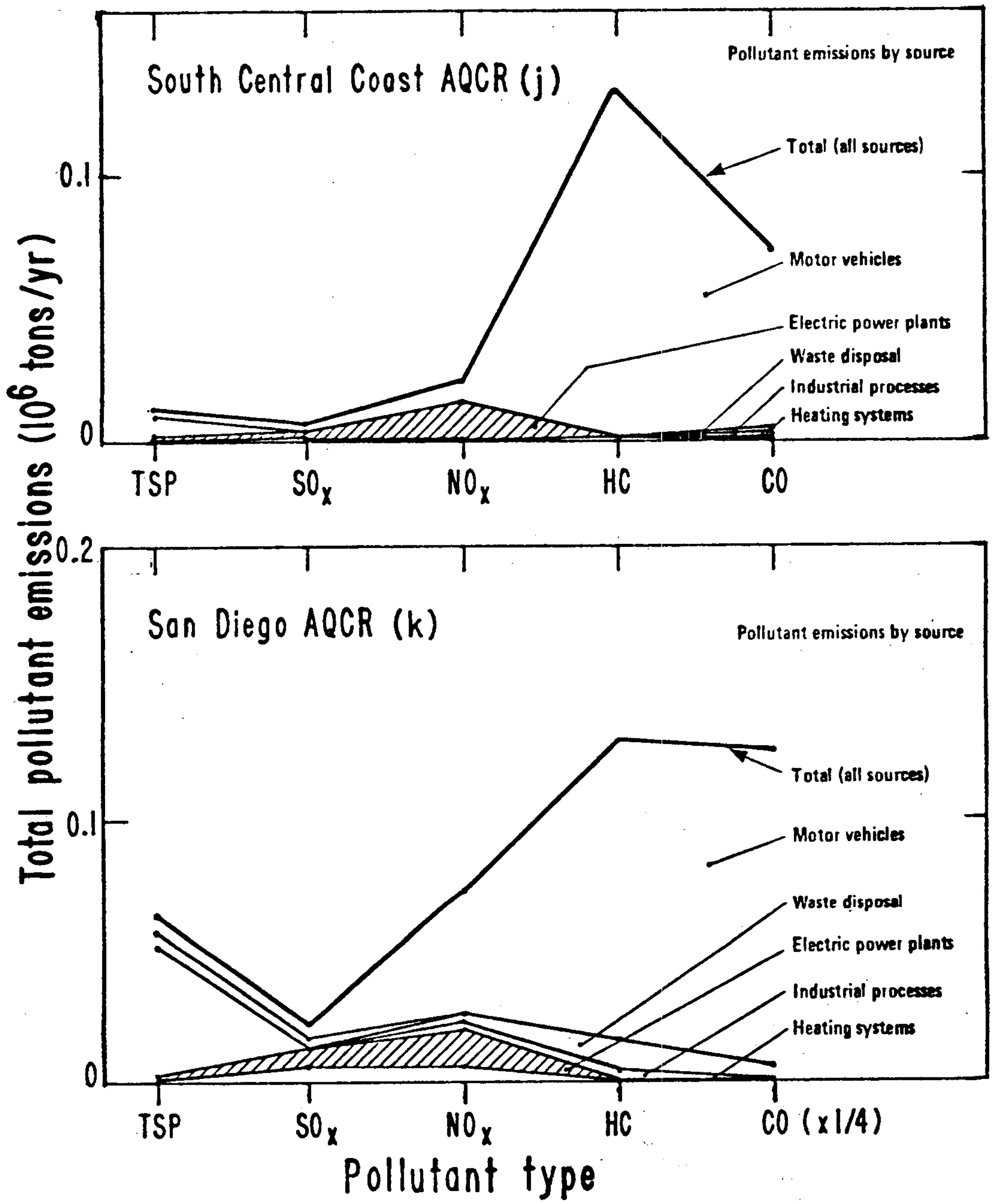

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Figure 3.1-1 (continued). (j) South Central Coast AQCR: (k) San Diego AQCR;

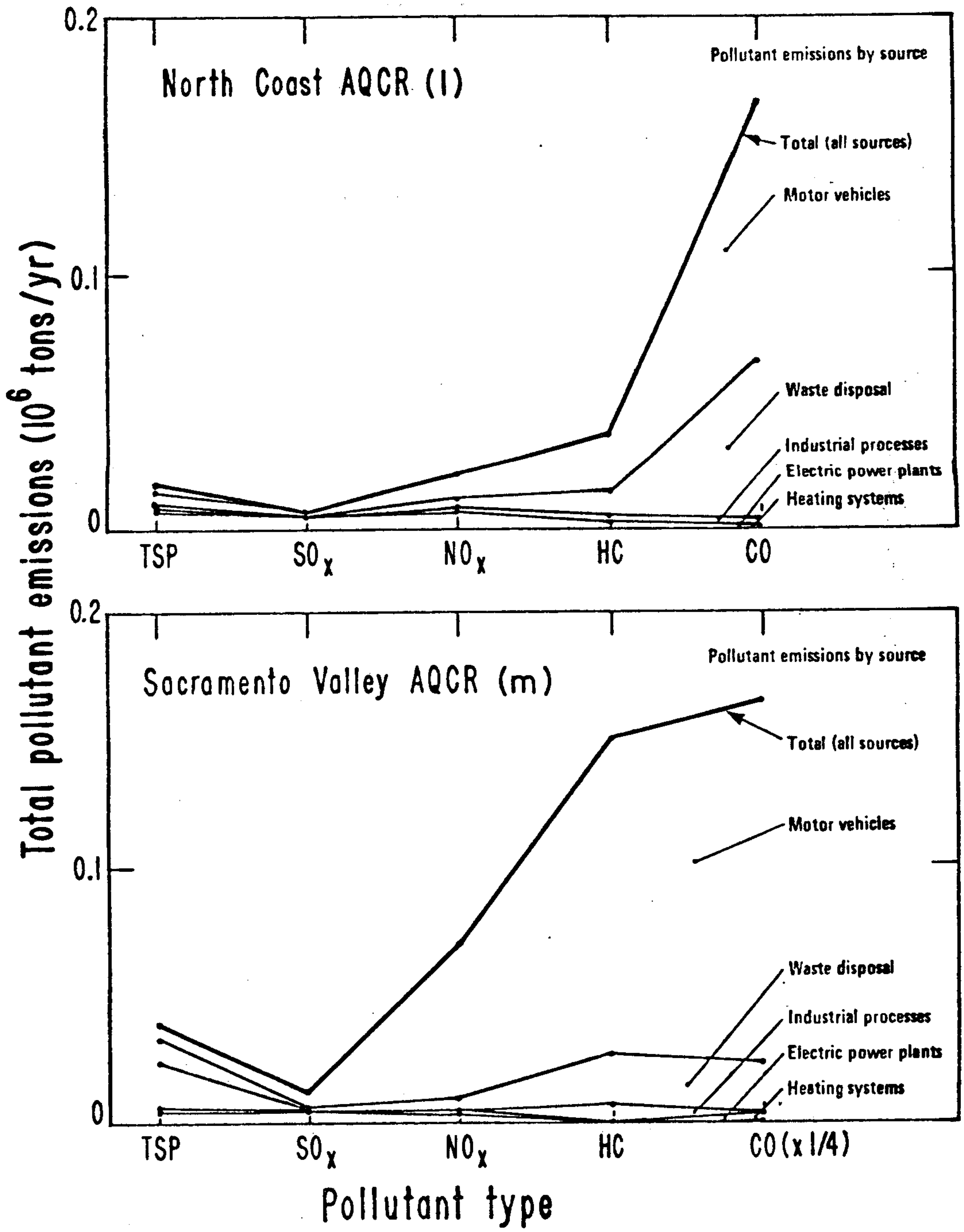

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Figure 3.1-1 (continued). (l) North Coast AQCR; and (m) Sacramento Valley AQCR.

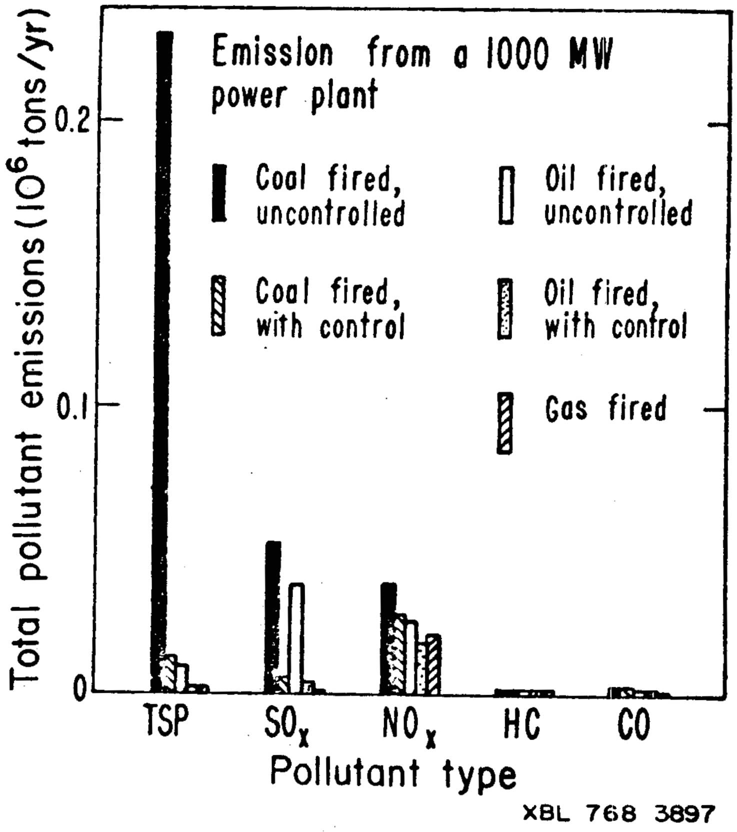


Figure 3.1-2. Pollutant emissions from a 1000 MWe power plant (based upon ref. 9). TSP is the total suspended particles, SO_x is all sulfur oxides, NO_x is all nitrogen oxides; HC is all hydrocarbons, and CO is carbon monoxide.

Table 3.1-1 Combustion Reactions of Nitrogen

Reaction	Temperature Range Favoring Right Side of Reaction (ref)
$4\ NH_3(NR_3) + 3\ O_2 \rightleftarrows 6\ H_2O(R_2O) + 2\ N_2$	< 700°C (22)
$4\ NH_3(NR_3) + 5\ O_2 \rightleftarrows 6\ H_2O(R_2O) + 4\ NO$	$\gtrsim$ 800°C (22)
$N_2 + O_2 \rightleftarrows 2\ NO$	> 1500°- 1900°C (22) > 1100°C (23)
$4\ NH_3(NR_3) + 7\ O_2 \rightleftarrows 6\ H_2O(R_2O) + 4\ NO_2$	> 1100°C (23)
$2\ NO + O_2 \rightleftarrows 2\ NO_2$	< 400°C (24)

This latter contribution to the total NO emitted by power plants may be as high as 75%,[22a] and cannot be reduced by emission control measures which rely on modified combustion conditions.

While nitric oxide is a poisonous gas in its own right, the principal problem with NO is its conversion into other oxides of nitrogen which are even more toxic.[22] Some of these oxides, dinitrogen trioxide (N_2O_3), dinitrogen pentoxide (N_2O_5), and nitrogen trioxide (NO_3) are unstable at temperatures above 5 to 10°C[24] and therefore do not accumulate to large concentrations in the atmosphere in the California air basins. They may be important as catalysts in the formation of photochemical smog, however[23] (see section 3.3.3 below). Nitrogen dioxide (NO_2) is the principal secondary product of NO emission into the atmosphere - the fraction of NO which oxidizes to NO_2 is usually at least 80%.[23,26] According to the EPA,[23] NO_2 is also formed directly as a primary combustion product, although primary NO_2 is almost certainly not more than a few percent of the initial NO_x. Whether this small fraction is due to residual primary NO_2 that does not decompose at the high flame temperature, or is formed in the first initial region of high NO and O_2 concentrations at cooler temperatures[23,24] is not clear. In any case, this "primary" NO_2 is present in concentrations which are small compared to those of the NO_2 which forms subsequently in the ambient atmosphere. Often the sum of NO + NO_2 concentrations is labeled as the NO_x emission, since the two forms do interconvert. Atmospheric reactions of NO_x are described in detail in section 3.3.3.3. Properties of particulate nitrates are discussed in section 3.1.1.3.2 below.

Figure 3.1-1 shows the 1972 annual emissions of NO_x (mostly NO) from fossil-fuel fired power plants in relation to all other sources of NO_x emissions. On a nationwide basis, power plants account for about 25% of the total NO_x emissions. This compares with 24% for emissions from heating systems and 37% for motor vehicle emissions (Fig. 3.1-1A; Ref. 8). In California (Fig. 3.1-1B; Ref. 8), electric power plants account for only 11% of the total NO_x emissions, as compared to 43% for both heating system and motor vehicle emissions. Part of the difference between the California fraction and the national average for power plant NO_x emissions can be explained by the relatively greater reliance on hydroelectric power in California and the large volume of vehicular traffic. In addition, NO_x emissions from oil-fired and natural gas-fired power plants are 30-40% lower than those for coal-fired plants, according to EPA emission factors,[9] and no coal-fired power plants presently exist in California. Drivas and Shair[9a] have presented evidence that one power plant in the South Coast Air Basin increases the atmospheric concentration of NO_x by 7.4 ppb over an area of 300 km^2. Provided that prevailing winds are sufficient to prevent a net regional accumulation of pollutants, they contend that the maximum 4-hour equivalent concentration of NO_x is not more than 120 ppb due to the power plant. Thus, while not by itself causing the air quality standard (250 ppb, 1 hour) to be exceeded in an area, an individual power plant can have a significant impact on NO_x air quality.

Because of the limitations of available control techniques, construction and startup of new fossil-fuel-fired power plants in California will almost certainly increase the local NO_x emissions. The three existing NO_x control methods involve: a) conversion to a lower NO_x-producing fuel such as natural gas, b) combustion modification, and c) flue-gas treatment. However, the option of converting power plant operations from coal or fuel oil combustion to the burning of natural gas is no longer open to California utilities except perhaps in air pollution episodes.[27] Moreover, combustion modification is not effective in reducing fuel nitrogen oxidation, and flue-gas treatment is still relatively ineffective.

3.1.1.3 Particulates

3.1.1.3.1 Size and Mass

Particulate matter is described by the EPA as "...a cloud of solid particles and/or liquid droplets smaller than 100μm in diameter, suspended in a gas."[31] Airborne particulates are also frequently called atmospheric aerosols, and should not be mistaken here for such by-products as spray can propellants and the like. Particulates may be characterized by their dimensions, mass, chemical composition, homogeneity, aerodynamic properties, optical properties, reactivity, and water solubility. References 3 and 31-33 give excellent descriptions of the properties of airborne particulates.

The size distribution of an atmospheric aerosol and its surface chemical composition determine the biological availability and reactivity of the particulates and therefore also the effects on human health. Most workers have used "effective particle diameter" or "aerodynamic diameter" to describe particle size.[3] For a true sphere, the aerodynamic diameter is identical to the physical diameter at constant density; but long fibrous particles possess an aerodynamic diameter which is (in the upper limit) 3.5 times the thickness of the fiber.[34] The ability of particles to remain suspended in the atmosphere is related to the aerodynamic diameter and is governed by competition between gravitational settling and other frictional and "buoyant" forces (see Ref. 33 for more details). Particles greater than a few tens of microns cannot remain suspended.[31] Settling of particles larger than a few microns (μm) occurs either as "dustfall" or during rainfall, and is widespread in urban areas and in many rural areas as well.[31] Particles smaller than about 0.1 - 1.0 μm may remain suspended in the air almost indefinitely.[3]

Whitby[35] has analyzed the size (particle diameter, D_p) distribution characteristics of several types of ambient urban aerosols, typical results of which are shown in Figures 3.1-3 and 3.1-4. The number density profile is greatest at small diameters, near 0.01 μm,[35-37] which probably reflects the concentration of primary combustion particulates.[35-40] Figure 3.1-5[35] summarizes the sources and behavior of the various size modes of particulates. The prevalence of these very fine particles is important because of their ability to grow by coagulation and to act as condensation nuclei.[35-38] The surface distribution curve in Fig. 3.1-3 reaches a maximum in the 0.1-0.2 μm size range[35] which forms the "accumulation mode." This mode is important because

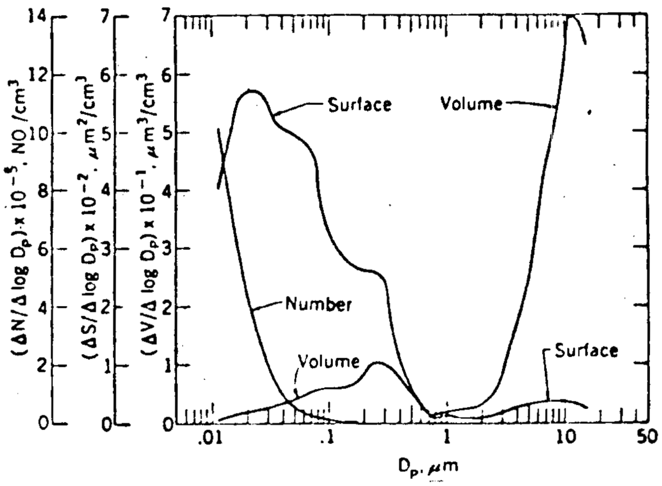


Figure 3.1-3. Normalized frequency plots of Number, Surface, and Volume Distributions. (For the grand average of October 1971 measurements at Denver's City Maintenance Yard. Reproduced from ref. (35).)

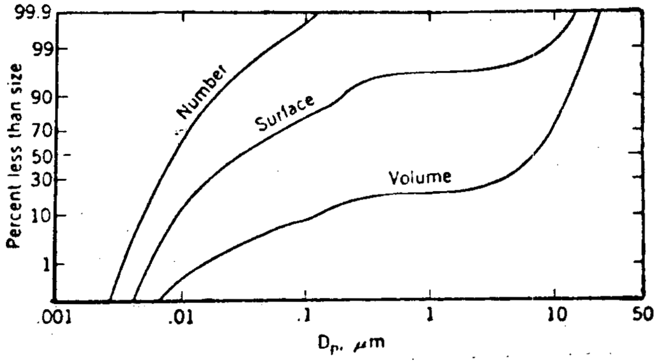
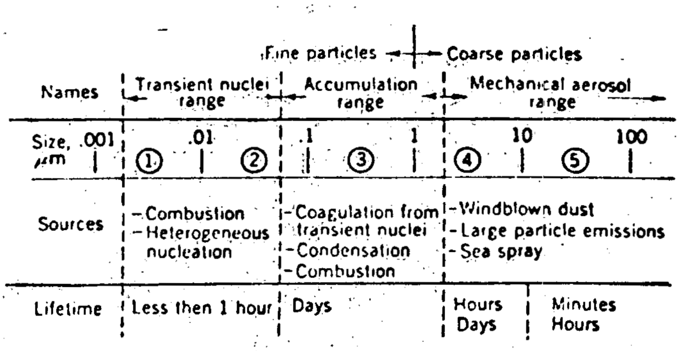


Figure 3.1-4. Cumulative Number, Surface, and Volume Distributions. (For the grand average of October 1971 measurements at Denver's City Maintenance Yard. Reproduced from ref. (35).)



	Fine particles		Coarse particles	
Names	Transient nuclei range	Accumulation range	Mechanical aerosol range	
Size, μm	.001 ① .01 ②	.1 ③ 1	④ 10	⑤ 100
Sources	– Combustion – Heterogeneous nucleation	– Coagulation from transient nuclei – Condensation – Combustion	– Windblown dust – Large particle emissions – Sea spray	
Lifetime	Less then 1 hour	Days	Hours Days	Minutes Hours

Figure 3.1-5. Nomenclature, origin, lifetimes, and sizes of aerosols. (Reproduced from ref. (35).)

most of surface-catalyzed secondary reactions of pollutants (see section 3.3.3 below) should occur with particles in this size range.[35,39-41] Figs. 3.1-3,3.1-4, and 3.1-5 also give the volume distribution curves for the same urban aerosol samples.[35] The volume distribution of ambient air particulates is almost invariably bimodal with maxima around 0.2-0.3 μm and 5-20 μm.[35-41] Nearly all mechanically generated particles occur in the larger of these two volume modes.[35]

Since the mass distribution curve is essentially indistinguishable from the volume curve, one can equate the mass median diameter (a term most conveniently used to describe aerosol size distributions) to the particle diameter (D_p) at which half the total particle volume is less and half is greater.[31] However, use of the "mass median diameter" (MMD), which is usually construed to refer to the median of a distribution that is log-normal and has a single mode,[31] may be misleading in the context of an urban aerosol or power plant plume. As an example, a particulate sample with MMD greater than 1.0 μm, such as that in Fig. 3.1-3, has surface and mass modes in the vicinity of 0.1 μm that are of considerable significance from the standpoint of health effects.

For isolated or artifically generated particulate samples such as those used to study particle deposition in the respiratory-pulmonary systems, the MMD of the particles may be an adequate indicator of particle size in some cases.[31] Curves such as those in Fig. 3.1-6, based on a MMD, lie behind the concept of a respirable fraction and a non-respirable fraction.[31] The upper limit for the "respirable" fraction of particles is between 0.5 and 2.0 μm MMD, depending on the definition of respirability. Within a factor of 2 or so, chemical composition of the aerosols appears to have little effect on respirability.[31,42-44] The smaller "respirable" particles tend to lodge in the pulmonary region (Fig. 3.1-6) and are more readily absorbed into the blood and lymph systems. Because the smaller particles also have greater surface-to-volume ratios than the larger "non-respirable" fractions, these tend to be more reactive and to dissolve in body fluids.[3,31]

Current Federal and State regulations for ambient air quality as well as stationary source emissions are addressed only to "total suspended particulate" (TSP) mass. As examples, the EPA primary standards for particulates are 75 $\mu g/m^3$ TSP for an annual geometric mean, and 260 $\mu g/m^3$ for a 24-hour average. The corresponding California standards are 60 and 100 $\mu g/m^3$ TSP. The reference method defined in both sets of regulations is the high-volume sampler (Hi-Vol),

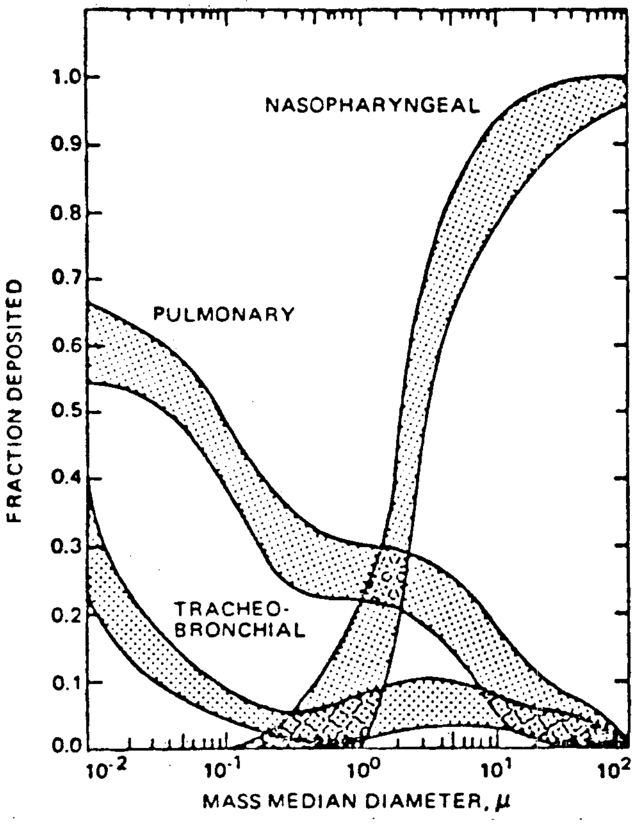


Figure 3.1-6. Fraction of Particles Deposited in the Three Respiratory Tract Compartments as a Function of Particle Diameter. (Reproduced from ref. (31).)

Table 3.1-2. 24-hour Source Identification based upon chemical element balance.[a,b]

	Pasadena 20 September 1972	Pomona 24 October 1972	Riverside 20 September 1972	Fresno 1 September 1972	San Jose 20 October 1972
Sea salt	0.7 ± 0.06	5.7 ± 0.6	1.3 ± 0.1	0‡ ± 0.4	19.4 ± 0.5
Soil dust	19.8 ± 0.1	15.1 ± 0.5	28.5 ± 0.9	51.1 ± 2.8	29.6 ± 1.1
Auto exhaust	5.1 ± 0.15	7.2 ± 0.3	3.9 ± 0.15	2.2 ± 0.1	8.3 ± 0.33
Cement dust	1.4 ± 0.15	3.3 ± 0.6	2.3 ± 0.15	0.5 ± 0.14	4.5 ± 1.3
Fly ash	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	<0.1 ± 0.01	0.1 ± 0.01
Diesel exhaust	1.4	1.9	0.9	0.6	2.2
Tire dust*	0.5	0.7	0.4	0.2	0.8
Indust. and Agric.	4.7	6.6	20.5	37.8	27.6
Aircraft	1.3	1.8	7.4	0.9	4.9
$SO_4^{=}$ †	2.9 ± 0.7	19 ± 5	5.9 ± 1.5	4.2 ± 1.0	16.6 ± 3.3
NO_3^{-} †	4.9 ± 0.4	36.4 ± 2.7	12.9 ± 1.0	7.9 ± 0.6	12.3 ± 0.9
NH_4^{+} †	2.3 ± 0.1	16.3 ± 0.8	5.7 ± 0.3	3.1 ± 0.15	7.2 ± 0.72
Organics	29.6	29.3	24.8	U	U
Water†	12 ± 6	18 ± 9	U	U	U
Total mass	86.7	161.5	114.6	108.5	133.5
Measured mass	64 ± 7	180 ± 20	125 ± 14	207 ± 23	189 ± 21

[a] Reproduced from ref. (39).

[b] Values are in micrograms/meter^3. Errors associated with sea salt, soil, dust, auto exhaust, cement dust, and fly ash are standard errors from least square fit for chemical element balance; errors associated with SO_4, NO_3, NH_4 and measured total mass concentration are analytical errors.

†Measured values.

‡Value found to be slightly negative.

U = unknown.

which collects nearly all particles in the atmosphere larger than about 0.3 μm in diameter.[3,45] Fragmentary evidences indicates that high-volume sampling also traps particles finer than 0.1-0.3 μm.[194] The Hi-Vol method does not allow one to discriminate between the small particles which become trapped in the lung from those larger ones which are either not depositied at all or are physically removed. Nor does the method discriminate between man-made particulates such as combustion effluents, and natural forms such as continental dusts or sea sprays. In order to obtain information on particulate levels in the air which is meaningful from the standpoint of effects on human health, the size distribution as well as the chemical composition should be more completely characterized. Methods for doing this are described in Reference 3.

3.1.1.3.2 Chemical Composition

The chemical composition of particulate matter obviously affects the health risks which these emissions pose, but the particle size and the surface distribution of chemical species are also important. Most particulate matter is likely to be heterogeneous in composition, with certain types of chemical agents accumulating preferentially on the surfaces where they are accessible to atmospheric vapors for catalyzing secondary reactions, or in the particle interiors, or aggregating into large particles as opposed to small ones, etc. Numerous studies have attempted to document the chemical composition of particulates as a function of particle size and origin; some of the results[31-126] are summarized below. In many cases, particular chemical constituents of ambient particulate matter may be used as "markers" to indicate the origin of the material.

Continental dusts contain, as one would expect, largely inorganic substances whose mineral composition closely resembles that of nearby soils. These particles are generally large, and in fact comprise the bulk of the nonrespirable fraction (MMD $\geqslant$ 5 μm), and contain mostly silicon (Si), aluminum (Al), potassium (K), calcium (Ca), and titanium (Ti).[46,47] Over 80% of these elements in TSP are found in the largest (dust) particles. Other elements such as iron (Fe), manganese (Mn), copper (Cu), and magnesium (Mg) are also probably derived from soil dust.[30,40,46,47] However, significant quantities of these elements also appear in the small particle fractions in urban areas such as Richmond, Sacramento, and the Los Angeles County air basins,[46] suggesting man-made sources for their origin. Soil dusts can account for a substantial fraction of TSP in many areas - as much as 50% of the total mass reported in Livermore, California[47] for example. One must therefore exercise extreme caution before using Fe or Mn as elemental markers for fly ash from power plants.[115]

Sea salt spray is also an important contributor to TSP in areas close to the ocean. Sea sprays are generally smaller in size than soil dust, averaging about 1 - 5 μm MMD.[39,40,48] The contribution of sea spray to TSP can be quite large - nearly 50% for a 21-month average in San Francisco. Changes in wind direction from offshore to onshore and vice-versa can markedly influence the composition of the total aerosols in a region, and occur regularly in California.[47] One must account for the contributions of sea sprays to the atmospheric sulfate burden[7] before attempting to use sulfates as a marker for power plant plumes.

When one considers the relative impact of natural aerosols and dusts on the particulate loading in the atmosphere, it becomes clear that "total suspended particulate" (TSP) mass is not a good indicator of particulate air pollution. What is needed, therefore, is a reliable indicator of particulates from man-made sources. General measures such as "TASP" (total anthropogenic suspended particulates) may be a suitable index for the San Francisco Bay Area APCD, but could be unreliable for a different air basin with different types of particulate pollution sources. For the present, it appears that several marker elements and compounds, along with size distribution mapping, will have to be used in order to obtain particulate data which can be related intelligently to health effects and pollution sources. This goal was the principal objective of the California Aerosol Characterization Study;[35,36,39-41] their breakdown of particulates by source is given in Table 3.1-2.[39] Anthropogenic particulates can be generalized into three categories: sulfates and nitrates, carbonaceous combustion particles (soot), and other inorganic materials, commonly called trace elements, from combustion and industrial processes. Although not explicitly stated in the ACHEX report,[40] one can define primary aerosols as particulates which occur immediately from combustion or industrial processes, while secondary aerosols (sulfates and nitrates, especially) are those from gas-particle or particle-particle reactions.

3.1.1.3.2.1. Sulfates

Sulfates are a class of aerosols which include sulfuric acid (H_2SO_4) mist, ammonium sulfate [$(NH_4)_2SO_4$], and other acidic and neutral salts of sulfuric acid. As defined by the current reference sampling and analytical methods,[5] the sulfate fraction contains as much as 10% particulate sulfites as well.[10,49] Natural background sulfates (as Na_2SO_4, for example) are thought to be neutral,[7,10,38,41,62] non-irritating,[10,50] and are present in California aerosols in concentrations of about 4 - 5 μg/m.[3,5] Most anthropogenic sulfates are not only present in higher concentrations,[5,10] but may also exist in the more acidic[2,19,51,52] and irritating[53] forms.

The coexistence of ammonium (NH_4^+) in the aerosols with sulfate has led several workers to conclude that the bulk of the sulfates exist as $(NH_4)_2SO_4$ and NH_4HSO_4.[38,54-58] Indeed, in the Arizona deserts, correlation between ambient sulfates and NH_4^+ coupled with the obvious lack of correlation with any other component in the aerosol points strongly to $(NH_4)_2SO_4$ as the dominant form.[54] Ammonium sulfates have been unequivocally identified in ambient air in St. Louis[51,59,60] and Sweden.[61]

However, in contrast with previous views, recent work by Novakov et al.[59,60] suggests that no chemical association between NH_4^+ and sulfate exists in California urban aerosols, in spite of the presence of NH_4^+ together with the sulfate.[58] Detailed analysis of aerosols in rural Long Island and New York City reveals that only about 10% of the total sulfate exists as ammonium sulfates, less than 5% as sulfuric acid, and less than 3% as sodium bisulfate[62] - in spite of the concurrent presence of NH_4^+ in the aerosols. Hence, it is not safe to generalize about the form in which sulfates exist in the urban air.

Sulfate aerosols are typically fine, with mass median diameter (MMD) approximately 0.4 m[39,40,52,65-67] and are therefore respirable and potentially dangerous. Less than 10% of ambient sulfates are found on particles larger than 3 μm diameter.[65]

Most sulfates are not primary emissions from man-made sources but occur as secondary pollution products in the atmosphere from other sulfur compounds.[10] The chemistry of the conversion of SO_2 and other sulfur compounds to sulfates is described more completely in Section (3.3.3.2) below, and is not discussed further here. It is worth noting, however, that in the South Coast Air Basin of California, ambient sulfate concentrations correlate linearly with regional SO_2 emissions.[67] In the eastern United States, ambient sulfate concentrations also correlate with the acidity of rainfall,[5,10,19,20,68] although no such correlation has yet been observed in California.[5] In the South Coast Air Basin, acidic sulfates comprise approximately 10-15% of the total particulate mass on an annual average basis.[5,39,40] On occasion, the sulfate fraction of TSP has been known to reach 30%.[2,5,10] However, in most other areas of California, anthropogenic sulfates represent only a very minor component of the total particulate burden.

3.1.1.3.2.2 Nitrates

Particulate nitrates present in aerosols include nitric acid (NHO_3), ammonium nitrate (NH_4NO_3), salts of nitric acid, organic nitrates, etc. Their existence as particulates occurs because of equilibrium interactions between liquid or solid nitrates and gaseous NHO_3.[58,68] Nitrates can be present in the atmosphere in either form, but are seldom detected in both states simultaneously.[58-60,69] Particulate nitrate concentrations representative of natural background levels have been observed on the order of 0.70 - 0.85 $\mu g/m^3$.[70,71] In urban areas, nitrate levels are typically around 2.4 $\mu m/m^3$,[65] but are usually 2.0 - 12.0 $\mu g/m^3$ (means = 2.8 $\mu g/m^3$) in the San Francisco Bay Area[67] and 4.9 - 36.4 $\mu g/m^3$ (mean = 13.5 $\mu g/m^3$) in the South Coast Air Basin.[39-41] Typical concentrations of gaseous NHO_3 in the South Coast Air Basin are on the order of 10 ppb (26 $\mu g/m^3$) and "track" directly with variations in ambient ozone (O_3).[69] Particulate nitrate levels, on the other hand, do not necessarily correlate with ozone. (Compare Refs. 58 and 195.) Because of the affinity of NHO_3 for only certain kinds of particulates,[58] measurement of either free NHO_3 or particulate nitrate alone may overlook total nitrate levels which could pose a threat to public health. For example, during a 1973 oxidant episode in Los Angeles County, O_3 levels of 0.67 ppm were accompanied by particulate nitrate levels which hit 60 $\mu g/m^3$, free NHO_3 levels in excess of 25 ppb (65 $\mu g/m^3$), and peroxyacetyl nitrate levels of 52 ppb.[58] Average nitrate levels which are a factor of 10 or so above natural background may be a common problem throughout most of California.[39,40] Friedlander[39,41] and Gordon and Bryan[65] have reported that the ammonium-to-nitrate ratio observed in Los Angeles County is consistent with NH_4NO_3 as the principal form in which nitrates occur in particulates. Like Like the sulfate aerosols, nitrates are found largely in the fine particle fractions, with MMD approximately 0.2 - 1.6 μm[30-41,72,195] and are therefore resprable.

Nitrates and HNO_3 in the atmosphere are the result of secondary reactions of nitrogen oxides (NO_x), and do not arise directly from primary combustion source emissions. (See section 3.3.3.3 on secondary chemical reactions.) There is some evidence that particulate nitrates are formed during the processes which also generate photochemical oxidants.[58,69] Particulate nitrates in the atmosphere often correlate with photochemical oxidants, whereas the correlation with either ambient NO or NO_2 concentration or with NO_x emissions is very poor.[67] On the other hand, during the winter of 1973-74 when a natural gas shortage occurred, daily average nitrate levels in the San Francisco Bay Area climbed to 20 - 24 $\mu g/m^3$ (from the more normal 2 - 12 $\mu g/m^3$). This increase occurred during periods in which photochemical smog formation was insignificant, and was attributed to the increased NO_x emissions from fuel oil combustion for electric power generation and space heating.[67] A similar nitrate episode occurred during November 1976.[67a]

Nitrate (including nitric acid) aerosols typically constitute about 5 - 20% of the total particulate mass in urban air samples,[39-41,58,73] and can rival sulfates as a threat to human health. It is expected that the effects of nitric acid and sulfuric acid mist should be similar, and in some cases it may be difficult to separate the effects of nitrates from those of sulfates during an air pollution episode (see Ref. 74, for example). In Southern California, average nitrate and sulfate levels are approximately equal.[39-41] However, if nitrates are produced principally by photochemical processes,[67] one might expect to observe especially high levels of nitrates in the air during oxidant smog episodes, regardless of the presence or absence of sulfates. In this regard, particulate nitrates (as nitric acid) should be given at least as high a priority for monitoring and control as currently being devoted to sulfates,[5] and development of better measurement techniques is sorely needed.

While nitrates have thus far received the most attention in research on particulate nitrogen species, recent work suggests that other nitrogen species may also be important. Novokov and co-workers[59,60] have obtained evidence that reduced nitrogen species can be the predominant forms of nitrogen on the surface of atmospheric particles. Among the species that may be important are ammonia not associated with sulfate or nitrate, amines, amides, and nitrites. More research is required to understand the implications of these findings.

3.1.1.3.2.3 Carbon

Carbonaceous particulates are usually defined as all organic and inorganic forms of carbon in the air which are not present in the vapor phase. These usually contain liquid or solid paraffinic, olefinic, and aromatic hydrocarbons as well as organic acides, alcohols, aldehydes, amines, esters, etc., and elemental carbon. Most people equate carbonaceous particles with soot or tars. However, carbonaceous particles should not be considered limited to these. Furthermore, soot and tars themselves are very poorly characterized mixtures of organic (C-H form) and elemental forms of carbon.

The fraction of total particulate matter which is estimated to be organic or elemental carbon depends heavily on the sampling and analytical method. Historically, the carbon content of aerosols has been equated to either the amount of material which extracts into benezene, or that fraction which "disappears" upon ignition.[31] While considerable effort has been devoted to determining the concentrations and origins of organic particulate constituents known to be hazardous, less effort has been devoted to characterizing the composition and origin of carbonaceous material more generally. Even the proportions of elemental and organic carbon present remain a matter for speculation, and those studies which addressed this problem have assumed highly operational definitions for organic and elemental carbon.

As an example, studies of carbonaceous particulate matter have primarily examined organic solvent-extractable fractions.[75-78] Detailed qualitative and quantitative analyses of cyclohexane extracts[79] and benzene extracts[80-82] of airborne particulate matter have been published. Unfortunately, the analyses, as sophisticated as these were, are only as good as the extraction procedures. Appel et al.(83) have recently shown that neither cyclohexane nor benzene extracts more than 50% of the organic carbon in airborne particulate matter. One assumes in these cases that organic solvents do not extract elemental (or inorganic) carbon.

Carbon analyses of particulate matter which rely on ignition losses may also be incomplete. In the presence of O_2, organic forms of carbon combust at temperatures between 50°C and 600°C, amorphous elemental carbon between 200°C and 700°C, and fine graphite particles between 700°C and 1100°C.(84) If the combustion temperature used in the analysis is not hot enough, some carbon remains unburned. The principal advantage of this method over organic solvent extractions is, of course, the ability in principle to ensure measurement of the total carbon content of aerosols.

The relative contents of organic and elemental carbon in atmospheric particulates has been the subject of considerable disagreement in the literature and is summarized in Table 3.1-3. If these studies present a reliable indication of the carbon content of airborne particulates, then it appears that organic compounds rather than elemental, free, or graphite carbon usually comprise the majority. No further generalizations at this point would seem justifiable, given the nature of the existing body of data.

However, numerous attempts to identify the types of organic compounds in particulate matter have been published, and the results are summarized in Table 3.1-4. Resolution by class of compound (acids, bases, polars, hydrocarbons, etc.) is generally determined by solvent extraction procedures and has been used by most workers. Analyses of specific substances (indicated by * in Table) by a variety of methods have been attempted in a few cases. Only a small fraction of the organic mass has been identified in terms of specific substances. The organic species in particulate matter which have received the greatest publicity and attention are the polycyclic aromatic hydrocarbons (PAH). Several of these compounds have been implicated as carcinogens (cancer-causing agents) when administered orally, subcutaneously, or by other routes.(72,93-97) Polycyclic aromatic hydrocarbons (PAH) have been detected in quantity in urban aerosols, along with a host of other organic compounds. Correlation of known carcinogenicity to these airborne PAH species is given in Table 4.3-2, in section (4.3) below. It is doubtful whether the PAH compounds comprise more than about 10% of the total organic carbon in urban aerosols. And if no more than 20% or so(83) of the total carbon is elemental (or inorganic), organics — especially aliphatic hydrocarbons and carboxylic acids — must be the major constituents.

Table 3.1-3. Tentative Estimates for Carbon Content of Airborne Particles (% TSP)

Origin	Total	Organic	"Elemental"	Reference
U.S. Average	———	6.5^a	———	(31)
U.S. Range	———	6.0 - 17^a	———	(31)
Pasadena, CA	———	34^b	———	(39)
Pomona, CA	———	18.2^b	———	(39)
Riverside, CA	———	21.6^b	———	(39)
Pasadena, CA	19^c	12.9 - 14.3^c	4.7 - 6.1	(41)
Los Angeles, CA	9.0 - 11.0^c	7.0 - 8.5^{c,d}	2.1 - 2.5	(75)
New York, NY	———	2.2 - 47.4^a	———	(70)
New York, NY	———	———	11^c	(77)
Ankara, Turkey	36.0 - 52.0^c	12.0 - 16.2^f	25.0 - 36.0^f	(78)
London, England	11.8 - 13.5^c	8.4 - 11.8^f	0.0 - 5.0^f	(78)
Chicago, IL	11.8 - 20.0^c	7.8 - 10.8^f	1.0 - 12.2	(78)
Tulsa, OK	———	———	8.0^e	(79)
Pittsburgh, PA	———	———	34.0 - 46.0	(79)
Secaucus, NJ	19.7^c	13.2	5.6^f	(81)
DIESEL EXHAUST	85.0 - 93.0	———	———	(82)
Soot	≡100	———	~12^g	(80)

a) Benzene soluble fraction, which is ~60% of total "organic" carbon (75).
b) Obtained from estimate of "carbon balance" (39).
c) Obtained from measurements of weight loss upon ignition.
d) Assumed from combined extractions with cyclohexane, benzene, and chloraform-methanol.
e) Residue which remains after exhaustive reaction with HF, NH_4OH, and HNO_3 at 150°C, but which subsequently burns to CO_2 upon high-temperature ignition.
f) Taken from measurements of fixed hydrogen content. Hydrogen was assumed to be in the form of paraffinic hydrocarbons with formula C_nH_{2n}. This assumption is justified by data of ref. (74).
g) Obtained from resonance Raman spectroscopy, which shows that "graphite domain" occupies half of the total particle radius. Number is very rough.

Table 3.1-4. Results of Some Measurements of Organic Compounds in Urban Aerosols

Form	Solvent Extract of Particulate			
	Benzene		Cyclohexane	"Polar" solvents
	μg/g C	μg/g TSP	μg/g C	μg/g C
Total Carbon	464,000(83)	46,000(83) 58,000(82) [c] 91,000(80) [c] 89,400(92) [h]381,000(58) [i]264,000(58)	288,000(83)	#313,000(83) # 65,000(82) #205,000(99)
Aliphatic Hydrocarbons		* 3,100(82) * 500(98)	[h]140,000(58) [d] 89,000(83) [e] 69,000(83) [i]200,000(58)	0(83)
Aromatic Hydrocarbons		*c 148(80) *b 1,500(81) * 300(82) *c 118(92)	[d] 43,000(83) [e] 23,000(83) [h]130,000(58) [i]150,000(58)	0(83)
Unidentified Hydrocarbons		34,300(82)	[h] 50,000(58) [i] 20,000(58)	
Polar Organic Compounds		* 1,500(82)	176,000(83)	a(83) [h]460,000(58) [i]420,000(58)
Organic Acids (Carboxylates)		13,054(82) *f 2,500(82) *g 465(82)		a(83) [h]200,000(58) [i]180,000(58) 30,000(100)
Organic Bases		5,630(82) * 75(82)	[h] 20,000(58) [i] 10,000(58)	a(83)

* Sum of individual components identified in air sample (by GC-MS, etc.)

\# Extraction was done on residue following a benzene extraction. In general, organic carbon is assumed to constitute 10-15% of TSP mass (75).

a Sum of polar, acidic and basic components assumed to equal total.

b TSP concentration was assumed to be 100 $\mu g/m^3$.

c Average of sampling sites in California. Distribution profile shows average to be justified.

d Exhaust gas from motor vehicle.

e Ambient air sample in Los Angeles area.

f Aliphatic acids only

g Aromatic acids only

h Aerosol sample from Pasadena CA during an oxidant episode. Numbers represent the sum of organic forms extracted from which organic compounds extracted in each solvent was not stated.

i Same as h, except that aerosol sample was taken in Pasadena, CA on a day in which "smog level" was "low".

( ) Numbers in parentheses are citations to literature.

Little information regarding the corresponding carbon composition of the primary particulates emitted from power plants exists.

One area of nearly universal agreement concerns the size distribution of carbonaceous particulates. Several investigations(39,36,37,40) have suggested that the 0.01 μm diameter particle number mode is greatly enriched in carbonaceous material. In view of the means by which particulate carbon must be formed during combustion,(102) this interpretation would appear reasonable. In fact, virtually all of the carbon found in all types of combustion emissions and in ambient air samples occurs in particles with MMD < 1 - 3 μm.(35-37,39,40,80,83,92,101,103,104) One should note that carbonaceous particlates are anything but inert (see section 3.3.3 below), and that their very small size makes control of their emissions very difficult.

Very fragmentary work has been done on the sources of particulate carbon in the atmosphere. Part of the problem lies in the multitude of organic compounds which can arise from primary combustion or from secondary atmospheric reactions. Friedlander(41) has attributed 68% of the ambient carbon in Los Angeles air basin to "tire dust" and the remainder to automobile emissions. While his tire dust factor appears to be grossly overestimated, more recent work from Friedlander's laboratory(39,58) attempts to demonstrate the large contribution of secondary oxidative reactions in the atmosphere to the formation of carbonaceous particulates. The hydrogen content is one to two times that of carbon by mole; that of nitrogen is 2-5% that of carbon by mole(38,86,89) but bound oxygen constitutes some 16% by mole of the carbonaceous material, or 12% of its weight.

Only a few compounds in atmospheric carbon particulates have been identified as source markers; most of these have been PAH substances and have generally not been useful as "fingerprints" of power plants emissions. Automobile emissions appear to be the major source of PAH in California,(80,92) because of the increasing use of unleaded gasoline(105) and the pyrolysis of hydrocarbons.(106)) (As the PAH in the fuel is increased to raise the octane rating, the emissions of higher order PAH climb disproportionately higher.(106) One of the PAH emission products which can be traced almost exclusively to the automobile is coronene.(80,92,106) As Table 3.1-5 shows for the South Coast Air Basin, the ratio of PAH compounds such as benzo(a)pyrene to coronene is lowest near the ocean (BAP/COR = 0.18) where no pollution sources other than vehicular traffic are significant.(92) This ratio is considerably higher (BAP/COR = 0.32) farther inland, indicating that contributions from stationary combustion sources are significant.(92) Power plant emissions appear to be enriched in benzo(a)pyrene-like PAH compounds relative to coronene (Table 3.1-5). Furthermore, it is evident that PAH emission factors for power plants overall are greatly reduced as the size of the power plant is increased, and as the fuel fed into the boilers becomes finer.(72)

Table 3.1-5 summarizes some typical PAH emission factors for various combustion sources.(80) However, to use all source emissions of benzo(a)pyrene as a mirror for particulate carbon emissions in general, the data in Table 3.1-6 are probably more meaningful. Only three types of sources—coal furnaces, coke production, and open burning—are major factors in atmospheric loading of benzo(a)pyrene in the U.S. None of these sources presently exist to any significant extent in California. Relative to other sources, electric power generating plants barely figure in the emission inventory at all.(80) In fact, the large differences in benzo(a)pyrene emissions between small coal-fired furnaces and boilers and small gas-fired or oil-fired furnace boilers vanish with increasing size of the plant unit. For power plants of the 200 - 1000 MW range, there is apparently no difference in the quantities of benzo(a)pyrene (and maybe also particulate carbon) emissions.(80) One must be careful to remember, however, that there presently exists no justification for equating benzo(a)pyrene emissions with total carbon. Hence the contribution of power plants to total carbon emissions is almost totally unknown. Over the past 25-30 years the concentrations of PAH in urban areas in most of the Western World have been declining.(80,92,107) This decrease is largely due to the conversion of residential and commercial heating systems from coal to "cleaner" fuels, and has been unaffected by the exponential growth of electric power generation.

Table 3.1-5. Emission Factors for PAH Compounds.(a)

Source	Type	Benzo(a)pyrene	Coronene	BAP/COR Ratio
Santa Monica, CA	Ambient Air (83)	0.36 ($\mu g/m^3$)	2.06 ($\mu g/m^3$)	0.18
West Covina, CA	Ambient Air (83)	0.76	2.38	0.32
Power Plants:	Coal Fired			
Pulverized	60 MW (72)	1.32 (mg/MW-yr)	0.91 (mg/MW-yr)	1.4
	400 MW (72)	7.70	0.41	19.0
	460 MW (72)	1.20	——	——
Crushed	485 MW (72)	24.47	0.10	241.
Coal Furnaces:	Residential			
Underfeed Stoked (72)		270. (mg/MW-yr)	13.2 (mg/MW-yr)	20.5
Hand Stoked (72)		13,300.	391.	34.0
Motor Vehicles:	Cars	——	——	0.16 - 0.18 (65,92)
Make "A"		5.0 (mg/1000 km)	20.0 (mg/1000 km)	0.25 (80)
Make "B"		21.3	40.0	0.53 (80)
Make "A"	Trucks	41.3	93.8	0.44 (80)
Make "B"		9.0	37.6	0.24 (80)

(a) From Ref. 80.

Table 3.1-6. Estimated Benzo(a)pyrene Emissions in United States, 1972.(a)

Source Type	Benzo(a)pyrene, Metric Tons
Stationary Sources:	
Coal, Residential Furnaces	270
Coal, Intermediate-Sized Furnaces	6
Coal, Steam Power Plants	<1
Oil, Residential through Steam Power	2
Gas, Residential through Steam Power	2
Wood, Home Fireplaces	23
Enclosed Incineration	3
Open Burning, Coal Refuse	281
Open Burning, Vehicle Disposal	5
Open Burning, Forest and Agriculture	10
Open Burning, Other	9
Petroleum Catalytic Cracking	6
Coke Production	0.05 - 153
Asphalt	<1
Mobile Sources:	
Gasoline-Powered Cars, Trucks	10
Diesel-Powered Trucks, Buses	<1
Tire Dust	10

(a) From Ref. 80.

3.1.1.3.2.4. Trace Elements

"Trace elements" represent the final major class of constituents in particulates in urban air. Their contribution to the total mass loading in the atmosphere is highly variable, and depends on their sources; hence, "trace" can be a misnomer. The term "trace elements" is generally used to describe all elements in particulate matter with atomic number greater than about ten. And since physical-chemical analysis of these elements can be carried out easily and unambiguously by a number of techniques, such as x-ray spectroscopy, atomic absorption, atomic emission, flame photometric methods, etc.[3] ; studies of the metal and elemental composition of ambient aerosols, fly ash, and fuels are abundant in the literature.(3,31,39-41,46-48,108-117) However, it is not enough to characterize the total concentrations of an element in a given particulate sample, since the size fraction, surface distribution, and chemical form all depend on the fuel source and combustion conditions. Lead in coal, for example, does not give rise to the same kinds of particulate emission products as lead in gasoline.(39-41,108-117)

Trace elements in the ambient air generally exist as metal oxides or other similar compounds, and may arise either from natural sources such as soil dust, or from man-made emissions such as fuel combustion. Table 3.1-7 shows some typical trace element concentrations in the ambient air for several (California) cities. It is clear that trace element concentrations are subject to wide variations which can, in part, be traced to seasonal fluctuations. In only a few cases is it obvious that any of these elements are due to anthropogenic activity. Only titanium, copper, and zinc in the Los Angeles-Azusa area, and possibly winter Zn in Sacramento, show concentrations which are much different from local soil dust concentrations.(39,46) Lead, bromine and chlorine levels are higher than natural background concentrations because of the lead halides (PbBrCl, mostly) from vehicular traffic.(39-41,115) However, mass balance calculations involving several elements simultaneously gives much better resolution of the sources for each element.(39-41,115) As examples, 92% of the vanadium and 76% of the copper in New York City air can be traced to fuel oil combustion, while 97% of the potassium is derived from soil dust.(115)

In some cases it is necessary to sort out the elemental compositions of particulate fractions as a function of aerosol size in order to resolve the origins of each element. Elements occurring in soil dust should be found on

Table 3.1-7 Trace Element Concentrations in California Urban Atmospheres ($\mu g/m^3$)

$\mu g/m^3$

Element	Sacramento		San Jose		Pasadena	Pomona	Riverside		Fresno	Los Angeles	Azusa	New York City
	a	b	c	b	d	c	d	b	d	b	b	
Sodium	0.23	0.62	6.71	0.73	0.716	2.06	1.13	0.27	0.84	0.83	0.48	0.55
Aluminum	0.093	0.90	2.56	0.60	1.03	1.30	2.35	1.02	4.97	0.44	1.14	- - -
Calcium	0.16	0.93	2.72	0.84	0.94	0.80	1.49	1.27	0.98	0.75	1.06	- - -
Vanadium	0.0020	0.0060	0.0110	0.0050	0.0048	0.0140	0.0088	0.0150	<0.02	0.025	0.043	0.102
Lead	0.89	0.70	3.34	1.06	2.03	2.89	1.55	1.70	0.87	1.90	1.41	2.00
Magnesium	0.048	0.13	3.5	0.20	<0.4	<0.04	0.97	0.074	0.86	0.17	0.10	- - -
Potassium	0.25	0.59	0.62	0.47	0.36	0.44	0.68	0.79	0.70	0.47	0.91	0.64
Manganese	0.006	0.036	0.047	0.030	0.023	0.025	0.040	0.050	0.051	0.031	0.049	0.033
Copper	0.019	0.008	1.5	0.005	0.043	0.025	0.29	0.0070	0.012	0.017	0.020	0.066
Chloride	0.25	0.34	7.9	0.89	0.44	0.93	0.76	0.11	0.38	0.12	0.10	- - -
Bromide	0.29	0.16	1.19	0.29	0.50	0.81	0.39	0.37	0.20	0.25	0.22	- - -
Chromium	0.011	- - -	0.032	- - -	0.006	0.025	0.013	- - -	0.012	- - -	- - -	0.017
Nickel	0.002	- - -	0.025	- - -	0.006	0.024	0.014	- - -	0.011	- - -	- - -	0.064
Iron	0.25	1.22	1.95	1.18	1.15	1.55	2.31	1.79	2.13	1.00	2.00	2.12
Zinc	0.043	0.030	0.16	0.098	0.097	0.23	0.13	0.085	0.12	0.18	0.19	- - -
Sulfur	0.74	1.02	5.5	0.87	1.0	6.3	5.9	2.9	1.38	4.01	3.08	- - -
Barium	0.002	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -
Silicon	0.55	3.37	- - -	3.15	- - -	- - -	- - -	4.02	- - -	2.42	3.75	- - -
Titanium	0.013	0.094	- - -	0.091	- - -	- - -	- - -	0.143	- - -	0.13	0.24	- - -
Cadmium	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	0.008

a) Mean concentrations for January 1974,(Ref. 46)
b) Mean concentrations for July-September 1973, (Ref. 46)
c) October 1972, Averages for one day, (Ref. 39)
d) September 1972, Averages for one day (Ref. 37).

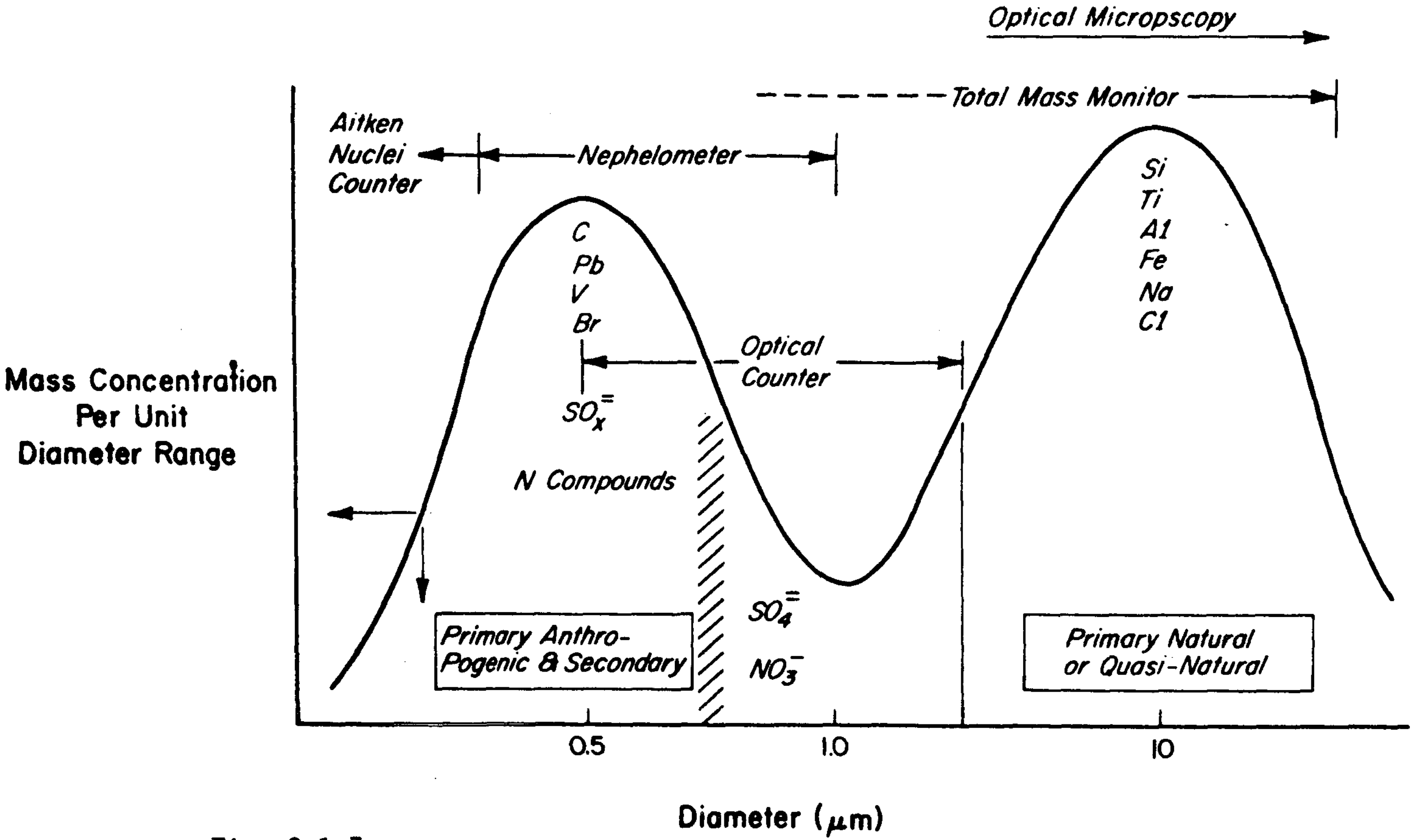


Fig. 3.1-7.
Typical Mass/Size Distribution for Suspended Particulate Matter. The portions of the size distribution detectable by various monitoring devices are indicated. An area under the curve is proportional to a fraction of the total mass. The relative areas may be expected to vary widely for different sampling situations.

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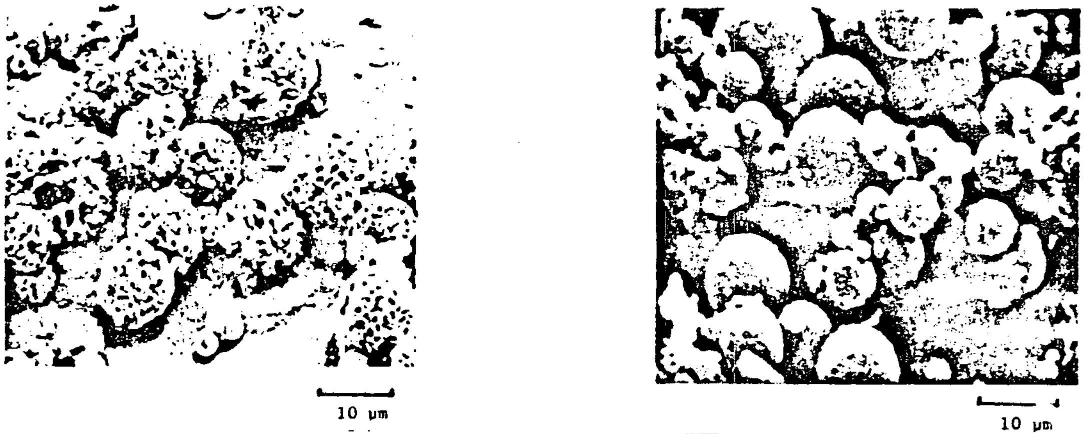
the largest airborne particles (larger than 5 μm MMD), while those attributed to such man-made sources as fuel combustion should also be detected on the smaller (respirable) particle modes.(31,35-41,46-48,115) Analysis of this type sometimes shows a bimodal size distribution for certain elements, indicating that both man-made and natural sources are important. This bimodal distribution has been observed for zinc,(46) lead,(115) manganese,(46,115,112,113) vanadium,(115) and chromium.(112,113,116) Figure 3.1-7 shows an example of size-resolved concentrations of selected elements in aerosols. On the other hand, Gladney et al.,(117) have shown enrichment factors of greater than ten times over natural crustal abundance for thallium, chromium, nickel, copper, zinc, arsenic, cadmium, tin, lead, selenium, sulfur, chloride, and bromide in Boston area particulates.

Enrichment of trace elements in aerosols can occur by two means. One is the escape of small particles from flue gas control systems designed to trap larger particles. The other, more important, involves the mechanism by which trace elements end up in coarse or fine particles in the first place. One explanation for the particle size dependence of specific element concentrations is the ashing characteristics of pyritic (FeS) inclusions that contain many of the trace elements.(118,119) However, Davison et al.,(108) have suggested that certain elements or their compounds in the fuel are volatilized in the high-temperature combustion zone and then either condense or adsorb onto entrained particles. The mass thus deposited is greatest per unit weight for the smallest particles. In support of the volatilization-adsorption-condensation hypothesis, all the elements which preferentially accumulate in the fine (2-3 μm) particle fractions have boiling points comparable to or below the temperature of the combustion zone (1300-1800°C). Table 3.1-8 categorizes some of these elements by boiling point. It is suggested that these elements can reach the vapor phase, if not as the oxides, as either the reduced metals or the carbonyls or chlorides. The same process ostensibly accounts for the prevalence of airborne lead (98% from vehicle emissions,(121)) in fine particles.(31,35,37,39-41,46)

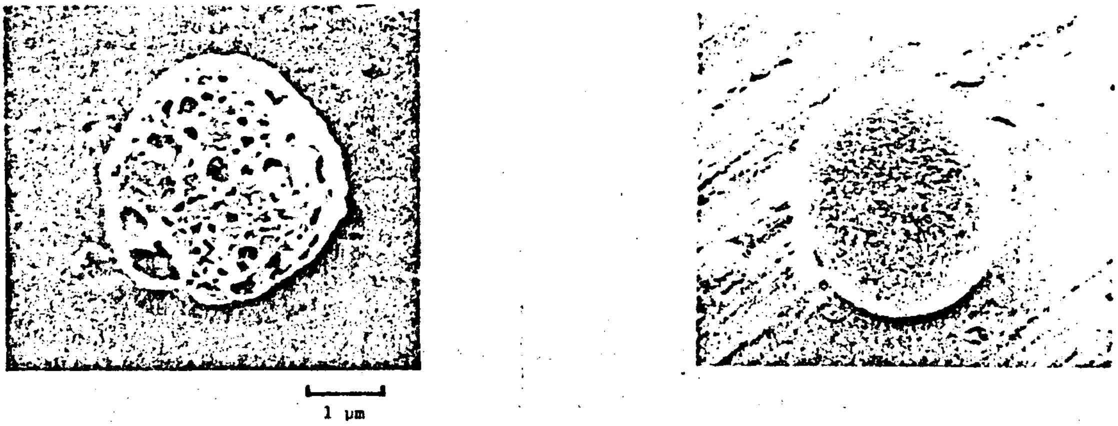
3.1.1.3.3. Fly Ash Emissions

Particulate emissions from oil-fired and coal-fired power plants are generally referred to as "fly ash" because of their size, consistency, and



a). Fly ash from an oil-fired power plant

b). Fly ash from a coal-fired power plant.



c). Higher magnification of a)

d). Higher magnification of b)

Figure 3.1-8. Surface features of particles with high magnification. (Reproduced from ref. (114).)

high mineral content. Figure 3.1-1 shows the relative and absolute contributions of fly ash from electric power generating stations to the overall particulate (TSP) loading in the U.S., California, and California air basins.(8,9) Typical particulate emission factors for the various types of power plants are shown in Figure 3.1-2 and discussed in more detail in sections 3.1.2 through 3.1.4.

Since TSP is not a particularly meaningful index of the aerosol pollution problem or of the effects of electric power plant emissions on particulate size, chemical composition, and reactivity, a further discussion of fly ash is clearly warranted. Fly ash particles are heterogeneous, as evidenced by the electron micrographs in Figures 3.1-8,(114) and are quite different for coal and oil emissions. Oil fly ash particles have rough honeycomb-like surfaces, while particles from coal-fired, power plants are smooth and glassy in appearance. Nearly all fly ash particles from both plants are

Table 3.1-8. Separation According to Boiling Point of Possible Inorganic Species Evolved During Coal Combustion.[a]

Species boiling or subliming, <1550°C	Species boiling or subliming, >1550°C
As, As_2O_3, As_2S_3	Al, Al_2O_3
Ba	BaO
	BeO
Bi	Bi_2O_3
Ca	C
Cd, CdO, CdS	CaO
$Cr(CO)_6$, $CrCl_3$, CrS (155°)	Co, CoO, CoS
K	Cr, Cr_2O_3
Mg	Cu, CuO
$Ni(CO)_4$, $NiCl_2$	Fe, Fe_2O_3, Fe_3O_4, FeO
$PbCl_2$, PbO, PbS	MgO, MgS
Rb	Mn, MnO, MnO_2
S	Ni, NiO
	Pb 1620-1750°C
Se, SeO_2, SeO_3	Si, SiO_2
Sb, Sb_2S_3, Sb_2O_3	Sn, SnO_2
	SrO
SnS	Ti, TiO_2, TiO
Sr	U, UO_2
Tl, Tl_2O, Tl_2O_3	
Zn, ZnS	ZnO

[a] Reproduced from Ref. (108).

spherical.(114) Fly ash emissions from coal-fired and oil-fired power plants also possess different (unimodal) size distributions, as shown in Figure 3.1-9.(111,114) In general, fly ash particles from the coal-fired

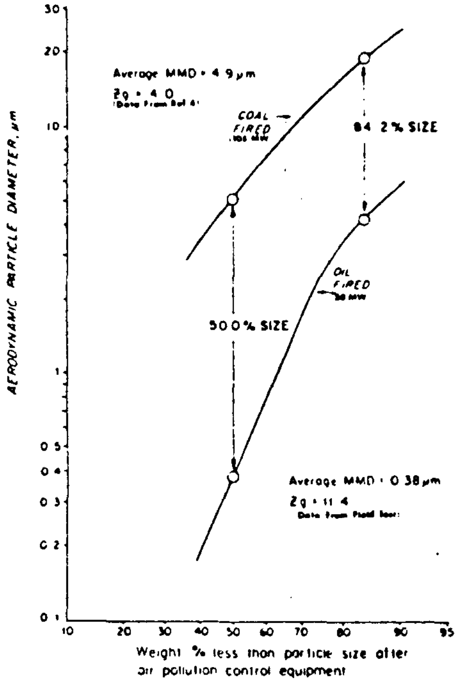


Figure 3.1-9. A Comparison of Particle Mass Size Distribution from Coal and Oil Fired Power Plants. (Reproduced from ref. (114).)

plants are an order of magnitude larger than those from oil-fired plants, such that most (80%) of the particulate mass from coal combustion is not of respirable size. On the other hand, much of the oil fly ash (60-70% by mass) is respirable.(111,114) Therefore, if one considers the total particulate emissions from coal and oil-fired power plants with control devices present, the total emissions of respirable range particulates by coal-fired and oil-fired power plants are about the same.

The chemical composition of fly ash from fuel oil or coal composition depends heavily upon the concentrations and chemical forms of elements in the fuel. Depending on the source of the fuel, or the specific drilling or mining site for that matter, trace element concentrations may vary over an order of magnitude. Typical ranges of concentration for specified elements usually found in fuel and fly ash are discussed in greater detail in sections 3.1.2 and 3.1.3. In general, fly ash from both oil-fired and coal-fired power plants is rich in silicon, aluminum, sodium, calcium, magnesium, iron and carbon. Potassium, titanium, and phosphorous are also present in massive quantities in fly ash from coal-fired plants, but are relatively insignificant in fly ash from oil-fired plants. Fuel oil combustion, on the other hand, releases large amounts of vanadium, nickel, and chromium, which are nearly absent in coal ash. The elements in power plant emissions whose atmospheric loan loading exceeds 10% of current ambient standards are lead, beryllium and nickel.

The distributions of various elements emitted in fly ash as a function of particle size and surface location have been reported by several workers, and the agreement has generally been good. Table 3.1-9 summarizes these results. The work of Hulett,(125) coupled with other investigations,(108-144,117,1[illegible]2) suggests that the elements which accumulate in the fine respirable (< 2-3μm) particle fractions are generally also enriched on the particle surfaces. This phenomenon has been ascribed to the accretions and condensation of the more volatile elements on particles existing in the solid state at the flame temperatures (1300°C-1800°C). Hence, the "condensation nuclei" would become the interiors of particles, and the degree of condensation on the particles would increase with the surface-to-volume ratio and would occur maximally in particles smaller than ~ 3μm.(108-110)

It is unfortunate from the point of view of effects on public health that some of the most volatile elements that are emitted (Table 3.1-8 and 3.1-9) are also the most toxic.(115) Recent studies(115) of the deposition of airborne metals in human tissues, on the other hand, have generally failed to reveal massive accumulations of elements traceable to specific sources. In fact, the only metals for which there was a significant elevation in body tissues from human subjects breathing polluted city air relative to a "clean air" control group were lead (concentrated in the lymph nodes) and nickel (concentrated in lung, lymph, and kidney). While the lead could be traced exclusively to motor vehicle emissions, the nickel was unquestionably derived from airborne effluents from fuel oil combustion, of which 11% was estimated to be from electric power generating plants in New York City after 1970.(115) While particulate emissions from power plants are potentially very dangerous to humans, it is not clear

Table 3.1-9. Preferential Accumulation of Elements in Fly Ash: Size & Spacial Distribution[a]

	Diameter		Locations		
Element	Fines (<2-3μm)	Coarse (>3μm)	Surfaces	Interiors	(Vapor Phase)
Si, Al, K Ca, Ti, Na	0	0	-	+	x
Hf, La, Eu Ce, Ta, Co, Y Bi, Sn, Sr, Nb	0	0	?	?	x
Pb, Cd, Ni Sb, Zu, Mo Tl, Cu, Cr	+	-	+	-	x
V, Ni, Cr	0,+	0	+	-	x
Zr	-	+	?	?	x
Fe	0,+	0	-	+	x
Mn, Cu, Be, U	0,+	0	?	?	x
As, Hg, Se	+	-	+	-	+
S, Br, Cl, F	+	-	+	-	+
Carbon	0	0	+	-	0

[a] From references: 108-114,117,122,125

+) Preferential accumulation
-) Preferential depletion
0) No Preferential accumulation or depletion
X) Not found

whether they pose a large threat to urban populations, in comparison to other local pollution sources.

Direct measurements of the impact of power plants on the concentrations of airborne metals have been reported for several elements. These studies have usually compared trace element concentrations downwind versus upwind from an existing power plant, or else before and after startup for a new power plant. An example of these data is given in Table 3.1-10.(113,126)

Table 3.1-10. A comparison for the Allen Steam Plant area between ambient air concentrations and ambient air standards.

Element	Concentration, μg/m^3		Concentration/standard	
	Maximum Instantaneous air level	Air standard[*]	Short time period	Maximum yearly average[b]
As	0.13	5	0.026	4.4 x 10^{-5}
Be	0.0033	0.01	0.3	5.6 x 10^{-4}
Cd	0.015	~ 1	0.015	2.4 x 10^{-5}
Hg	0.0025	1	0.025	4.8 x 10^{-5}
Ni	0.22	~10	0.02	3.8x 10^{-5}
Pb	0.19	~ 1.5	0.13	2.1 x 10^{-4}
Se	0.16	~ 2	0.08	1.7 x 10^{-4}
Zn	1.7	~50	0.034	5.6 x 10^{-5}

[*] Based on EPA or ACGIH standards. The values for Be and Hg are EPA ambient air standards. The values for the other elements are the ACGIH workroom TLV's divided by a factor of 100.

[b] These values are based on the maximum yearly average ambient air concentration calculated in the vicinity of the plant.

[c] Reproduced from ref. (112).

In general, the contribution of power plant emissions are not sufficient to elevate the airborne concentrations of trace elements in urban or rural areas above the prevailing ambient safety standards. The contribution of a power plant to the community level of TSP can be as high as 25 μg/m^3, which may suffice to raise the ambient level above existing air quality standards.(127) However, TSP is probably the least reliable index of particulate air pollution in terms of implications for human health.

Control of particulate emissions is accomplished by any of several methods, all of which are discussed at greater length in sections 3.1.2 and 3.1.3 as well as in references.(3,128-133) Methods employed for control of particulate emissions from industrial sources include inertial separation, fabric filtration, electrostatic precipitation, gravity settling and wet scrubbing. Control of particulates in the narrow sense means using devices for removing particles from the air. However, we also have to control particulate-forming gases and vapors in order to control the ambient levels of particles. This point is nowhere more apparent than on sunny days in cities like Los Angeles where photochemical particulate smog is formed from reactions between nitrogen oxides and hydrocarbon fragments. In general, particulate removal devices for large particles are more successful in an economic sense than gaseous control techniques. The control of submicron particulates, however, is harder and has not been seriously attempted on a large scale even though it is the most important size range for health effects, visibility reduction, atmospheric dynamics, and length of residence in the atmosphere.

Serious efforts to control the smaller particles on a large scale still lie in the future. A study of the options and economics was recently undertaken by the Midwest Research Institute.(134) Taking "fine particles" to be those below 2 μm in size, they concluded that, in general, emissions standards for this size fraction are both technologically and economically feasible. Fabric filters and high efficiency electrostatic precipitators are the only presently available methods for efficient and economical collection of fine particles from large industrial sources. Thus, while large particles can be adequately controlled by existing equipment, emerging and new technology will be relatively more important in the problem of fine particle control. Some of this new technology is described in the MRI report. Instruments capable of determining particle size distribution will play an important role in measuring and understanding the size dependence of existing and new particulate control devices.

3.1.1.4. Hazardous Metal Vapors

Several trace elements found in coal or oil fly ash are actually or potentially hazardous to human health. Most of these occur in the particulate emissions from power plants and were discussed in section 3.1.1.3. There are, on the other hand, trace elements emitted from coal and fuel oil combustion which enter the air in the vapor phase rather than as particulates. Most notable of these are mercury (Hg) and selenium (Se). In addition, significant portions of arsenic (As) and tellurium (Te) are also discharged as vapors from power plants.(3,108,110,113) Control devices which are designed to remove particulates from the fuel gas do not trap these vaporous elements.(3)

In the U.S., coal and fuel oil combustion for electric power generation are believed to account for some 2000 T/yr, or about 30% of the man-made Hg emissions,(3,138) and about 1100-3600 T/yr, or 65-70% of the man-made Se emissions.(139-142) Contributions of these elements from natural sources are not precisely known, but could be comparable to those from fossil fuel combustion.(138,139)

Particulate emissions from a single 870 MW coal-fired power plant reveal that Hg and Se levels at the plant are enriched several thousand-fold over the natural ambient background (see Table 3.1-11 or Ref. 113) aerosol. Observed concentrations in the ambient air within 40 km of the plant, however, suggests that much of the Hg and Se present in aerosols is derived from sources other than the power plant.(113) Concentrations of Hg and Se in power plant stack gases are clearly above(3,138,139) existing ambient and occupational standards (100 $\mu g/m^3$ for Se, 1 $\mu g/m^3$ for Hg, Refs. 3,138,139,144). In the immediate plant neighborhood, typical daily inhaled doses of either Hg or Se [138,145] would be approximately 10μg. This dose is well below the threshold limit standard for Se,(144) and closely approaches that for Hg.(138) But in the surrounding community, upwind versus downwind measurements show that a 870 MW power plant adds approximately 0.05 $\mu g/m^3$ to the atmospheric mercury concentration,(145a) which is less than 10 per cent of the existing threshold limit standard for mercury.(45,138) No data on occupational levels of Hg or Se are readily available for power plants at the present time. Whether the power plant effluents of metal vapors pose a direct threat to human health needs to be studied more closely. Especially important is an accurate assessment of the potential of power plant Hg and Se emissions to contaminate food and water supplies.

Major control technology for mercury and selenium emissions from stationary sources has yet to be fully developed. Control methods for small-scale Hg emissions which have been discussed(3) include: a) refrigeration to condense the Hg vapors; b) solid absorbents; c) scrubbing solutions

Table 3.1-11. Comparison of Enrichment Factors of aerosols from Walker Branch Watershed and fly ash collected at Allen Steam Plant.[a,c]

Element	EF	
	Aerosol	Fly ash
Ag	236	–
Al	1.9	0.9
As	35.2	57
Au	35.4	35
Br	982	–
Ca	4.2	1.4
Cd	402	30
Cl	295	–
Co	4.1	5.2
Cr	2.0	4.5
Cs	0.3	1.0
Cu	13.7	35
Eu	1.1	1.0
Fe	1.2	2.9
Hf	0.6	0.4
Hg[b]	504	5800
I	100	–
K	1.6	0.7
La	1.6	0.6
Lu	1.0	–
Mn	1.8	0.4
Na	3.7	0.3
Pb	485	17.5
Rb	1.0	1.1
S	4.8	–
Sc	1.1	1.8
Se[b]	380	2174
Ta	0.5	1.3
Tb	1.0	–
Th	1.1	1.4
Ti	2.7	1.6
V	8.1	13.3
Zn	7.2	9.2

[a] $EF = \frac{[\text{Element}]/[\text{Ce}]\ \text{fly ash or deposit}}{[\text{Element}]/[\text{Ce}]\ \text{soil}}$

[b] EF here is the sum of particulate plus gaseous effluent. EF for Hg when just the particulate phase is taken into account is ~0.5; for Se it is 160.

[c] Reproduced from ref. (112).

designed specifically for Hg and Se. However, operation of these types of devices in large-scale plants has not been successful.

3.1.1.5. Gaseous Hydrocarbons and Carbon Monoxide

Hydrocarbons (HC) are a class of organic compounds which are composed strictly of carbon and hydrogen. For our purposes, the term hydrocarbons refers to those alkanes, olefins, and aromatics which exist in the gaseous or vapor state in the atmosphere, as opposed to those which exist in particulate matter.

Both hydrocarbons (HC) and carbon monoxide (CO) are emitted from fossil fuel combustion processes, and are indicators of wasted or lost energy.(3,146,147) Storage tank losses could represent a source of HC emissions at oil-fired power plants, not directly associated with fuel combustion. Since electric power generating stations operate with very efficient combustion conditions, their emissions of CO and hydrocarbons are low. This is shown very graphically in Figures 3.1-1 and 3.1-2.(8,9) Power plants account for less than 2% of these emissions, the largest contributions to the total coming from motor vehicle exhausts. Hence, power plants may not be a significant source of these pollutants. Power plant emission control devices for these pollutants might therefore not have significant effect on ambient air quality. It would probably be difficult to justify the costs associated with control procedures in terms of the limited benefits that would be realized.

3.1.1.6 Water waste effluents

The basic heat transfer fluid at a conventional steam power plant is water, either in liquid or vapor form. Water discharged from the basic power system or from various treatment and cleaning systems contain a number of substances subject to control, including both heat and chemical pollutants. For a fossil-fuel plant many of these effluent sources are indicated schematically in Figure 3.1-10. We will first discuss water effluents from two fundamental plant systems, the cooling system and the boiler, including their associated water treatment and cleaning equipment. We will then summarize effluents from cleanup of combustion products, an important consideration in fossil-fuel power plants. The present discussion, based largely on reference 148, is intended to broadly characterize the water effluents from conventional steam-generating power plants (including, to some extent, nuclear plants), giving some indication of the type of substances which may find their way into the effluent stream, typical amounts of these materials, and the manner in which they may be controlled. The emissions into water and their potential impacts are not treated substantially in the remainder of this report, which is devoted primarily to emissions into air.

Cooling systems

The plant cooling systems are a major source of potential emissions into water resources. The basic function of these systems is to remove from the basic power systems that portion of the combustion, geothermal, or nuclear heat which is not converted into work (electrical energy) and, particularly in the case of fossil-fuel plants, which does not escape with flue gases. This heat removal occurs at the condenser, where the steam exiting from the turbine is condensed, usually for recycle in the steam supply system (except possibly for geothermal plants). This condensation is accomplished by the transfer of heat to a secondary fluid, usually water.

The heated water from the condenser may transfer heat to the general environment in several distinct manners. "Once-through" cooling, the simplest and currently prevalent type, pumps water from some body of water, through the condenser, and finally out to a receiving body, without

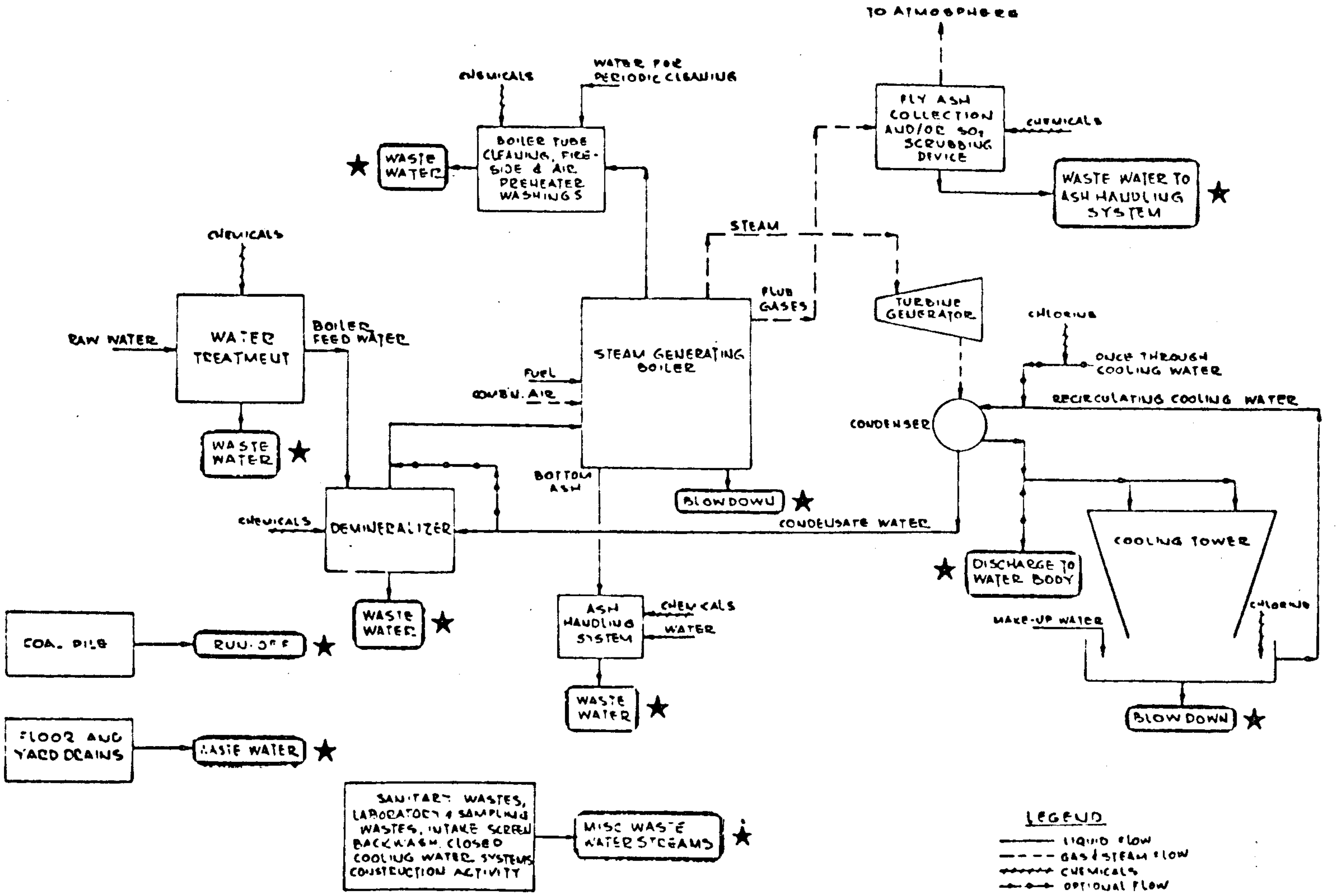


Figure 3.1-10. Typical Flow Diagram for Fossil-Fired Power Plant. Sources of chemical wastes are indicated. [Reproduced from ref. (148).]

any recirculation. The waste heat is simply transferred, via a condenser, to a body of water. More sophisticated cooling systems effect a transfer of heat to the air in a cooling tower, either through evaporative (or "wet") cooling or through "dry" cooling. In wet cooling, water from the condenser is evaporated into a forced or natural draft of air. Due to the water's latent heat of vaporization, a relatively small amount of water can carry off the waste heat, and most of the water can recirculate to the condenser. Even less water is used in a dry cooling system, where heat is transferred from the condenser water to the air across a heat transfer surface which prevents evaporation of the water. In general, however, dry cooling towers require steam conditions at the turbine exhaust that reduce the power plant efficiency, as compared with wet cooling systems.

For any wet cooling system, whether once-through or evaporative, there is a priori a substantial thermal effluent, either to water or to air resources. There are also notable chemical effluents. The latter is also true of dry cooling systems. Regulations[149] from the California Water Resources Control Board place specific limits on the degree to which temperatures may be raised in cold interstate waters, warm interstate waters, and the open ocean. Once-through cooling is only permitted at coastal sites; however, due to developmental controls in the coastal zone, few power plants are likely to be built at such sites in the near future. Due to the decreased plant efficiency and increased expense associated with dry cooling methods, most plants will use evaporative (wet) cooling, primarily with forced (mechanical) draft. (An alternative which requires more space is use of cooling ponds or canals, possibly with spray modules to increase evaporation rates.) Such wet cooling systems recirculate the water to the condenser, but the systems suffer losses due to "drift", loss through the evporative process, and "blowdown", removal of water to maintain a satisfactory chemical environment. Flows associated with a typical wet cooling tower are given in Table 3.1-12.

Blowdown is required because of the concentration of dissolved substances, primarily salts, which would occur as water is lost to evaporation and makeup water is added to maintain the system inventory. This makeup water, added at a rate of about 10,000 gallons per minute for a 1000 MWe power plant,[150-152] contains substances which, if they are concentrated sufficiently in the cooling water, could reach their solubility limit and precipitate as scale in the system. This would impede heat transfer and therefore reduce the system's efficiency. To prevent this, a portion of the circulating water is periodically discharged as blowdown and replaced in the makeup water.

Table 3.1-12. (Reproduced from [a]) Cooling Tower Quantities for Coal-Fired Power Plant — 1000 MWe

Thermal load	11.07×10^9 kwh/yr
Circulating coolant	574,000 gal/min
Blowdown discharge rate	4,290 gal/min
Dissolved solids released in blowdown	4,270 Te/yr
Make-up water rate	11,430 gal/min
Drift rate	287 gal/min
Dissolved solids released in drift	286 Te/yr
Evaporated water	1.37×10^7 Te/yr

[a] T.H. Pigford, et al., Ref. (152).

Most natural waters contain calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^+), and other metallic ions, and chloride (Cl^-), carbonate (CO_3^{--}), bicarbonate (HCO_3^-), sulfate (SO_4^{--}), and other negative ions in solution. An example of salt concentrations in blowdown water (and other effluent streams) is given in Table 3.1-13. These substances occur largely from their presence in the makeup water. However, chemicals are also added to reduce corrosion, scaling, and biological fouling (the last would be particularly true of once-through systems, not the topic of the present discussion). Sulfuric acid is used to maintain the pH; scale and corrosion are controlled by phosphates and chromates; and chlorine is frequently used as a biocide. Algae in water storage reservoirs can be controlled with copper sulfate.

Table 3.1-13. Wastewater Quality[d]

Stream[a]	Chemical Analysis in mg/ℓ									
	Ca	Mg	Na	Cl	HCO_3	SO_4	PO_4	SO_3	SiO_2	TDS[e]
Cooling tower blowdown	702	228	2688	3840	35	2946	9	-	78	10350
Demineralized water system										
Reverse osmosis blowdown	461	151	1687	2373	525	1821	6	-	45	6850
Spent regenerant	59	11	2665	1464	-	3874	-	-	59	7673
Filter backwash[b]	117	38	448	640	6	491	2	-	13	1725
Floor drains from miscellaneous services[b]	117	38	448	640	6	491	2	-	13	1725
Combined wastewater streams (wastewater storage reservoir)	642	208	2470	3512	57	2712	8	-	72	9681
SO_2 absorber thickener underflow	1144	3686	17040	31639	61	9427	52	214	495	63758
Solids mix tank discharge and wastewater to evaporation pond[c]	704	947	6563	8453	61	6678	14	160	135	23715

a. Boiler blowdown returned directly to the raw water storage reservoir.

b. Taken same as AWT water

c. Saturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$)

d. Reproduced from ref. (150).

e. TDS = total dissolved solids

Drift properly refers to droplets of circulating water entrained in the updraft through the cooling tower, and not to the water which is actually evaporated (the latter is discussed immediately below). Drift losses actually have a potential for removing not only water, but dissolved solids (such as the salts discussed above) from the cooling system; these materials then constitute an emission into air, which may be deposited on ground or water surfaces nearby or may become more generally part of the atmospheric mixture. Cooling tower entrainment rates have been estimated to be from 0.001 to 0.01% of the circulating water for mechanical draft cooling (and about half this for natural draft towers).[150-151] The amount of salts entrained depends on their concentration in the water and on the drift control systems. Observed loss rates vary widely; reference 148 quotes rates of from 25 to 500 tons per year from a number of environmental statements for nuclear power plants (which differ little in this respect from fossil-fuel plants) using non-ocean waters — the plants all had similar outputs, the largest being 1700 MWe, twice the smallest; there was not an observable correlation among the six examples between type of cooling (wet or dry) and expected solid loss rate. Comparable rates for salt deposition from coal-fired plants of 1000 MWe output have been given as 300 to 600 tons per year.[151,152]

By their very nature, evaporative cooling towers are sources of water vapor, which may cause visible vapor plumes, ground fogging and/or icing, reactions with SO_2, and, perhaps, weather modification. The visible plumes arise from condensation, into visible droplets, of water vapor from the air as it cools, causing it to change from being nearly saturated to supersaturated; roughly the third of California that is closest to the coast is considered to have a high potential for fogging. Mechanical draft towers, in contrast to the much taller natural draft towers, may emit such plumes close to ground level, causing a potential nuisance, if not hazard (for example, to motorists). However, the principal health impact of the vapor emitted arises from possible interactions with sulfur dioxide (SO_2), perhaps in combination with other substances, to form sulfuric acid mist. (See elsewhere in Section 3 of this report.) Explicit attention should be given to preventing the mixing of vapor and stack exhaust plumes, where this could be a hazard. Finally, the potential for weather modification has not been verified in detail, although "precipitation enhancement" has been suggested.

The boiler produces steam by the transfer of heat from a combustion zone to water inside the boiler tubes. Although this water circulates in a closed system, scaling presents a potential problem, since the solubility of salts decreases with increasing temperatures. At boiler operating temperatures, the salts precipitate out of solution onto heat transfer surfaces. Calcium and magnesium salts are the most troublesome. To prevent such scaling in the boiler, salts are precipitated out as a sludge and discharged as boiler blowdown, either continuously or intermittently (often daily). Sodium phosphates are often used to carry this out, as well as chelating or complexing agents. Tetrasodium salt of ethylenediaminetetraacetic acid (Na_4 — EDTA) and trisodium salt of nitrilotriacetic acid (Na_3 — NTA) are the most common chelating agents.

The solubility of iron in water increases as the pH decreases below 7 (acidic); to prevent corrosion, alkalis such as sodium carbonate, sodium hydroxide, and/or ammonia are used to neutralize any acidic tendencies of the boiler water. Dissolved oxygen in the boiler water may also cause corrosion of metallic surfaces; to control corrosion,mechanical or chemical deaeration may be used — for example, hydrazine is used in high pressure boilers to remove dissolved oxygen via the reaction

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$

Because of these additives, boiler blowdown has a pH of 9.5 - 10.0 and a total dissolved solids concentration of about 10 - 100 mg/l, with 0 - 2 mg/l of ammonia from the hydrazine. Representative overall releases are given in Table 3.1-14.

Water treatment

Water streams in the plant must be treated for a variety of reasons; the discussion which follows is based on reference (148). The treatments include both pretreatment of water for introduction into the cooling and boiler systems and processing of waste streams from cleaning and other operations, including blowdown.

Table 3.1-14. (Reproduced from [a].) Boiler Blowdown Releases in Liquid Wastes — 1000 MWe

Component	Releases lb/day	Releases Te/yr
Suspended solids	3,000	497
Non-degradable organics	400	66.2
Biological oxygen demand	15	2.4
Acids	500	82.5
Alkalinity	63	10.4
Chlorine	160	26.3
Phosphates	250	41.7
Boron	2,000	331
Chromates	15	2.4

[a] Pigford, T. H., et al., Ref. (152).

To minimize blowdown, the makeup water for the cooling towers and the boiler-feed water is pretreated to remove suspended and dissolved solids and salts. Clarification, ion exchange, and evaporation are commonly used for this purpose. Clarification is the chemical precipitation of suspended and dissolved solids (coagulation and water softening, respectively). Aluminum sulfate, ferric sulfate, and sodium aluminate are the most common coagulants, while calcium hydroxide, which is hydrated (slaked) lime, and sodium carbonate are the principle water softeners used. Ion exchange units can remove all mineral salts in one operation, producing high-quality water suitable for boiler and feed purposes. Evaporators are also used to purify boiler feed water, by boiling and then condensing the water. A portion of the boiling water is drawn off as blowdown during the process.

The wastes from water pretreatment can be characterized by pH and concentrations of suspended solids and other substances characteristic of each process. Clarification wastes consist of clarifier sludge and filter washes. The sludge could either be alum or iron salt sludge from the coagulants, while lime water-softener sludge is a calcium carbonate/magnesium hydroxide sludge; filter backwash is a more dilute waste stream. All ion exchange wastes are either acidic or alkaline, except sodium chloride solutions which are neutral. These wastes do not naturally have any significant amount of suspended solids, but certain chemicals such as calcium sulfate and calcium carbonate have very low solubilities and are often precipitated because of common ion effects.* Evaporator blowdown consists of salts concentrated (usually by a factor of 3 - 5) from the feed water. Due to their low solubility, calcium carbonate and calcium sulfate may precipitate out in the blowdown if present in the feed water, while the decomposition of bicarbonate to carbon dioxide and carbonate ion causes the blowdown to be alkaline (pH 9 - 11).

Even with pretreatment of the boiler feed water and the addition of corrosion and scale control agents, scale and corrosion products build up in the boiler tubes. To maintain maximum heat transfer rates, these products must be removed from time to time. Acidic, alkaline, and chelating cleaning mixtures are used and result in waste flows containing high concentrations of metallic species, especially copper and iron, and having a high chemical oxygen demand (COD). Acidic cleaning mixtures are usually inhibited hydrochloric acid (see note next page) with hydrofluoric acid or fluoride salts added for silica removal. The principle pollutants released in waste streams from this type of cleaning are "acidity", phosphates, fluorides, and organic compounds with biological oxygen demand (BOD). Large quantities of copper, iron, "hardness", phosphates, and "turbidity" are also released from the dissolved scale. Alkaline mixtures may contain free ammonia and ammonium salts, an oxidizing agent (e.g., potassium or sodium bromate, or chlorate) for copper removal, ammonium persulfate, nitrates or nitrites, and sometimes caustic soda. The resultant waste stream contains ammonium ions, oxidizing agents high in alkalinity, and large concentrations of iron and copper ions from the dissolved scale. Common chelating agents, EDTA, NTA, citrates, and gluconates, are used with alkaline cleaning mixtures, often after acid

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*If one ion of a slightly soluble salt has its concentration increased, the other ion may be forced out of solution (maintaining the product of their concentrations constant).

cleaning, to neutralize residual acidity and remove additional amounts of iron, copper, alkaline earths and silica.

Other plant components require cleaning. One example is the condenser; although the steam side does not require frequent cleaning, depending on boiler water quality, the water side is typically cleaned with (uninhibited) hydrochloric acid. Feedwater heaters, condensate coolers, hydrogen coolers, air compresser coolers, stator oil coolers are some of the other system components requiring infrequent cleaning. Inhibited hydrochloric acid* is commonly used to clean these items.

A steam electric power plant has other miscellaneous sources of waste-water, including piping, equipment leakage, and drainage. Floor drains collect these wastes, which can include dust, fly ash, coal dust, cleaning agents, oil and grease. Sanitary wastes from workers and plant laboratory wastes can be handled as appropriate.

Wastes associated with the combustion process itself are the next topic for discussion.

Liquid wastes from combustion products

Liquid wastes can arise from processes in the burner area, in the stack, and — ultimately — from handling and storage of resulting sludges.[148-151] Combustion processes leave a residue of soot and fly ash deposited on the fireside of the boiler tubes, air preheater surfaces, and in the exhaust stacks. High-pressure water is used to wash the soot and fly ash from these components. Water is used to clean the buildup of scale from the cooling tower basins. Water is also used to handle air pollution control equipment wastes. An electrostatic precipitator for fly ash removal, followed by a wet lime or limestone scrubber to absorb SO_2, is the most likely combination of equipment for a coal-based power plant, since burning coal results in the emission of large quantities of particulates and SO_2.

When pulverized coal is burned most of the ash is entrained along with the exhaust gases as fly ash (about 80%), while the rest settles out in the furnace as bottom ash. The bottom ash is sluiced out of the furnace

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*Hydrochloric acid to which an inhibitor has been added to slow its reactivity.

by water and then placed in dewatering bins, requiring about 2,400 - 40,000 gallons per ton of ash conveyed. The fly ash collected by the electrostatic precipitators is pneumatically transferred to storage silos with air. Operation of the lime or limestone SO_2 scrubbers will result in the generation of a sludge (thickener underflow), mainly composed of calcium sulfite, calcium sulfate, and water containing numerous dissolved solids (see Table 3.1-13). These wastes can be either disposed of as landfill or by ponding. If the wastes are buried as landfill, the fly ash and scrubber sludge are mixed to reduce the water content of the sludge and avoid dust problems with the ash, and trucked to the disposal site along with the bottom ash. Ponding involves mixing the fly ash and sludge with water and pumping the mixture to a lined pond where the water drains through a porous underdrain system of bottom ash (which was laid down during pond construction). The drainage water is piped to a lined evaporation pond. (See the section on coal-fired power plants for more details.)

Oil-fired plants also produce ash, collected by mechanical collectors, which is disposed of by burial. Oil contains less ash than coal so the quantities generated are much less. Any bottom ash can be washed out with the hot, high pH, boiler water.

Both coal and oil ash contain trace elements, including heavy metals, and must be disposed of so that none of these contaminants enter any water supplies. (See the tables on coal and oil ash analysis later in this report.)

Coal-fired plants have an additional waste stream resulting from leaching from exposed, inactive coal storage piles. These storage piles usually contain enough coal for 90 days of operation. For a 1000 MWe plant, up to 2,340,000 cubic yards of coal might have to be stored, covering an area from 15 to 75 acres, depending on the height of the coal pile. Active coal storage would be in enclosed silos holding 3 to 6 days supply. Since the inactive coal storage pile is open to the atmosphere, moisture and air can oxidize the metal sulfides contained in the coal to sulfuric acid. Oxidation also results in the precipitation of ferric compounds. Rainfall will wash these acids and compounds out in the runoff, which might average 22 to 26 million gallons per year (see Table 3.1-15).

Coal pile runoff is characterized by a low pH (high acidity), high concentrations of dissolved solids, including iron, magnesium, sulfate,

Table 3.1-15. Typical Chemical Wastes from a Coal-Fired Power Plant.[a]

Waste Stream	Flow,[1] GPD/Mw	Typical Concentrations of Major Pollutants[1], mg/l				
		TSS	Iron	Copper	Sulfate	Hardness
Ion exchange	88	46	-	-	2085	-
Boiler blowdown	52	25	-	-	-	-
Boiler cleaning	0.25	127	2100	380	-	520
Boiler fireside cleaning	4.44	582	142	-	1650	4661
Air preheater cleaning	11.7	1882	1610	-	1130	3700
Miscellaneous cleaning	1.11	1000[2]	-	-	-	-
Laboratory operations	10	100[2]	-	-	-	-
Floor drains	30	100[2]	-	-	-	-
Recirculating bottom ash sluicing blowdown	400	1000[2]	-	-	-	-
Ash pond overflow (once-through fly ash)	5000	60	-	-	510	244
Coal pile drainage	-[3]	864	-	-	6880	1025

Notes:
1. Based on the average of available data
2. Assumed values
3. Based on 0.02 acres/Mw coal pile and 40 inches of rainfall per year; the flow is calculated to be 59,500 GPD for a 1000 Mw plant

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[a] Reproduced from ref. (148).

and coal dust. The acid will dissolve other metals so that aluminum, sodium,manganese, copper, zinc, and other metals are present. The runoff will also wash any chemical sprays used for dust control (phenol, ether, and polyethylene glycol or calcium chloride) or to prevent freezing (oil, saline solutions or calcium chloride). Runoff must be prevented from reaching any ground or surface water supplies. This can be done, for example, by using a vinyl liner under the coal pile with a 6" bed of sand on top to prevent the coal from puncturing the liner. The water can then be collected for treatment and/or disposal.

Water recycle and disposal

Because of the large variety of uses of water and the wide range of water quality required in a power plant, it is possible to cascade the use of the various levels of water quality in a waste management system which incorporates a high degree of water reuse and prevents the discharge of any effluent to surface or ground water supplies.[148] The water consumption of such a plant would consist only of evaporation from receiving ponds and/or ash-scrubber sludge disposal areas, and evaporative and drift losses from the cooling towers.

The highest water quality is required for boiler feedwater (about 2 mg/l TDS). Because of this, boiler blowdown is generally purer than the original source of supply and can be recycled for almost any other use. Cooling system blowdown is also usually reusable after a softening process. Without softening, it is still suitable for low water quality uses, such as ash sluicing, SO_2 stack scrubber makeup water, and coal pile dust control. Another possible source of water is the drainage from coal piles, roads, and buildings, which can be filtered and recycled. Power plants receiving coal by slurry pipeline can dewater the coal and use this water in their service systems.

Some power plants collect all of the reusable water, such as boiler and cooling tower blowdown,into a reservoir which is the source for all lower quality water needs, such as ash sluicing. Other plants assign specific uses for the recycled water from the various sources. An example would be the taking of cooling tower makeup water from boiler blowdown and of makeup for the ash sluicing equipment from cooling tower blowdown.

One of the simplest ways to dispose of the nonreusable waste water is to pump it to lined evaporation ponds for final disposal. Such ponds can occupy a large area. An alternative means of disposal is to use waste water to slurry the ash, scrubber, and water treatment sludges to disposal ponds, which can also be rather large.

Many power plant sites are too small to allow the use of disposal ponds. Careful water management could minimize water consumption and wastewater generation allowing for water disposal in a low moisture ash and waste sludge mixture. Closed-loop bottom ash sluicing and SO_2 scrubbing systems together with dry pneumatic fly ash handling equipment can be used to significantly reduce water use. Makeup water for these closed-loop systems can come from boiler and cooling tower blowdown, while blowdown from the closed loop systems can be combined with ash, SO_2 scrubber sludge, and water treatment wastes to form a semisolid mixture which can be trucked to a disposal area. This solid waste can be used as landfill either on or off of the site, or, for mine-mouth plants, at the coal mine. Mine-mouth power plants can also use waste water in coal preparation and mining activities.

Summary of power plant liquid waste streams

A number of tables are included at this point to summarize the major waste streams from steam power plants; they are characteristic primarily of fossil-fuel plants, but — with the exception of streams that result directly from the fuel, combustion process, or flue gas cleanup systems — they are also characteristic of nuclear power plants.

Table 3.1-15 summarizes the chemical wastes from a coal-fired power plant process. A summary of important effluents and their limitations are given in Table 3.1-16. Chemical waste flow rates are given in Table 3.1-17. Table 3.1-18 lists many of the chemicals used in power plants, while Table 3.1-19 summarizes chemical waste treatment and control technology.

Table 3.1-16. Summary of Effluent Limitations Guidelines and Standards for Pollutants other than Heat.[a]

SOURCE	POLLUTANT PARAMETER	EFFLUENT LIMITATIONS*		
		BPCTCA (1977)	BATEA (1983)	New Sources
Nonrecirculating cooling water	Free available chlorine		0.2 (0.5 max) **	
	Total residual chlorine	←	**	→
Cooling tower blowdown	Free available chlorine		0.2 (0.5 max) **	
	Total residual chlorine		**	
	Chromium, total	No limitation	0.2 (0.2 max)	-
	Zinc, total		1.0 (1.0 max)	-
	Total phosphorus (as P)		5.0 (5.0 max)	-
	Corrosion inhibiting materials other than Cr, Zn, and P		Case-by-case	-
	All corrosion inhibiting materials		-	No discharge
Ash transport	Total suspended solids	30 (100 max)	-	-
	Oil and grease	15 (20 max)	-	-
Bottom ash transport	Total suspended solids	-	2.4 (8.0 max)	1.5 (5.0 max)
	Oil and grease	-	1.2 (1.6 max)	0.75(1.0 max)
Fly ash transport	Total suspended solids	-	30 (100 max)	No discharge
	Oil and grease	-	15 (20 max)	No discharge
Low-volume wastes				
Boiler blowdown	Total suspended solids		30 (100 max)	
	Oil and grease		15 (20 max)	
	Copper, total		1.0 (1.0 max)	
	Iron, total		1.0 (1.0 max)	
Metal equipment cleaning wastes	Total suspended solids		30 (100 max)	
	Oil and grease		15 (20 max)	
	Copper, total		1.0 (1.0 max)	
	Iron, total		1.0 (1.0 max)	
Others, except sanitary wastes and radwastes	Total suspended solids	←	30 (100 max)	→
	Oil and grease		15 (20 max)	
Rainfall runoff from materials storage piles and construction activities	Total suspended solids		Not to exceed 50mg/l	
Rainfall runoff from other sources ***	All pollutant parameters		No limitation	
Sanitary wastes and radwastes	All pollutant parameters		No limitation	
All sources	Polychlorinated biphenyls		No discharge	
	pH value ****		Within the range 6.0-9.0 at all times	

* Note: Numbers are concentrations, mg/l, except for pH values. Effluent limitations, except for pH and rainfall runoff, are quantities of pollutants to be determined by multiplying the concentration indicated times the flow of water from the corresponding source. Effluent limitations are averages of daily values for 30 consecutive days (maximum values for any one day are determined from the numbers in parentheses), except for pH and rainfall runoff. In the event that waste streams from various sources are combined for treatment or discharge, the quantity of each pollutant attributable to each waste water source shall not exceed the limitation for that source. No limitations are prescribed for sources/pollutants not specified in this table.

** Note: Neither free available chlorine nor total residual chlorine may be discharged from any unit for more than two hours (aggregate) in any one day and not more than one unit in any plant may discharge free available chlorine or total residual chlorine at any one time. Exceptions to be made, on a case-by-case basis, if discharger demonstrates that limitations must be exceeded in order for the cooling system to operate efficiently.

*** Note: ...and from facilities designed, constructed, and operated to treat the volume of material storage runoff and runoff from construction activities that is associated with a 10 year, 24 hour rainfall event.

**** Note: From all sources except nonrecirculating cooling water, rainfall runoff from sources other than materials storage piles and construction activities ***, sanitary wastes and radwantes.

[a] Reproduced from ref. (148).

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Table 3.1-17. Flow Rates and Chemical Wastes[a]

	Reported Data		Typical		
Waste Stream	Waste Flow or Volume	Frequency	Flow or Volume	Basis	Remarks
Condenser Cooling Water					
Once-Through	-	-	500-1500 GPM/Mw	-	Flow reported in FPC Form 67.
Recirculating	20-7200 x 10^3 GPD	-	Varies from 0.3% to 4% of curculating water flow.		Blowdown depends on water quality and varies from 2-20 concentrations.
Water Treatment					
Clarification	No Discharge				
Softening	No Discharge				
Ion Exchange	1-533,00 x 10^3 GPD	52-365 cycles/yr.	-	-	Extremely variable-depending on raw water quality.
Evaporator	0.1-1060 x 10^3 GPD	300-365 cycles/yr.	-	-	Extremely variable-depending on raw water quality.
Boiler Blowdown	0.05-1120 x 10^3 GPD	25-365 cycles/yr.	-	-	Flow reported in FPC Form 67.
Chemical Cleaning					
Boiler Tubes	3-5 Boiler Volumes	once/7 mos.-once/100 mos.	1 boiler vol.per 1-2 hrs.-Boiler draindown time.	Frequency-once per 24-30 mos.	
Boiler Fireside	24-720 x 10^3 GAL.	2-8/yr.	300,000 GAL.	5/yr.	
Air Preheater	43-600 x 10^3 GAL.	4-12/yr.	200,000 GAL.	6-12/yr.	
Misc. Small Equip.	No reported data	-	-	-	
Stack	No reported data	-	-	-	Cleaned infrequently
Cooling Tower Basin	No reported data	-	-	-	Cleaned infrequently
Ash Handling	5-32,000 x 10^3 GPD	-	-	-	Overflow from ash ponds reported in FPC Form 67.
Drainage					
Coal pile	17-27 x 10^6 GAL/YR.	Dependent on rainfall	-	Reported data based on 43-60 inches of rain year.	Flow dependent upon frequency; duration and intensity of rainfall
Floor & Yard Drains	No reported data	-	-	-	Flow dependent upon frequency & duration of cleaning and stormwater runoff.
Air Pollution Control Devices	No Discharge				
Misc. Waste Streams					
Sanitary Wastes	No reported data	-	25-35 gal/capita/day	Personnel: operators-1 per 20-40 Mw maintenance-1 per 10-15 Mw administrative-1 per 15-25 Mw	
Plant Laboratory and Sampling	No reported data	-	-	-	Nominal, variable flow
Intake Screen Backwash	No reported data	-	-	-	Guideline requires collection & removal of debris-flow data not significant.
Closed Cooling Systems	No reported data	-	5 gal./day	-	-
Low Level Rad Wastes	No reported data	-	-	-	Flow extremely variable depending on treatment techniques, leakage, etc.
Construction Activity	No reported data	-	-	-	Flow depends primarily on rainfall.

[a] Reproduced from ref. (148).

Table 3.1-18. Chemicals Used in Power Plants.[a]

Use	Chemical
Coagulant in clarification water treatment	Aluminum sulfate
	Sodium aluminate
	Ferrous sulfate
	Ferric chloride
	Calcium carbonate
Regeneration of ion exchange water treatment	Sulfuric acid
	Caustic soda
	Hydrochloric acid
	Common salt
	Soda ash
	Ammonium hydroxide
Lime soda softening water treatment	Soda ash
	Lime
	Activated magnesia
	Ferric coagulate
	Dolomitic lime
Corrosion inhibition or scale prevention in boilers	Disodium phosphate
	Trisodium phosphate
	Sodium nitrate
pH control in boilers	Ammonia
	Cyclohexylamine
Sludge conditioning	Tannins
	Lignins
	Chelates such as EDTA, NTA
Oxygen scavengers in boilers	Hydrazine
	Morphaline
Boiler cleaning	Hydrochloric acid
	Citric acid
	Formic acid
	Hydroxyacetic acid
	Potassium bromate
	Phosphates
	Thiourea
	Hydrazine
	Ammonium hydroxide
	Sodium hydroxide
	Sodium carbonate
	Nitrates
Regenerants of ion exchange for condensate treatment	Caustic soda
	Sulfuric acid
	Ammonex
Corrosion inhibition or scale prevention in cooling towers	Organic phosphates
	Sodium phosphate
	Chromates
	Zinc salts
	Synthetic organics
Biocides in cooling towers	Chlorine
	Hydrochlorous acid
	Sodium hypochlorite
	Calcium hypochlorite
	Organic chromates
	Organic zinc compounds
	Chlorophenates
	Thiocyanates
	Organic sulfurs
pH control in cooling towers	Sulfuric acid
	Hydrochloric acid
Dispersing agents in cooling towers	Lignins
	Tannins
	Polyacrylonitrile
	Polyacrylamide
	Polyacrylic acids
	Polyacrylic acid salts
Biocides in condenser cooling water systems	Chlorine
	Hypochlorites
Additives to house service water systems	Chlorine
	Chromates
	Caustic soda
	Borates
	Nitrates
Additives to primary coolant in nuclear units	Boric acid
	Lithium hydroxide
	Hydrazine
Numerous uses	Numerous proprietary chemicals

[a] Reproduced from ref. (148).

Table 3.1-19. Chemical Wastes Control and Treatment Technology.[a]

Pollutant Parameter	Control and/or Treatment Technology	Effluent Reduction Achievable	Industry Usage	Costs	
				Capital	Operating
Common: pH	Neutralization with chemicals	Neutral pH	Common	$10-20,000 (tanks, feeder, etc.)	$3-30,000 (Chemicals, labor, etc.)
Dissolved Solids	1. Concentration and evaporation	Complete Removal	Not generally in use - Desalinization technology	$250,000-$1,660,000 from Table A-VIII-5; costs are significantly less in areas where evaporation ponds are feasible.	$150,000-$450,000 from Table A-VIII-6; costs are significantly less in areas where evaporation ponds are feasible.
	2. Reverse Osmosis	50-95%	Not in use - Desalinization technology.	50-80 ¢/1000 gal. total cost.	
	3. Distillation	60-90%	Not in use - Desalinization technology.	80-150 ¢/1000 gal. total cost.	
Suspended Solids	1. Sedimentation	90-95%	Extensive	$1000-$20,000/Mw based on 500 gpd/Mw	1-20¢/1000 gallons
	2. Chemical Coagulation and Precipitation	95-99%	Moderate	$10,000-$35,000/Mw based on 500 gpd/Mw	1-20¢/1000 gallons
	3. Filtration	95%	Not generally practiced-water treatment technology.	$7,000-$30,000/Mw based on 500 gpd/Mw	1-20¢/1000 gallons
Specific: Phosphate (Blowdown, Chemical Cleaning, Floor & Yard Drains, Plant Laboratory & Sampling)	1. Chemical coagulation and Precipitation		Not generally practiced-water treatment technology.	$10,000-$35,000/Mw based on 500 gpd/Mw	1-20¢/1000 gallons
	2. Deep Well Disposal	Ultimate Disposal	Not practiced	Costs extremely variable-dependent primarily on geologic conditions.	
Iron (Water Treatment, Chemical Cleaning Coal Ash Handling, Coal Pile Drainage)	1. Oxidation, chemical coagulation & precipitation	Removal to 0.1 mg/l	Limited usage	$150-4,000x$10^3$	10-100¢/1000 gal.
	2. Deep Well Disposal	As described above			
Copper (Once-through Condenser Cooling)	1. Replace condenser tubes with stainless steel or Titanium.	Elimination of discharge.	Done in several plants where tubes have erroded or corroded-not done for environmental reasons.	Prohibitively expensive-would not be done except where retubing is required for process reasons.	No incremental operating cost.
Copper (Blowdown, Chemical Cleaning)	1. Chemical Coagulation and Precipitation	Removal to 0.1 mg/l	Limited usage	$100-$9,000/1000 gpd capacity.	10-350¢/1000 gal.
	2. Ion Exchange	Removal to 0.1 mg/l	Not Practiced	$400-$1200/1000 gpd capacity	31-81¢/1000 gal.
	3. Deep Well Disposal	As described above			
Mercury (Coal Ash Handling & Coal Pile Drainage)	1. Reduction & Precipitation	Removal to 0.3 mg/l	Limited usage	$700/1000 gpd	7¢-27¢/1000 gal.
	2. Ion Exchange	Removal to 0.1 mg/l	Not practiced	$18,000-$22,000/1000 gpd	$1/1000 gal.
	3. Adsorption	Removal to 50 μg/l	Not practiced	$5000-$50,000/1000 gpd	$0.50-$2/lb. mercury removed
Vanadium (Chemical Cleaning)	1. H_2S Treatment Precipitation	Removal of low concentrations difficult to achieve	Not practiced	Cost Data Not Available	
	2. Ion Exchange		Not practiced	Cost Data Not Available	
Vanadium (Oil Ash Handling)	1. Convert to Dry Collection	Ultimate Disposal	Practiced in several plants	Cost Data - Not Available	
	2. Total Recycle with Blowdown & Precipitation	Complete recycle of liquid	Not generally practiced	Cost Data Not Available	

[a] Reproduced from ref. (148).

Table 3.1-19. Chemical Wastes Control and Treatment Technology (continued)

Pollutant Parameter	Control and/or Treatment Technology	Effluent Reduction Achievable	Industry Usage	Costs	
				Capital	Operating
Chlorine (Once-through Condenser Cooling)	1. Control of Residual Cl_2 with automatic instrumentation	Control to 0.2 mg/l	Limited usage in the industry-Technology from sewage treatment practiced in some plants-all systems are not capable of being converted to mechanical cleaning.	$5,000	Negligible
	2. Utilize mechanical cleaning	Eliminates Cl_2 discharge		No Cost Data Available	
Chlorine (Recirculating)	1. Control of Residual Cl_2 with automatic instrumentation	---------------As described above---------------------------------------			
	2. Reduction of Cl_2 with sodium bisulfite	Below detectable limits	Being installed in a new nuclear facility;however excess $NaHSO_3$ is discharged.	No Cost Data Available	
Aluminum/Zinc (Water Treatment, Chemical Cleaning, Coal Ash Handling, Coal Pile Drainage)	1. Chemical Precipitation	Removal to 1.0 mg/l	Limited usage	$500-$3000/1000 gpd	10-180¢/1000 gal.
	2. Ion Exchange	Similar to Copper	------------------------	------------------------	--------------
	3. Deep Well Disposal	--------As described above--			
Oil (Chemical Cleaning, Ash Handling, Floor & Yard Drains)	1. Oil-water Separator (Sedimentation with skimming)	Removal to 15 mg/l	Common usage	$1,500-$15,000 based on 500 gal/Mw 25-400 Mw range	No data
	2. Air Flotation	Removal to 10 mg/l	Limited usage	$5,000-$50,000	No data
Phenols (Ash Handling, Coal Pile Drainage, Floor & Yard Drains)	1. Biological Treatment	Removal to 1 mg/l	Not practiced in the industry.	$150 $2800/1000 gpd	22¢/1000 gal.
	2. Ozone Treatment	Removal to < 0.01 mg/l	Not practiced in the industry.	No data	No data
	3. Activated Carbon	Removal to < 0.01 mg/l	Not practiced in the industry.	$50-$350/1000 gpd	4¢-15¢/1000 gal.
Sulfate/Sulfite (Water Treatment, Chemical Cleaning, Ash Handling, Coal Pile Drainage, SO_2 Removal)	Ion Exchange (Sulfate) Oxidation & Ion Exchange (Sulfite)	75-95%	Not practiced in the industry.	Total cost of $2.00/1000 gal.	
Ammonia (Water Treatment, Blowdown, Chemical Cleaning, Closed Cooling Water Systems)	1. Stripping	50-90%	Not practiced; several installations in sewage treatment	Total cost - 3¢/1000 gal.	
	2. Biological Nitrification	Removal to 2 mg/l	Not practiced for these waste streams	No Data Available	
	3. Ion Exchange	80-95%	Not practiced	Total cost - 10¢/1000 gal.	
Oxidizing Agents (Chemical Cleaning)	Neutralization with reducing agent and precipitation where necessary.	Neutral pH & > 95% removal	Limited usage	No Data Available	
BOD/COD (Sanitary Wastes)	Biological Treatment	85-95%	Common practice	$25,000-$35,000	Negligible
COD (Water Treatment, Chemical Cleaning)	1. Chemical Oxidation	85-95%	Limited usage	No Data Available	
	2. Aeration	85-95%	Not practiced	No Data Available	
	3. Biological Treat.	85-95%	Not practiced	No Data Available	
Fluoride (Chemical Cleaning)	Chemical Precipitation	Removal to 1 mg/l	Limited usage	Total cost - 10-50¢/1000 gal.	
Boron (Low Level Radwastes)	Ion Exchange	Removal to 1 mg/l	Not generally practiced-radioactive material would concentrate on ion exchange resin requiring inclusion in solid radwaste disposal system.	No Data Available	

3.1.1.7 Noise

Mechanical and combustion noise from a power plant may be caused by the operation of conveyors, pumps, steam lines, furnaces, exhaust ducts, turbines, generators, vehicles, transformers, transmisssion lines, and virtually anything else that moves. Noise abatement is necessary both for the protection of power plant personnel, and also to prevent noise transmissions from the general vicinity of the power plant. The Walsh-Healy Act, which regulates noise levels in industries with federal contracts, set maximum limits to exposure to noise (see Table 2-8)[154], largely on the basis of potential hearing impairment (see Table 3.1-20). The EPA has established community noise limitation standards in EPA Document No. 550/9-74-004 (March 1974), by recommending that noise levels at the property line, from the onset of construction and station operation activities, should not exceed 55 dBA.

Table 3.1-20 Percentage Risk of Developing a Hearing Handicap

Percentages of exposed population

Exposure level (dBA)	Age	20	25	30	35	40	45	50	55	60	65 Years
	Exposure (age - 20)	0	5	10	15	20	25	30	35	40	45
80	Total	0.7	1.0	1.3	2.0	3.1	4.9	7.7	13.5	24.0	40.0
	Noise-induced	No increase in risk at this level of exposure									
85	Total	0.7	2.0	3.9	6.0	8.1	11.0	14.2	21.5	32.0	46.5
	Noise-induced	0.0	1.0	2.6	4.0	5.0	6.1	6.5	8.0	8.0	6.5
90	Total	0.7	4.0	7.9	12.0	15.0	18.3	23.3	31.0	42.0	54.5
	Noise-induced	0.0	3.0	6.6	10.0	11.9	13.4	15.6	17.5	18.0	14.5
95	Total	0.7	6.7	13.6	20.2	24.5	29.0	34.4	41.8	52.0	64.0
	Noise-induced	0.0	5.7	12.3	18.2	21.4	24.1	26.7	28.3	28.0	24.0
100	Total	0.7	10.0	22.0	32.0	39.0	43.0	48.5	55.0	64.0	75.0
	Noise-induced	0.0	9.0	20.7	30.0	35.9	38.1	40.8	41.5	40.0	35.0
105	Total	0.7	14.2	33.0	46.0	53.0	59.0	65.5	71.0	78.0	84.5
	Noise-induced	0.0	13.2	31.7	44.0	49.9	54.1	57.8	57.5	54.0	44.5
110	Total	0.7	20.0	47.5	63.0	71.5	78.0	81.5	85.0	88.0	91.5
	Noise-induced	0.0	19.0	46.2	61.0	68.4	73.1	73.8	71.5	64.0	51.5
115	Total	0.7	27.0	62.5	81.0	87.0	91.0	92.0	93.0	94.0	95.0
	Noise-induced	0.0	26.0	61.2	79.0	83.9	86.1	84.3	89.5	70.0	55.0

a) From Ref. 154

Power plants meet these limitations by enclosing and/or insulating all noise producing components or processes that would violate these standards. The main power building is enclosed to the elevation of the turbine-generator operating deck, and enclosures surround induced-draft and forced-draft fans, along with the coal pulverizer and all coal handling equipment, (e.g. conveyers, railroad car unloading equipment, etc.). The fuel pipes, steam lines, air inlets and exhaust ducts are wrapped with insulation.[155,156,157] Sound panels are located around yard activities, auxiliary equipment, and ductwork that might cause excessive noise. Mufflers and baffles are used wherever necessary. Low power public address systems and quiet-type electric motors also help reduce "noise pollution".[156,157] The enclosures and sound panels (free-standing walls) are usually two inches thick, made of a solid structural skin on the outside, acoustical fill (usually a glass fiber material) and perforated sheeting inside. Doors and latches are equipped with bulb seals to prevent acoustic (air) leaks. Ductwork and pipes are insulated with fiber glass held on by perforated muffler steel.[157]

Table 3.1-21 shows the predicted noise level increases caused by the operation of a 2000 MWe coal-fired plant at the nearest residence, about 2 miles away from the center of the power generating facilities (which does not includ the waste disposal ponds). The next nearest residence, which is about 3 miles from the generating facilities, is not expected to experience any increases in noise levels due to the power plant's operation.[155]

Table 3.1-21 Noise Levels at a Point Two Miles from the Center of a 2000 MWe Coal-Fired Power Plant (center of plant, excluding evaporation ponds)[a]

	(dBA re 0.0002 dyn/cm^2)				
	Leg	Ldn	L_{10}	L_{50}	L_{90}
before power plant	58	63	52	37	26
after power plant	59	64	52	43	42

A-Weighted noise levels:

Leg:	energy equivalent average noise level
Ldn:	energy equivalent day-night level (24 hour equivalent sound level with 10dB nighttime penalty)
L_{10}:	noise level exceeded 10% of the time
L_{50}:	noise level exceeded 50% of the time
L_{90}:	noise level exceeded 90% of the time

a) From Ref. (155)

However, noise (unwanted sound) can cause more than hearing loss. It can bring about hypertension, dilate the pupils, cause dryness in the mouth, contract muscles and blood vessels, cause excess production of epinephrine and norepinephrine, stop the flow of gastric juices, and accelerate cardiac stimulation (studies have correlated heart disorders with noise). It can also cause psychological effects.

Such effects are typically specific to individuals and are not used as the quantitative basis for noise standards. However, they and more subjective considerations are a primary reason for formulation of community noise (nuisance) standards, such as that suggested by the EPA.

Eighteen million Americans suffer from some hearing loss. Half of those exposed to 95dB of noise for 40 hours a week will join them over the next 10 years. These are permanent losses in hearing, there are many more cases of temporary hearing losses. Table 3.1-20 shows a hearing loss risk chart. The noise threshold for discomfort is about 117dB at 2000-5000 Hz, while the pain threshold is about 143dB.(154)

3.1.2 Coal-Fired Power Plants

Coal represents one of our largest fuel resources available for large central station power plants and is one of the dirtiest. The properties of coal vary widely, even among Western coals, and indeed among samples from the same field (see Table 3.1-22), making it difficult to predict the exact emission characteristics of any given plant. Using "average" properties for Western coal (Table 3.1-22) with even the best pollution controls presently available for large power plants, the enormous coal consumption rates of these plants result in substantial emissions of gaseous and particulate pollutants (Table 3.1-23). Burning coal within California for future electric power generation will depend on the demonstration of environmental acceptability.

3.1.2.1 Coal Combustion Processes

The various types of coal-fired power plants which are presently in operation differ from one another in the manner in which coal is fed into their boilers. These are principally pulverized coal furnaces, cyclone furnaces, crushed coal furnaces, and stoker-fed boilers.[21] Stoker-fed boilers are found in small, older power plants. Their principal advantage is that fairly large, non-uniform sized chunks of coal can be burned. On the other hand, the efficiency of the stoker limits the size of this type of coal-fixed power plant (typically 60 MWe).[80] Other disadvantages include high air/fuel ratio requirements that reduce operating efficiency. In addition, PAH emissions from a stoker-fed power plant are much higher than those from other types,[80] suggesting that carbon losses may also be higher.

Cyclone furnaces and pulverized coal-fired units have the following advantages over stoker-fed units:[21]

1) ability to handle the larger coal feed rates of larger coal plants.
2) ability to use any size of coal available
3) improved response to load changes
4) increased thermal efficiency due to lower excess air for combustion and lower carbon loss
5) lower NO_x emissions (uncontrolled)
6) reduced manpower for operation
7) improved ability to use substitute fuels (oil or gas).

Table 3.1-22. Selected Properties of Western Coals as Received by the Power Plant.[a)]

Location	Moisture %	Ash %	Sulfur %	Nitrogen %	Heat Value Btu/lb
Montana Richland County (county average)	35.4	6.9	0.3	0.7	6706
	33.3-38.4	4.6-9.6	0.2-0.5	0.6-0.8	6120-7450
Utah, Kane County (Kaiparowits Plateau)	14.8	7.0	0.42	0.98	10,800
	14.0-16.5	6.5-9.0	0.35-0.75	0.84-1.03	10,300-11,000
Utah, Carbon Co. (price coal field)	4.6	6,8	0.4	1.3	12,730
	3.6-13.5	4.0-8.0	0.2-1.1	1.2-1.5	10,620-12,960
New Mexico (State average)	7.3	6.0-19.5	0.6	—	11,900
	2.4-20.1	10.0	0.4-1.2	—	9,560-13,250
Colorado (State average)	11.8	7.2	0.5	—	11,160
	2.2-31.9	4.8-70.4	0.3-2.4	—	7,470, 13,780
Arizona (Black Mesa Coal	10.74	7.93	0.51	1.03	10,725
	9.75-16.0	5.84-12.2	0.36-1.26	0.90-1.07	10,000-11,500
Wyoming (State average)	17.3	7.5	0.6	0.8	9,190
	10.4-27.1	4.1-15.0	0.3-0.9	0.7-1.0	8,530-10,280
Utah Alton (coal field average)	25.3	7.19	0.86	0.79	8,897

a) From references 123 and 124.

Table 3.1 - 23

Emissions From a Coal-Fired Power Plant, 1000 MWe (net), 100% load

Emission	Emission Factor $(LB/T_{coal})^a$	Uncontrolled (T/HR)	Controlled (T/HR)	NSPS ($LB/10^6$ Btu)	Max. Allowed (T/HR)
Particulates	17 x A	29	0.15	0.10	0.52
SO_x (as SO_2)	32 x S	4.6	0.49	1.2	6.2
NO_x (as NO_2)	18	4.3	3.6*	0.70	3.6*
CO	1	0.24	0.26	-	-
Hydrocarbons (as CH_4)	0.3	0.072	0.078	-	-
Aldehydes	0.005	$1.2 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	-	-

A = ash content of coal in percent, S = sulfur content of coal in percent

Assumptions:

85% of ash in the coal becomes flyash and 95% of the sulfur in the coal is oxidized to SO_x (calculated as (SO_2)).

Coal properties: ash content, 7.0%; sulfur content, 0.5%; heating value, 10,000 Btu/LB; density, 81 LB/Ft^3

Fuel consumption (where η stands for thermal efficiency):

uncontrolled, 1070 MWe (gross) @ 38% η:481 T_{coal}/HR (total waste heat:$6.0 \cdot 10^9$ Btu/HR)

controlled, 1120 MWe (gross) @ 37% η:517 T_{coal}/HR (total waste heat: $6.5 \cdot 10^9$ Btu/HR)

Internal Power Consumption	MW (% of net output)
auxiliary equipment	70 (7%)
SO_x stack gas scrubber	20 (2%)
Stack gas reheat	20 (2%)
electrostatic precipitator	10 (1%)
TOTAL (controlled)	120 (12%)

Collection Efficiencies of Pollution Controls[13,14]	
electrostatic precipitation	99.5%
SO_x stack gas scrubber	90.0%
NO_x controls: sufficient to meet NSPS*	

[a] From reference (161)

[b] Net Plant efficiency: 33%

In a cyclone furnace, crushed coal is fed into a cylindrical chamber into which air is blown tangentially, imparting a whirling motion to the coal. The conditions in the furnace are such that the ash forms a slag. The coal is held in the slag on the cylinder surface where it is "scrubbed" by the incoming air. Coals with very high ash contents can be burned in a cyclone furnace, and the slagging serves to reduce the amount of fly ash. However, some coals are not suitable for combustion in a cyclone furnace. Hence, the flexibility and usefulness of the cyclone furnace may be limited where coal quality is variable.[21]

The most energy-efficient type of furnace for large coal-fired power plant is the pulverized coal type. In this case, coal which has been ground into a fine power is blown into the combustion chamber. Almost any kind of coal can be burned pulverized, so that limitations on power plant size and coal quality are not particularly stringent.

3.1.2.2 Coal-fired Plant Emissions Characteristics

Hypothetical emission factors for coal-fired electric power plants have been published by the EPA,[8,9,161] and are summarized in Figure 3.1-2 and Table 3.1-23. Emissions of sulfur oxides (SO_x) depend heavily on the fuel sulfur content, as indicated by the EPA formula.[161] Table 3.1-23 shows that they are relatively independent of the particular coal combustion process used in the power plant. Assuming that all the SO_x emitted is SO_2,[2] and that 95% of the fuel sulfur is oxidized to SO_x, uncontrolled SO_x emissions from a 1000 MWe power plant should be on the order of 6 tons per hour for 0.6% sulfur coal.[161,162]

The only other gaseous pollutant emissions from power plants which are subject to control measures at the present time are <u>nitrogen oxides</u> (NO_x), which are emitted primarily as nitric oxide (NO). Unlike particulate or sulfur oxide emissions, which depend on the ash and sulfur content of fuel, the NO_x discharged into the atmosphere is governed by the combustion process conditions as well as nitrogen content of the fuel. Primary factors are flame temperature and furnace temperatures, residence time of the combustion gas at the flame temperature, heat release and removal rates, and the amount of excess air.[161-164] Nitrogen oxides result from the oxidation of nitrogenous compounds in the fuel (up to 75% total emissions[22a]) or from the high-temperature oxidation of atmospheric nitrogen (see Table 3.1-1 and also Ref. 8). Figure 3.1-11 shows the predicted flue gas NO concentration as a function of combustion temperature under "typical" boiler furnace conditions.[167]

For coal-fired power plants, combustion temperatures in the range of 1500°C - 1900°C (2700°F - 3400°F) are required for optimum operating performance. Hence, flue gas concentrations of NO in power plants should range between 50 - 1000 ppm (Figure 3.1-11). High temperatures, coupled with rapid heat removal from the combustion gases, prevent the decomposition of NO, so that, once formed in the flame, NO remains in the flue gas.[22,165,166] Table 3.1-24 shows some representative NO_x emission factors for the various types of coal-fired boilers. It is evident that cyclone furnaces emit much more NO_x (about 2.5 times) than either stoker-fed boilers or pulverized coal units. In comparison with current EPA emission standards (0.70 pounds NO_2 per 10^6 BTU input, Ref.(161)) cyclone furnace NO_x emissions are far too high. NO_x emissions from the other types of boilers all lie within ±25% of the current EPA standard.[161,168]

Particulate emissions from coal-fired power plants have generally been characterized as fly ash, and analyzed principally in terms of mineral or inorganic elemental composition. Table 3.1-25 shows typical fly ash emissions for the various types of coal-fired power plants in common use. Pulverized coal fired units emit more total particulate mass than any other firing methods. About 80% of the ash contained in the feed coal is entrained in the flue gas stream, with the remainder retained in the furnace for dry-bottom pulverized units.[21,168] On the other hand, wet-bottom or slag-tap pulverized furnaces, in which the ash is molten, can retain as much as 50% of the combustion-generated ash in the furnace, but can only utilize certain types of coal. Fly ash emissions from cyclone furnaces are generally about half of those from pulverized coal-fired boilers, on a total mass (fly ash to flue gas) basis.

As shown in Table 3.1-26 the size distribution of ash particles emitted from coal-fired power plants can vary dramatically with the firing process. Stoker-fed boiler particulates are primarily larger than 22 μm diameter. Only 4% of the TSP mass occurs in the respirable fraction (MMD < 2.5 μm).[169] In contrast, 65% of the total particulate mass emitted from cyclone furnace fired boilers has mean radius <2.5 μm. Obviously, an even larger fraction of the particle number and surface area lies in this size range.[35] Pulverized coal-fired power plants emit particulates whose mass is approximately evenly distributed on a log-normal scale among size ranges between 2.5 - 22 μm.[169,170] The fact that the fly ash mass is not dominated by the very largest particles indicates that most of the particulates (by number) are of respirable size.

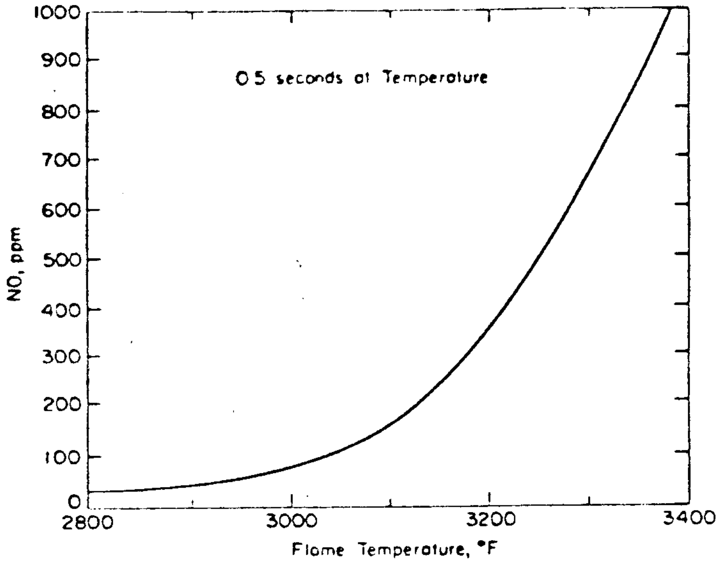

Figure 3.1-11. Theoretical Production of Nitric Oxide by Fossil Fuel Combustion as a Function of Flame Temperature. (Reproduced from ref. (167).)

Table 3.1-24. Nitrogen Oxide Production as a Function of Boiler Type.[f]

Full-load tests[a]				
	ppm[b]		$Lb/10^6 Btu$	
Type of boiler firing	B[d]	A[e]	B[d]	A[e]
Vertical *	221	310	0.38	0.55
Corner *	526	413	0.95	0.71
Front-wall *	416	606	0.68	0.95
Spreader-stoker	431	437	0.65	0.76
Cyclone	1204	1160	2.5	2.2
Horizontally opposed *	393	350	0.65	0.59
Partial-load tests[c]				
	ppm[b]		$Lb/10^5 Btu$	
Type of boiler firing	B[d]	A[e]	B[d]	A[e]
Vertical *	161	171	0.28	0.31
Corner *	393	325	0.73	0.57
Front-wall *	500	453	0.82	0.74
Spreader-stoker	430	390	0.73	0.68
Cyclone	742	784	1.9	1.8
Horizontally opposed *	395	328	0.66	0.56

[a] Average values for three or four tests at each unit.
[b] Reported as NO_2, at stack conditions.
[c] Average values for two tests at each unit.
[d] B: Before fly-ash collector.
[e] A: After fly-ash collector.

* Pulverized coal firing.

[f] Reproduced from ref. (168).

Table 3.1-25. Fly ash Concentrations and Collection Efficiencies of various Coal-Fired Boilers.[1]

Type of boiler firing	Ash in coal,[a] %	Concentrations				Type of fly-ash collector[d]	Collector efficiency, %
		gr/scf[b]		lbs/1000 lb[c] dry flue gas			
		B[g]	A[h]	B[g]	A[h]		
Full-load tests[e]							
Vertical *	20.2	4.8	0.18	8.8	0.27	C, E	96.4
Corner *	14.9	3.7	0.23	6.9	0.42	C, E	93.9
Front-wall *	10.3	2.5	0.44	4.6	0.82	E	63.1
Spreader-stoker	8.4	2.3	0.36	4.2	0.66	C	83.9
Cyclone	7.7	1.5	0.39	2.8	0.62	E	74.5
Horizontally opposed *	8.2	4.9	0.65	8.9	1.27	C	83.9
Partial-load tests[f]							
Vertical *	19.0	4.7	0.11	8.7	0.21	C, E	97.5
Corner *	13.5	2.9	0.13	5.5	0.21	C, E	95.7
Front-wall *	9.2	2.4	0.22	4.4	0.41	E	91.3
Spreader-stoker	8.7	1.5	0.19	2.8	0.35	C	87.3
Cyclone	7.4	1.8	0.22	3.1	0.36	E	86.3
Horizontally opposed *	7.8	2.9	0.61	5.1	1.1	C	77.7

[a] Moisture-free basis.

[b] Corrected to 12 percent CO_2, dry volume basis.

[c] 1000 pounds of dry flue gas corrected to 50 percent excess air.

[d] C designates cyclone; E designates electrostatic precipitator.

[e] Average values for either three or four tests of each unit.

[f] Average values for two tests at each unit.

[g] Before fly-ash collector.

[h] After fly-ash collector.

* pulverized coal firing

[1] Reproduced from ref. (168).

Table 3.1-26. Particle Size Distributions (by Mass) Emitted from Coal-Fired Power Plants.[a,b,c]

Particulates	Type of unit			
	Pulverized[a,b]	Spreader stoker[a]	Cyclone[a]	Pulverized[c]
(*R* = particle radius in microns)				
Total	8.0 kg/T 16 lb/t	6.5 kg/T 13 lb/t	1 kg/T 2 lb/t	
R > 22	25%	61%	10%	24%
22 > *R* > 10	23	18	7	18
10 > *R* > 5	20	11	8	16
5 > *R* > 2.5	17	6	10	16
2.5 > *R*	15	4	65	26

[a] From ref. (169).

[b] From ref. (162).

[c] From ref. (170).

The inorganic chemical composition of coal-fired power plant fly ash has been scrutinized by numerous investigators.[31,113,123,124,163] Much of the work has attempted to determine the mass balance distribution of elements from the feed coal to the various bottom ash and fly ash fractions. Typically, many elements are enriched in fly ash relative to the feed coal. Table 3.1-27 summarizes the concentrations of the most important elements in coal and fly ash observed from several power plants.[31,113,123,124] Elements such as silicon, aluminum, and the alkali metals and alkaline earths are the dominant soil and rock constituents, and are probably fused into glass-like materials during combustion (see Figures 3.1-8 and 3.1-9, and also Ref. 114.) In addition, iron is present in fly ash from coal combustion in large quantities, and may account for much of whatever reactivity is associated with fly ash. For more detailed analyses of the elemental composition, refer to the original reports. From Tables 3.1-27 and 3.1-28, one can assess the enrichment of elements in fly ash relative to concentrations in coal. Much more important, however, is the enrichment of elements in fly ash relative to ambient aerosols or to elements in soil. This information is available for the Allen Steam Plant in Tennessee,[113] and is shown in Table 3.1-11 in Section 3.1.1.4. It is evident that while iron in fly ash is enriched 8-15 fold compared to the feed coal, it is enriched by only a factor of 2.9 compared to neighboring soils, and only a factor of 2.5 compared to the background aerosol. Other elements in coal-derived fly ash which are enriched relative to the soil include (with respective enrichment factors) lead (17.5), vanadium (13.3), zinc (9.2), copper (35.), cadmium (30.), gold (35.), and arsenic (57.). These can all be considered trace elements in coal fly ash. It is noteworthy to point out that elements such as manganese, nickel, and vanadium,which form a substantial fraction of the fly ash from oil-fired power plants are of only minor importance as coal-related emissions. Table 3.1-29 shows estimates of the trace element emissions characteristics from a 1000 MWe power plant, based on information[163] from the Kaiparowits proposal. The particulate mass fractions retained in the furnace, captured by a precipitator, and emitted through the stack have differing size distributions. Many trace elements in the coal preferentially concentrate on certain size fractions when burned in a coal-fired power plant. The elements favoring the largest particles tend to be retained in the furnace bottom ash, while those concentrating in the smaller particles can escape collection (particularly if a precipitator is the chosen control), so that their emission rates will not be decreased by the rated efficiency of the pollution

Table 3.1-27 Trace element concentrations in coal and in ash fractions from coal-fired power plant (ppm)

Element (as free X)	USGS[a] Coal	USGS[a] Fly Ash	USGS[a] Bottom Ash	Swanson[b] Coal	EPA[c] Fly Ash
Carbon[d]	750,000-800,000	---	---	720,000-770,000	3,700-362,000
Silicon	10,000- 70,000	200,000-300,000	260,000-300,000	---	84,000-300,000
Aluminum	10,000- 44,000	60,000-140,000	120,000-140,000	---	50,000-300,000
Sodium	100- 4,500	750- 15,000	3,000- 15,000	---	1,500- 7,000
Potassium	250- 2,000	7,500- 12,500	4,000- 13,000	---	23,000- 25,000
Calcium	1,400- 12,000	32,000-120,000	31,000- 90,000	---	840-100,000
Magnesium	500- 2,000	6,000- 13,500	6,000- 9,600	---	360- 38,700
Iron	1,400- 7,700	24,000- 77,000	20,000- 70,000	---	14,000-190,000
Sulfur	600- 3,200	1,600- 6,800	800- 2,000	3,000- 13,000	500-100,000
Phosphorus	100- 700	250- 4,000	250- 4,000	---	320-210,000
Arsenic	---	3-15	1	1-5	---
Fluorine	---	110-610	50	20-200	---
Antimony	---	0.6-3.7	0.05-0.6	0.1-43	---
Thallium	---	1.1-1.7	0.2 -0.4	---	---
Europium	---	10-30	10-20	---	---
Cadmium	6	1	1	0.1	---
Copper	1-18	36-128	33-39	5-50	---
Lithium	3-29	45-110	50-80	1-122	---
Zinc	3-17	50-105	22-48	1.5-54	---
Manganese	---	100-300	100-700	5-200	---

(continued)

Table 3.1-27 (continued)

Element (as free X)	USGS[a]			Swanson[b]	EPA[c]
	Coal	Fly Ash	Bottom Ash	Coal	Fly Ash
Boron	---	200-700	100-300	20-100	---
Barium	---	2,000-5,000	1,500-5,000	50-700	---
Beryllium	---	3-7	2-7	1	---
Chromium	---	20-150	15-70	1.5-15	---
Cobalt	---	7-20	7-15	5	---
Gallium	---	15-50	15-30	1-20	---
Titanium	---	3,000-7,000	3,000-5,000	70-5,000	22,400
Nickel	---	10-70	10-30	0.5-15	---
Lead	---	20-70	20-30	1.5-70	---
Scandium	---	10-20	10-15	1-15	---
Strontium	---	300-3,000	300-1,500	20-500	---
Vanadium	---	70-150	70-100	3-50	---
Yttrium	---	30-70	30-50	1-10	---
Zirconium	---	150-300	150-300	3-150	---
Lanthanum	---	70	70	3-10	---

a) Average range of concentrations for coals from Western and Southwestern states. The fly ash concentrations are the range of values for power plants in Colorado, Arizona, Utah, Nevada, and the "Four Corners" site. (ref. 123).

b) Ref. 124.

c) Ref. 31.

d) Measured by the weight loss upon ignition.

Table 3.1-28. Enrichment factors for Elements on Suspended Particles Relative to the Input Coal at two Coal-Fired Power Plants.[a]

Element	Ref. (171)		Ref. (117)	
Ba	2.6	0.9	0.92	0.08
As	7.3	3.2	6.3	1.7
Sb	6.7	1.6	4.0	0.9
V	3.8	1.0	0.72	0.06
Ga	3.1	0.7	1.0	0.2
Se	2.5	1.1	5.7	1.3
Zn	6.4	4.4	2.9	0.6
Co	2.2	0.3	1.0	0.2
Cr	2.0	0.3	0.92	0.08
Fe	1.2	0.1	0.83	0.33
Mn	0.66	0.08	1.3	0.2
Ti	0.54	0.14	0.78	0.14
Sm	0.83	0.16	0.69	0.07
Ta	0.95	0.40	0.66	0.02
Th	0.91	0.10	0.80	0.03
Sc	≡ 1.0		≡ 1.0	
Mg	0.42	0.26	1.2	0.3
Na	0.85	0.17	0.92	0.17
Al	0.41	0.06	0.83	0.08
La	0.98	0.09	0.71	0.05

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[a] Reproduced from ref. (171).

Table 3.1-29. Estimated trace element emissions from 1000 MW coal plant with 90% SO_2 scrubber and 99.5% electrostatic precipitator.[a]

Element and molec.wt.	Conc in total ash (ppm)	Fly ash / total ash	Emitted ash / fly ash	Emitted / total	Emission lb/hr
Sb (121.8)	2.8	1	0.01	0.01	$1{,}7\cdot10^{-3}$
As (74.9)	0.9(coal)	—	—	0.25	0.24 (GAS)
Ba (137.4)	2290	0.8	$5.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.54
Be (9.01)	3.4	0.8	$5.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	$8.0\cdot10^{-4}$
B (10.8)	1400	0.8	$4.9\cdot10^{-3}$	$3.9\cdot10^{-3}$	0.32
Cd (112.4)	1.0	0.8	$4.3\cdot10^{-3}$	$3.5\cdot10^{-3}$	$2.1\cdot10^{-4}$
Cr (52.0)	70	1	$6.7\cdot10^{-3}$	$6.7\cdot10^{-3}$	0.028
Co (58.9)	20	0.8	$5.2\cdot10^{-3}$	$4.1\cdot10^{-3}$	$4.8\cdot10^{-3}$
Cu (63.5)	80	1	$4.2\cdot10^{-3}$	$4.2\cdot10^{-3}$	0.020
F (19.0)	54(coal)	—	—	0.25	14 (GAS)
Ga (69.7)	26	1	$6.5\cdot10^{-3}$	$6.5\cdot10^{-3}$	0.010
Pb (207.2)	38	1	$4.4\cdot10^{-3}$	$4.4\cdot10^{-3}$	0.010
Li (6.94)	72	0.8	$5.7\cdot10^{-3}$	$4.5\cdot10^{-3}$	0.019
Mn (54.9)	210	0.8	$4.5\cdot10^{-3}$	$3.6\cdot10^{-3}$	0.045
Hg (200.6)	0.06(coal)	—	—	1	0.063 (GAS)
Mo (95.95)	6	1	$5.6\cdot10^{-3}$	$5.6\cdot10^{-3}$	$2.0\cdot10^{-3}$
Ni (58.7)	34	1	$3.7\cdot10^{-3}$	$3.7\cdot10^{-3}$	$7.4\cdot10^{-3}$
Se (78.96)	3(coal)	—	—	0.18	0.60 (GAS)
Sr (87.63)	560	0.8	$5.2\cdot10^{-3}$	$4.1\cdot10^{-3}$	0.14
Sc (44.96)	14	0.8	$4.4\cdot10^{-3}$	$3.5\cdot10^{-3}$	0.12
Tl (204.4)	0.34	0,8	$6.0\cdot10^{-3}$	$4.8\cdot10^{-3}$	$9.6\cdot10^{-5}$
Ti (47.9)	3000	0.8	$5.0\cdot10^{-3}$	$4.0\cdot10^{-3}$	0.71
U (238.07)	6	0.8	$5.7\cdot10^{-3}$	$4.5\cdot10^{-3}$	$1.6\cdot10^{-3}$
Y (50.95)	92	1	$5.6\cdot10^{-3}$	$5.6\cdot10^{-3}$	0.030
Y (88.92)	44	0.8	$4.7\cdot10^{-3}$	$3.7\cdot10^{-3}$	$9.6\cdot10^{-3}$
Yb (173.04)	4	0.8	$5.3\cdot10^{-3}$	$4.2\cdot10^{-3}$	$9.9\cdot10^{-4}$
Zn (65.38)	64	1	$5.2\cdot10^{-3}$	$5.2\cdot10^{-3}$	0.020
Zr (91.22)	150	0.8	$5.5\cdot10^{-3}$	$4.4\cdot10^{-3}$	0.039

$$\left(\begin{array}{l}\text{PARTICULATE}\\ \text{EMISSION}\end{array}\right) = (\text{CONC IN ASH})\times\left(\begin{array}{l}\text{TOTAL UNCONTROLLED ASH}\\ \text{PRODUCTION RATE}\end{array}\right)\times\left(\frac{\text{EMITTED}}{\text{TOTAL}}\right)$$

$$\left(\begin{array}{l}\text{GASEOUS}\\ \text{EMISSION}\end{array}\right) = (\text{CONC IN COAL})\times\left(\begin{array}{l}\text{TOTAL CONSUMP-}\\ \text{TION RATE}\end{array}\right)\times\left(\begin{array}{l}\text{EMITTED}\\ \text{TOTAL}\end{array}\right)$$

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[a] Values calculated from reference 163.

control equipment. The elemental size distribution is an important consideration for assessment of the health effects of fly ash emission.

Table 3.1-30 and Table 3.1-31 show the size distributions of iron and several other (trace) elements which exhibit enrichment in fly ash, before and after an electrostatic precipitator in the flue gas stream. Prior to the electrostatic precipitator, a large percentage of the iron, chromium, nickel, lead, cadminum, and zinc are found in particles with diameter greater than 20 µm. In contrast, the stream which is discharged into the atmosphere is enriched in smaller particles (MMD between 1 - 5 µm) containing iron, vanadium, chromium, nickel, lead, antimony, cadmium, zinc, and selenium.[111] Combinatio of Tables 3.1-30 and Table 3.1-31 allows determination of absolute concentrations of size-resolved fly ash minerals.

Information on the elemental and organic carbon composition of fly ash from coal-fired power plants is relatively sparse, and shows a high degree of variability (Table 3.1-27, also Ref.(31)). Current understanding of the proportion of total carbon emitted as particulate from coal-fired boilers as polynuclear aromatic hydrocarbons (PAH, also called "polycyclic particulate organic matter" or "PPOM" in Ref.(80)) is totally lacking. The PAH emissions from power plants, with their higher combustion efficiencies, are usually very low when compared to other sources.[80,172] Coal-fired power plants generally emit less than 1.6 micrograms (µg) of particulate polycyclic organic matter per million calories (Mcal) of heat input, compared to over 1600 µg/Mcal for hand-stoked residential furnaces.[80] Figure 3.1-12 shows the correlation between benzo(a)pyrene emissions and the heat input rate for fossil fuel furnaces. Benzo(a)pyrene emissions are the highest for the smallest units, and decrease with increasing furnace size.[80,172] Presumably, this results from the higher combustion efficiencies of the larger units.[172] The data also indicate that oil and gas fired units emit lower amounts of PAH than coal-fired units, although the difference in emission rates due to the type of fuel burned approaches zero as the size of the unit increases (Fig. 3.1-12).[80,172]

In addition to containing trace elements, coal ash is also slightly radioactive. Table 3.1-32 shows a typical radionuclide analysis of coal and coal ash, plus an estimation of the radioactivity emitted with the coal ash of a 1000 MWe power plant operating at 100% load. Moore and Poet[158] have surveyed measurements of radioactivity which escape from coal-fired power plants into the surrounding environment. Typical counts of fly ash specimens from Poland, New York, and Alabama power plants range between 37.8-300 Picocuries per gram

Table 3.1-30. Concentration and Mass Median Diameter of Emitted Particles. (Reproduced from ref. (111).)

	Power plant			
	Inlet		Outlet	
Component	Concn, μg/m³	MMD, μm	Concn, μg/m³	MMD, μm
TP	38×10^5	18	8700	4.7
Fe	3×10^5	6	1340	2.6
V	970	5	1.5	1.6
Cd	8.5	8.4	0.1	5.0
Cr	300	12	0.7	<0.5
Co	0	0	0	0
Ni	395	11.2	1.3	5.4
Mn	600	15	0	0
Cu	[a]	[a]	[a]	[a]
Pb	189	5	1.4	1.1
Sb	689	<1	6.8	0.6
Zn	162	8.6	0.7	4.7
TP	23×10^5	16	9600	4.7
Se	114	0.9	6.5	4.7

Set A analyzed by graphite furnace atomic absorption.
Set B analyzed by neutron activation.

[a] Component could not be reliably distinguished from background material in the blank collection surfaces. [b] Not analyzed.

Table 3.1-31. Percent of Particles and Elements Emitted as a Function of Size. (Reproduced from ref. (111).)

Coal-fired power plant[a]

	Sample set A																				Sample set B			
	Total particulate		Fe		V		Cr		Ni		Mn		Pb		Sb		Cd		Zn		Total particulate		Se[b]	
Size range, μm	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Above 30	24	5	15	8	6	0	16	0	40	0	0	0	18	0	0	0	12	12	15	2	21	5	7	8
20–30	21	6	6	5	7	0	14	0	4	0	8	0	6	0	0	0	11	8	6	6	19	6	5	6
10–20	38	17	15	9	17	12	26	0	18	13	89	0	20	1	0	0	22	10	21	30	31	18	9	16
5–10	13	20	16	14	20	10	7	0	23	43	33	0	6	9	0	0	15	20	26	10	19	19	19	18
1–5	3	38	30	45	31	43	25	20	7	30	0	0	29	40	0	38	5	30	17	8	7	37	9	22
0–1	1	14	18	19	19	35	12	80	8	14	0	0	21	50	100	62	35	20	15	44	3	15	51	30

[a] Samples collected at the inlet and at the outlet of an electrostatic precipitator control device. [b] Analysis by neutron activation.

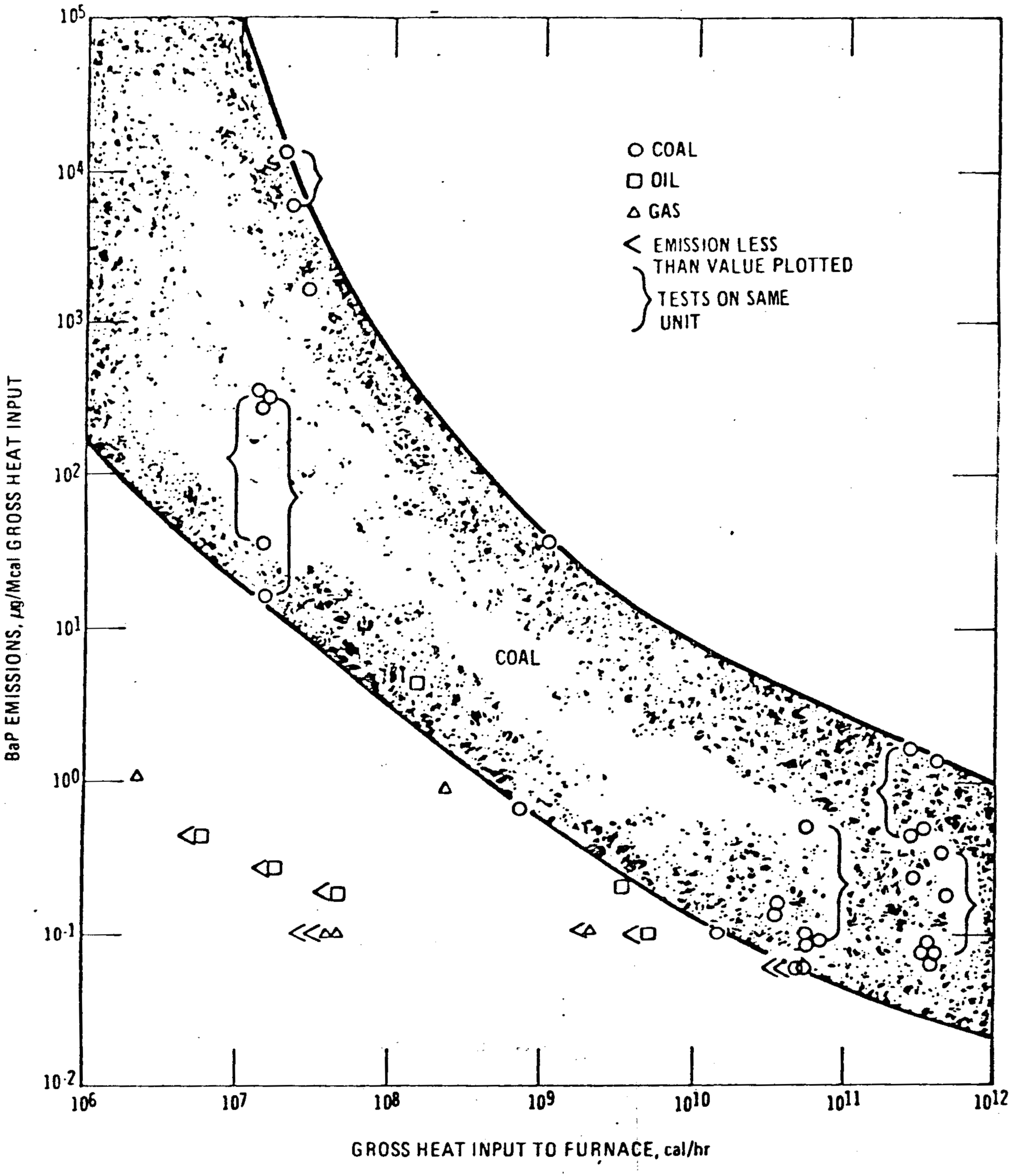

Figure 3.1-12. Benzo(a)pyrene Emissions from Coal, Oil, and Natural Gas Heat-Generation Processes. (Reproduced from ref. (80). The heat input for a 1000 MWe power plant operating at 38% efficiency is 2.3×10^{12} cal/ hr.)

Table 3.1-32 Radioactive emissions from a 1000 MWe coal-fired power plant.[a]

Radionuclide	pCi/gm Coal	pCi/gm Ash
Radium-226	0.018 - 0.13	0.24 - 1.86
Radium-228	0.022 - 0.18	0.30 - 2.57
Thorium-230	0.069 - 0.20	0.96 - 2.86
Thorium-232	0.024 - 0.17	0.33 - 2.43
	0.133 - 0.68	1.83 - 9.71
pCi/lb →ash	60.3 - 308	830 - 4404

Assumes all the radioactivity in the coal remains in the ash and is equally distributed between fly and bottom ash.

	pCi/hr	Ci/yr
Uncontrolled (total)	$5.80 \cdot 10^7 - 3.08 \cdot 10^8$	0.508 - 2.70
Emitted in fly ash	$4.63 \cdot 10^7 - 2.46 \cdot 10^8$	0.406 - 2.16
Emitted in bottom ash	$1.17 \cdot 10^7 - 6.19 \cdot 10^7$	0.103 - 0.543
Controlled, 99.5% (total)	$6.12 \cdot 10^7 - 3.25 \cdot 10^8$	0.536 - 2.85
Emitted from stack	$0.015 \cdot 10^{-7} - 0.013 \cdot 10^8$	0.0022-0.011
Retained in the plant in the solid wastes (collected fly ash)	$6.10 \cdot 10^7 - 3.24 \cdot 10^8$	0.535 - 2.84

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[a] Values were calculated from references 164 and 168.

(pCi/gm). Global background counts in soils, however, are on the order of 5.4-227 pCi/gm. Evidently, radioactivity emitted from coal-fired power plants is preferentially concentrated in the fly ash. Upwind versus downwind measurements of radioactivity have also been reported for the Four Corners power plant of Southern California Edison.[158] Radionuclide counts were reported to be 48.6 $pCi/10^6m^3$ at a distance of 9.3 km upwind from the plant, but 91.8 $pCi/10^6m^3$ at a distance of 5.6 km downwind. Hence, one might expect a large coal-fired power plant to cause some increase in the existing background level of radioactivity.[158] Since variations in the background radioactivity range from 45-760 $pCi/10^6m^3$, one cannot argue that coal-fired power plants are a significant global or regional source.

3.1.2.3 Effects of Emission Control Measures

The above discussion of emissions from coal-fired power plants has focused on uncontrolled emissions. However, both presently operating and planned power plants incorporate some kind of emissions control strategy. The discussion in the previous sections provides a baseline for judging the effectiveness of emission control technologies, and suggests possible emissions from a given power plant during malfunction of an emission control system. The present section discusses the various types of emissions control technologies available, their effectiveness, their by-products and waste disposal problems.

3.1.2.3.1 Sulfur Oxides Control

The principal methods for controlling sulfur oxides emission are: a) use of low-sulfur fuels, b) fuel desulfurization prior to combustion, c) removal of sulfur oxides from gases after combustion, d) modification of the combustion process, and e) increasing stack height (which alters dispersion characteristics). Debate over which control technology offers the best promise of success has been heated. Conflicting recommendations have been advanced by the EPA, the electric power companies, and other government agencies, based on the proven or hypothesized effectiveness of certain procedures versus the cost of installation and operation. Several reviews of the various SO_x control measures have appeared in the literature[10-18,21] and should be consulted for detailed information.

Conversion to a low-sulfur fuel would require the substitution of coal or oil containing less than 0.5 - 1.0% total sulfur by weight for unregulated coal or oil with higher sulfur content (up to 4.5% weight). The sulfur content of fossil fuels burned in some California air basis is currently limited by regulation to less than 0.5% (see Section 2.2, above).

An alternative to the combustion of increasingly scarce low-sulfur fuels is the removal of sulfur compounds from the fuel that is consumed, regardless of its grade. This can be done either before it is burned (fuel desulfurization) or after combustion (flue gas desulfurization). While technologies for coal and oil fuel desulfurization are still in their early stages of development, devices which scrub sulfur oxides from stack gases are already commercially available from many vendors.[18] The efficacy of existing flue gas scrubbers is dependent upon the chemical composition of the coal and the homogeneity of this composition. The available technology is inadequate for some coal. Slack[12] has reviewed the various types of stack gas scrubbers that are presently in use in power plants. Most of these involve absorption of SO_2 into either solid or liquid matrices of metal oxides or metal carbonates, although catalytic oxidation systems are also now operational.

Invariably, the scrubbers accumulate large quantities of sulfite or sulfate sludge for which disposal must be arranged. For some of these systems, the product can be recycled into a commercial grade of H_2SO_4 plus the original absorbing material. Reclaimed sulfur compounds from power plant emissions would have a substantial impact on the world sulfur market, as would sulfur extracted from pre-combustion fuel desulfurization.[159] Alternatively, disposal of the sludge as solid waste may introduce problems with land and water use. For most scrubbing systems, resulting sulfite and sulfate sludges are sufficiently water-soluble that leaching into the soil and nearby drinking water supplies is a potential problem.

The two most advanced SO_2 stack gas removal systems are limestone ($CaCO_3$) scrubbing and lime (CaO) scrubbing.[28] These are both throwaway processes, which involve disposing of large quantities of solid wastes. Both the lime and limestone systems can reliably remove 90% of the SO_2 in the stack gases.[166] This would reduce the SO_2 emissions from a 1000 MWe coal fired plant to about 0.15 tons per hour at full load.

The lime process is more expensive, requiring additional energy expenditures and pollution controls for the calcining kiln. Lime, however, is more reactive with SO_2, so that less reactants are used, generating less solid wastes, when compared to the limestone process. During full scale tests at the Mojave Coal Plant, lime was shown to cause fewer operating and maintenance problems than limestone.[163]

Table 3.1-33 Estimated sludge effluent from a SO_x flue gas scrubber for a 1000 MWe coal-fired power plant operating at full load.[a)]

	LIME WASTE		LIMESTONE WASTES	
	%	Rate (T/hr)	%	Rate T/hr)
$CaSO_3\ \frac{1}{2}\ H_2O$	73	6.2	58	6.7
$CaSO_4\ 2\ H_2O$	11	0.9	9	1.0
$Ca(OH)_2$	11	0.9	—	—
$CaCO_3$	5	0.4	33	3.8
Total dry wt	100	8.4	100	11.5
Total wet wt (50% solids)		17		23

a) Calculated from reference 174.

Table 3.1-34. Chemical analysis of sludge liquor from a lime SO_2 flue gas scrubber.[a)]

Element	Mg/ℓ
Ca	1144
Mg	3686
Na	17040
Cl	31639
HCO_3	61
SO_4	9427
PO_4	52
SO_3	214
SiO_2	495
TDS	63758

a) From reference 164.

Both systems use a scrubber, where the lime or limestone slurry is introduced to the flue gas, a reaction tank which allows time for the following overall reactions to take place:

1) $CaCO_3$ (limestone) + $SO_2 + \frac{1}{2} H_2O \rightarrow (CaSO_3 \cdot \frac{1}{2} H_2O) + CO_2$

or

2) CaO (lime) + $SO_2 + H_2O \rightarrow (CaSO_3 \cdot \frac{1}{2} H_2O) + \frac{1}{2} H_2O$

and

3) $CaSO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4$.

A thickner is used to concentrate the underflow from the reaction tank from 5-15% solids to 30-50% solids.[162,164,174] The solids are mainly calcium sulfite crystals that can retain as much as 50% water in the interstices of its crystalline structure. Figure 3.1-13 shows the approximate rate at which scrubber sludge is produced as a function of power plant capacity and sulfur content of the coal burned for different stoichiometrics. Table 3.1-33 shows the dry solids composition of the sludge, and Table 3.1-34 shows the composition of the liquid solution entrained in the sludge.

Both of these scrubber systems require about 2% of the power station's gross energy output for basic operation.[114] Moreover, since these are wet processes, the flue gases are cooled by the scrubber. To restore buoyancy and to prevent condensation, the flue gas must be reheated, reducing the gross energy output from the power plant by another 2 - 4%. Increased buoyancy allows the plume to rise faster and higher to aid dilution-dispersal,[175] an effect which is also augmented by the use of tall, large diameter stacks.[175] The scrubbers are located downstream of particulate control devices in order to avoid 1) having to handle ash in the scrubber, and 2) lowering the temperature and raising the humidity of the flue gas going into the particulate control devices (see Section 3.1.2.3.3), alterations which would adversely affect operation of precipitators or filters.

Besides the lime and limestone scrubbing techniques, there are three other methods that show promise. They are magnesia slurry scrubbing, the Wellman-Lord process, and catalytic oxidation, all of which can achieve 90% removal efficiencies.[163,164,166] All of these are regenerative processes that avoid the problem of having to dispose large quantities of solid wastes. However,

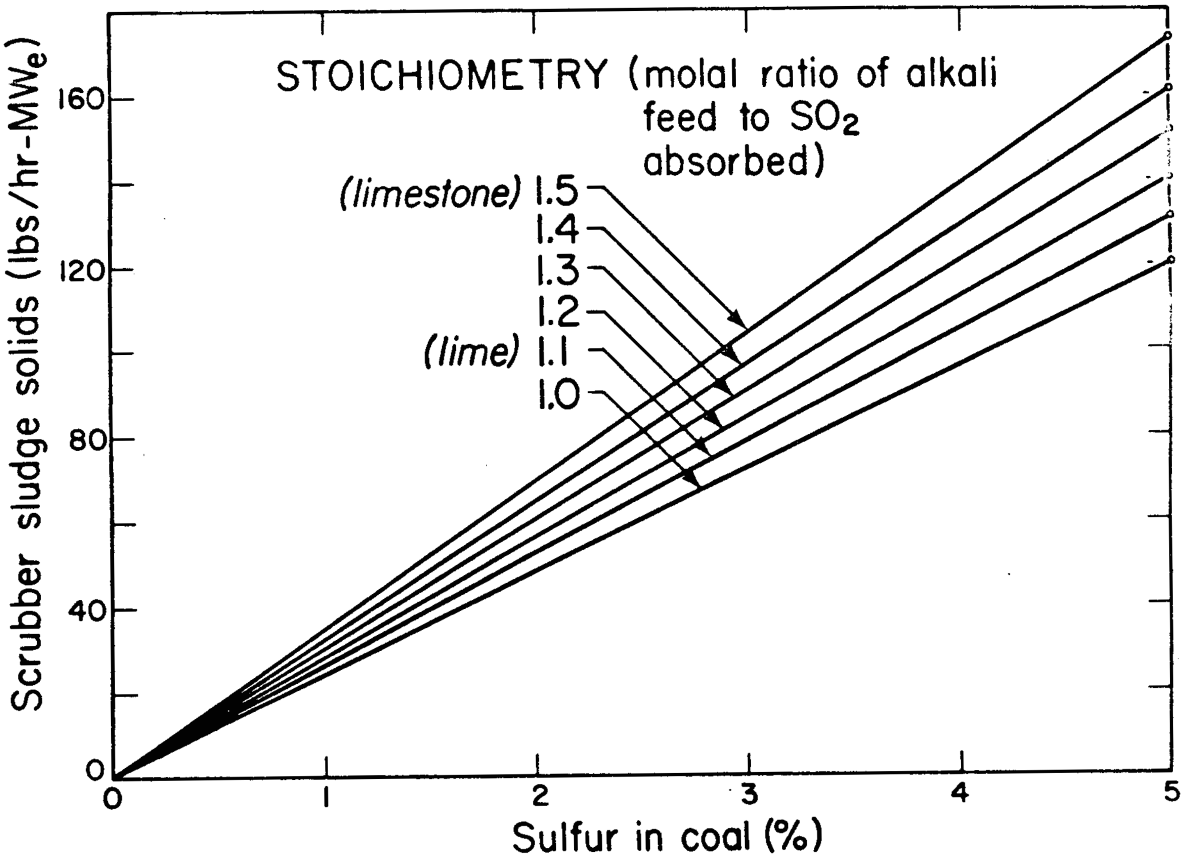

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Figure 3.1-13. The amount of waste produced by a throwaway flue gas scrubber as a function of sulfur content in the coal and the stoichiometric ratio of the scrubber material. (Reproduced from ref. (173).)

these processes have not been extensively tested in coal-fired power plants, and require a large capital investment for an auxiliary regeneration plant.[3]

The magnesia slurry process operates with the same principle as the lime scrubbing process, except that the by-products, $MgSO_3$ and $MgSO_4$, are regenerated. Trapped SO_2 can be sent to an acid/chemical plant to be processed into 98% sulfuric acid (H_2SO_4) or elemental sulfur(S). The regeneration step uses process water and fuel and is an additional source of particulate, SO_2 and NO_x emissions. Like the lime scrubber, the magnesia scrubber by itself uses about 2% of the plant's gross output. Additional energy is required for stack gas reheat, MgO regeneration, and H_2SO_4 or S production.[163,164,166,173]

The Wellman-Lord system utilizes a sodium sulfite-sodium bisulfite scrubbing solution to absorb SO_2. The $NaHSO_3$ is then thermally stripped to obtain concentrated SO_2 which can then be converted to H_2SO_4 or S. Fairly large quantities of Na_2SO_4 are also generated and must be sold or disposed. Three to 6% of the power plant's output is also required to operate the process, in addition to large quantities of steam and water, resulting in 1½ times the increment in emitted air pollutants as the magnesia scrubbing process.[163,164,166,173]

The catalytic oxidation process uses a vanadium pentoxide catalyst to convert SO_2 to SO_3. The SO_3 reacts with moisture in the flue gas to form H_2SO_4 mist, which is scrubbed out with a recirculating acid stream to yield 80% H_2SO_4 acid. The heat from this exothermic process is used to minimize the energy consumption from the power plant and also any pollutants from the process.[13,14,28,29] Table 3.1-35 summarizes the additional pollutants and waste products from these five types of flue gas SO_2 removal systems.

An alternative catalytic method which has been tested successfully on laboratory-scale units reduces both SO_2 and NO using CO. The reaction is carried out in hot stack gas, and no scrubber is used. According to the work of Killick,[160] the best catalyst appears to be a promoted iron oxide bed. If the system can be operated on a commercial scale, advantages could include effective emission reduction combined with low capital cost, elimination of sludge problems, and minimal thermal losses.

The relative advantages and disadvantages of other control techniques such as increased stack height, or the <u>intermittent</u> use of desulfurization systems are discussed in ref. 14 and 15. Raising the height of the stack will result in the amelioration of ground level SO_x concentrations in the vicinity of the power plant.[2,15] At the same time, the area over which SO_2

Table 3.1-35 Pollutant/Wastes Generation from various types of Scrubbers.[b]

A. Limestone Slurry Scrubber[a]
(Tons/Year)

	Particulate	SO_2	NO_x	Solid	Water soluble
Primary source					
$CaSO_4/CaSO_3$	—	—	—	156 400	[b]
Secondary source					
Utility					
Steam	493	740	173	—	—
Water	—	—	—	44	—
Electricity	787	1 181	275	—	—
Chemical					
Limestone	nil	nil	nil	—	—
Total	1 280	1 921	448	156 444	[b]

[a] Capacity, 500 MW; fuel, coal; SO_2 removal, 90%; sulfur content of the fuel, 3.5%. [b] Not estimated for leaching of $CaSO_4/CaSO_3$ and that in the purge stream.

B. Lime Slurry Scrubber[a]
(Tons/Year)

	Particulate	SO_2	NO_x	Solid	Water soluble
Primary source					
$CaSO_4/CaSO_3$	—	—	—	156 400	[b]
Secondary source					
Utility					
Steam	490	735	172	—	—
Water	—	—	—	42	—
Electricity	741	1 112	259	—	—
Chemical					
Lime	3 045	—	—	—	—
Total	4 276	1 847	431	156 442	[b]

[a] Capacity, 500 MW; fuel, coal; SO_2 removal, 90%; sulfur content of the fuel, 3.5%. [b] Not estimated for leaching of $CaSO_4/CaSO_3$ and that in the purge stream.

C. Magnesia Slurry- Regeneration to H_2SO_4[a]
(Tons/Year)

	Particulate	SO_2	NO_x	Solid	Water soluble
Primary source					
H_2SO_4	—	—	—	—	(110 400)[b]
Secondary source					
Utility					
Steam	440	660	154	—	—
Water	—	—	—	386	—
Electricity	711	1 067	249	—	—
Fuel oil	791	1 187	277	—	—
Heat credit	−20	−30	−7	—	—
Chemical					
MgO	41	—	—	—	—
Lime	5	—	—	—	—
Coke	nil	nil	nil	nil	—
Catalyst	[c]	[c]	[c]	[c]	—
Total	1 968	2 884	673	386	—

[a] Capacity, 500 MW; fuel, coal; SO_2 removal, 90%; sulfur content of the fuel, 3.5%. [b] Treated as salable by-product. [c] Data not available.

D. Sodium Solution Scrubbing- SO_2 Reduction to Sulfur[a]
(Tons/Year)

	Particulate	SO_2	NO_x	Solid	Water soluble
Primary source					
Sulfur	—	—	—	(32 700)[b]	—
Na_2SO_4	—	—	—	—	(13 000)[b]
Secondary source					
Utility					
Steam	2 138	3 207	749	—	—
Water	—	—	—	1 742	—
Electricity	742	1 113	260	—	—
Natural gas	255	—	102	—	—
Heat credit	−63	−95	−22	—	—
Chemical					
Lime	5	—	—	—	—
Soda ash	—	—	—	560	—
Antioxidation catalyst	[c]	[c]	[c]	[c]	[c]
Total	3 077	4 225	1 089	2 302	—

[a] Capacity, 500 MW; fuel: coal; SO_2 removal: 90%; sulfur content of the fuel: 3.5%. [b] Treated as salable by-product. [c] Data not available.

E. Catalytic Oxidation[a]
(Tons/Year)

	Particulate	SO_2	NO_x	Solid	Water soluble
Primary source					
H_2SO_4	—	—	—	—	(109 900)[b]
Secondary source					
Utility					
Steam	179	269	63	—	—
Water	—	—	—	55	—
Electricity	904	1 356	316	—	—
Heat credit	−987	−1 481	−345	—	—
Chemical					
Catalyst	[c]	[c]	[c]	[c]	[c]
Total	96	144	34	55	—

[a] Capacity, 500 MW; fuel, coal; SO_2 removal, 90%; sulfur content of the fuel, 3.5%. [b] Treated as salable by-product. [c] Data not available.

b Reproduced from ref. (166).

in the plume is transported becomes much wider, and the resultant lengthening of the SO_2 residence time in the atmosphere. This may facilitate the formation and distribution of acid sulfates.[19] Hitchcock[20] has shown, however, that one cannot rule out biological activity as the source of the ubiquitously elevated acid sulfate concentrations in the Eastern U.S., which Altshuller[19] had attributed to power plant emissions. If Altshuller[19] is correct, increases in the stack heights of power plants in Air Basins where the rate of air exchange is slow (such as the South Coast or San Francisco Bay Area) could lead to greatly elevated sulfate levels locally.

Basically, emission control measures for SO_x from power plants which operate by either fuel or flue gas desulfurization would compel any utility planning to erect a new facility to propose a satisfactory plan for solid and liquid waste disposal which would protect local communities from deterioration of soil and water quality.[175] Other "halfway" measures such as intermittent desulfurization or readjustment of stack heights may be satisfactory in remote areas of California, but clearly not in regions which are presently experiencing chronic air pollution problems.

3.1.2.3.2 Nitrogen Oxides Control

Construction and startup of new fossil fuel-fired power plants in California will certainly increase the local NO_x emissions, since existing techniques for NO_x control cannot reduce emissions by a substantial factor (Figure 3.1.2; also Ref. [9]). The three existing NO_x control methods involve: a) conversion to a lower NO_x-producing fuel such as natural gas, b) combustion modification, and c) flue-gas treatment. Since the option of converting power plant operations from coal or fuel oil combustion to the burning of natural gas is no longer open to California utilities except in air pollution episodes,[27] future electric power generation will require an alternative method.

Combustion modification techniques that have been conceived or demonstrated are low-excess-air operation, staged or off-stoichiometric combustion, flue gas recirculation, reduced air preheat, steam or water injection, or a combination of these methods.[28,30] The <u>off-stoichiometric</u> method relies on creating a fuel-rich mixture for primary combustion so that there is a decreased supply of N_2 and O_2 available for NO_x formation when the fuel is burned at the peak flame temperature. Excess air is then introduced to oxidize the remaining fuel at lower temperatures. This can be accomplished by "biased firing" which lets air flow through only selected burners, by "over firing," which adds "NO_x ports" above the burners. Recirculating a portion of the exhaust gases back into the intake dilutes the fuel and air mixture with a noncombustible gas which provides an additional heat sink to lower combustion temperatures. Temperature reduction of the incoming air simply involves reducing the amount of air preheating but requires a larger economizer and reduced feed water temperatures.[162,165] While combustion modification methods substantially reduce the NO_x formed from air nitrogen, these are ineffective for controlling NO_x formation from fuel nitrogen.

Flue-gas treatment results in the removal or decomposition of the NO_x after it has been formed, and the methods include such systems as wet scrubbing with alkaline solutions or aqueous sulfuric acid. Catalytic reduction, adsorption on solid matrices, and catalytic decomposition have also been reported experimentally.[28, 160] Either catalytic reduction or decomposition of NO_x in hot stack gas offers the best promise because the method could be simple, and no waste management problems would exist as long as the catalyst remains active. Additional development effort should definitely be encouraged, since effective controls do not now exist and since it has been shown that NO emissions from power plants are a substantial contributor to photochemical oxidant formation over wide areas.[25]

3.1.2.3.3 Particulate Emission Control

The chief methods employed for industrial particulate emissions control involve inertial separation, filtration, electrostatic precipitation, gravity settling and wet scrubbing. Two manuals, one by AIHA[128] and the other by the LAAPCD,[129] provide good coverage of the principles and practical aspects of industrial air cleaning devices; other manuals are available. A summary of the state of the art has also been published by NAPCA (now EPA), "Control Techniques for Particulate Air Pollution."[130] More recently, a series of manuals on wet scrubber, fabric filter, and electrostatic precipitator technology have been prepared by the EPA.[131-133]

Inertial separators include the single cyclone, high-efficiency cyclone, multiple cyclone, and mechanical centrifugal separators. In these, the gas is directed along a circular path or undergoes an abrupt change in direction, causing the larger particles to move out of the air stream by their inertia. Generally they are suitable for medium size (15-40 μm) particulates, but some with smaller orifices will work down to 5 μm. Fine dusts and metallurgical fumes, which are 5-10 μm and smaller, cannot be adequately collected; neither can low density particles. Versatility and low cost, however, make the single cyclone the most widely used of dry centrifugal separators.[129] Since a large fraction of the fly ash produced from high-temperature coal combustion occurs in the larger diameter ranges, cyclones should serve to remove much of the particulate mass generated in coal-fired power plants. They are recommended as a preliminary stage in particulate removal, to be used in conjunction with either high-efficiency electrostatic precipitators or fabric (baghouse) filters downstream.

Electrostatic precipitation of particulates is currently the most popular method for fly ash emission control in power plants. Basically, a high voltage corona discharge produces gas ions, which readily attach themselves to particles, allowing the particles to be drawn out of the gas stream by the high electric field. *Reference 135 provides a detailed theoretical treatment of precipitator* operation. The collected dust is removed periodically by vibrating the collection electrodes so that the dust falls into storage trappers.[21,162,164]

Electrostatic precipitators work more efficiently when the resistivity of the fly ash is between 10^3 and 10^{10} ohm-cm;[196] that is, when either the sulfur[133] or carbon[196] content or the temperature of the fly ash is high. To compensate for the use of low sulfur coal (sulfur content less than 1.0%), the precipitator is located before, or on the hot side, of the air preheater.* In this position, exhaust gases enter the precipitator at about 345-455°C (650-850°F) instead of the 120-180°C (250-350°F) temperature of the exhaust gases coming out of the preheater. This keeps the preheater cleaner, but the higher temperatures put greater stresses on the precipitator components and increases slightly the energy requirements for the electrostatic precipitator. Hot precipitators use about 0.4 to 0.7% of the power plant's gross output compared to 0.3-0.5% for cold-side precipitators.[163,164] The high voltage required presents shock (and explosion, if flammable vapors are present) hazards against which personnel must be protected.[31]

Overall particulate collection efficiencies of 99.5% by weight can be attained,[163-165] resulting in an emission rate of about 0.15 tons/hour for a 1000 MWe power plant. Figure 3.1-14 shows a fairly typical

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*Air flowing into the combustion chamber is preheated by heat transfer from the flue gases.

size distribution of fly ash particles before and after treatment of the flue gas stream with an electrostatic precipitator. Collection efficiencies better than 99% for particles larger than 5 µm are clearly demonstrated.[111] For particles smaller than 1 µm, high-efficiency electrostatic precipitators are still capable of removing 92-93% of the number and mass, under optimum conditions (see Fig. 3.1-14). However, the efficiency in the submicron range may not be better than 50% for most precipitators.[3,129] Ragaini[171] has reported a different submicron size distribution of fly ash particles which escape the electrostatic precipitator of a 430 MWe coal-fired power plant. The MMD is typically on the order of 1.0 µm, with particle number modes at 0.06 µm and 0.6 µm (Figures 3.1-15 and 3.1-16). Numerous other studies[108.109.111.171.133] have reached the same conclusions, indicating that the principle particulate

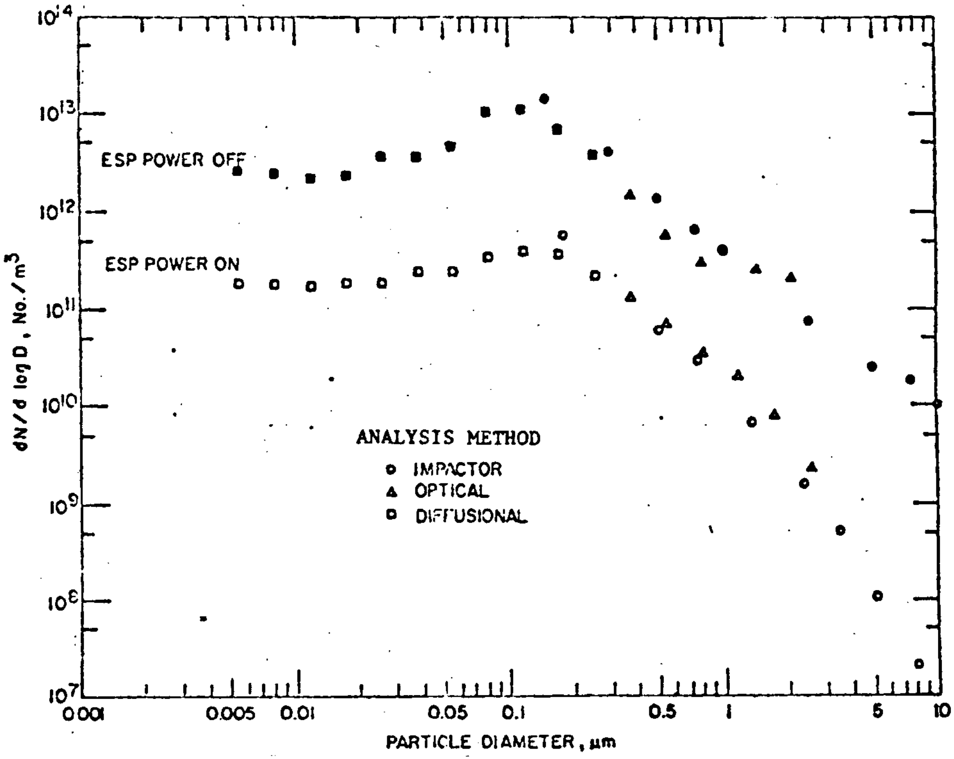

Figure 3.1-14. Number-averaged Particulate Concentrations at the inlet and outlet of an Electrostatic Precipitator (ESP) of a Coal-Fired Power Plant as a function of Particle Diameter. (Reproduced from ref. (157).)

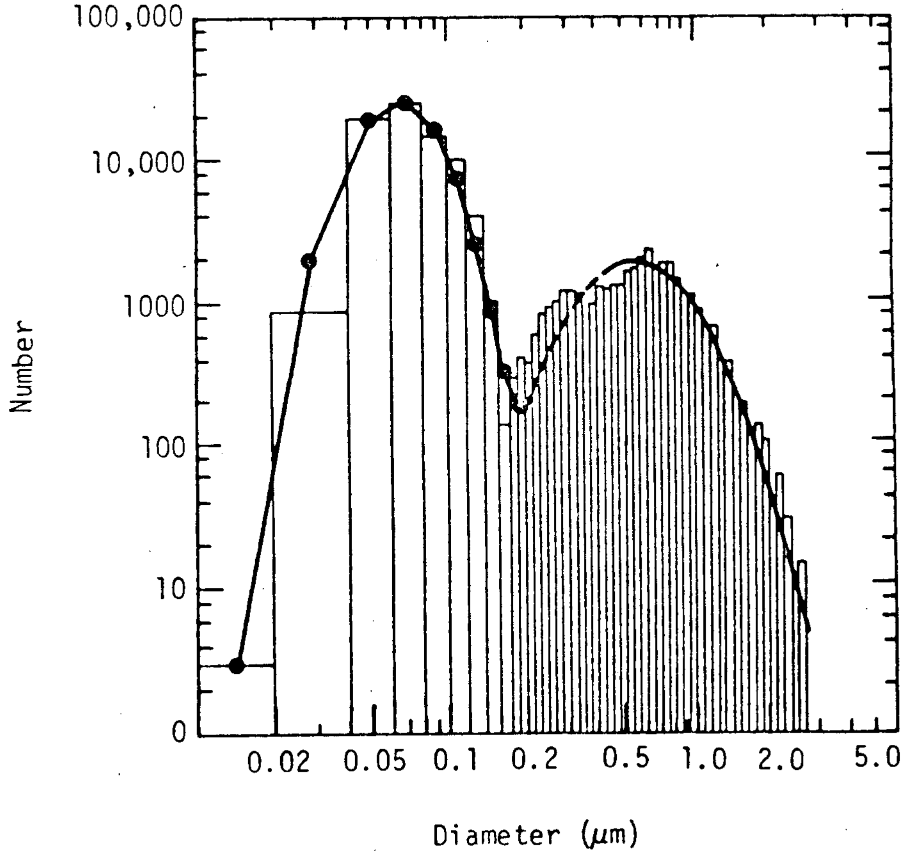

Figure 3.1-15. The Number-Size Distribution of Particles collected from a 430 MWe Coal-Fired Power Plant, equipped with a 99.5% Effective Electrostatic Precipitator. (Reproduced from ref. (171).)

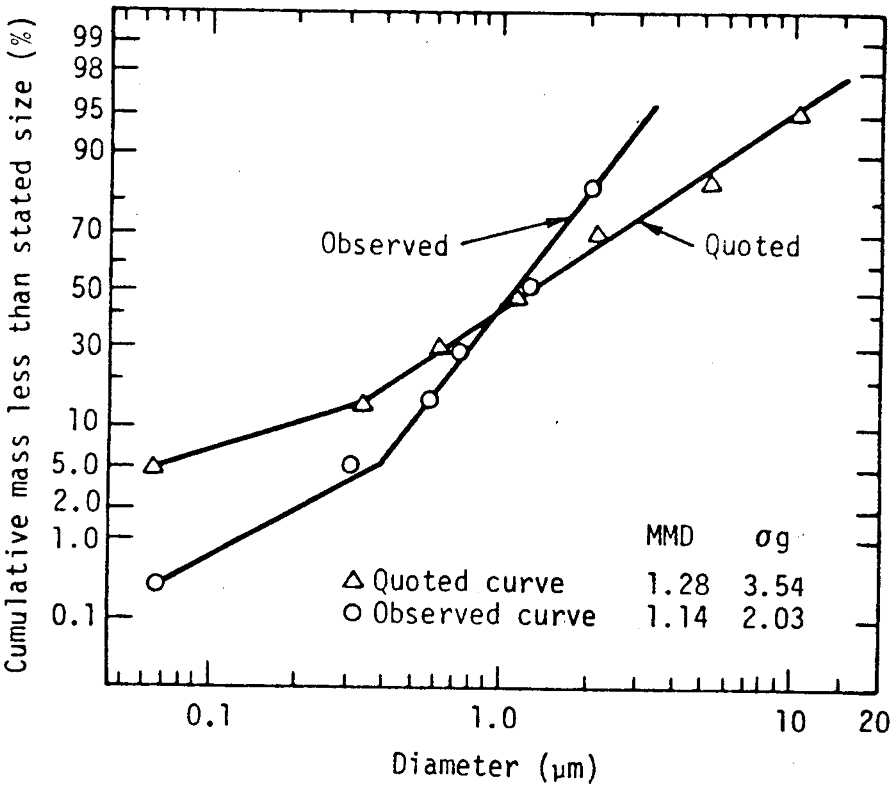

Figure 3.1-16. The Mass-Size Distribution of Particles collected from a 430 MWe Coal-Fired Power Plant, equipped with a 99.5% Effective Electrostatic Precipitator. (Reproduced from ref. (171).)

emissions from coal-fired power plants equipped with an electrostatic precipitator are enriched in respirable range (< 2 μm) particles.

Electrostatic precipitators are fairly temperamental and their efficiencies can drop if overloaded, if the particle sizes decrease (different types of firing result in different size particulate emissions (see Table 3.1-34)), or if the sulfur content and/or temperature of the flue gases fluctuate greatly.[163] The lower efficiency of the precipitator for the smaller particles in the Lee[111] study might be attributed to any of these factors. For this reason, incorporation of a cyclone in the flue gas stream prior to the electrostatic precipitator may serve to improve the performance of the latter device.[129] One should also note the fact that a variation of just one tenth of one percent in the collection efficiency of a particulate removal devise can increase the emission of small particles by 20%, or 60 lb/hour for a 1000 MWe plant.

Filtration can be performed by a baghouse, a collection of large porous fabric bags, made of natural, synthetic, and mineral fibers, and hung vertically in a large enclosure. They are open at the bottom so that the dust-laden flue gases can pass up through them. This arrangment allows the unit to have a low enough flow resistance to be practical for the high exhaust flow rates typical of large power plants. As the particles collect in the filter pores, they form a cake which itself acts as a filter and makes possible efficient filtration of very small particles. The collection efficiency of the filter bags increases until they become sufficiently clogged to require cleaning by shaking or by reversing the direction of gas flow. (Trapped particles fall into a hopper for storage.) This cleaning may require shutdown of the plant (or bypass of the baghouse) unless a second system is available or the baghouse is designed so that not all the bags need be emptied at once. Immediately after cleaning, the collection efficiency for small particles may be low until a cake builds up. Precoating with coarse dust is sometimes used to prevent such decreases in efficiency.

Factors which might limit the usefulness of fabric filters[164] include the temperature limits imposed by the fabric material (currently 90-230° C) and the moisture content of the flue gas (too much moisture can cause cold spot condensation which cakes solids or accumulates acids).

The principal advantages of baghouse filters are their simplicity and their efficiency of particulate removal, particularly for fine particles. Although unusable for mists and hydroscopic particles, the baghouse controls almost any dry dusts and fumes with virtually complete ($\geqslant 99.8\%$) efficiency.[129] Basic filtrations mechanisms are the same as those for analytical filters and are discussed in Ref. 3 . Figure 3.1-17 compares the collection efficiency of the baghouse filter with other types of particulate removal systems. Under optimum operating conditions, the baghouse filter is at least as efficient as the best types of electrostatic precipitators for virtually any size range of particles encountered.[3] Figure 3.1-17, however, does not adequately display the fact that detailed data on submicron particle collection efficiency are difficult to obtain. Once baghouse filters have been proven reliable for large coal-fired power plants, they will probably become the recommended method of particulate removal because of their ability to remove very small particles.[3,162,163] Development of ceramic and non-corrosive fabrics for baghouse filters will certainly aid their acceptance, because of the resulting improvement in energy efficiency and maintenance requirements. Combination of baghouse filter with cyclones (as pretreatment devices) is recommended for coal-fired power plants, to extend the usable life and efficiency of the filter.

Wet collection devices have a wide range of costs (initial plus maintenance), efficiencies, and power requirements. They include spray chambers, cyclone-type scrubbers, orifice-type scrubbers, mechanical scrubbers, mechanical-centrifugal collector with water sprays, high pressure sprays, Venturi scrubbers, packed towers, and wet filters, as well as combinations of these. These can usually handle high-temperature moisture-laden emissions, and the collected dust is securely held in a liquid rather than dry and loose. (There remains the problem of disposal of the scrubbing liquid.) Particle collection efficiency declines for particle sizes below 10 μm. The aerosol is wetted by contact with a liquid droplet and then removed by impingement on a collecting surface followed by flushing of the liquid. Particles make contact with the drops by impaction, diffusion, turbulent processes, condensation, and other possibly important processes. The droplets have to be large enough so they can be removed by gravity settling, centrifugal action, and impaction.[129] Some efficiency vs. particle size curves given in Ref. 2 indicate good collection efficiency down to about 1 μm and poor efficiency below a few tenths of a μm.

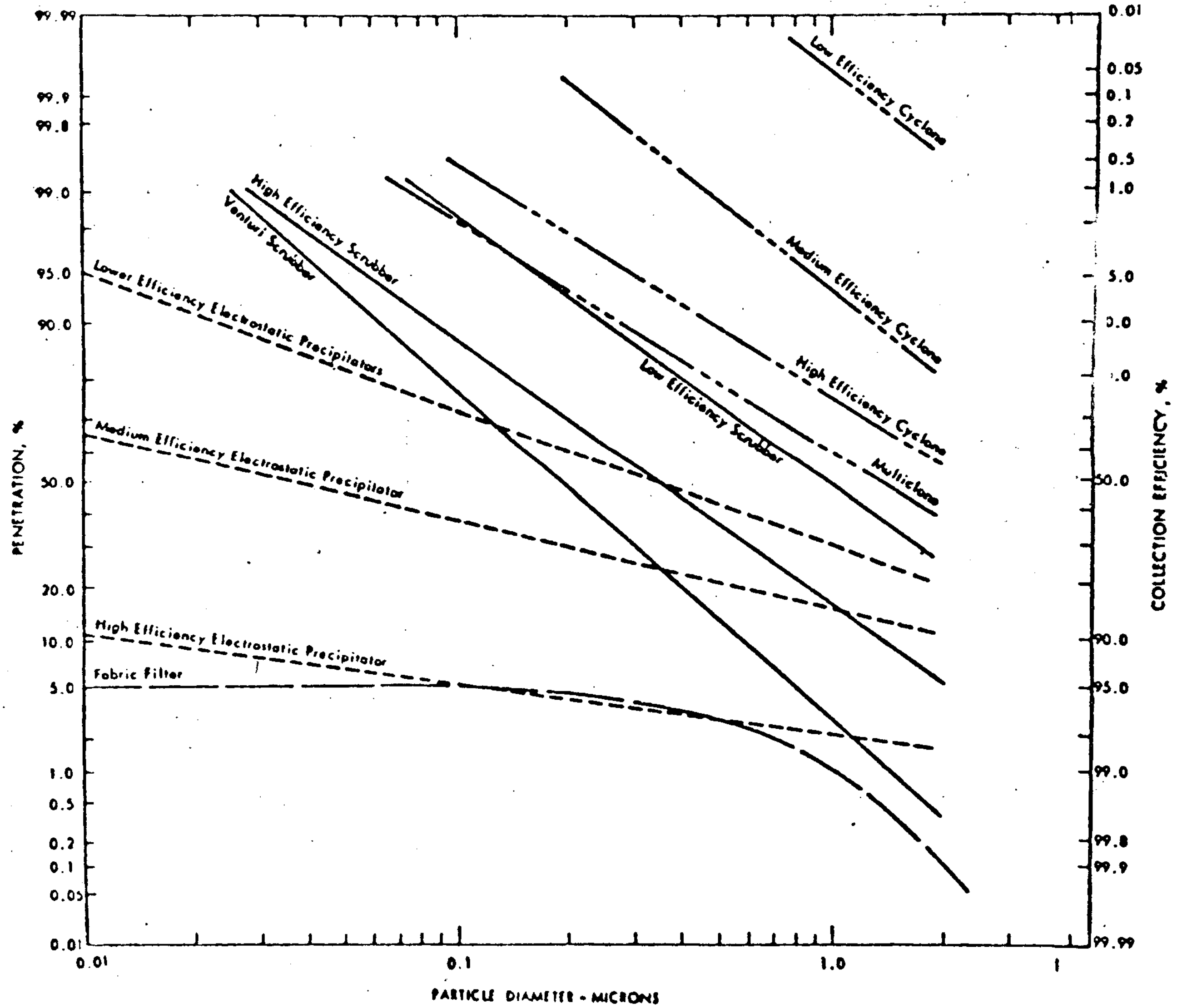

Figure 3.1-17. Extrapolated Fractional Efficiencies of Particulate Control Devices as a Function of Particle Size. (Reproduced from Ref. 134).

An experimental scrubber for gases and fly ash was built several years ago by the Braxton Company in Massachusetts. It was a pilot plant with 20,000 cfm capacity and worked with the aid of a 400 Hz sound wave which increased the gas flow past the liquid droplets. Efficiencies in excess of 99.8% were reported for gases and particles, and the amount of waste liquid was substantially smaller than that from more conventional scrubbers.[3] A test report on one of these systems has just been completed.[3] Acoustic and ultrasonic scrubbing technology are reviewed briefly in Ref. 134, as are other advanced particulate removal methods.

Particulate collection efficiencies for the various control devices described above do not necessarily apply to specific elements or compounds even when accounting for size distributions. Ample data on the efficiency of mineral removal by electrostatic precipitators is available, as discussed in Section 3.1.2.2. Polynuclear aromatic hydrocarbons (PAH) and other carbon species are also emitted from the stacks of coal-fired power plants.

Studies of the formation of PAH by combustion processes have shown that airborne PAH are almost entirely absorbed onto the particulate or soot emissions. Only trace amounts of vapor phase PAH are emitted.[172] Because of this, present control methods for sulfur oxides (SO_2 stack gas scrubbers) and particulate matter (filters, cyclones, and electrostatic precipitators) should help reduce PAH emissions.[68,80,172] Several tests of a vertically-fired coal furnace showed <u>negligible reduction</u> of total benzene-soluble organics and benzo(a)pyrene by the fly ash collector. However, a single test of a front-wall-fired furnace shows a 73% reduction of the benzo(a)pyrene emission rate by the fly ash collection system.[172] Table 3.1-36 summarizes the results of these PAH emission control studies. Although the data are scant, it appears that the various particulate removal devices are not as effective in removing PAH as other constituents of fly ash.[172] Unfortunately, the proposed method of NO_x reduction which initiates the combustion in a fuel-rich mixture and then completes it at lower temperatures using less excess air may increase PAH emissions. In the first stage of this process, combustion is incomplete, favoring PAH formation, while the lower amounts of excess air reduce the oxidation of the PAH that is formed. According to Ref. 35, no test results are cited in the literature concerning PAH from two-state combustion.

Table 3.1-36 Polycrylic Aromatic Hydrocarbon Emissions From Pulverized Coal-Fired Power Plant (Dry Bottom Furnace), 1000 MWe, 100% Load.

	Vertically-Fired		Front-Wall-Fired		Tangentially-Fired	
Ref. (80)	Emission Factor ($\mu g/10^6$ Cal)	Emission Rate (g/hr)	Emission Factor ($\mu g/10^6$ Cal)	Emission Rate (g/hr)	Emission Factor ($\mu g/10^6$ Cal)	Emission Rate (g/hr)
Fluoranthene	1.29	3.00	0.83	1.93	2.11	4.91
Pyrene	1.16	2.70	1.04	2.41	0.76	1.77
Benzo(a)pyrene	0.12	0.28	0.09	0.21	0.76	1.77
Benzo(e)pyrene	-	-	0.29	0.67	0.46	1.07
Benzo(ghi)pyrene	-	-	0.07	0.16	0.81	1.88
Coronene	-	-	-	-	0.04	0.093
Perylene	-	-	-	-	0.38	0.88
Phenanthrene	-	-	1.04	2.42	0.19	0.44
Anthanthrene	-	-	-	-	0.03	0.070
Ref. (168)*						
Fluoranthene	200	1.90	80	0.76	390	3.70
Pyrene	155	1.47	180	1.71	140	1.33
Benzo(a)pyrene	19	0.18	19	0.18	140	1.33
Benzo(e)pyrene	-	-	23	0.22	86	0.82
Benzo(ghi)pyrene	-	-	7	0.066	150	1.42
Coronene	-	-	-	-	7	0.066
Perylene	-	-	-	-	71	0.67

* The measurements from Ref. 168 were taken after the Fly Ash Collector.

3.1.2.3.4 Waste Disposal

Often, reducing one type of pollutant creates another; controlling the emission of air pollutants results in a solid waste problem. There are two proposed methods to dispose of the vast quantities of ash and scrubber sludge generated by the operation of large coal-fired power plants (see Table 3.1-37): a "dry" method which uses the solid wastes as land fill and a "wet" method in which the wastes are pumped into man-made ponds. Care must be taken with any disposal scheme to isolate the solid wastes from any water supplies, since the wastes include all the trace elements found in the bottom ash and fly ash (Table 3.1-27) plus the dissolved solids of the scrubber sludge (Table 3.1-34 .

In the dry method, scrubber sludge is mixed with fly ash to reduce its moisture content to about 27%. The remaining fly ash and bottom ash are mixed with a little water to form a mixture of about 20% moisture to avoid dust problems. Both mixtures are then trucked to the disposal site. The burial is staged so that one section of the disposal area is filled at a time. Each section should be a single drainage area isolated by ridge lines forming a low profile fill area.[163]

The trucks then spread and compact the ash as they traverse the fill section. After the ash is placed to its greatest depth, a layer of scrubber sludge and ash mixture is spread over the ash. This mixture sets into a mortar-like crust which becomes chemically stable and relatively inert. An earth cover, typically one-foot thick, is then placed and compacted over the crust. After 35 years of operating a 1000 MWe power plant, at 70% average capacity factor, seventeen million cubic yards of solid wastes would need to be disposed; this would cover an area of 214 acres to an average depth of 50 feet. Drainage ditches and an earth dam would be constructed to collect and hold any water runoff from the fill area to allow for its evaporation. Such a collection pond might cover 8-10 acres of land.[163,164]

The wet disposal method involves mixing the fly ash and scrubber sludge with power plant waste water. The resulting waste slurry, containing about 20% by weight suspended solids and about 24% dissolved solids, is then pumped to a lined disposal pond. The ash-sludge mixture would settle to a nominal 60% solids content as the waste water used to slurry the ash and sludge percolates through the settling solids into a porous underdrain system composed of bottom ash previously trucked to the disposal area and laid down during pond construction. This waste water and rain water runoff is collected and transferred to a nearby lined evaporation pond for final disposal. As each pond becomes full, the surface is stabilized to prevent the formation of either airborne dust[164] or quicksand.[21]

The disposal area for ponding is much larger than a comparable dry disposal area, since larger quantities of water must be evaporated and because the ponds are shallower than the land fill sites. For 35 years of operation at 70% capacity, a 1000 MWe power plant using the wet disposal method would need ponds to accommodate 12,300 acre feet (19.8×10^6 cubic yds) of sludge and ash mixture containing 40% water. The disposal pond area would cover about 410 acres at a 30-foot average depth, with the evaporation ponds covering another 200 - 300 acres.[21,164]

Alternatively, fly ash, bottom ash, and/or scrubber sludges may be utilized successfully for commercial applications. Capp[176] has reviewed the properties of building materials which contain fly ash. Concrete products containing fly ash can be structurally superior to their conventional counterparts. Commercial-scale utilization of fly ash in building materials has been ongoing for at least the last 15 - 20 years — this market outlet for ash wastes may be expanded. Ash wastes from power plants can be used in asphalt and road-bed materials as well. Many highways in Michigan and other states are presently paved with fly ash.[176] Another very important use for power plant ash wastes is in strip mine reclamation, and in conventional agriculture. The high percentages of calcium, potassium, and phosphorous make ash wastes excellent fertilizers. For surface mine reclamation, the high pH of many fly ash specimens alleviates the effects of acid drainage from the abandoned mines. However, the presence of trace elements, some of which are toxic, may limit the types of vegetation which can grow on the reclaimed soil. Grasses and legumes appear to be most tolerant, so that these plants may be excellent pioneer crops for reclaimed lands.[176] Corn and alfalfa grow especially well on fly ash, but barley and spinach crops will not survive.[176] Commercial utilization of SO_x scrubber wastes is presently limited to sulfur or sulfuric acid manufacture, where technology permits. Sulfur-deficient soils are generally rare, and the use of SO_x scrubber wastes in construction has not been successful.

3.1.2.3.5 Fugitive Emissions

In addition to the public health and environmental implications of emissions from coal-fired power plants, there are potential occupational hazards within

Table 3.1-37. Solid wastes from a 1000 MWe pulverized coal-fired power plant with a 90% lime SO_2 scrubber and 99.5% electrostatic precipitator operating at full load.a)

Bottom and economizer ash	7.4	tons/hr
Collected fly ash	29.4	
Pulverizer rejects	5.3	
Lime scrubber sludge (50% solids)	17*	
	59.1	tons/hr

*23 tons/hr for limestone scrubbing

a)From references 161, 168, and 173.

Table 3.1-38. OSHA Standards for Fugitive Dust[b]

Substance	Milligrams per Cubic Meter (mg/m^3)	Million Particles Per Cubic Foot (Mp/ft^3)
Coal dust (respirable fraction less than 5% SiO_2)(a)	2.4	
Coal dust (respirable fraction more than 5% SiO_2)(a)	$\left(\frac{10}{\%SiO_2 + 2}\right)$	
Inert or nuisance dust (respirable fraction)	5	15
Inert or nuisance dust (total dust)	15	50
Crystalline quartz (respirable)	$\left(\frac{10}{\%SiO_2 + 2}\right)$	$\left(\frac{250}{\%SiO_2 + 5}\right)$
Crystalline quartz (total dust)	$\left(\frac{30}{\%SiO_2 + 2}\right)$	

a. Intent of law is to regulate free silica (crystalline portion; i.e., quartz)

[b] Reproduced from ref. (164).

Note:

The OSHA standards for fugitive emissions of combustion gases are the same for coal-fired power plants as for other industrial sources. These include : SO_2, 5 ppm; NO , 25 ppm; NO_2, 5 ppm; and CO_2, 50 ppm. All of these maximum permissible concentrations are averaged over an 8-hour working day, and assume that the workers are in a "reasonably normal" state of health.

the power plant itself. Coal, coal ash, and exposed and unstable soil surfaces are all sources of dust at a coal-fired power plant. Fugitive dust concentrations in all new power plants are therefore subject to the U.S. Occupational Safety and Health Administration (OSHA) regulations summarized in Table 3.1-38

Dust is created whenever coal or coal ash is transported, processed, or stored. Both coal and coal ash have to be transported in closed systems, enclosed coal conveyors, and closed pneumatic hydraulic fly ash transport systems.

Active coal and fly ash storage must be in enclosed concrete silos. The inactive coal storage is compacted and stabilized to prevent fugitive dust. At any transfer points, water, fans, hoods, and fabric filters are used to minimize dust. Water and/or non-toxic chemical sprays containing phenol, ether, and polyethylene glycol, or calcium chloride are used for coal dust abatement in storage piles.[163,164,167]

If calcium chloride (0.1 - 0.5% solution) is used as an antifreeze or dust control agent on coal storage piles, increased amounts of hydrogen chloride could be emitted in the flue gases of the power plant. Coal contains about 0.1% (range 0.01 - 0.46%) chlorine. With the use of calcium chloride sprayed on the coal pile and a 60% emission as hydrogen chloride, 0.09 - 0.3 lb per 10^6 Btu, or about 0.32 tons/hr of hydrogen chloride could be emitted from a 1000 MWe power plant,[167] as a result of dust abatement procedures.

All surface roadways that are extensively used should be paved, while utility roadways and working areas should be surfaced with crusted rock and treated with deliquescent chemicals or water.

OSHA standards for fugitive emissions of combustion gases are the same for coal-fired power plants as for other industrial sources. These include: SO_2, 5 ppm; NO, 25 ppm; NO_2, 5 ppm; and CO, 50 ppm. All of these maximum allowable concentrations are averaged over an 8-hour workday, and assume that the workers are in a reasonably "normal" state of health.

3.1.3 Oil-Fired Power Plants

Electric generating plants which utilize fuel oil to fire the boilers generally operate by spraying the oil into the furnace in fine streams, for optimum efficiency. Frequently, oil-fired power plants are constructed so as to permit the combustion of a variety of fuels, including natural gas and in some cases pulverized coal. Oil-fired power plants can usually burn either distillate fuel oil (refined) or residual fuel (undistilled residue from other petroleum refinery operations). Because of the price, residual fuel oil is usually preferred. It is often the case that the heavier, more viscous fuel oils contain higher percentages of sulfur and ash.

3.1.3.1 Specific emissions characteristics

Oil-fired power plants emit essentially the same kind of pollutant as coal-fired power plants, although the amounts differ. Table 3.1-39 shows the emissions from a typical 1000 MWe power plant at maximum load. Similar data on gaseous and particulate mass emissions is contained in Figure 3.1-2 (Section 3.1.1). Sulfur oxide emissions are, as with coal combustion, determined almost solely by the fuel sulfur content. In practice, the range of fuel sulfur concentrations in oil is about the same as for coal.

Nitrogen oxide emissions, also as with coal combustion, are governed by both the combustion temperature and the fuel nitrogen content[8] (see Sections 3.1.1.2 and 3.1.2.2 for details). Fuel oil and oil fly ash are slightly radioactive, although less so than coal combustion emissions, so that the radionuclide output of an oil-fired power plant is only about 1/10 that of a coal-fired plant (only 0.18 pCi/gm ash).

On the other hand, since virtually all the ash in the oil becomes fly ash upon combustion, particulate emissions can vary greatly depending on the grade of fuel oil burned.[150] In general, residual oil contains the highest level of fuel ash[115] and is therefore expected to emit the greatest mass of fly ash upon combustion. Consequently, any absolute particulate mass emission factors quoted may be inappropriate in some cases.

The size distribution of particulates from fuel oil combustion in a power plant is invariably shifted toward smaller particles compared to

Table 3.1-39

Emissions From a Residual Fuel Oil-fired Power Plant, 1000 MWe (net), 100% Load

Emission	Emission Factor (LB/10^3 gal)[a]	Uncontrolled (T/HR)	Controlled (T/HR)	NSPS (LB/10^6 Btu)	Max. Allowed (T/HR)
Particulates	78.8 x A	1.2	0.19	0.10	0.49
SO_2	157 x S	2.5	1.3	0.80	3.9
SO_3	2 x S	0.031	0.016	-	-
NO_x (as NO_2)	105	3.3	1.5*	0.30	1.5*
CO	3	0.094	0.098	-	-
Hydrocarbons	2	0.063	0.065	-	-
Aldehydes (HCHO)	1	0.031	0.033	-	-

A = ash content of fuel oil in percent, S = sulfur content of fuel oil in percent.

Assumptions:

All the ash in the fuel oil becomes fly ash, 99% of the sulfur is oxidized to SO_2, and 1% of the sulfur to SO_3.

Residual fuel properties: ash content, 0.5%; sulfur content, 0.5%; heating value, 19,000 Btu/LB ($1.5 \cdot 10^5$ Btu/gal); density, 59 LB/ft^3 (7.88 LB/gal)

Fuel consumption (where η stands for thermal efficiency):

uncontrolled, 1050 MWe (gross) @ 38% η:62,900 GAL/HR (total waste heat: $5.8 \cdot 10^9$ Btu/HR)

controlled, 1060 MWe (gross) @ 37% η:65,200 GAL/HR (total waste heat: $6.2 \cdot 10^9$ Btu/HR)

Internal Power Combustion	MW	(% of net output)
auxiliary equipment	50	(5%)
cyclone particulate collector	10	(1%)
TOTAL (controlled)	60	(6%)

Collection Efficiencies of Pollution Controls	
cyclone collector (ash collected: 1.1 T/HR)	85%
SO_x control (switch from 0.5% sulfur oil to 0.25% sulfur oil)	50%
NO_x control: sufficient to meet NSPS*	

[a] From reference (161)

[b] Net plant efficiency: 35%

coal fly ash (see Table 3.1-31, for example). While reports of the particle size distribution may disagree slightly, nearly all of the existing work suggests that oil fly ash particles are small. The exact particle size distribution probably depends on the grade of fuel oil and on combustion process conditions, as well as the sampling methods. It can be assumed safely that at least 50% of the uncontrolled particles are smaller than 5 μm diameter.[167]

The trace element composition of fuel oil and the resulting fly ash is highly variable depending on the geological characteristics of the oil field and the degree of oil processing, and for fly ash composition, on the burner temperature, fuel-to-air ratio and stack size.[115] Table 3.1-40 shows an analysis of various grades of fuel oil and ashes. If one compares the mineral composition of oil fly ash with that from coal combustion (Tables 3.1-27, 3.1-28, and 3.1-29), it immediately becomes obvious that oil fly ash is greatly enriched in vanadium, whereas coal ash contains large amounts of iron. Furthermore, oil fly ash contains significant amounts of manganese and nickel, neither of which is an important constituent of coal fly ash. Tables 3.1-41 and 3.1-42 give estimated emission rates for trace elements.

3.1.3.2 Effects of emission control measures

The emission control techniques used to limit the discharge of gaseous and particulate fuel oil combustion products are identical to those used to control coal combustion effluents. They are not discussed in any detail here. The reader should refer to Section 3.1.2.3 for further information.

Since fuel oil is a refined product, the easiest way to control SO_2 emissions is to burn low-sulfur oil. Many air pollution control districts have already adopted regulations banning the use of fuel oils with sulfur content greater than 0.5%.[178] However, this course of action presumes the continued availability of low-sulfur fuel oil. It is unlikely that fuel sulfur limitations can remain the principle method for SO_x emissions control for the long-term future. Eventually, oil-fired power plants will have to be equipped with desulfurization devices similar to those in use or under development for coal-fired power plants.

Table 3.1-40. Elemental Concentration in Fuel and Fly Ash of an Oil-Fired Power Plant (ppm).

Element (as free X)	EPRI		EPA[c]	LACAPCD[d]	Gordon et.al[e]	
	Fuel Oil[a]	Residual Fuel Oil[b]	4° API Fly Ash	Fly Ash	Fuel Oil	Fly Ash
Carbon[f]	~80,000	-	181,000	581,000	~85,000	-
Vanadium	1-221	40-113	312,000	17,000	36	32,000
Nickel	⩽32	20-90	104,000	14,000	-	
Manganese	⩽ 0.8	0.2-1.0	250	g	0.28	50
Iron	3-40	10-20	26,000	22,000	-	-
Chromium	< 0.3	0.7-4.0	1,850	g	-	-
Cobalt	-	-	2,100	g	-	-
Silicon	-	8-30	45,000	2,800	-	-
Aluminum	-	-	76,000	8,600	5	1,100
Barium	-	0.3-5	900	g	12	-
Magnesium	-	2-3	4,200	g	<60	-
Lead	-	1-4	2,000	g	-	-
Calcium	-	17-400	2,800	g	26	300
Sodium	-	30	22,500	6,700	130	4,000
Copper	-	0.2-1.0	2,000	g	<3	-
Titanium	-	-	30	g	-	-
Molybdenum	-	-	220	g	-	-
Boron	-	0.02-0.15	290	g	-	-
Zinc	-	0.4-2.0	500	g	-	-
Sulfur	-	-	100,000	70,000	8,700	-
Chlorine	-	-	5,000	g	90	-
Bromine	-	-	g	g	21	-

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[a] Mean value for oil obtained from various reservoirs in the United States, the Middle East, South America, and Canada (ref. 115).

[b] Ref. 139.

[c] These data were obtained from an oil-fired power plant in Southern California (ref. 39).

[d] These data were obtained from an oil-fired power plant in Southern California (ref. 40).

[e] These data were obtained from an oil-fired power plant in the Boston metropolitan area (ref. 122).

[f] Measured by the weight loss upon ignition.

[g] The concentration of this element in the fly ash was well below 10,000 ppm.

Table 3.1-41. Trace Element Emissions from a 1000 MWe Residual Fuel Oil-Fired Power Plant, Operating at 100% Load.[a]

Element	Ash concentration (ppm)	Emission rate (LB/HR)
Carbon	581,000	2.0
Iron	22,000	8.0
Chromium	1,350	0.67
Cobalt	2,100	0.76
Silicon	2,800	1.0
Aluminum	8,600	3.1
Barium	900	0.33
Magnesium	4,200	1.53
Lead	2,000	0.73
Calcium	2,800	1.0
Sodium	6,700	2.4
Copper	2,000	0.73
Titanium	30	0.011
Molybdenum	220	0.80
Boron	290	0.11
Zinc	500	0.18
Chlorine	5,000	1.8

[a] Values calculated from Table 3.1-40 with neither preferential concentration onto different size particles nor vaporization assumed.

Table 3.1-42. Trace Element Emissions from a 1000 MWe Residual Fuel Oil-Fired Power Plant, Operating at 100% Load.[b]

Element	Emission Factor (LB/10^3 GAL.)	Emission rate Uncontrolled (LB/HR)	Emission rate Controlled (LB/HR)
Arsenic	0.001 (VAPOR)	0.060	0.015
Beryllium	0.0007/0.0002	0.042	0.012
Cadmium	0.02	1.2	0.160
Manganese	0.001	0.060	0.0092
Mercury	0.0004 (VAPOR)	0.024	0.024
Nickel	0.1	6.0	0.69
Vanadium	0.3	18.0	2.8

[b] Values calculated from ref. 177

Nitrogen oxide controls are very similar to those used in coal-fired power plants. Since the objective has been to avoid production of NO from atmospheric nitrogen, the principle methods in use or planned involve some sort of combustion modification procedure. To date, these methods have been limited in their effectiveness, possibly due to the inability of combustion modification to lower the formation of NO_x from fuel nitrogen.

Since oil contains less ash by weight than coal, less efficient methods of fly ash control can be used and still comply with the EPA's New Source Performance Standards for particulate emissions (Section 2.2). Hence, multiple cyclone collectors are commonly used since they are relatively simple and inexpensive to operate.[3] However, as indicated earlier in Section 3.1.2.3.3, cyclone collectors are relatively efficient for large (> 10 μm) particle control, but do not remove any more than 40% of the respirable particles (< 2 - 3 μm) (see Figure 3.1-17, also reference 13 and 161). Fly ash particles from fuel oil combustion, on the other hand, are rich in small respirable (< 2 μm) particles. Consequently, the use of cyclones should have little effect on the concentration or composition of particulates from oil-fired power plants.[114] As Table 3.1-43 shows, the mass concentration of respirable range (< 3 μm) particulates which escape from the multicyclones of an oil-fired boiler can be 20 times greater than for the comparable particulates emitted from the same size coal-fired power plant equipped with an electrostatic precipitator. This occurs in spite of the fact that the uncontrolled oil-fired combustion emissions are only 12% of those from the coal-fired plant.

Table 3.1-43 Comparison of Particulate Emissions.[114]

Description	Oil fired boiler	All Data From* Coal fired boiler
	(mg/m^3)	(mg/m^3)
Average particulate concentration		
Before the control device	435[a]	3070
After the control device	87	9.2
Particulate emissions in stack gases		
3 μm or smaller	67.4[b]	3.2[c]
larger than 3 μm	19.6	6.0

[a] Based on 80% control efficiency.

[b] 87 × 77.5% = 67.4 mg/m^3 (after the multicyclones).

[c] 9.2 × 35.0% = 3.2 mg/m^3 (after the electrostatic precipitator).

From the standpoint of impacts on public health, therefore, the incoporation of more effective particulate removal systems such as baghouse filters or even electrostatic precipitators in place of multicyclones alone should be pursued. These emission data also point out the deficiency in existing standards, since both types of power plants shown in Table 3.1-43 comply.

Solid wastes and dust are not significant problems at oil-fired power plants at the present time. However, inclusion of scrubbers for SO_x removal would introduce the same sludge disposal problems as are encountered in coal-fired power plants. The only dust that could occur would be from fly ash handling equipment and from the ground. Enclosing the ash handling equipment and using water to moisten the ash and any loose ground would minimize dust problems. The solid wastes to be disposed of are the collected ash, which is about 1.5% the weight of the solid wastes from a coal plant with lime SO_2 scrubbers, and any sludge from sulfur control equipment.

Analogous to coal dust from coal storage piles, oil storage tanks have evaporative hydrocarbon losses. There are three basic types of tanks for oil storage: fixed roof, floating roof, and variable vapor space.[161] Fixed roof tanks are the simplest and least expensive tanks, but result in the greatest losses. These are the working losses that occur when the tanks are refilled, since the incoming fluid displaces the vapor which is in the tank, which is simply vented to the atmosphere. Breathing losses also occur due to thermal expansion, barometric pressure changes, and added vaporization of the fluid. Floating roof and variable vapor space tanks are more expensive and complicated, but are designed to eliminate or lessen these vapor losses. Variable vapor space tanks have a telescopic roof or flexible diaphram that essentially eliminates breathing losses (but not refill losses). Floating roof tanks prevent both breathing and refill losses but allow standing storage losses through leakage of the seals of the floating roof. Table 3.1-44 gives an approximate emission factor and emission rate from a 60-day-capacity tank farm for a 1000 MW plant operating at 70% capacity. Under the assumptions listed below in the table, the losses from fixed roof tanks are almost five times the losses from floating roof tanks.[161]

Table 3.1-44. Evaporative Hydrocarbon Losses from the Oil Storage Tanks of Oil-Fired 1000 MWe Power Plants, Operating at 70% Capacity[a]

DISTILLATE AND RESIDUAL OIL

Type of Storage Tank	Emissions Factor (LBS/Unit of Time-10^3Gal)[b]	Rate of Emissions (Tons/60 Days)	
		Distillate	Residual
1. FLOATING ROOF (new/old tank)			
Daily Losses	0.0052/0.012	10/24	9.7/22
Refill Losses[c]	-	-	-
Total Emissions		10/24	9.7/22
2. FIXED ROOF (new/old tank)			
Daily Losses	0.036/0.041	72/81	67/76
Refill Losses[c]	1.0	33	31
Total Emissions		105/114	98/107
3. VARIABLE VAPOR			
Daily Losses	-	-	-
Refill Losses[c]	1.0	33	31
Total Emissions		33	31

CRUDE OIL

Type of Storage Tank	Emissions Factor (LBS/Unit of Time-10^3Gal)[b]	Rate of Emissions (Tons/60 days)
1. FLOATING ROOF (new/old tank)		
Daily Losses	0.029/0.071	57/140
Refill Losses[c]	-	-
Total Emissions		57/140
2. FIXED ROOF (new/old tanks)		
Daily Losses	0.150/0.170	290/330
Refill Losses[c]	7.3	240
Total Emissions		530/570
3. VARIABLE VAPOR	not used	

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[a] Based upon Ref. (161).

[b] The unit of time for the daily emissions factors is per day, while the refill losses are per storage tank capacity (which we will assume in the calculation of the emissions rate is once every 60 days).

[c] Refill losses assume that each tank is completely emptied and then refilled every 60 days.

3.1.4 Natural Gas-Fired Steam Power Plants

Natural gas is the most desirable fuel for a fossil-fuel power plant. It is piped directly to the power plant, eliminating any need for storage. Since it is a gas, it can be mixed completely with air, allowing precise control of its combustion. Complete combustion can easily be attained with low excess air, virtually no smoke, and relatively low NO_x emissions.[161,21] Table 3.1-45 summarizes the operating characteristics and pollutant emission factors for a natural gas-fired power plant (see also Figure 3.1-2, Section 3.1.1.1).

Natural gas itself consists of methane, with minor proportions of ethane and a few higher alkanes, nitrogen gas, carbon dioxide, and a sub-part-per-million trace of mercaptans for detection of fugitive emissions.[21,161] Natural gas contains virtually no ash, and is processed to remove most of the sulfur-bearing compounds (mainly H_2S). Consequently, combustion of natural gas produces negligible emissions of sulfur oxides and fly ash. Most of the particulate emissions consist of organic and tarry carbonaceous matter.[21] In general, all of the emissions from gas-fired power plants are well below current existing emissions standards, with the notable exception of NO_x. Production of nitrogen oxides is governed solely by the flame temperature during the burning of gas, so that NO_x emissions from gas-fired power plants are sufficiently high to warrant emission control procedures. Essentially the same methods for reducing NO_x emissions from coal-fired and oil-fired plants are used for natural gas-fired plants.[21,161,164]

Because of present and projected shortages in natural gas supplies, and the higher priorities assigned for residential uses, natural gas firing of power plants will be restricted in the future. The principle function of gas-fired power plants will be to supply peak loads and to serve as power sources during periods of air pollution episodes in which combustion of other fuels might significantly aggravate the threat to public health. However, use of gas in power plants is increasingly restricted to use in more advanced cycles discussed in Sections 3.1.5 and 3.1.6.

Table 3.1-45

Emissions From a Natural Gas-Fired Power Plant, 1000 MWe (net), 100% Load

Emission	Emission Factor ($LB/10^6\ ft^3$)	Uncontrolled (T/HR)	Controlled (T/HR)	NSPS ($LB/10^6$ Btu)	Max. Allowed (T/HR)
Particulate	5-15[a]	0.022 - 0.066	0.023 - 0.068	0.10	0.48
SO_x (as SO_2)	0.6[a]	$2.6 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	-	-
NO_x (as NO_2)	700[a]	3.08	0.95*	0.20	0.95*
CO	17[a]	0.075	0.077	-	-
Hydrocarbons (as CH_4)	1[a]	$4.4 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	-	-
Aldehydes	3[b]	0.013	0.014	-	-
Organics	4[b]	0.018	0.018	-	-

Assumptions:

Natural gas properties: ash content, nil; sulfur content, nil; heating value, 22,000 Btu/LB (1050 Btu/ft^3); density, 0.048 LB/ft^3

Fuel consumption (where η stands for thermal efficiency):

uncontrolled, 1030 MWe (gross) @ 38% η:$8.81 \cdot 10^6\ ft^3$/HR (total waste heat: $5.7 \cdot 10^9$ Btu/HR)

controlled, 1030 MWe (gross) @ 37%[c] η:$9.05 \cdot 10^6\ ft^3$/HR (total waste heat: $6.0 \cdot 10^9$ (Btu/HR)

Auxiliary power consumption: 30 MW (3% of net output)

NO_x control efficiency: sufficient to meet NSPS* (no other pollution controls)

[a] From reference (161)

[b] From reference (179)

[c] Net plant efficiency: 36%

3.1.5 Combined Cycle Power Plants

Instead of burning gas or oil in a boiler, the hot gases from combustion may be used to drive a turbine directly (in a Brayton cycle, rather than the Rankine steam cycle). Such plants have many operational advantages, particularly for peak loading,[180,181] an appropriate use because of their relatively high operating costs.[179,181]

However, a pure gas turbine suffers from low efficiencies (24 - 27%, as compared with 35% to 38% for fossil steam plants), primarily due to the high turbine exhaust temperatures (~ 1000°F). The efficiency can be greatly increased by using the hot exhaust gases to generate steam for a steam turbine, operated in addition to the gas turbine, as shown in Figure 3.1-18. Present generation "combined cycle" plants have efficiencies of about 40%, slightly better than any other type of presently operating, large central station power plant. Improved combined cycle plants could achieve efficiencies as high as 50% and burn low-BTU gas from coal[181,182] (see the next section for further discussion of the latter possibility).

Tables 3.1-46, 47 show the emissions from a hypothetical present generation 1000 MWe combined cycle power plant. The newest combined cycle power plants (planned or under construction) are only about half this size.[180] Emissions and fuel consumption from a combined cycle plant are slightly less than the same sized conventional power plant fueled with the same type of fuel (refer to Table 3.1-45).

Combined cycle facilities burning distillate fuel oil will also have evaporative hydrocarbon losses associated with oil storage tank farms (see Table 3.1-44).

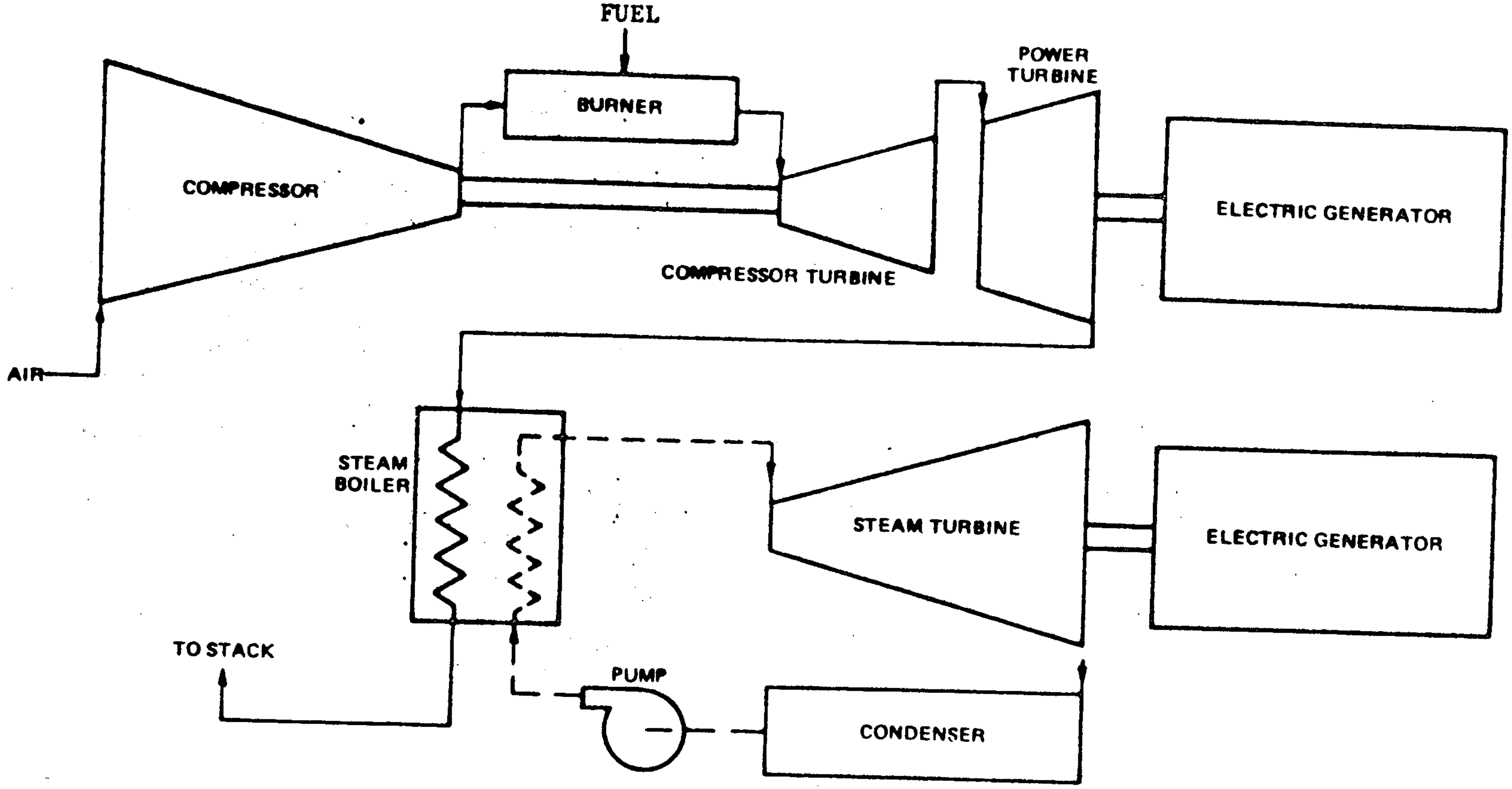

Figure 3.1-18. Schematic diagram of a Combined Cycle Power Plant.(Reproduced from ref. (183).)

Table 3.1-46

Emissions From a Distillate Fuel Oil-Fired Combined Cycle Power Plant, 1000 MWe (net), 100% Load

Emission	Emission Factor ($LB/10^3$ gal)[a]	Uncontrolled (T/HR)	Controlled (T/HR)	NSPS ($LB/10^6$ Btu)	Max. Allowed (T/HR)
Particulate	5.0	0.16	0.16	0.10	0.45
SO_x	140 x S	0.87	0.90	0.80	3.6
NO_x	67.8	2.1	1.3*	0.30	1.3*
CO	15.4	0.48	0.49	-	-
Hydrocarbons	5.57	0.17	0.18	-	-

Assumptions:

Distillate fuel properties: ash content, 0.02%; sulfur content, 0.2%; heating value, 20,000 Btu/LB ($1.4 \cdot 10^5$ Btu/gal); density, 53 lb/ft^3 (7.05 lb/gal)

Fuel consumption, no fuel is burned in the heat recovery boiler (where η stands for thermal efficiency):

uncontrolled: 1050 MWe (gross) @ 41% η:$6.24 \cdot 10^4$ gal/HR (total waste heat: $5.2 \cdot 10^9$ Btu/HR)

controlled: 1050 MWe (gross) @ 40%[b] η: $6.40 \cdot 10^4$ gal/HR (total waste heat: $5.4 \cdot 10^9$ Btu/HR)

Auxiliary power consumption: 50 MWe (5% of net output)

NO_x control efficiency: sufficient to meet NSPS* (no other pollution controls)

[a] From reference (161)

[b] Net plant efficiency: 39%

S is sulfur content of fuel oil in %.

Table 3.1-47

Emissions From a Natural Gas-Fired Combined Cycle Power Plant, 1000 MWe (net), 100% Load

Emission	Emission Factor (LB/10^6 ft^3)[a]	Uncontrolled (T/HR)	Controlled (T/HR)	NSPS (LB/10^6 Btu)	Max. Allowed (T/HR)
Particulate	14	0.057	0.059	0.10	0.44
SO_x	940 × S	0.038	0.039	-	-
NO_x	413	1.7	0.88*	0.20	0.88*
CO	115	0.47	0.48	-	-
Hydrocarbon	42	0.17	0.18	-	-

Assumptions:

Natural gas properties: ash content, nil; sulfur content, 0.01%; heating value, 22,000 Btu/LB (1050 Btu/ft^3); density, 0.048 LB/ft^3

Fuel consumption, no fuel is burned in the heat recovery boiler (where η stands for thermal efficiency):

uncontrolled: 1030 MWe (gross) @ 41% η: $8.17 \cdot 10^6$ ft^3/HR (total waste heat: $5.1 \cdot 10^9$ Btu/HR)

controlled: 1030 MWe (gross) @ 40%[b] η: $8.37 \cdot 10^6$ ft^3/HR (total waste heat: $5.3 \cdot 10^9$ Btu/HR)

Auxiliary power consumption: 30 MWe (3% of net output)

NO_x control efficiency: sufficient to meet NSPS* (no other pollution controls)

[a] From reference (161)

[b] Net plant efficiency: 39%

S = sulfur content of gas in %.

3.1.6 Advanced Technologies

Many new advanced technologies are being developed to burn fossil fuels, mainly coal, to generate electricity more efficiently and/or with less pollutant emissions. Although none of these technologies are now economically competitive with conventional power plants, some of these hold the promise of widescale use, if and when they are developed to the level of reliability necessary for commercial application. Some of the most promising are fluidized bed combustion, combined cycle power plants utilizing low-Btu power gas synthesized from coal, and MHD power generation.

Most of the technologies being developed to clean up pollutant emissions are primarily concerned with sulfur compounds. Currently, these compounds (mainly SO_2) are scrubbed out of the stack gases after the combustion process. The new technologies, however, are aimed at removing sulfur compounds during or before combustion of the fuel.

The major technology being developed for the control of SO_2 during combustion is fluidized bed combustion. This method involves burning ground coal with particles of limestone in a stream of air which flows up through the boiler at a rate sufficient to suspend or fluidize a bed of these particles. The SO_2 evolved during combustion is absorbed within the bed by the limestone particles. The absorption process produces calcium sulfate in the form of a dry solid, which is continually removed and replaced with fresh limestone.[184,191,192]

Unlike stack gas scrubbers, the sulfur removal efficiencies of fluidized bed boilers seems to be limited to 70 to 95% of the sulfur present in the fuel that is burned.[197] This type of boiler also uses about as much limestone as a scrubber for a conventional boiler of similar size, but the dry, solid calcium sulfate waste from a fluidized bed will be easier to handle and dispose of than wet scrubber sludge. It may be possible to use regenerative absorbants such as magnesium oxide instead of limestone to eliminate the disposal problem posed by solid wastes.[184,191,192]

The particulate emissions characteristics of uncontrolled fluidized bed units are still uncertain, especially for small particulate matter.[184] Particulate control equipment, probably similar to existing equipment (electrostatic precipitators, cyclones, and baghouse filters) might still be needed on fluidized bed units to comply with particulate emission regulations.

This is especially important if higher ash content fuels are burned which cannot be used in other processes.

Fluidized bed boilers have a potential for becoming more efficient, more versatile, and more economical than conventional boilers equipped with flue gas desulfurization equipment. The design of fluidized bed units can be relatively independent of the type of coal or other fuel to be burned because they operate at about 1100°C which is below the melting point of coal ash. (Because of the high combustion temperatures of conventional boilers (1500-1800°C), the ash fusion temperature of the particular coal to be burned must also be considered as a specific design criterion.) Fluidized bed combustion also offers lower NO_x emissions than conventional boilers, probably because the prolonged contact time in the hot bed facilitates the spontaneous decomposition of fixed nitrogen.[22a,184,198,199] Oxidation of atmospheric nitrogen only occurs at temperatures above 1500°C, but operating at lower temperature could also result in greater emissions of CO and carbonaceous particulate matter when compared to conventional power plants.

The temperature is controlled by a series of tubes located within the fluidized bed through which water is pumped to carry away heat and generate steam. The tubes are in direct contact with the hot solid particles, which permits a heat transfer rate several times that of a conventional boiler. As a result, fluidized beds are expected to be more compact, of standard designs, and possibly fabricated in the shop rather than in the field, while maintaining emission characteristics comparable to conventional boilers equipped with the best pollution control equipment.[184,191]

The advantages of fluidized bed combustion have yet to be demonstrated, however. A recently completed 30 MW fluidized bed unit is now being tested in Rivesville, West Virginia. This plant represents a significant jump in size from previous pilot plants and its success or failure could have a major impact on the utility industry's confidence in the technology.[184,192]

Another technology under development is coal gasification, which cleans up the fuel before it is burned, offering the potential for improved emissions characteristics as compared with burning the coal directly in a conventional power plant. There are two classifications for the fuel obtained by gasification: synthetic natural gas, SNG, which has a heating value of around 1000 Btu per standard cubic foot (SCF), and low Btu power gas, which has a much lower heating value (about 150 Btu/SCF).[181] Synthetic natural gas is made to be a direct substitute for natural gas. Low Btu gas, on the other hand, is simpler to synthesize than SNG, but, because of its low heating value, cannot be economically transported very far.[181] Attempts to make coal gasification an economically viable source of fuel for electricity generation focus on integrating a low-Btu gasification and raw gas cleanup facility with a modern combined cycle power plant using a gas turbine capable of burning the low-Btu power gas[181,183,185,193] (see the section on combined cycle power plants). With the anticipated advances in gasification technology, such an integrated power plant would have lower SO_2 and particulate emissions than a comparably sized conventional power plant in which these air pollutants are cleaned up in the exhaust gases, in addition to economic advantages. The sulfur removed from the coal gas would be in the form of elemental sulfur, which would be much easier to dispose than SO_2 stack gas scrubber sludge.

Air emissions from an integrated coal gasification and combined cycle power plant would be well within the limits imposed by the Federal New Source[186,187] Performance Standards (NSPS) for solid fossil fuels (coal), except for NO_x. Particulate emissions will be very low because of the strict requirements for control of particulate loading in gas turbine fuel, to prevent turbine blade erosion by particulate matter.[186,187] Usually the SO_2 emissions from the raw gas cleanup unit account for 60 - 90% of the total SO_2 emitted from the integrated plant (see Table 3.1-48). These emissions can therefore be further reduced by employing a tail gas scrubber at the raw gas cleanup plant.[186,187]

The NO_x emission rate from an integrated system depends largely on the type of gasifier and raw gas cleanup system used. Some gasifiers convert much of the nitrogen in the fuel into ammonia (NH_3), which, if present during combustion, is oxidized along with the nitrogen in the air to NO_x. High temperature cleanup systems, which increase system thermal efficiencies, also raise turbine flame temperatures (possibly increasing NO_x production). Their effect on the NH_3 level of the fuel gas is not known.[193] Low temperature cleanup systems, however, can remove much of the NH_3 from the fuel gas before it is burned in the turbine, permitting much lower NO_x emissions. Table 3.1-48 gives emission factors and emission rates for 1000 MWe versions of four types of integrated coal gasification, combined cycle power plants.

Table 3.1-51. Emissions from Representative Integrated Coal Gasification, Coal Gas Cleanup Process, and Combined Cycle Power Plant, 1000 MWe (net), @100% load.

	Bureau of Mines Fixed Bed Gasifier[a]		Bituminous Coal Research, Inc. entrained flow gasifier[b]	
	Delexol[c] Desulfurization	Iron Oxide[d] Desulfurization	Delexol[c] Desulfurization	Conoco[e] Desulfurization
EFFLUENTS: Emission Rate for 1000 MWe Plant in tons per hr[f]/Emission Factor in lb per 10^b Btu Coal Input [Maximum Emission Rate Allowed by Fed. New Source Performance Standards, if applicable, in tons per hr.[f]]				
Particulates[g]	< 0.084/ 0.016 [0.53]	< 0.16/ 0.032 [0.49]	< 0.044/ 0.01 [0.44]	< 0.18/ 0.04 [0.44]
SO_x[g]	2.1/0.408 [6.3]	4.4/0.909 [5.8]	1.7/0.388 [5.3]	2.4/0.553 [5.3]
NO_x[g]	3.0/0.574 [3.7]	25/5.17 [3.4]	7.2/1.633 [3.1]	7.5/1.71 [3.1]
Solid wastes[h]	77/14.6	71/14.6	31/7.1	31/7.1
Sulfur[h]	16/2.96	12/2.51	12/2.74	12/2.72
Ammonia[h]	7.3/1.38	---	4.2/0.96	---
Waste water[h]	1300/246	130/27	2400/544	420/97
WASTE HEAT[i]: Thermal Discharge in 10^6 Btu/hr[f]/Ratio of Heat Rejected to Heat Input[h]				
	53/0.005	180/0.018	140/0.016	18/0.002
NET PLANT EFFICIENCY:[g]				
	32.4%	35.1%	38.6%	39.0%

a A first generation combined cycle plant

b A second generation combined cycle plant

c A low temperature desulfurization process using polyethylene glycol ether as a physical solvent

d A high temperature desulfurization process using sintered iron oxide and fly as as the absorbent

e A high temperature desulfurization process using half-calcined dolomite as the absorbent

f Calculated for a 1000 MWe power plant from the emission factors and net plant efficiencies given in the table

g Emission factors & net plant efficiencies from reference (186)

h Emission factors & heat ratios from reference (187)

i Assumes the use of mechanical draft cooling towers

Magnetohydrodynamic plants offer one method to increase operating temperatures and hence the efficiency at which fossil fuels are utilized to generate electricity. Binary-cycle power plants incorporating a magnetohydrodynamic (MHD) topping cycle in conjunction with a conventional Rankine (steam) cycle generator work on this principle and have the potential of generating electricity at efficiencies of 50 - 60%.[181,182,188-190]

An MHD cycle is a method of generating electricity from a conducting fluid moving through a magnetic field. MHD generators are essentially expansion engines which convert the thermal energy of the hot combustion gases directly into electricity.

After the fuel is burned with compressed, preheated (1200° - 1800°C) air (oxygen enriched air can also be used, but is usually too expensive), the hot combustion gases are seeded with an easily ionizable material such as potassium, cesium, or other alkali metal, to increase its conductivity.[181,188,189] The hot conducting gas, or plasma, is accelerated through a nozzle and directed in a channel through a transverse magnetic field, inducing a direct current, which is picked up by electrodes located along the walls of the channel. The plasma then passes through an air preheater and a steam generator to extract more of its energy. Steam from the steam generator powers a Rankine turbine to generate additional electricity, which amounts to about half of the output from such a binary-cycle power plant.[181,188,189]

Although first-generation MHD-steam power plants will have efficiencies only slightly better than advanced combined (Brayton and Rankine) cycle power plants, coal can be burned directly in a MHD unit, as opposed to being gasified and cleaned of sulfur and particulate matter before combustion in a gas turbine.[188] However, there are still many problems to work out before the first MHD-steam binary cycle power plant comes on-line (perhaps around 1985[190]). Second-generation MHD-steam plants could have efficiencies closer to 60%.[181,189,190] Their use could greatly extend the life of our fossil fuel reserves and significantly reduce the thermal pollution generated by power plants, while generating electricity with very little air pollution.

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3.2 Geothermal Emissions

3.2.1 Characteristics of Geothermal Resources

Convecting magma transports heat from the earth's interior to the solid crust. The heat is then conducted through rocks toward the surface at a rate on the order of 10^{-6} cals/cm^2/sec. On crustal plate margins the earth's crust is thinner, and heat is conducted at a rate of up to 7.9×10^{-5} cals/cm^2/sec in areas such as California's Imperial Valley.[1] When water is coincident at depth with such higher heat flows, a hydrothermal reservoir exists. Such reservoirs within several kilometers of the surface comprise the world's geothermal resources. Depending on reservoir geology, geochemistry, water inflow, and temperature, the subterranean water can be either predominantly liquid or vapor. Each of these requires a slightly different technology to harness and produce electricity, and has varying environmental impacts. The following discussion will highlight the differences between the types of geothermal resources, and then describe the environmental effluents of current and future geothermal power plants in California.

Liquid dominated geothermal resources contain liquid phase fluid composed of water, dissolved gases, and dissolved minerals from the water-bearing rock formation. This type of reservoir is usually found in permeable sedimentary or volcanic rokcs with water inflows that are equal to or greater than outflows.[2] Reservoir temperatures and enthalpies are in the 200 to 350°C and 200 to 300 cal/gm ranges, respectively.[3] Mineral concentrations can reach several hundred thousand ppm by weight due to the high temperatures and pressures. Geothermal wells typically yield liquid and flashed steam which is the result of declining temperature and pressure during ascent up the well. The fluid can be voluminous, hot, and laden with solutes. Table 3.2-1 shows characteristics of the East Mesa, Long Valley, Niland, and Salton Sea liquid dominated California geothermal fluids.

Vapor dominated geothermal resources contain vapor phase fluid composed of water, gases, and a small amount of minerals. This type of reservoir is rare and comprises only 5% of the world's geothermal resources.[4] It is thought to exist in competent rock into which less water flows than escapes, and may be underlain by a liquid dominated region.[2] Reservoir

Table 3.2-1. Characteristics of California Geothermal Fluids*

		Castle Rock Springs	Geysers	East Mesa	Long Valley	Niland	Salton Sea
enthalpy	cals/gm		670			240	248
reservoir press.	psig		475				
surface press.	psig		125				
reservoir temp.	°C		245		220	300	340
surface temp.	°C		101	180	219		101
salinity	ppmw		0.001			260,000	
pH		5.1	7		9.2		
TDS.	ppmw		28.38		1420		
(references		29	5,36,44	44	15,44	5	44,37)
Minerals	ppm by weight						
sodium	Na	117.0	0,12		390	53,000	50,400
potassium	K	86.0	0.10		45	16,500	17,500
lithium	Li		0.002		2.8	210	215
rubidium	Rb				0.48	70	137
cesium	Cs				0.6	20	16
calsium	Ca	0.10	0.20		0.9	27,800	28,000
magnesium	Mg	37.0	0.06		0.1	10	54
strontium	Sr		0.1		0.14	440	609
barium	Ba					250	235
iron	Fe				0.05	2000	2090
manganese	Mn				0.02	1370	1560
zinc	Zn				0.10	500	790
copper	Cu				0,03		8
silver	Ag				0.04		0.8
silicates		0.50				400	
floride	F	8			12		15
chloride	Cl	10	20		280	155,000	155,000
lead	Pb				0.1	80	84
mercury	Hg	0.054	0.005		0 0001		0.006
arsenic	As		0.019		2.2		12
boron	B	24.1	16		15	390	390
(references		29	14,43		29	30	29)
Gases	ppm by weight (by volume)						
carbon dioxide	CO_2	216(142)	3260(2150)				
hydrogen sulfide	H_2S	96(82)	222(190)				
methane	CH_4	4(7)	194(350)				
ammonia	NH_3	140(239)	194(330)				
nitrogen	N_2	2	52(54)				
hydrogen	H_2	2(28)	56(809)				
ethane	C_2H_6	1.8	nil				
total		460(502)	3980(3785)				
(references		1	14)				

* Blanks in table indicate no accurate data, not zero values.

pressures are lower than the hydrostatic pressures at similar depths in a liquid dominated reservoir. Temperatures and enthalpies are in the 200 to 250°C and 600 to 700 cal/gm ranges, respectively.[5] Geothermal wells yield dry superheated steam and a small amount of gas, minerals, and particulates. Table 3.2-1 shows characteristics of the Castle Rock Springs and Geysers vapor-dominated California geothermal fluids.

Few generalizations about the environmental impact of geothermal electric power plants are accurate. Impacts are technology and fluid specific. The more the generating hardware isolates the fluid from the environment, the less the impact. Fluid enthalpy tends to be inversely related to potential impact. Lower enthalpy fluids require higher mass flow per MW-hr, and increase the potential amount of emissions for a given size power plant.

It is tempting to generalize fluid characteristics within a geographic region, and assume that they and their potential impacts are homeogeneous. This is an error. The East Mesa, Niland, and Salton Sea fluids are all in the Imperial Valley and differ widely, as Table 3.2-1 shows. Adjacent wells in the Broadlands, New Zealand geothermal field have H_2S concentrations which differ by as much as an order of magnitude.[6] For this reason the experiences of development and impact at Cerro Pieto, Mexico, just over the border from the Imperial Valley, are not considered representative of potential geothermal development impacts in California.

The impacts discussed herein are divided into seven categories. Noncondensible gases, fluid wastes, solid wastes, waste heat, and noise are examined in this section. Problems of subsidence and seismicity, not as directly health related, are also discussed. The preponderance of impact information exists for the Geysers development in Sonoma County. Imperial Valley development is at the test stage only, and much remains to be learned. The Long Valley in central-eastern California has attracted a small amount of attention, and is periodically mentioned.

3.2.2 Noncondensible Gases

3.2.2.1 Hydrogen Sulfide, Ammonia, and Sulfur

Geothermal fluids contain a small amount of gaseous impurities which remain vaporous in the steam condenser. These are the so-called noncondensible gases which comprise about one percent by weight of most fluids.

Carbon dioxide is the main component, with lesser concentrations of hydrogen sulfide, methane, ammonia, nitrogen, hydrogen, and ethane. Table 3.2-1 shows the concentrations of these gases in several California geothermal fluids. H_2S and NH_3 exist in high enough concentrations that they are a nuisance result of geothermal electricity production. The emission points of all noncondensible gases can be divided into natural, drilling, preplant, and power plant sources.

Noncondensible gas concentrations in the geothermal fluid tend to decline with exploitation.[7] This decline is, however, intimately tied to the geochemistry of the reservoir. For example, at Wairakie, New Zealand the H_2S emissions remained constant while the total gas mass evolved declined by 50% during the period between 1960 and 1969.[8]

H_2S is best known for its rotten eggs odor. This odor is detectable by humans in a range around 0.03 ppm, which represents the California State Standard established by the Air Resources Board. The American Congress of Government and Industrial Hygienists (ACGIH) has adopted a threshold limit of 10 ppm hourly average exposure, based on several occupational toxicology studies.[9] Typical background concentrations of H_2S range up to approximately 0.005 ppm over most of the earth.[10-11] The gas has an atmospheric life of between 2 and 48 hours depending on meteorologic conditions, and is naturally oxidized to sulfur oxides and sulfates.[3] H_2S is heavier than air, and tends to sink in still conditions. The gas and its oxidation products tend to be highly soluble and their distributions are greatly influenced by rain. Measured H_2S concentrations are two to ten times higher during dry periods than wet.[12]

NH_3 is detectable by humans in a range around 47 ppm.[3] Although there is no Federal or State ambient air quality standard for NH_3, the ACGIH has established an occupational threshold concentration of 50 ppm for an 8 hour average exposure, because of its strong irritant properties.[7] This lighter-than-air gas is highly soluble in water and enhances the solubility of H_2S. Hence, NH_3 is also readily washed out by rain. Its presence as ammonium in steam condensate, in addition to boron, led to the curtailment of releasing the condensate into streams at the Geysers in 1968. All unevaporated condensate is now reinjected.

Natural releases of gas occur constantly from fumaroles common to geothermal regions. In the Geysers area, reports of a strong sulfur odor appear as early as 1860. Such natural emission has decreased due to an ebb in reservoir pressure; however, natural sources still account for 54.4 kg/day of H_2S to the air.[13] Assuming a constant relationship between H_2S and NH_3 emissions, approximately 47.5 kg/day of NH_3 are released. Some fumaroles exist in the Imperial and Long Valleys. However, no accurate data exists on their noncondensible gas emissions.

Drilling gas releases occur from the time the fluid first comes to the surface until the well is shut in. Gases escape with the vented steam in vapor dominated fields, and from the geothermal fluids dumped in ponds in liquid dominated fields. Drilling emissions per well at the Geysers in 1974 averaged 8274 metric tons of steam, or 184 and 160 metric tons of H_2S and NH_3 respectively.[13] Drilling is concluded by well testing and clean out. Average Geyser emissions for this 3 day to 2 week process are 141 and 123 metric tons of H_2S and NH_3. Blown out or uncontrolled wells are very infrequent and venting lasts from 4 days to 15 years. No data exists on Imperial Valley drilling emissions. Some estimates place them 5 times higher than the Geysers.[3]

Pre-plant noncondensible gas emissions occur from shut in wells, geothermal fluid line vents, and "stacking". Wells are shut in while waiting to come on line after drilling, or if the power plant will be out of operation more than 3 days. Such wells are vented to maintain some steam flow. Ordinarily this steam is collected and reinjected. Wells typically emit about 0.01 tons per hour of both H_2S and NH_3 at the Geysers. Elapsed release times vary widely. Geothermal fluid lines have separators in them which remove particulate matter. At the Geysers most of these vent emissions are collected in another pipe system. In the event of a power plant shut down of less than 4 days duration, fluid may be vented just before it enters the power plant. This is called stacking. All pre-plant emissions account for less than 5% of the total at the Geysers. Imperial Valley development is insufficient to have these sources, or data on them.

Power plant emissions of noncondensible gases depend on the technology used. They are negligible if a binary system is used and all geothermal fluid remains pressurized and is reinjected. If fluid from a liquid dominated reservoir is flashed, or vapor dominated reservoir steam is used, gas will escape from the off-gas ejectors and wet cooling towers. Off-gas ejectors are vacuum pumps which remove noncondensible gases from the condenser. If the condenser is the direct contact type, a substantial amount of gas will dissolve in the condensate and be stripped out in the cooling towers. The amount of each gas dissolved, of course, depends on its solubility. Most NH_3 dissolves and is exhausted at the cooling tower.[14] H_2S is fairly soluble and 65 to 80% dissolves in a direct contact condenser and goes to the cooling towers.[13] All power plant emissions of H_2S depend on abatement, if any.

Total Geysers noncondensible gas emissions are 250 metric tons/MW-yr, according to 1975 Northern Sonoma County Air Pollution Control District data,and mean fluid compositions shown in Table 1.[13] This emission rate implies that 12 to 14 metric tons of NH_3 and H_2S are released per MW-yr. No NH_3 intoxication problem has been observed; however, H_2S standards are frequently exceeded. Previously discussed power plant emission sources release gas having H_2S concentrations as high as 16,000 ppm.[13] Substantial mixing occurs before off-gas ejector and cooling-tower plumes reach the ground; however, ambient concentrations around some units frequently range between 5 to 10 ppm.[15] During the start up of Unit 7, concentrations of over 20 ppm were detected in working areas.[15] Extension of gas ejector stacks ameliorated the problem before normal operation began. Above-standard H_2S levels are not restricted to the power plant site and work areas, but pervade the region. During nocturnal inversions in the lower elevation Big Sulfur Creek Valley, H_2S concentrations over 100 ppm have been measured.[16] Residents of neighboring Lake County also complain of H_2S originating from the Geysers. These conditions have stimulated the iron catalyst H_2S abatement of Unit 11, planned Stretford process abatement of Unit 13, and retrofitting of older Units. It should be noted that the cumulative effect of individually complying Units may still exceed the 30 ppm standard.

SO_2 has not been found in geothermal fluids. It has been detected in ambient air at the Geysers only after H_2S has been present for several hours.

During atmospheric inversion conditions, SO_2 concentrations of up to 10% of the simultaneous H_2S concentrations have been measured, but have never exceeded 0.01 ppm.[16] The California State Standard for ambient air is 0.50 ppm for one hour, and 0.04 ppm for a 24 hour average.

Imperial Valley geothermal development consists of several test facilities and no on-line power production plants. No definitive noncondensible gas emissions per MW-yr estimations exist. Due to the liquid dominated field's low enthalpy and higher H_2S fluid concentrations, emissions could be 5 times those at the Geysers.[3]

3.2.2.2 Radon

Uranium-238 is common in soil and rock. It is localized around geothermal reservoirs by the reducing environment afforded by hydrogen sulfide and the precipitation of uranyl carbonate.[17] Its presence in geothermal fluid-bearing formations is indicated by the existence of one of its natural gaseous decay products, Radon-222. The association between radon gas and geothermal resources has stimulated its use as a prospecting tool. Radon is a chemically "inert" noble gas with a 3.82 day half-life. Its three decay daughters, polonium-218, lead-214, and bismuth-214, eventually decay into stable lead-206. Radon's low water solubility allows the gas to escape from the geothermal fluid at the surface with the other noncondensible gases.

Radon is ubiquitous in nature. The largest natural source is diffusion through the ground from soil and rock containing U-238. The magnitude of this diffusion averages 1 pCi/m^2-sec over the United States, and accounts for 110.7 metric tons emitted into the atmosphere per day world-wide.[18-19] Ambient air concentrations due to this source can be as high as 1400 pCi/m^3.[20] Fumaroles common to most geothermal regions emit radon at significantly higher rates.

Radon is emitted from geothermal development everywhere that steam and noncondensible gases are exhausted. Table 3.2-2 shows the concentrations in several geothermal fluids, emission points, and spaces occupied by humans. The four principle sources are well drilling operations, steam venting, off-gas ejector, and cooling tower exhausts. Well drilling, testing, and cleanout radon release concentrations are those of the geothermal fluid. Total releases during this phase of development are small compared to power plant operation.

Power plant emissions depend on the type of generating facility. When a binary system is used, such as that being tested at Niland, California, releases are negligible if the fluid remains under pressure and is reinjected. When steam or flashed liquid systems are used,the first source is vented steam. Radon is exhausted at vents in high concentration but low volume. The main emission source is the off-gas ejectors which remove noncondensible gases from the condenser. Radon exhaust concentration and volume is relatively high; however ejector stacks are 60 to 85 feet high and substantial mixing occurs before the plume reaches the ground.[20] In systems using direct contact steam condensers,a small amount of radon gas will dissolve in the condensate and condenser fluid, and be transported to the cooling tower. There it is stripped from the fluid and exhausted.

Sludge composed of sulfur from oxidized H_2S and air and steam particulates accumulates in the bottom of the cooling towers, and has been found to contain lead-210. When an iron catalyst H_2S abatement system is used, such as a Geysers Unit 11, the sludge is voluminous. Pb-210 occurs naturally and is scrubbed from the cooling tower air, rather than originating in the geothermal fluid.[21]

Radioactivity at all physically occupiable positions at the Geysers is below the 3000 pCi/m California State Standard. No other producing geothermal plants presently exist in California. Geysers ambient air concentrations range from < 0.01 to 0.2 pCi/ℓ, and are similar in the working environment as shown in Table 3.2-2 .[20] Some investigators have concluded that an employee could indefinitely spend all working hours in the physically occupiable atmosphere having the highest measured concentration, and not exceed applicable standards.[22] Radon and lead concentrations in soil and vegetation in the Geysers region do not appear to be elevated, and no other indications of increased exposure rates have been found.[22,23]

Total radon emissions at the Geysers are 1.56 Ci/MW-year. If the gas is released from power plants in the Imperial Valley, releases will be comparatively quite high. Referring to enthalpy in Table 3.2-1, and assuming equal plant efficiency, 2.8 times as much fluid by weight is needed to provide the same energy at Niland (Imperial Valley) as at the Geysers. Converting from kilograms to liters, and assuming that Imperial Valley fluids have a specific gravity of 1.3 because total dissolved solids are as high as 330,000 ppm, the ratio becomes 2.15. If 1.56 Ci/MW-yr are produced from Geysers steam having mean radon concentration of 8150 pCi/m^3, then Imperial Valley plants with concentrations from 1.24 to 10.0 $\mu Ci/m^3$ could emit from 510 to 4115 Ci/MW-yr. This figure assumes 16% thermal efficiency, and the actual figure is likely to be closer to 10%.

3.2.3 Liquid Wastes

3.2.3.1 Water Pollution

Geothermal development can degrade both surface and ground water qualities by addition of geothermal fluid to existing waters, and extraction of good quality water from lakes, streams, or wells.

Subterranean aquifers may be damaged if extraction or injection well casings are not sealed. Because the fluid pressure in the well is greater than the aquifer pressure, it will seep out and may foul well water quality or damage spring fed lakes and rivers. The dissolved mineral and gases could affect the drinking water supplies of residential, municipal, and agricultural users. The problem of well casing integrity exists during both drilling and power production phases of development. According to Rex, withdrawal of geothermal fluids in the Imperial Valley may cause near-surface aquifer levels to subside.[25] If this happens, well water quality and availability may decline even though geothermal wells are sealed from the agricultural or drinking water reservoir.

Surface waters can be polluted during drilling and power production in different ways. Pollution opportunities endemic to the well site are the sump and the possibility of a blow out. The sump is an earthen reservoir constructed to the standards of a California State Water Resources Control Board Class II-1 disposal site and approved by the Water Quality Control Board.[26] It is designed to hold all drilling muds and cuttings, and must be much larger for liquid dominated fields because of the voluminous drilling effluent. No waste may overflow the sump, and at East Mesa they are plastic lined due to the highly porous soil.[1] The drilling waste contains several toxic sodium compounds and detergents, and is buried once it has dried. No sump failures have been reported, and no studies have been done to check their integrity several years after abandonment. Pacific Energy Co. has attempted to use large tanks in lieu of a sump, and had poor results.[27] With some

Table 3.2-2. Radon concentrations in California geothermal fluids, at emission points, and alternative electric energy source comparisons.

	Radon Emissions
*USBR Mesa Well 5-1, I V	1.612±0.041 μCi/m^{3*}
*USBR Mesa Well 6-1, I V	1.673±0.079 μCi/m^{3*}
*Sinclair No. 4, I V	13.000±0.055 μCi/m^{3*}
Geysers steam 700 mm Hg pressure	
Geysers steam line noncondensible gas vents	6.100-9.600 μCi/m^3
Geysers off-gas ejector	3.660-5.300 μCi/m^3
Geysers ambient air	10.-200 pCi/m^3
Geysers operators desk inside turbine building	0.20±0.10 pCi/m^3
Typical geothermal power plant	1500 Ci/GW-yr
Mean USA ground diffusion	1 pCi/m^2 sec
California State Standard	0.003 μCi/m^3

*Assuming specific gravity of 1.3 for conversion to μCi/m^3

Source: 19,20,24

innovation this method appears to have promise.

Well blow outs in vapor dominated fields have minimal water pollution problems, because of the gaseous nature of the escaping fluid. At liquid dominated fields approximately 20% of the fluid flashes to steam and a hot and voluminous toxic flow remains. The addition of this liquid to surface waters for even a very short time would seriously foul their quality. There have been three blow outs at the Geysers and two at Cerro Prieto.[18]

Power plant water pollution can result from spent geothermal fluids and the uptake of local water supplies for make up water. Since 1968 no fluid has been released into local streams at the Geysers, and 1.3×10^6 gallons are reinjected per day.[15] Even though the waste fluid from plants in liquid dominated fields is 15 times as large, reinjection is the only acceptable production-scale method of fluid disposal.[3] Water may be taken from local sources during drilling to add to drilling muds, and during power production as condenser make up water. Make up water replaces that which is evaporated in the cooling tower that is needed in the condenser. The Geysers need no make up water; however, this may not be the case in the Imperial Valley. Water extraction from local sources may cause a decline in downstream and lake water qualities and volumes. Geothermal wells in California are monitored for leakage, pressure changes, and infiltration by the Division of Oil and Gas.

3.2.3.2 Toxic Minerals

High levels of mercury are associated with geothermal fluids in Hawaii, Iceland, and New Zealand. California fluids have lower concentrations; however, in view of the Minimata incident it is worthwhile to examine toxic mineral pollution closely. The concentrations of arsenic, boron, and mercury in various California geothermal fluids are shown in Table 3.2.1.

The minerals are released at all fluid emission points which were examined in section 3.2.2 above. Boron in fluid released into a local Geysers tream stimulated reinjection of all unevaporated fluid in 1968. There is no other mention that ambient concentrations of these toxins are worthy of concern in any of the literature surveyed.

Cooling tower sludge mercury concentrations at the Geysers reach 5 ppm; the sludge is trucked to industrial waste disposal sites.[18]

Imperial Valley development is insufficient to indicate where toxic minerals might accumulate and in what concentrations.

3.2.4 Solid Wastes

Solid wastes of several types are created during the drilling and power production phases of geothermal development. Liquid drilling wastes are discussed in section 3.2.3. Power plant waste characteristics depend on the method of geothermal heat utilization, and the method of H_2S abatement.

Vapor and liquid dominated resources require different types of power plants, which create different wastes. Vapor dominated plants, such as the Geysers, produce a small amount of cooling tower sludge and sludge from the reinjection settling ponds. These wastes have created no disposal problems. Liquid dominated reservoir fluids are typically high in total dissolved solids, which can create voluminous waste if the plant is engaged in desalinization or evaporative brine concentration. If all fluid is reinjected solid waste is negligible. No Imperial Valley facilities yet emit solid waste on a production scale.

H_2S abatement equipment being put into use at the Geysers creates a toxic sludge in the cooling towers composed of iron oxides, sulfur, and air and steam particulates. This iron catalyst system reduces H_2S emission 92% and produces 33 barrels of sludge per MW-yr at 110-MW Unit 11.[28] The waste is then transported to an industrial waste disposal site in Contra Costa County, as no suitable place can be found in Lake or Sonoma Counties. The Stretford process[13] is scheduled to be used at Geysers Unit 13, and will produce saleable elemental sulfur and much less solid waste.[26]

3.2.5 Waste Heat

Geothermal fluids have low enthalpy and the thermal efficiency of electricity production utilizing such fluids is therefore also low. Thermal efficiency is 16% at the Geysers, and in the Imperial Valley it is expected to be as low as 10%. Because of these low efficiencies, a large amount of unusable waste heat is produced per MW-year. This heat is released to the environment in wet or dry cooling towers or cooling ponds by conduction and evaporation. These cooling methods are discussed briefly in section 3.1.1.6.

The Geysers mechanical-draft wet cooling towers release approximately 4.2×10^{17} cals /MW-yr.[29] A 1000-MW development is expected to raise the local atmospheric moisture content 50%.[30] No definitive estimations of the impact of these releases on the local climate have been made.

Imperial Valley power plants will release more waste heat because of the lower geothermal resource enthalpy and production thermal efficiency. Cooling methods are not yet defined, but are projected to release 7.2×10^{17} cals/MW-yr.[29] Water evaporation from wet cooling towers would have little climatic effect, because total evaporation would still be less than in the past due to a decline in agricultural water use and evaporation.[31]

3.2.6 Noise

Geothermal developments create characteristically low frequency high energy sounds from several sources. The sound levels vary depending on source and muffling. Mechanical sources produce constant levels, and fluid emission sources produce oscillating levels proportional to the rate of flow. The sources and associated sound levels appear in Table 3.2-3 and are discussed below, using the table as a reference.

The first noise from development emanates from heavy machinery constructing the well pad. Once drilling begins the diesel engines powering the bit and mud pumps increase sound levels to 90 dB day and night for the duration of drilling.[31] In vapor dominated fields mud is not used when steam producing formations are penetrated, because it would quench and plug the aquifer. Air is forced into the well to cool the bit and carry the cuttings to the surface. Compressed air, steam, and cuttings exit a "Blooie" line and can increase sound levels by 12 dB. If a water injected cyclonic separator muffler is used, sound levels can be reduced to that of mud drilling for the 2 to 6 week duration.

Wells are cleaned and tested once drilling is complete. In vapor dominated fields this is the noisiest action in development. Wells vented straight to the atmosphere create peak sound levels of 125 dB in the 1100 to 4000 Hz range.[33] 40 dB reduction can be achieved with a cyclonic separator muffler; however, fist-size debris often is ejected from the well. An expansion muffler is less prone to damage from such debris, but provides less attenuation. No information exists on sound levels produced by flowing, unrestricted, liquid-dominated wells. The fluid partially flashing to steam, however, is known to create a 100 dB sound level, as shown in Table 3.2-3.

Wells are shut in while waiting to come on line or whenever the power plant is closed for more than several days. At the Geysers they are bled through a 1/4 inch line to maintain well casing temperature and some flow. Sound levels created thereby are equal to production field ambient levels. No similar data exists for liquid dominated fields.

The only production facility in California is the Geysers, so only its noise emissions can be discussed or shown in Table 3.2-3. The largest source is the off gas ejectors which produce sound levels over 117 dB.[15] Insulation of lead and mineral wool reduces the emission to less than 88 dB.[34] The other plant sources are the cooling towers and turbine-generator machinery. Table 3.2-3 shows the associated sound levels.

Post-emission sound level attenuation is caused by barriers and meteorological conditions. Buildings, fences, ridges, and trees limit sound spreading. Wind tends to bend sound waves upward if they are travelling the opposite direction, and downward toward the ground if they are travelling in the same direction. Oxygen molecules absorb sound energy. However, they absorb little of the low frequency sound characteristic of geothermal developments.

3.2.7 Seismic Effects

Geothermal resources exist where subterranean fluid and high heat flow are coincident. High heat flow is caused by thinning of the earth's crust over convecting magma.[4] Such conditions occur in zones of recent volcanism and mountain-building which are on the margins of crustal plates.[35] Seismic activity is natural and frequent in such regions, and some evidence indicates that geothermal development may change natural seismicity.

Extraction and injection of fluid in faults may aggravate their activity. Extraction could allow fault stress to build up by increasing frictional resistance, and thus increase the magnitude of a quake when it does occur. Injection could reduce the frictional resistance to shear, and promote rupture.[30] At the Rocky Mountain Arsenal near Denver, Colorado, waste injected

Table 3.2-3. Sound levels associated with geothermal well construction and power plant operation.

Phenomena	Dist.	dB(A)	Duration
site preparation	15.2m	80-90	8-10 hrs/day, 2 weeks
drilling-mud	15.2m	90	24 hrs/day, 2-6 weeks
-air	15.2m	102	24 hrs/day, 2-6 weeks
-air muffled	15.2m	80-90	24 hrs/day, 2-6 weeks
testing and cleanout	15.2m	110-125	24 hrs/day, 3-4 days
muffled	15.2m	85-95	24 hrs/day, 3-4 days
venting shut in well	15.2m	65-75	---
pipeline noise	15.2m	75	installation life
stacking steam	15.2m	100	shutdown duration
off gas ejectors	0	117	installation life
insulated	0	< 88	installation life
developed production field	---	40-50	installation life
cooling towers	5	80	installation life
inside turbine building	---	88-91	installation life
Unit 13	---	< 85	installation life
flashing geothermal liquid	15.2m	100	---

Source: 15,18,26,32

into the ground was shown to increase the frequency of small earthquakes.[15] A similar phenomenon occurred at the Rangely oil field in northwestern Colorado. In both cases evidence implies that reservoir rocks were subject to large tectonic sheer stress. This situation exists in California geothermal resource areas.

The Geysers and surrounding known geothermal resource areas are made of Franciscan metasedimentary and metavolvanic rock of Jurassic and Cretaceous age. Geothermal fluid is born from a Franciscan graywacke sandstone producing formation.[36] The region has several faults which characterize the fault and sheer zone-riddled Franciscan formation.[37] The nearest active fault, the San Andreas, is 30 miles west of the Geysers. Condensate reinjection began in 1968 and the U.S. Geologic Survey has been monitoring the area seismically and by methods of triangulation. Current data show that there has been no noticeable change in regional seismic activity.[3] Apparently the Coloradoan experiences will not be repeated at the Geysers.

The Imperial Valley is part of the East Pacific Rise structural rift which creates the Salton Trough. Although the Valley floor is below sea level,[37] it is full of water-saturated sediments up to 6.15 kilometers deep. It is crisscrossed by the Coyote Creek, Imperial, San Andreas, San Jacinto, and Superstition Hills faults, which have all moved since 1968.[35] Seismic monitoring of the East Mesa area has shown 1 to 2 Richter magnitude quakes to be common, and nanoearthquakes to occur at a frequency greater than 100 per day.[38] The focal depths of many of these quakes are less than 2.5 km, which is within the range penetrated by wells. Parts of the Imperial Valley are being monitored for seismicity and subsidence; however, insufficient development of the resource has taken place to afford any results.

The Mono-Long Valley known geothermal resource area is of volcanic origin, and no data or development exists on which to base an estimate of the seismic effects of geothermal development.

The principle seismic hazards to geothermal power plants are ground shaking and landslides. Ground shaking could shear and crack well casings, and damage all surface hardware. In sedimentary mediums, such as the Imperial Valley, shakes are expected to have a larger verticle range and longer period than in harder rock mediums.[26] Mountainous areas, such as the Geysers, are prone to landslides, which can damage surface hardware. Some Geysers wells are sunk through landslide material. The blow out of geothermal well GDC 65-28 was caused by movement of slide material at a depth of 41 meters.[39]

3.2.8 Subsidence

Geographic surface elevation and contour changes can be introduced by fluid extraction and injection, hydraulic and thermal gradients, landslides, and tectonism. Geothermal fluid extraction and injection cause subterranean reservoir pressure changes that can cause subsidence or rebound. Subsidence occurs under conditions where the fluid actually aupports the overlying rock.[40] When this support is reduced or removed the rock may sink. Because geothermal resources exist where tectonism is active and where thermal gradients are large, separating the effects of geothermal development from other forces is difficult. Further, subsidence is endemic to only a certain type of geothermal reservoir.

Vapor dominated geothermal fields, such as the Geysers, can only exist where host rocks are competent.[40] The steam-bearing formation is fractured self-supporting rock. Reservoir pressure changes caused by fluid extraction or injection hence have no effect on geographic elevations and contours. There is no evidence of any subsidence in vapor dominated steam fields, including the Geysers and the Lardarello field in Italy, which has been in operation since 1904.[40]

Liquid dominated geothermal fields can experience subsidence because the fluid-bearing formation is both porous and incompetent.[30] Reservoir pressure changes modify the support given by the fluid to overlying rock, and may cause it to sink. Geothermal fluid extraction from the Wairakie, New Zealand liquid-dominated field has caused subsidence up to 4 meters at a rate of 40 cm/yr since 1956.[41] Similarly, withdrawal from the Wilmington oil field at Long Beach, California has caused subsidence of up to 8.3 meters.[15]

Unlike the Geysers fractured rock, the Imperial Valley is filled with water-saturated porous sedimentary strata. There is a shallow, cool, fairly saline aquifer underlain by a deep, very hot, hypersaline geothermal pool.[31] Some natural subsidence is occurring, and has been measured at Cerro Prieto, Mexico.[15] Geothermal fluid is extracted at Cerro Prieto, but its effect on subsidence rates is unknown. Lofgren has been studying subsidence in the Imperial Valley; however, too little geothermal development has taken place to produce results.[42] Geographic deformation in this region will have disastrous consequences to agriculture, because most irrigation canals have slopes of less than feet per mile.[15]

Geothermal fluid reinjection could maintain reservoir pressure and may ameliorate land subsidence problems. For example, one to one saltwater reinjection is now being done in the Wilmington oil field and seems to be successful. The Imperial Valley has two problems in this respect. The first is the low availability of reinjection water. A binary system in which all fluid is reinjected may be the best solution. Second, the surface effect of the subterranean hydraulic gradient between extraction and injection wells is unknown.

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3.3 Dispersal and Population Exposure

Once pollutants have been emitted from their sources into the atmosphere, several processes can occur. Some pollutants may fall to the ground either close to the source, or farther along the path of the plume. Nearby deposition occurs generally for large ($\gtrsim 10\ \mu m$) particles in the air, so that only fine particles and gases remain in the plume at distances greater than a few km downwind from the source.[1] Deposition by rainfall or condensation can occur anywhere, and often depletes the air and increases soil concentrations of acid sulfates, acid nitrates, etc.[2,3] If the raindrops or mist particles are large enough to fall to earth, they are probably too large to be inhaled or to represent a primary health hazard to the population.[1]

Gaseous and particulate matter may also remain suspended in the air and undergo secondary reactions. The products of these secondary reactions are not found in the primary source emissions, but are formed sometime after the pollutants have been in the atmosphere. Many secondary pollutants are more reactive, dangerous, and toxic than their primary emission precursors, and include ozone, peroxyacetyl nitrate (PAN), aldehydes, organic acids, sulfates, nitrogen dioxide, nitrates, and so on.[4-7] Secondary reactions are described in greater detail in part 3.3.3 below.

Finally, as discussed in section 3.3.2, pollutants from stationary sources that are not deposited on the ground near the plant are transported, often over vast distances and covering large areas. It is this fate that poses the threat to public health from any primary or secondary pollutants in ambient air, and which must be assessed in order to determine the likely doses of pollutants that people in an urban or a rural area would receive from power plant emissions.

3.3.1 Urban and Non-Urban Ambient Air Quality

3.3.1.1 Global Background Processes

On a worldwide scale, emissions from natural sources account for a large fraction of the total inventory of some species. Processes yielding these emissions include biological decay sources, rock weathering, volcanic activity, transport, electric discharges, natural fires, and so on. The contributions of these processes to total world-wide emissions and global air quality are shown in Table 3.3-1.

Table 3.3-1. Contributions of Natural Processes to Air Pollution.

Species	Background concentration*	Total burden by mass (%)	Reference
SO_x	0.1 - 3 ppb (SO_2)	65-90	(8, 11)
NO_x	10 - 30 ppb (NO or NO_2)	90	(10)
O_x	10 - 70 ppb (O_3)	--	(4, 9)
CO	~ 1 ppm (CO)	80	(8, 12)
Hydrocarbons	1.0-1.5 ppm (CH_4)	5	(8, 13-15)
mercury	≤ 1 ppt (Hg)	38-83	(8, 16)
selenium	3 ppt (Se)	?	(17)

*Form in which concentrations are expressed is shown in parentheses.

3.3.1.2 Urban Air Quality

The data in Table 3.3-1 give some idea of man's impact on global pollution. However, ambient air pollutant concentrations in urban areas can be much higher than the natural background levels. The Environmental Protection Agency (EPA) has compiled an extensive catalog of air quality and source emissions data for SO_2, NO_x, oxidants, CO, hydrocarbons, and particulate matter for the various monitoring areas in the United States.[18,19] In addition, the California Air Resources Board (ARB) has independently maintained continuous compilations of air quality data for several California monitoring stations for several years, which examine CO, oxidants, NO, sulfates, particulate matter, and hydrocarbons.[20] The reader should consult these sources for specific information on air quality and source emissions data; some of the emissions data are summarized in Figure 3.1-1 of this report.

Typical urban concentrations of SO_2 have been reported to range from 0.01 ppm in San Francisco to 0.2 ppm in Chicago,[21] on an annual average basis. Levels as high as 1.5 ppm have been observed during "smog episodes" in London.[21] Corresponding levels of sulfates (as H_2SO_4) have been observed to be 4.0 $\mu g/m^3$, 20 $\mu g/m^3$, and 220 $\mu g/m^3$, respectively.[21] In California, SO_2 concentrations have rarely exceeded either the EPA or ARB air quality standards during the past three years.[19,20,21] Sulfate levels in California, particularly in the South Coast Air Basin, however, frequently exceed the ARB 24-hour standard of 25 $\mu g/m^3$.[20] California sulfates show a definite seasonal trend, with maximum concentrations observed in summer.[20]

Nitrogen oxides concentrations in U. S. urban air typically range from 0.03 ppm NO and 0.02 ppm NO_2 in St. Louis to 0.073 ppm NO and 0.05 ppm NO_2 in Chicago on an annual average basis.[10] Twenty four-hour average concentrations as high as 0.16 ppm have been observed in Anaheim,[8] and one-hour levels in excess of 0.6 ppm have frequently been observed in South Coast Air Basis monitoring stations.[20] NO_2 concentrations in California are highest during the winter months[20] in which photochemical activity is at a minimum. Ambient NO concentrations have not been studied as extensively as NO_2 in California; however, the impact on Los Angeles school children[26] suggests that NO should and will be analyzed more extensively in the future.

Photochemical oxidants are a class of secondary pollutants that are formed from primary emissions (NO_x, HC, etc.) in the atmosphere. These oxidants are comprised mainly of ozone (O_3) and to a lesser extent peroxyacetyl nitrates (PAN), and related compounds. Because of variations in meteorological conditions and seasonal and diurnal fluctuations (see Figure 3.3-1) instantaneous levels usually do not correlate well with long term values. In general, total oxidant levels can be equated with the ambient O_3 concentration.[4,8] Because O_3 is a secondary pollutant, comparison of rural with urban oxidant concentrations is probably not a reliable index of man-made urban air pollution. Considerable evidence now exists[22,23] to suggest that O_3 precursors emitted in urban areas result in high oxidant levels in non-urban areas as well. O_3 concentrations in excess of 0.1 ppm have been observed over large areas of the eastern United States, including most of the states of Ohio,[19] [illegible]vania[19], and New York.[24] In California, photochemical-produced oxidants are a principal pollutoin problem. Oxidant concentrations frequently exceed the ambient air quality standards through most of California. It is rare for any of the major urban centers in California to experience a summer season without at least one oxidant smog episode.[20] Table 3.3-2 summarizes various smog episodes reported in California during the years 1973-1975. For California, O_3 and CO are the only pollutants which have routinely led to major episodes, although sulfates may be important contributing factors.[20]

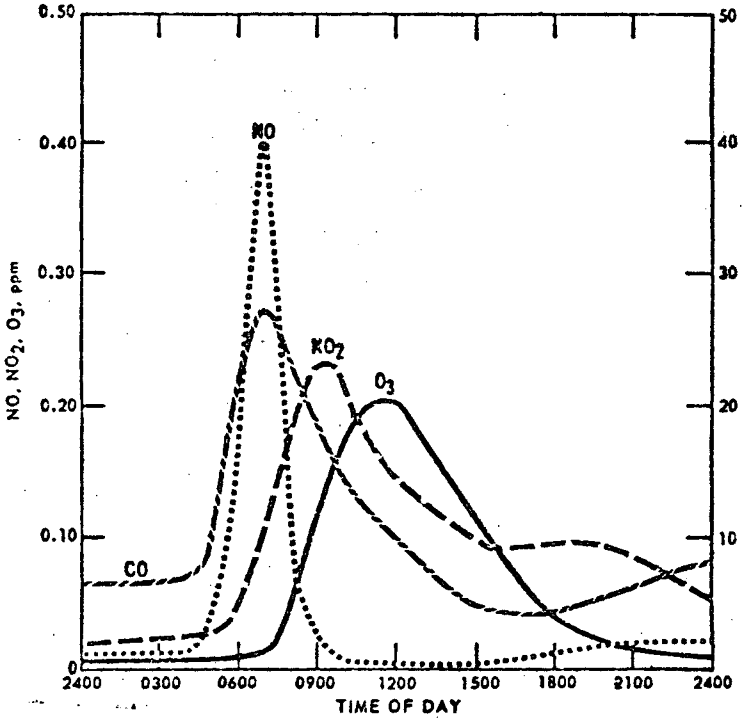

Figure 3.3-1. Average daily 1-hour Concentrations of selected Pollutants in Los Angeles, July 19, 1965. (Reproduced from ref. (8).)

For other pollutants, typical California concentrations range between 1-50 ppm for CO,[20] 0.1-7.0 ppb for mercury vapor,[8,16] and in excess of 45 for non-methane hydrocarbons.[25]

3.3.2 Dispersion of Emissions

The processes by which emissions from isolated sources become a community-wide air pollution problem are highly dependent on the modes of atmospheric transport which can occur. The volume of air in which mixing takes place, the rates of mixing due to diffusion* or atmospheric turbulence, the directions in which plumes travel, and other factors, reflect the influences of weather and climate,

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*Usually meaning eddy mixing, rather than molecular diffusion.

TABLE 3.3-2. AIR POLLUTION EPISODES IN CALIFORNIA# – 1973-1975†

Air Basin: Air Quality Control District	Pollutant	Number of Days in which Pollutant Level Exceeded Episode Criteria								
		Alert (Stage 1)			Warning (Stage 2)			Emergency (Stage 3)		
		1973	1974	1975	1973	1974	1975	1973	1974	1975
South Coast Air Basin:		*(**)								
Los Angeles County	Oxidant	63(26)	81(35)	79(41)	9	2	1	1	0	0
	CO	4	15(10)	5	0	0	0	0	0	0
Orange County	Oxidant	15	6(4)	15(10)	0	0	0	0	0	0
	CO	0	1	3	0	0	0	0	0	0
San Bernardino County	Oxidant	132(90)	142(97)	102(72)	30	18	4	4(2)	1	0
Riverside County	Oxidant	81	96(73)	40(23)	9	2	2	1	0	0
Ventura County	Oxidant	7	20(3)	1	0	0	0	0	0	0
Santa Barbara County	Oxidant	3	1	1	0	0	0	0	0	0
Southeast Deserts Air Basin	Oxidant	35	38	0	0	0	0	0	0	0
San Francisco Bay Area	Oxidant	6(2)	10(5)	4(2)	0	0	0	0	0	0
San Diego Air Basin	Oxidant	5(4)	0	0	0	0	0	0	0	0
Sacramento Valley Air Basin	Oxidant	2	1	1	0	0	0	0	0	0
San Joaquin Valley Air Basin	Oxidant	2	3(2)	1	0	0	0	0	0	0

---

‡ Data were obtained from "California Air Quality Data", Vol. 5, Issues 1-4 (1973); from Ibid., Vol. 6, Issues 1-4 (1974); from Ibid., Vol. 7, Issues 1-3 (1975) which are all published by the California Air Resources Board, 1102 Q Street, Sacramento, CA 95814; and from "State Implementation Plan Progress Report: July 1 to December 31, 1975", Publication EPA-450/2-76-006 (April 1976), published by the Environmental Protection Agency, Washington, D.C.

* Number of days in which at least one monitoring station in the District reported pollutant concetrations in excess of the episode threshold.

**Number of days in which at least half of all the stations in the District reported pollutant concentrations in excess of the episode threshold. Numbers are in parentheses.

Episode criteria are defined in California Air Pollution Emergency Plan, 11th Revision, California Air Resources Board, Sacramento, CA 95814 (July 26, 1976), and are given in Section 2.6.

topography, and the community-wide distribution of pollutant sources. These factors determine whether ground-level ambient air concentrations of pollutants are uniform for only a limited area or for an entire community, and whether emissions from sources such as power plants can account for the pollution burden in a given sector of the community. After a brief look at observed seasonal fluctuations (section 3.3.2.1), the manner in which atmospheric conditions may be characterized is discussed (3.3.2.2), the influence of these conditions on plume behavior is summarized (3.3.2.3), and a brief introduction to meteorological modeling is provided (3.3.2.4). A more specific discussion of modeling considerations is the subject of a separate report.[26a]

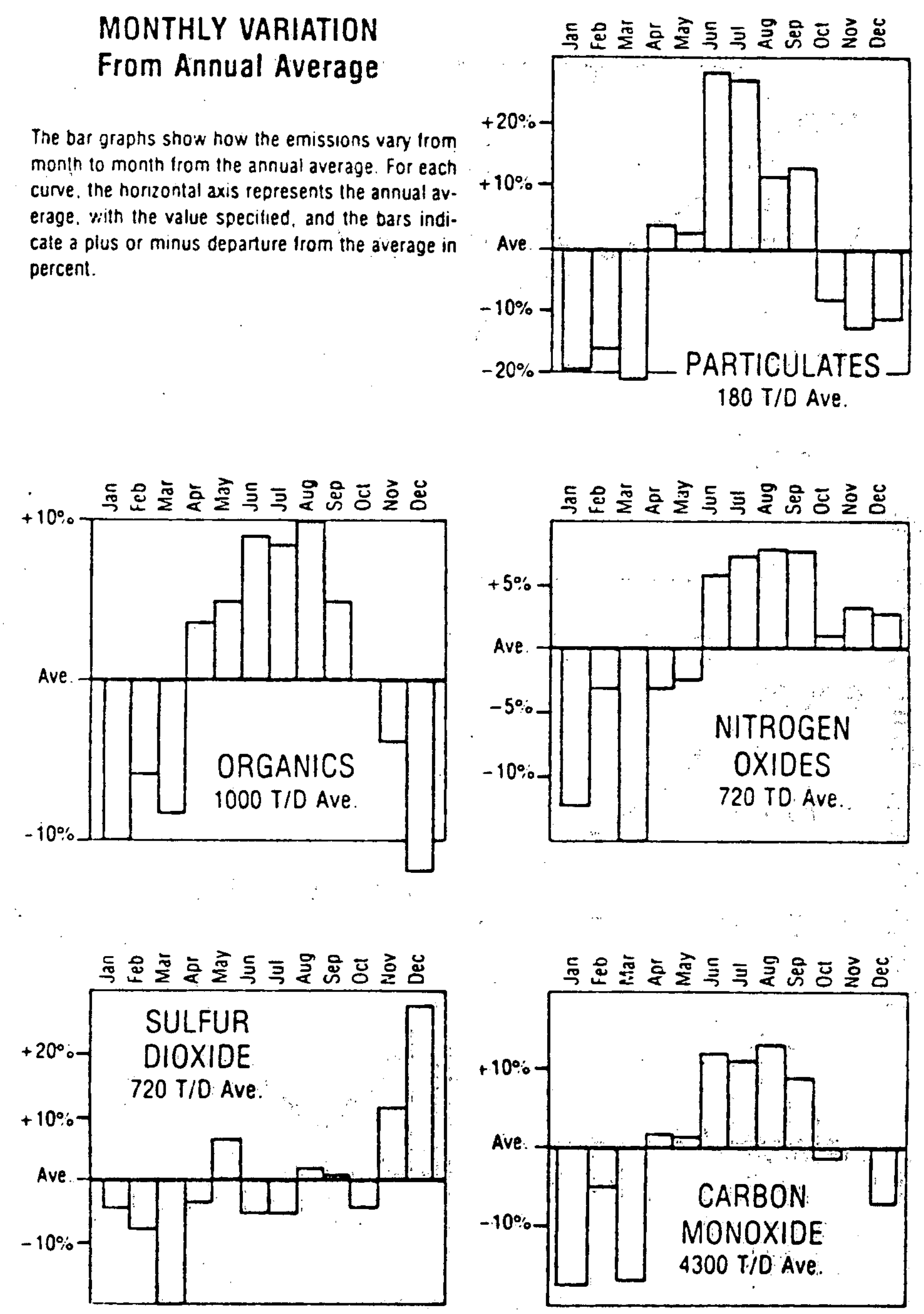
3.3.2.1 Seasonal fluctuations

Both ambient air concentrations and emission rates of pollutants show seasonal variations. Generally, however, the seasonal variations in emission rates are small compared to those in ambient levels. Figure 3.3-2, for example, shows that emissions of various pollutants in the San Francisco Bay Area vary by only about ± 30% from their annual averages. Similar data for power plant emissions in Los Angeles County (Figure 3.3-3) show emission values for SO_2 and NO_x to be within 50% of their yearly averages.

Ambient air concentrations, however, show very large seasonal fluctuations as is seen in Figures 3.3-4,5. As an example, the oxides of nitrogen average maximum hourly concentrations climb, in the winter, to twice the annual average value in both San Francisco and Los Angeles. These fluctuations in ambient air concentrations are much larger than the variations in pollutant emissions and do not correspond to the seasonal pattern of emission rates. They arise from seasonal variations in meteorological conditions.

3.3.2.2 Atmospheric characterization

Ambient air quality depends, not only on the emission inventory, but also on the dispersion or dilution that takes place after the pollutants are emitted into the atmosphere. The two main factors determining these processes are winds, primarily causing horizontal movement of the pollutants, and the atmospheric stability, which affects vertical movement.



MONTHLY VARIATION
From Annual Average

The bar graphs show how the emissions vary from month to month from the annual average. For each curve, the horizontal axis represents the annual average, with the value specified, and the bars indicate a plus or minus departure from the average in percent.

Fig. 3.3-2. Emission Inventory for the San Francisco Bay Area from the Bay Area Air Polution Control District[27]

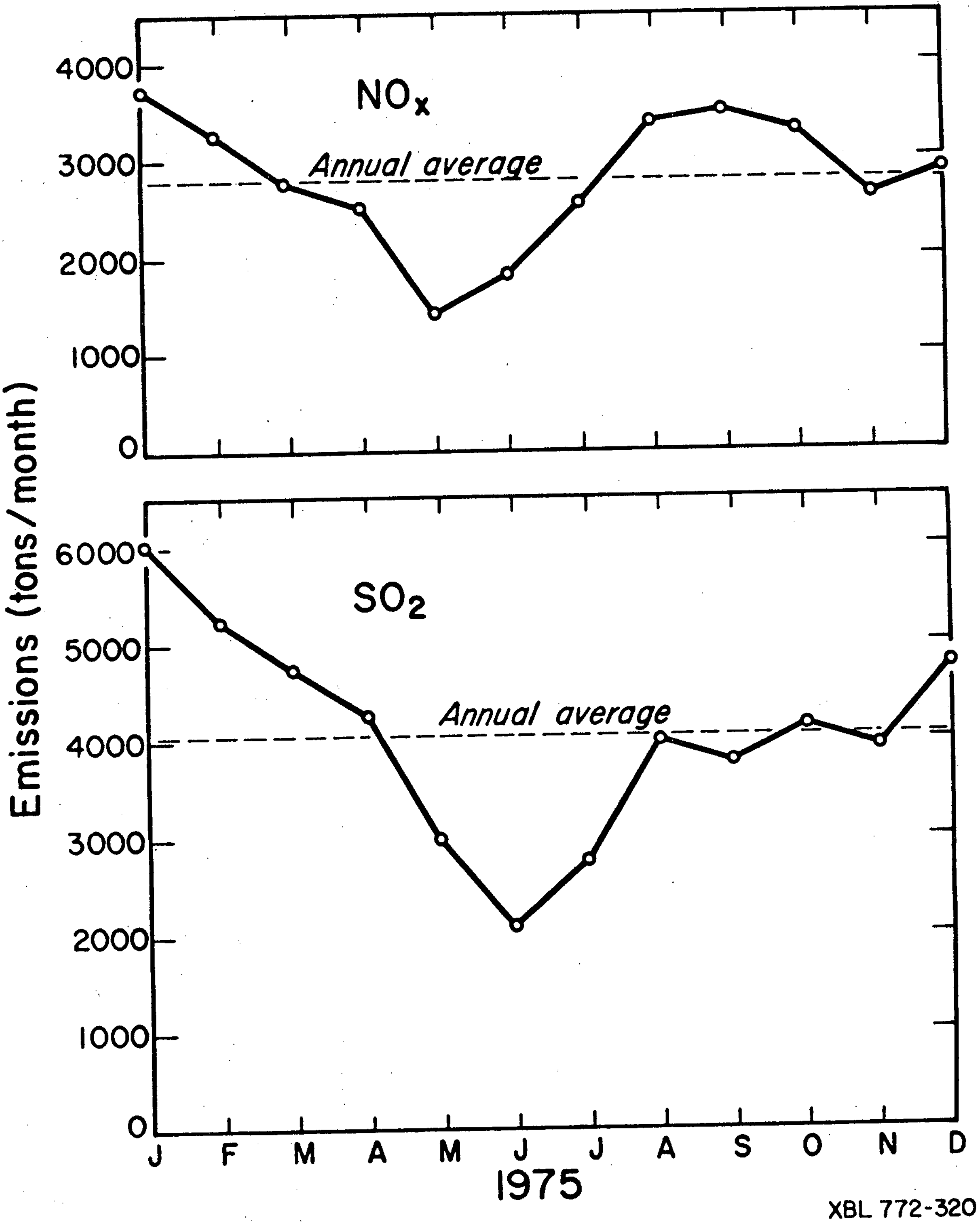


Figure 3.3-3. Emissions from oil and gas fired power plants in Los Angeles county (1975). (Based on ref. 29.)

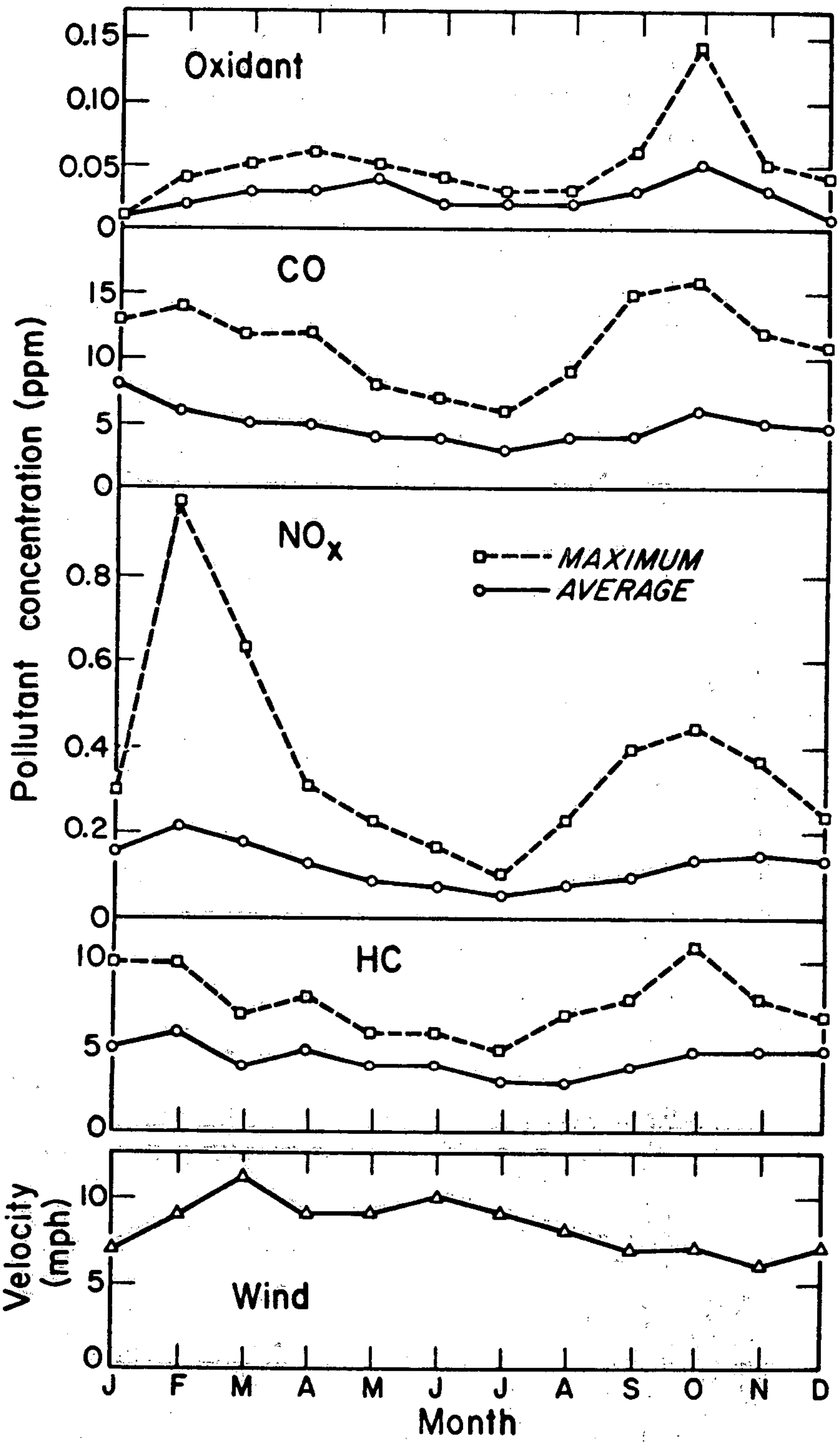


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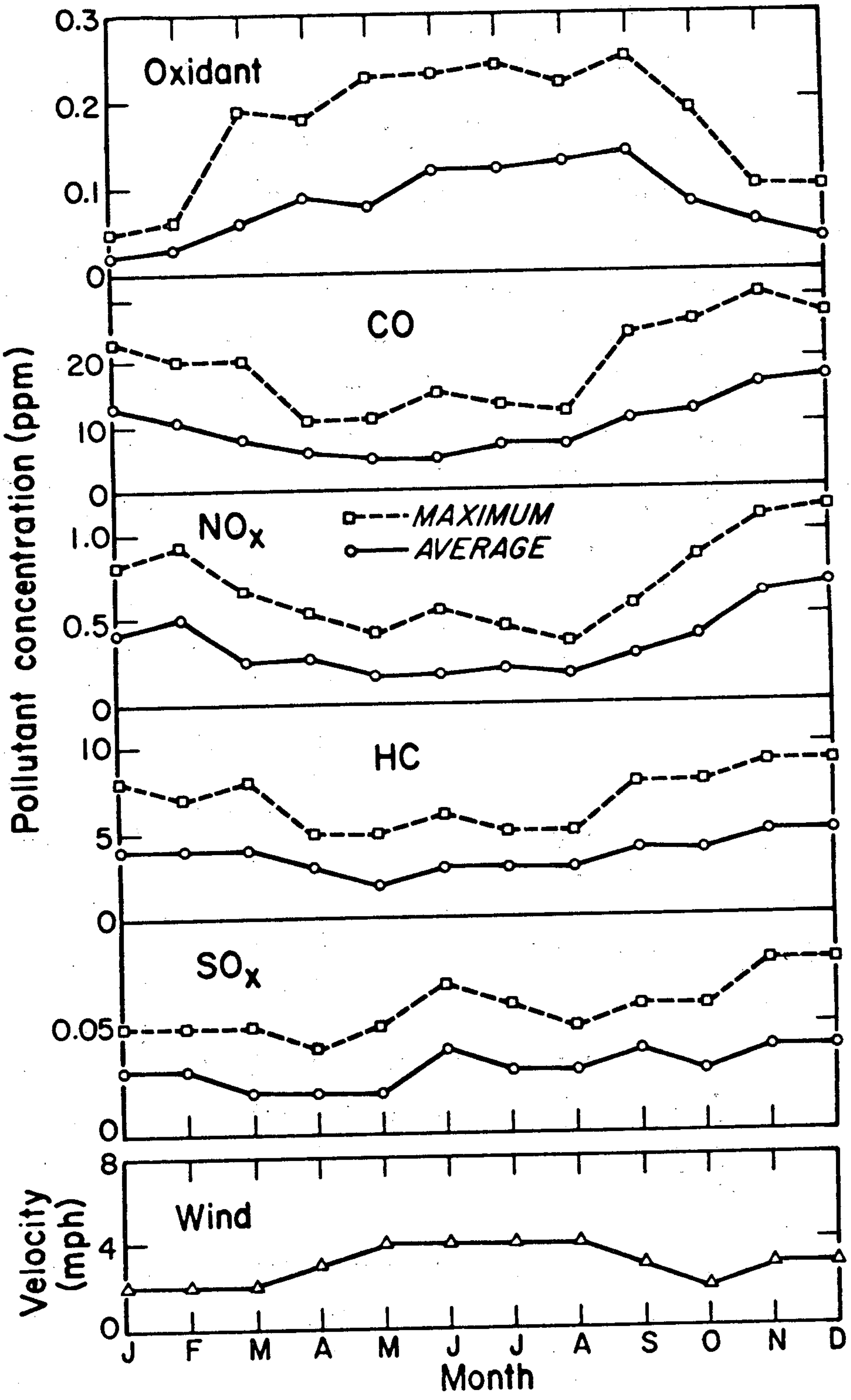
Figure 3.3-4A. The monthly maximum and average of maximum daily hourly-averaged pollutant concentrations; and the monthly average of the daily wind velocity; San Francisco (1974). (Based upon ref. 20.)



XBL 772-326

Figure 3.3-4B. The monthly maximum and average of maximum daily hourly-averaged pollutant concentrations; and the monthly average of the daily wind velocity; Los Angeles county (1974). (Based upon ref. 20.)

References 27-31 serve as a general introduction to these transport mechanisms.

A basic question to be answered in characterizing atmospheric stability and plume dispersion is the behavior of a sample or parcel of air released at a specified location. Such a parcel may, of course, be moved due to transport by winds — even in a vertical direction (particularly if large surface irregularities are present). However, its vertical movement may also be influenced greatly by more subtle characteristics of the atmosphere, in particular its stability and, a closely related matter, its vertical temperature profile.

This temperature profile is typically parameterized by the "lapse rate," which is the rate of change of temperature with decreasing altitude. (The lapse rate is positive if the temperature decreases with height.) The lapse rate is described as "adiabatic" if it is equal to the rate at which an air parcel would change temperature as it rises and expands adiabatically (i.e., without heat transfer to the parcel). As a result, if the lapse rate is adiabatic (numerically equal to 10°C/km), a parcel of air which is displaced upward or downward will maintain a constant temperature difference compared with its surroundings. This is a relatively neutral condition as compared with superadiabatic or subadiabatic lapse rates, where the temperature decreases, respectively, faster and slower than 10°C/km. In the first case, a rising parcel of air will cool as it rises, but less rapidly than its surroundings, so that it will tend to continue to rise; conversely, a falling parcel will tend to continue to do so. On the other hand, in subadiabatic conditions, the rising parcel would eventually become cool compared with its surroundings and start to fall; whereas a falling parcel would eventually tend to rise. (See Figures 3.3-6,7 for temperature profiles.) The first condition is unstable and favors mixing; the second is stable, hinders vertical mixing, and hence encourages pollutant buildup. Subadiabatic conditions become even more stable when the lapse rate becomes negative, i.e., the temperature increases with altitude. Such a temperature inversion essentially stops vertical mixing, effectively trapping pollutants. Such inversions may occur in two circumstances, either where a layer of air moves in such a way as to trap a warmer layer below it, or when air at low altitude is cooled by contact with ground that has been radiatively cooled. Figure 3.3-8 shows possible temperature profiles for inversion conditions.

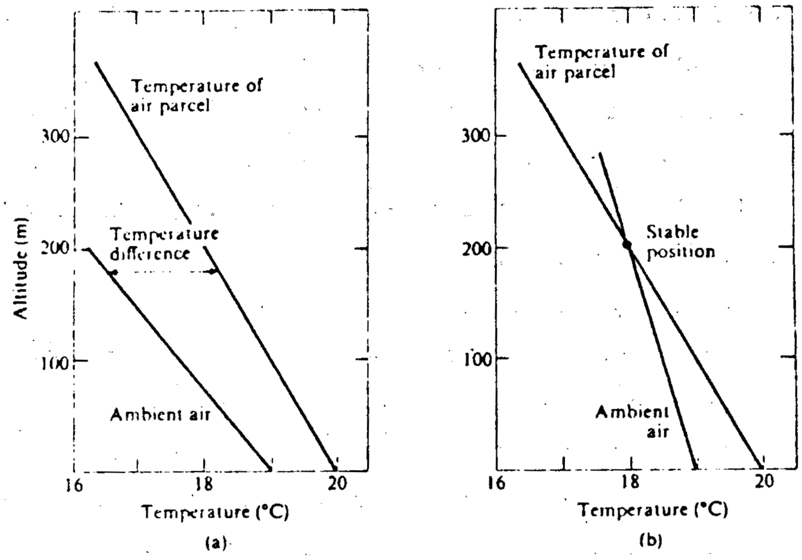


Figure 3.3-6. Temperature profiles. a) A rising parcel of air will continue to be buoyed upward if the ambient lapse rate exceeds the dry adiabatic lapse rate. b) The same parcel will cease its upward motion if at some point its temperature is equal to the ambient temperature and the ambient lapse rate is less than the adiabatic rate. (Reproduced from ref. 30).

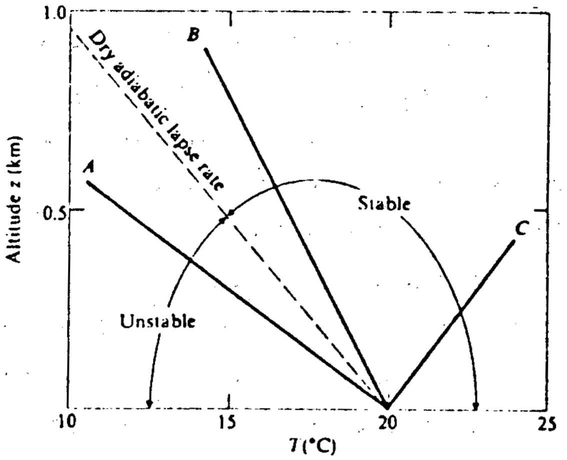


Figure 3.3-7. Temperature profiles to illustrate Lapse Rates in a dry atmosphere. (A) unstable, (B) stable, and (C) very stable (inversion). (Reproduced from ref. 30.)

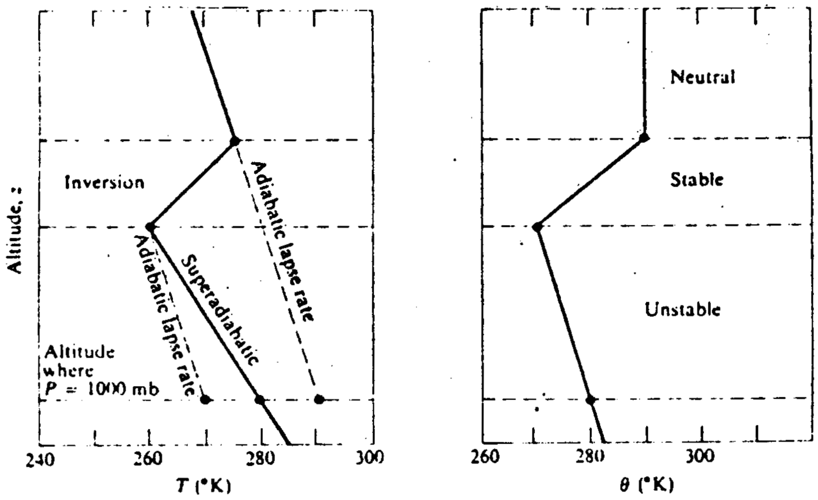


Figure 3.3-8. Profiles for the absolute temperature and potential temperature for a situation with an elevated inversion layer. The dashed line at the left shows how the temperature of the two parcels of air would change if the parcel were lowered adiabatically to an altitude where the pressure was 1000 mb. (Reproduced from ref. 30.)

3.3.2.3 Plume behavior, atmospheric mixing, and pollutant dispersion

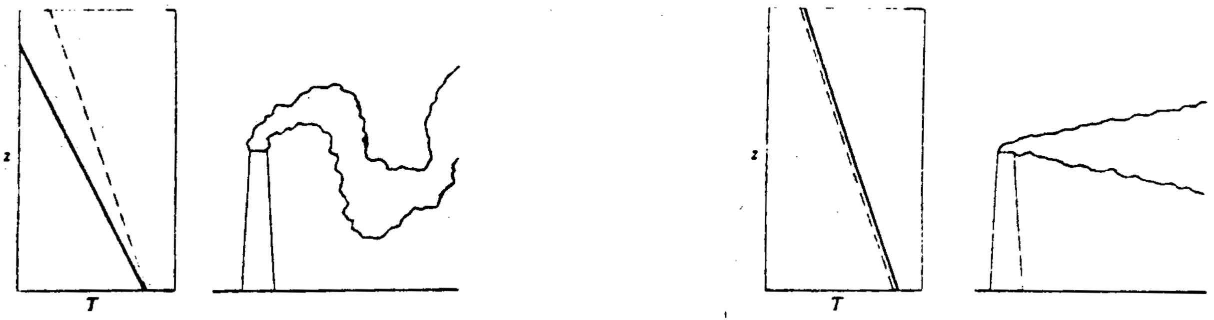
Atmospheric stability directly affects the behavior of a power plant plume and of pollutant mixing in general. Of the two basic mechanisms through which pollutants may be dispersed, the one which may have effects on a larger scale is transport due to winds, but an equally important mechanism in many circumstances is what is called turbulent diffusion, a mechanism which is directly influenced by atmospheric dispersion. These mechanisms give rise to various types of gross plume behavior, such as the examples given in Figure 3.3-9, but they are also the important factors in pollutant dispersion within regional air basins.

Figure 3.3-9 shows vertical plume profiles associated with various temperature profiles. With superadiabatic lapse rate (a), the atmosphere mixes, and "looping" occurs. Under neutral conditions (b), the plume simply expands due to small-scale diffusion processes. In the other cases (c,d,e), inversions exist and, depending on whether the plume is above, below, or within the inversion layer, the plume's dispersion is inhibited downward, upward, or in both directions, respectively. The point of a very tall stack is to emit the plume above potential inversion layers, so that the emissions are not trapped near the earth. If the emissions are trapped, removal must depend on horizontal air flow (an aid that is not characteristic of inversions).

An important parameter associated with inversions is the mixing depth, the thickness of the mixing layer that lies beneath the inversion layer. This mixing layer is effectively the volume into which pollutants are emitted. If the mixing layer is an effective container, it is also the cauldron in which various atmospheric chemical processes may occur.

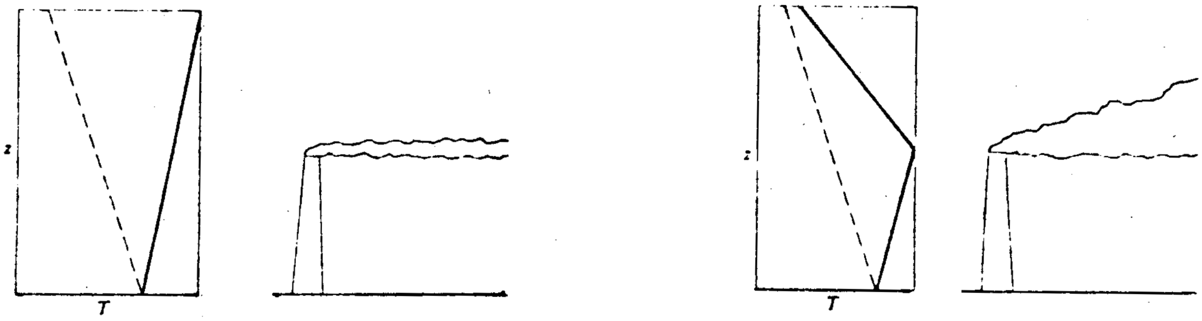
Emitted pollutants remain in the atmosphere until they are removed or altered by physical or chemical processes. Physical removal of particulates occurs due to sedimentation, washout and rainout, and impaction. Smaller particles may combine by agglomeration, leading to increased removal rates via these mechanisms. Gases may be removed by absorption into liquids (such as SO_2 into water droplets) or by adsorption onto solids.

The chemical reactions which occur in the atmosphere are important, not only in that they may remove a primary pollutant, but also in that harmful secondary pollutants may be formed. Such reactions have been referred to in section 3.1 and are the specific subject of section 3.3.3. In California, a major example is the formation of photochemical smog, an important constituent



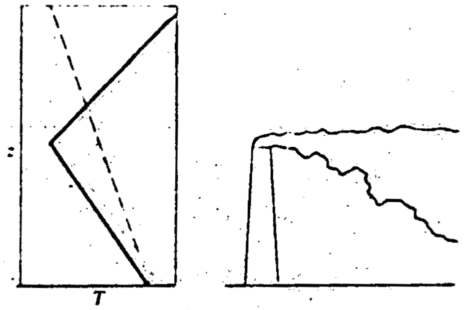
a). Looping under highly unstable conditions

b). Coning under neutral conditions



c). Fanning in an inversion layer

d). Lofting above an inversion layer



e). Fumigation below an inversion layer

Figure 3.3-9. Plume behavior as a function of Lapse Rate above and below the Release Height. (The dashed line in the temperature profiles is the adiabatic lapse rate. Reproduced from ref. 30.)

of which is the oxidant, ozone (O_3), shown in Figure 3.3-1.

Overall, air quality is determined by a number of interrelated factors, many of which have been indicated in this section. In addition to the actual emissions inventory, these are: meteorological (and the associated topographical) conditions, removal processes, and atmospheric chemistry. The design of the stack itself and the character of the plume as it is emitted may also be important. Information on these factors forms the basis for any attempt to predict or calculate pollutant concentrations.

3.3.2.4 Meteorological Modeling

Models for calculating pollutant concentrations are useful for understanding and evaluating the effects of emissions on ambient air quality. Such models are the subject of a separate report.[26a] In general, they require some selection of several possible types of information including emissions data, meteorological characterization (wind and/or stability), and chemical reactions. Site-related information, such as local topography,is closely associated with meteorological conditions. Depending on their sophistication, various models require differing selections of these data, and their specification in different manners, including level of detail. The main emphasis in the following discussion (based largely on Refs. 32-37) is on deterministic models, as distinguished from the statistical models mentioned at the end of this section.

The emissions data may range from the description of a single source to the specification of location and emissions for an array of point and even continuous sources. The basic information required is the pollutant source inventory, but additional information may include stack height and diameter, along with exhaust gas temperature and velocity.

The most fundamental meteorological data can be the wind speed and direction. For simple models, a single value of wind speed will suffice, but for more elaborate models this information might have to be known for each grid point or computational cell. Some models require information describing the vertical variation in wind velocity. This information can be related to the local terrain, so that topographical information is also often required. In addition to wind data, models typically require information on the atmospheric stability class or eddy diffusivities. These may be described either in terms of the standard classification system (see reference 26a) or by an explicit vertical temperature profile or may be parameterized as a function of wind speed, inversion height, etc.

Finally, any detailed modeling of ambient air quality requires additional information on other substances which may be present (in addition to the specific emissions source(s) being considered) and on the atmospheric chemistry which may take place. The latter may require specification of an array of possible chemical reactions and of factors other than concentrations of reacting substances, an important example being the intensity of solar radiation.

One basic model is the "Gaussian" plume model, which uses data of only the first two types, normally ignoring chemical reactions. In its simple form, this model assumes a single steady-state source and a specified wind velocity (speed and direction), and permits diffusion perpendicular to the specified direction. The resulting equation for these simplified assumptions is satisfied by an expression which gives the concentration in terms of a standard mathematical form known as a "normal" or "Gaussian" distribution, hence the name. The standard deviations of the Gaussian distribution are related to downwind distances by "Pasquill-Gifford" curves, which are characteristic of the atmospheric stability classes ("Pasquill" classes) mentioned above.

This basic approach may be modified to take account of plume deposition, and reflection off of ground or inversion layers; it may also be constructed for instantaneous (puff) and multiple sources and for variable winds. Although these modifications allower wider application of the model, they do not remedy its basic shortcomings, which are non-realistic modeling of wind fields and limitation to non-reactive pollutants. Other models simulate dispersion and reaction of pollutants by numerical solution of the basic conservation of mass equations (of which the Gaussian diffusion equation is a simplification). They typically require specification of a "wind field" for the region being considered, usually on the basis of detailed meteorological data modified (effectively "smoothed" and made self-consistent) for use of the model. The dispersion modeling itself may use a variety of techniques, following cells of air or using volumes fixed in position and considering transport processes across the cell boundaries. These approaches typically require more difficult mathematical techniques and more computer time than the rather simple Gaussian model. However, they have the potential for more realistic calculation of concentrations in ambient air.

An extremely different approach than those mentioned above is to use statistical information, i.e., historical air quality data, to predict future concentrations. Versions of this technique are often employed in predicting conditions during air pollution episodes. Basically, empirical formulas are used, including correlation coefficients based on previous pollutant concentrations. No attempt is made to connect, on the basis of any fundamental formulation, ambient concentrations with emissions, meteorological conditions, or chemical processes. Statistical models basically amount to an extrapolation on the basis of historical data. They have, however, been found to be useful for making predictions during the course of air pollution episodes.

3.3.3 Secondary Chemical Reactions

Secondary chemical reactions of pollutants are those processes in which pollutants emitted from sources such as power plant stacks undergo or catalyze reactions in the atmosphere to give rise to new products not present in the original emissions. These reactions are usually either oxidations or reductions of primary pollutants and often require catalysts such as sunlight, free radical mediators, soot, or other solid particulate matter. In some cases, water vapor (high humidity) is essential; in others, water may only interact with the final product of the atmospheric cauldron.

3.3.3.1 Formation of Photochemical Oxidants

Photochemical oxidant formation is the secondary pollutant reaction which has received the greatest attention in recent years because of the magnitude of the pollution problem which this has caused in the Los Angeles area over the last three decades.[4,20] As a result, the atmospheric reactions leading to the formation of photochemical oxidants are reasonably well understood in a broad, if not detailed, sense. It is known that certain hydrocarbon pollutants interact with the photolytic cycle of nitrogen dioxide and, as a result, the hydrocarbons are oxidized to form various products. The product mixtures contain substantial concentrations of ozone, as well as such hydrocarbon products as aldehydes, ketones, and peroxyacyl nitrates. This section briefly explains the photochemistry of ozone formation.

Oxidation of NO to NO_2 in air is normally very slow;[39] however, under certain atmospheric conditions (in the presence of sunlight and reactive hydrocarbons) NO is converted to NO_2 very rapidly. Ultraviolet regions (300 to 400 nm wavelength) of the solar spectrum are absorbed by NO_2 giving rise to three reactions, referred to as the NO_2 photolytic cycle:

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

(M is a third body [collisional molecule] in the system which removes excess energy, allowing formation of O_3).

The NO_2 photolytic cycle explains the initial formation of ozone, O_3, but it alone does not account for the rapid build-up of O_3 and NO_2 levels which occur in the atmosphere. If no additional mechanisms were involved, under steady state conditions NO and O_3 would be formed and destroyed in equal quantities.

Laboratory and field studies have shown that the presence of hydrocarbons in the atmosphere provides a mechanism for buildup of the O_3 and NO_2 levels. Studies suggest that oxygen atoms react with the hydrocarbons, and the resultant oxidized compounds and free radicals react with NO to form more NO_2. Thus the rate of NO_2 formation is upset so that NO_2 levels build up while NO levels become depleted. As the NO becomes depleted, O_3 levels also build up. A schematic of the overall photochemical reactions is shown in Figure 3.3-10.

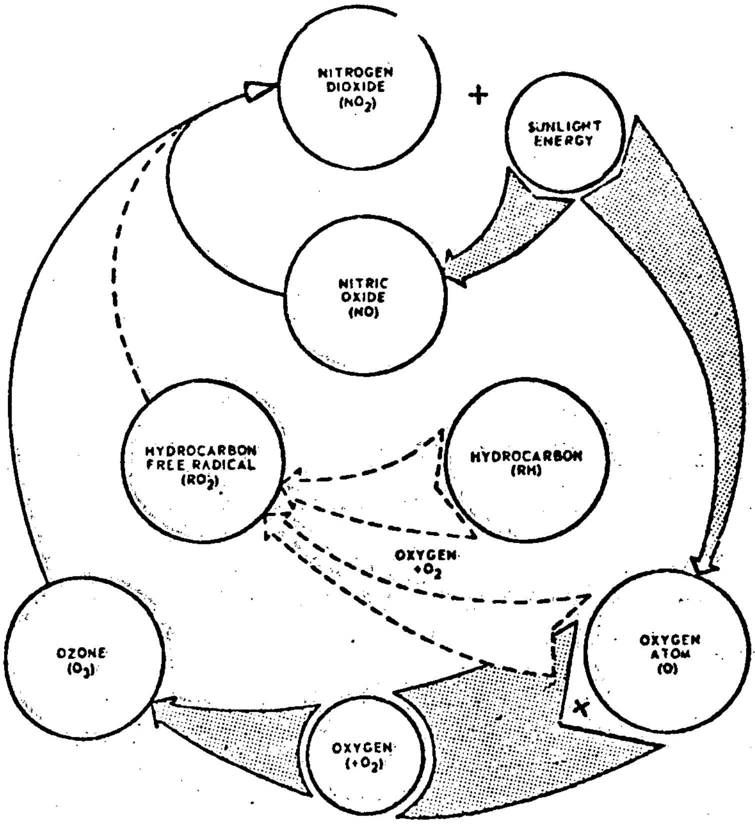


Figure 3.3-10. The Photochemical Cycle. (Reproduced from ref. (4).)

Some of the major reactions involving hydrocarbons are:

$$O + HC \rightarrow \text{(hydrocarbon)} \rightarrow HCO$$
$$HCO + O_2 \rightarrow HCO_3$$
$$HCO_3 + HC \rightarrow RCHO \text{ (aldehydes)} + R_1R_2CO \text{ (ketones)}$$
$$HCO_3 + NO \rightarrow HCO_2 + NO_2$$
$$HCO_3 + O_2 \rightarrow HCO_2 + O_3$$
$$HCO_x + NO_2 \rightarrow RCOOONO_2 \text{ (peroxyacyl nitrates)}$$

Calvert[40] has proposed a truly detailed scheme for the formation of photochemical oxidants in which some 72 intermediate reactions are required. Rather than describe this scheme, it is appropriate to note that the most essential ingredients for O_3 formation are NO_2 (or NO only, if it can be photo-oxidized to NO_2), hydrocarbons, oxygen (O_2), and ultraviolet irradiation. For most of the U. S., including parts of California, the limiting reagent appears to be oxides of nitrogen, since hydrocarbons from natural and man-made sources can usually be considered ubiquitous.[22-25] Depending on the specific pollutants involved, O_3 levels can either be enriched or depleted by the constituents of power plant plumes. In some cases, such as in the San Francisco Bay Area, NO_x is present in excess, thereby suppressing oxidant level.

Ozone will react with NO to generate NO_2, O_2, and light in a chemiluminescent process (Figure 3.3-10).[4] This reaction has been shown to occur in the plumes of fossil-fuel fired power plants at distances less than 20 km from the stack[22,41] and results in a decrease in ozone. However, at distances farther from the power plant, the plume constituents appear to greatly increase the O_3 concentration in the atmosphere.[22-25] Davis et al.[22] have observed increases of 20-50 ppb O_3 at distances as far as 70 km from a coal-fired power plant. Presumably, at the longer distances, NO will have totally oxidized to NO_2, so that reactions with O_2 and ubiquitous hydrocarbons result in net O_3 production rather than O_3 consumption.[22]

Like NO, unsaturated hydrocarbons (olefins) also react with O_3 in rapid fashion to form organic acids and aldehydes[4,7] in a reaction which is also chemiluminescent.[42] Where olefinic organic compounds are present, therefore, O_3 levels in the atmosphere should become depleted.[43] However, reactions of olefinic hydrocarbons with NO_2 in the atmosphere purportedly generate O_3 *de novo*.[4,10,25] Hence, if unsaturated organic compounds were found to be emitted with the carbonaceous particulate fraction from power plants, the effects on O_3 concentrations would be identical to those produced by NO. Near the stack, O_3

would be depleted, but farther away O_3 would increase. In view of the high NO_x emissions from power plants, however, it is believed that NO and NO_2 are the pollutants responsible for O_3 trends in down wind areas.[22]

O_3 has been suggested by several investigators as an essential factor in other atmospheric secondary reactions, such as the oxidation of SO_2 to sulfates or NO_2 to nitrates. These are discussed below in sections 3.3.3.2 and 3.3.3.3.

3.3.3.2 Oxidation and Reduction of Sulfur Compounds

The primary sulfurous pollutants emitted from stationary sources are SO_2, from fossil fuel-fired power plants, and H_2S, evolved from geothermal plants. Once in the ambient atmosphere, both substances undergo oxidation spontaneously to give sulfites and sulfates.[11,21] Spontaneous oxidation is usually very slow, and may require several hours or days for complete reaction. This section deals with reaction mechanisms by which sulfur compounds in power plant plumes can be oxidized more rapidly. These are summarized below:

$$SO_2 + O_2 \xrightarrow[[\quad]]{h\nu} SO_3; \qquad [\quad] = O_3,\ OH\cdot,\ NO_2\cdot,\ \text{etc.}$$

$$SO_2 + O_2 \xrightarrow[H_2O]{h\nu} SO_2\cdot^{-}$$

$$SO_2 + O_2 \xrightarrow[H_2O]{MeO_x} SO_3,\ H_2SO_4$$

$$SO_2 + MeO_x \longrightarrow MeSO_x \quad (\text{Me} = \text{metal})$$

$$SO_2 + O_2 \xrightarrow[H_2O]{C} SO_3,\ H_2SO_4,\ SO_4^{=}$$

3.3.3.2.1 Homogeneous Processes

Homogeneous oxidation of H_2S or SO_2 is defined as those reaction processes which occur strictly in the gas phase. No solid or liquid suspended particulate matter is involved either in the reaction or in catalysis. While little effort has been applied to investigating the mechanisms of H_2S oxidation in the atmosphere, ultraviolet irradiation is believed to be required[11] for photo-oxidation.

Theories and controversy abound concerning facilitated oxidation mechanisms for SO_2. Several investigators have suggested that photochemical oxidation of SO_2 to SO_3 or H_2SO_4 is the dominant mechanism in the atmosphere.[7,11,21,44,45] According to Sidebottom et al.,[46] the light-dependent oxidation of SO_2 to SO_3 requires O_3, as all other potential photochemical oxidation pathways are spin-forbidden. Calvert[45-47] has detailed likely photochemical mechanisms for SO_2 oxidation to acid sulfates. Interestingly, hydroxyl radical (OH·) is assumed to play a central catalytic role in this process, and the detection of parts-per-trillion levels of OH· in ambient air[48] suggests that photochemical oxidation of SO_2 to acid sulfates is indeed possible in urban atmospheres. On the other hand, Eickenroht, et al.[49] have recently demonstrated that ultraviolet irradiation of aqueous solutions of SO_2 in the presence of oxygen gives rise to the thionite anion radical ($SO_2^{\dot{-}}$) and hydroxyl radicals (OH·). While OH· is an extremely strong oxidant, the formation of $SO_2^{\dot{-}}$ raises the possibility that atmospheric photochemistry causes reduction and not oxidation of the sulfurous species.

SO_2 can also be oxidized to sulfates in a homogeneous non-photochemical reaction, involving O_3. The kinetics of this non-photochemical oxidation have been studied in solution and laboratory model atmospheres,[50,51] and the results suggest that times on the order of weeks may be required for complete reaction. Hence, homogeneous gas phase oxidation of SO_2 which is not "pumped" by ultraviolet irradiation is not a significant pathway in the atmosphere.[22]

3.3.3.2.2 Heterogeneous Processes

Heterogeneous oxidation of SO_2 is defined as those reaction mechanisms which require gas-particle interactions either for the catalysis or for the combination of actual reactants. Three types of oxidation mechanisms have been proposed for SO_2 to sulfate conversion which involve suspended particulates in the atmosphere: a) oxidation facilitated by water and ammonia, b) oxidation catalyzed by metal oxides and salts, and c) oxidation catalyzed by carbonaceous matter.

Reaction of SO_2 with water droplets yields quantitative conversion to sulfurous acid (H_2SO_3) which can, in turn, react spontaneously to give H_2SO_4. This oxidation mechanism has been suggested in urban atmospheres[21,52-55] and is though to involve ambient ammonia (NH_3).[52] The frequent occurrence of ammonium sulfate aerosols have suggested a direct reaction with aqueous NH_3 to give ammonium sulfate.[7,56,57] Measurements of gaseous ammonia compounds in West Germany, Sweden, and Hawaii,[58-61] intended to find out whether sufficient NH_3 is present for catalysis, suggest a concentration range between 1 - 25 ppb as NH_3. Accordingly, the formation of acid sulfates should deplete the atmospheric level of NH_3 below 0.01 ppb.[58] In the U.S., gaseous levels of NH_3 are estimated to be typically 0.001 ppb on the East Coast, less than 0.01 ppb everywhere east of the Mississippi River, and less than 0.1 ppb on the West Coast.[58] Free NH_3 concentrations are maximal in the Rocky Mountain and Great Plains states, and approach 3 ppb in these areas.[58] The correlation between ambient sulfates and NH_3 depletion is therefore striking. Hence, heterogeneous SO_2 oxidation in water droplets, facilitated by ambient NH_3, does have some observational basis. On the other hand, other heterogeneous oxidation mechanisms are not ruled out by the coincidence of ammonium sulfates.

Metal oxides have been known to catalyze the oxidation of SO_2 to SO_3 for many years. In fact, the principal catalyst used in the commercial synthesis of H_2SO_4 is vanadium pentoxide (V_2O_5). Numerous other metal oxides have a demonstrated capability of oxidizing SO_2 to sulfates.[8,62,63] Trace metals, as the metal oxides, are abundant in ambient urban and rural aerosols[2,3,7,64-69] and in power plant plumes,[68-74] so that there should be, in principle, ample opportunity for metal-catalyzed SO_2 oxidation. Iron oxides from coal-fired power plants and vanadium oxides from oil-fired power plants are especially prevalent elements in fly ash emissions,[74] and both are rated as excellent catalysts for SO_2 oxidation. Several workers[74-77] have suggested that metal catalyzed oxidation is the dominant pathway for SO_2-to-sulfate conversion in power plant plumes and in ambient air.[78] The mechanism and conditions of this reaction have been detailed by Freiberg,[76,77] and the suggestion is made that metal oxide catalysis is most efficient at high relative humidity and relatively cold temperatures. The high humidity dependence of SO_2-sulfate conversion in power plant plumes observed by Newman et al.[79] may indicate that metal oxide catalysis is the dominant mode of SO_2-sulfate conversion. This view may be supported by the observation[80] that ammonium sulfates account for less than 10%

of the total particulate sulfate in the New York City-Long Island area. Hence, NH_3 catalyzed SO_2 oxidation in water droplets would appear unlikely.

Along the same lines, recent work[81] in Utah has demonstrated that a major reaction of SO_2 with transition metal oxides is the formation of transition metal sulfites. Since these sulfites occur in particulate form, they are often mistaken for sulfates[81] by other investigators. Metal sulfites in the Utah aerosols were also found to be totally inert to oxidation.[81] In addition, SO_2 can react with certain metal oxides to give rise to metal sulfates directly.[62,81] The consumption of SO_2 and metal oxides by these processes serves to deplete the aerosols of surface-localized[82] metal oxide catalysts, except for those species like $MnSO_4$ which remain excellent SO_2 oxidation catalysts as the sulfite or sulfate adduct.[63] Thus, metal oxides might serve to remove SO_2 from the atmosphere without oxidizing it to an acid sulfate.

The difficulty with unambiguously assigning heterogeneous SO_2 oxidation to either H_2O/NH_3 or metal catalysis on particulates, is the association of carbon with combustion. Novakov and his coworkers[83-89] have demonstrated that carbonaceous soot also catalyzes the oxidation of SO_2 to (acid) sulfates. Sulfate formation from SO_2 has been observed in the presence of commercial activated carbon,[86] propane smoke,[86] or benzene smoke.[89] Sulfates so formed were found to be not acidic (HSO_4^-) but neutral ($SO_4^=$).[89] Hence, the respiratory irritant properties might be very different from those observed for H_2SO_4 mist.[90] High relative humidity enhances the soot-catalyzed oxidation of SO_2 to sulfate.[83,86] In addition, in some cases soot-catalyzed <u>reduction</u> of SO_2 to sulfide ($S^=$ or H_2S) has been observed.[83,86,88]

Extension of this work to analysis of ambient urban aerosols has been most revealing. Several different valence states of sulfur have been detected in California aerosols, including sulfates, sulfites, elemental sulfur, and sulfides.[86,88] The diurnal variations in sulfate show a mid-afternoon maximum in California air samples,[83,86,87,91] which coincides in phase with photochemical oxidants[91,96] and particulate carbon,[83,86,87,91,96] but not with particulate lead.[83,86,87,96] Hidy and Burton found equally good correlations between sulfate formed and carbonaceous aerosols, and between sulfate and O_3.[91] Hence, although these workers attributed sulfate formation to the photochemical oxidation of SO_2, their data support equally well the heterogeneous SO_2 oxidation catalyzed by carbon. Brosset and his colleagues[92-95] have also compared particulate sulfate levels in Sweden to other atmospheric pollutants on a daily basis for periods exceeding a year, including several periods of "white episodes" (particulates mostly mineral ash-like) and "black episodes" (particulates mostly carbonaceous). Seasonal variations in ambient sulfate in Sweden show a winter maximum,[92-95] contrary to the summer maximum observed in Southern California.[5] More interestingly, however, sulfate levels correspond almost quantitatively to the particulate carbon in the air, and much poorer correlations are observed between sulfates and metals in the air.[92,93] Since sulfate concentrations are maximal in winter in Sweden, photochemical oxidation of SO_2 can effectively be ruled out as a significant reaction mechanism.

One reason for discussing the reported mechanisms of sulfate formation from SO_2 in the present work is to develop an idea of the effects of certain control measures in electric power plants and in the community on the rates of SO_2 to sulfate conversion in ambient air. Measured rates of sulfate formation from SO_2 in power plant plumes have been reported to be about 20% (of initial SO_2) per hour in New York,[78] and 1.5 - 5.0 percent/hr in St. Louis. However, other studies in California[97] and England[98-103] show no detectable contribution of electric power generating plants to the ambient sulfate or SO_2 burden, suggesting that no conversion of power plant SO_2 emissions to sulfate had occurred at all. Sensitivity problems and high background levels may have hampered the latter groups of studies.[97-103] SO_2-to-sulfate conversion in ambient urban atmospheres occurs at a typical rate of 1-2% per hour over most of the U.S.[5,21,78] but at a rate as high as 7-13% hour in the California South Coast Air Basin.[5,78] During oxidant smog episodes, the conversion rate is at its maximum, as are also the concentrations of O_3 and particulate carbon.[5,78,96]

Until more is known about the relative importance of the mechanisms of SO_2 oxidation to sulfate in the atmosphere, the only reasonable approach for containing in urban sulfate burden is to limit SO_2 emissions from all sources. Additional measures to control particulate metal and carbonaceous emissions may help to retard SO_2-sulfate conversion, but in view of the multiplicity of pathways believed to exist for this process, there can be no guarantee of success. Moreover, retarding the conversion to sulfate, while allowing a greater mixing volume, may only shift the sulfate problem down wind. This effect can be seen in the increasing sulfate concentration in the prevailing westerlies as they sweep across this continent and possibly in the Swedish acid rain problem. Controlling particulates, on the other hand, may be important and useful for other purposes. Metal oxides, carbon, and photochemistry are all involved in reactions with other kinds of pollutants than sulfur oxides.

3.3.3.3 Reactions of Nitrogen Compounds

Combustion of fossil fuels occurs at sufficiently high temperatures in steam electric power plants that the only major nitrogenous pollutant produced in the fire is nitric oxide (NO). However, cooling and exposure to molecular oxygen, ozone, metal oxides, carbonaceous particulates, hydrocarbons, and ultraviolet irradiation gradually convert the NO to a host of other nitrogen compounds.

3.3.3.3.1 Formation of NO_2 and HNO_3

At temperatures below 400° C, NO reacts spontaneously with O_2 to form NO_2. The kinetics of this reaction are such that by the time flue gases leave the stack, as much as 10 - 20% of the original NO may have oxidized.[22] In ambient air, however, spontaneous oxidation occurs too slowly to account for the subsequent NO_2 formation. Considerable evidence for the formation of NO_2 from NO by photochemical processes has been advanced.[10] Figures 3.3-1 and 3.3-9 indicate key features of the photochemical reactions of NO_x.

In addition to NO_2, oxidation reactions of NO_x can also give rise to nitric acid (HNO_3) and particulate nitrates. Nitric acid exists as an equilibrium mixture of HNO_3 gas and liquid droplets in the atmosphere, so that both forms are important.[96,104] Several investigators[40,45-48,66,68,91,96,104] have suggested that nitrate formation occurs as a result of photochemical activity. Most likely, nitrates occur as precursors or at least earlier products in photochemical smog formation, and the reader should refer to the original literature[40,45-47,66,67,91,96,104] for detailed mechanisms of HNO_3 formation in smog. The fact that diurnal fluctuations in HNO_3 concentrations show a noon maximum[66,67,91,96] instead of the late afternoon peaks observed for O_3, sulfates, and particulate carbon, suggest that nitrates are not formed by gas-particle interactions.

However, Chang and Novakov[105] have recently shown that ammonium nitrate is formed from: a) activated carbon + NO in humid air, b) soot from combustion of propane and benzene in air, c) exhaust particles from an internal combustion engine, and d) airborne particles collected in a freeway tunnel. Activated carbon has been known to catalyze the oxidation of NO to NO_2[106] as well, so that a multiplicity of reactions involving NO_x may occur as a result of heterogeneous catalysis. It is not known to what extent heterogeneous catalysis accounts for nitrates in urban air, since diurnal patterns for nitrates differ from those observed for other pollutants. At the same time, direct examination of combustion emissions shows that some nitrates have already been formed. More effort should be directed toward the elucidation of these processes.

3.3.3.3.2 Ammonia

The widespread attention being given to ammonium sulfates and ammonium nitrates in atmospheric sulfate and nitrate aerosols[56,57,66,67,80,86,87,88,91,96,105,107,108] justifies discussion of the origin of atmospheric ammonium (NH_4^+). Lau and Charlson[58] have made the suggestion that sufficient gaseous NH_3 from primary natural and man-made (industrial and geothermal) emissions exists in the atmosphere to account for ammonium in urban particulates. In relation to other earlier work,[57,61] the general depletion of free NH_3 from the air in heavily populated regions of the United States[58] means either that no NH_3 emissions occur in the first place in these localities or that something in the air acts as an NH_3 sink.

There is one additional source of atmospheric NH_4^+ in urban atmospheres, which makes NH_3 and NH_4^+ important as secondary pollutants. Chang and Novakov[105,108] have demonstrated that the reaction of NO (emitted from primary combustion sources) with particulate carbon results in substantial formation of NH_4^+ on the soot particles. The soot-catalyzed reduction of NO to NH_4^+ occurs on either hot or cold particles, and appears to be the dominant heterogeneous reaction of NO in the atmosphere.[108] Most of the NH_4^+ formed in this manner is volatile and is not associated with either sulfate or nitrate.[84,85,105,108] Much of the NH_4^+ observed in California aerosols is also "volatile",[84,85] suggesting that its origin is probably the heterogeneous reduction of NO emitted from fossil fuel combustion sources rather than primary NH_3 emissions.[58,66,67] For reasons given in the following subsection (3.3.3.3.3), the formation and chemical reactivity of NH_3 and NH_4^+ should be scrutinized very carefully.

3.3.3.3.3 Organic Nitrogen Compounds

Very little is now known about organic nitrogen compounds as air pollutants, except that their existence in the atmosphere may be very hazardous to public health. Among the classes of organic nitrogen species which have been identified in urban air are: heterocyclic aromatics (quinolines, isoquinolines, pyridines, acridines, etc.),[109,110] amines,[84,85,86,108] and N-nitroso-amines or nitrosamines.[111,112] Detailed concentrations in urban air are given in Table 4.3-2 in Section (4.3.4), in which the carcinogenic properties of these compounds are examined.

According to the work of Novakov and colleagues,[84,85,86,108] these organic forms of nitrogen appear in atmospheric aerosols as the result of soot-catalyzed NO reduction. High temperatures seem to enhance the formation of organic nitrogen on soot particles from either NO or NH_3.[108] The mechanism for this process is unknown. Nitrosamines are classically formed by the reaction of nitrous acid (HNO_2) with NH_3 or an organic amine[111] and evidently occur widely in urban atmospheres.[112] Several organic aromatic amines are also demonstrated carcinogens.[116,117] However, these have not been identified in air samples because of instrumental shortcomings. Future efforts in this area should concentrate on the development of analytical methods for resolving the organic nitrogen species on soot.

3.3.3.4 Aerosol Coagulation

One of the properties of atmospheric particulates is the propensity for smaller particles to collide and form large particles. Several reports dealing with the kinetics and mechanisms of aerosol coagulation[113-115] suggest that both homogeneous and heterogeneous nucleation processes can occur. Most particulates created in the initial combustion process are extremely small, with mean particle diameters in the 0.01-0.02 μm size range. Since the number of these small particles is large, interparticle collisions should occur frequently. Since most of these particles initially possess a common size distribution, one can view coagulation in the early part of particle growth as homogeneous. Later on, however, as collisions give rise to larger particles, nucleation begins to take place in which fine particles collide with and stick to the larger particles. The resulting process is considered heterogeneous because the colliding particles are no longer of equal size. Heterogeneous particle growth can also result from the condensation of vapors in the atmosphere around a small "seed" particle.[118]

Most particles which coagulate by homogeneous mechanisms are very small, since the number density of particles larger than 0.1 μm is so low that interparticle collisions are nearly non-existent. Hence, one should expect that homogeneous coagulation occurs only in very fresh aerosols.[114,119] Heterogeneous nucleation and coagulation should occur over much longer times, and accounts principally for the "aerosol aging" process pictured in Figure 3.3-11. One can adequately account for the kinetics of aerosol coagulation by simple second order collision theory,[113-115] so that the chemical composition of an atmospheric aerosol has virtually no bearing whatever on particle growth. Bekowies[119] has modeled the recent ACHEX data[65,66,113] to determine whether the absolute age of an urban California aerosol can be measured from particle size distributions. Preliminary results appear very promising, and indicate that the average "age" of combustion-generated ambient particulate matter in the South Coast Air Basin is about one hour. The closer one comes to the combustion source, however, the "younger" and smaller the size distribution becomes.[119]

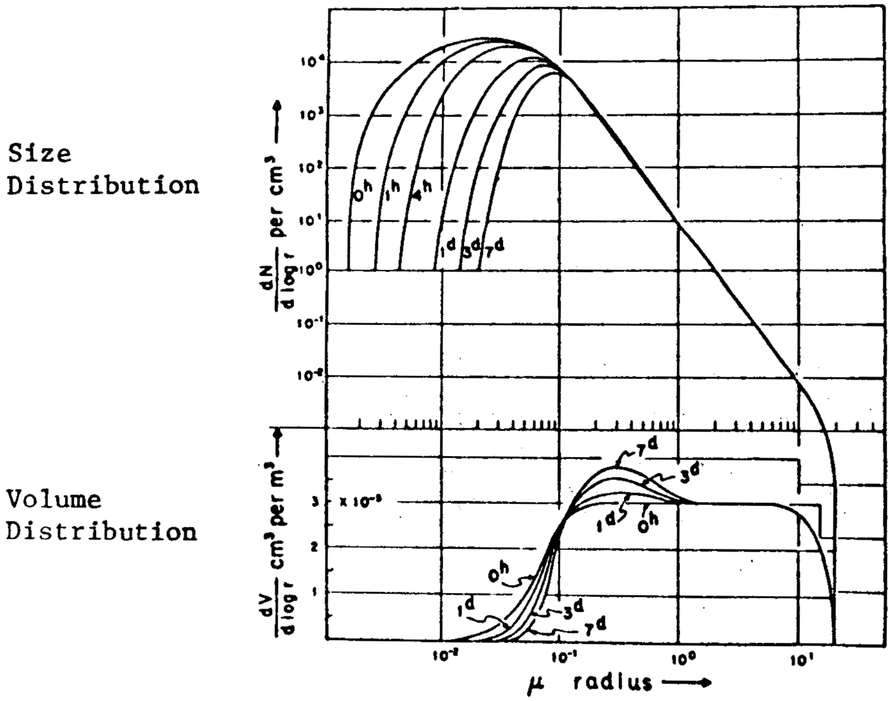


Figure 3.3-11. Calculated change in the size and volume distribution of continental aerosols due to coagulation. The labels on the curves represent the time elapsed since the original aerosol (0^h) began to coagulate. h = hours, d = days. (Reproduced from ref. (113).)

Aerosol coagulation occurs almost exclusively with the respirable submicron particulate fraction (Figure 3.3-11, also Ref. (113)). It is not presently known whether the changes in surface area of particulates during coagulation affect either their reactivity or toxicity. The effects of the 0.01 - 0.02 μm particles on atmospheric chemistry in exhaust and flue gases is not known either, since relatively few studies have attempted to deal with the chemical and physical dynamics of these particulates.

3.3.4 Alternate Sources of Human Exposure

In order to make a realistic assessment of the health risks associated with fossil-fuel or geothermal power plants, it is instructive to note that what most people breathe is either outdoor ambient air or indoor ambient air. In addition people also eat food and drink water which may or may not be contaminated by alternative pollution sources.

3.3.4.1 Industrial Effluents

Industrial (non-power plant) processes of nearly every kind emit common gaseous and particulate pollutants into the ambient air at a rate which contributes significantly to the total pollution burden in the area. In California, smelters and petroleum refineries contribute substantially to the total emissions of sulfur oxides, nitrogen oxides, carbon monoxide, particulates, etc. — generally much more so than equivalently sized steam electric generating plants (cf. Figure 3.1-1, for example). Nor should smelters and refineries necessarily be singled out as the worst offenders in a given urban area. However, recent emissions data from the San Francisco Bay Area[27] shows that steam electric power generation accounts for no more than about 10% of the sulfur oxide, nitrogen oxide, or particulate emissions. Industrial sources are responsible for at least 4 - 5 times the emissions of these pollutants by steam electric generating stations.

3.3.4.2 Vehicular Emissions

Figure 3.1-1 in section 3.1.1.1 shows very graphically the contributions of motor vehicle emissions to the total pollution problem[18,19,20,120] in California. Vehicular emissions of hydrocarbons and carbon monoxide are orders of magnitude higher than those from electric power plants or virtually any other source. Vehicular NO_x emissions are also sizeable — about 40% of the California total[18,27] or some four times the NO_x emissions from power plants. As shown by Friedlander and coworkers,[7,66,96] the contribution of vehicular traffic to the total particulate loading cannot be correlated to vehicular particulate emissions, since vehicle-related particulates may arise from secondary atmospheric reactions as well as from the primary combustion process. These vehicle emissions are, therefore, believed to be the principle contributors to photochemical smog in California.[4,10,20,66,96]

3.3.4.3 Residential Sources

Unlike industrial process and motor vehicle pollutant emissions, residential heating and appliance operations are not believed by most responsible agencies to be an important contributor to ambient air quality deterioration.[18,19] In fact, the NEDS report[18] attributes less than 3% of ambient air pollutant loading to domestic sources. On the other hand, what is important from the point of view of impact on human health is not the contribution which residential combustion makes to outdoor ambient air pollution (see 132,133), but to the quality of the air inside the home. In this light, regulatory agencies should consider home heating and cooking appliances as important pollution sources which may affect the quality of indoor air.

To date, only a handful of studies have attempted to document the impact of domestic combustion sources on indoor, as opposed to outdoor, air quality. Among these, investigators have discovered the airborne build-up of CO and suspended particulate matter from cigarette smoking,[121] NO and NO_2 from gas ranges,[122-125] formaldehyde from construction materials,[126] vinyl chloride[127] and fluorocarbons[128,129] from the use of aerosol spray cans, and mercury from interior wall paint and unidentified sources.[130,131] Hollowell et al.[134] have surveyed indoor combustion sources for a wide range of gaseous and particulate pollutants. NO and NO_2 levels indoors were found to frequently exceed corresponding outdoor ambient levels by factors of 5 - 20; indoor concentrations of CO were also found to exceed outdoor ambient levels by 1 - 5 on many occasions. Indoor sulfate accounted for 20% of the total sulfur oxides[134] in contrast with 1 - 3% (for SO_3) reported for SO_x emitted into the atmosphere.[21] NO_2 levels indoors regularly exceed the EPA annual average standard, and occasionally violate even the 1-hour standards, even when outdoor levels are "safe."[134]

One must keep in mind that people spend the major portion of their time in indoor environments rather than exposed to outdoor ambient air. If it is generally true that conventional pollutant (SO_x, NO_x, CO, etc.) levels indoors are much higher than those routinely surveyed outdoors,[123] then it may be necessary to reexamine the existing body of epidemiology literature. Most epidemiology studies have neglected indoor pollutant levels as a matter of convenience, since routine ambient air measurements have been reported for outdoor levels only, and these at central monitoring stations most of the time. Consideration of indoor pollutant exposures may result in positive correlations with observable health effects where none had been previously thought to exist. Furthermore, examination of health effects due to combined indoor-outdoor exposures may affect some of the associations previously made with air pollutants. Considerable emphasis should be directed toward resolving the impacts of indoor pollutant exposure on human health, to determine the relative health risks of power generation at the electric generating plant and combustion processes in the home.[134,135]

3.3.4.4 Other Routes of Administration of Pollutants

One must also realize that not all pollutants need be breathed to be dangerous. Nitrates and nitrites in food and drinking water have effects which are comparable to and nearly indistinguishable from breathing NO or CO in the air.[135,137] Furthermore, nitrosamines such as those found in urban air[111,112] are also common in food and water supplies[138] and are carcinogenic from either source.

Contamination of water or food with toxic metals can also occur without the aid of airborne contamination. In some cases, the health effects may be similar regardless of the route of administration; however, in others, oral ingestion may turn out to have a much less significant impact on health for a given pollutant than inhalation. Sulfur oxides are a classical example of this latter point. SO_2 (as sulfites) and sulfates are almost totally harmless when ingested orally,[139] but, can be dangerous when inhaled.[5,6,8,21] Consequently, epidemiology studies which attempt to establish health effects of given pollutants must also determine the relative importance of how the substances enter the body.

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4. THE HEALTH EFFECTS OF FOSSIL FUEL AND GEOTHERMAL EMISSIONS

Emissions from the combustion of fossil fuels or the discharge of geothermal steam for the purpose of generating electric power are a matter of concern because of the potential harm these substances can cause to the public health and welfare. For this reason State and Federal regulations are formulated to limit the ambient air concentrations or the point source emissions of specified pollutants. This section surveys the epidemiological and biomedical investigations which have elucidated the effects of conventional pollutants on health and which have formed the technical basis for the existing standards and regulations.

Types of studies

In general, research into the health effects of pollutant exposure concentrates on one of the following: a) mortality during catastrophic episodes; b) mortality and morbidity (the incidence of specific illnesses) under more routine circumstances; or c) physiological, structural and metabolic alterations in cells and tissues. The first two types of studies may yield data directly associating exposures and health effects. Studies at the biomedical level can have an important bearing on the interpretation of what symptoms or responses indicate a threat to public health from a given pollutant. Either type of study may use animals as exposure subjects.

Much of this research was sparked by what have been called the classic air pollutions episodes, i.e., those which occurred in the Meuse Valley of Belgium in 1930; Donora, Pennsylvania in 1948; Poza Rica, Mexico in 1950; London, England in 1952; and New York City in 1963 and 1966. During these episodes, populations were exposed to extremely high concentrations of pollutants. Excess mortality, a term derived from the difference between observed and expected deaths, is the datum sought from analysis of these episodes. Based on these results (discussed in Section 4.1.1), there is little room to argue that intense air pollution does not have serious health effects.

In epidemiological studies of morbidity and mortality (Section 4.1.2), it is difficult, if not impossible, to prove cause and effect. Exposure atmospheres, for one thing, contain complex mixtures of pollutants which cannot be adequately controlled. It is, however, possible to establish correlations or associations. As an example, the association John Snow (1755) made between a contaminated well on Broad Street in London and the prevailing cholera epidemics was strong enough to effect the removal of the pump handle to prevent further consumption of water, even though he could not prove causation. Therefore, a question of reliability and validity is asked: do existing morbidity and mortality data implicate pollution from fossil fuel sources as causes of sickness and death? A review of the literature in this area suggests that while considerable room exists for alternative interpretations, the evidence is sufficient to warrant the conclusion that combustion-generated pollution may pose a serious health problem.

In an attempt to tighten control of the variables that are encountered in health effects studies, numerous investigations of clinically observable health effects (physiological and/or cellular) are carried out under laboratory conditions (see Section 4.2). In these experiments, either animal subjects or human subjects are exposed and examined for evidence of illness. By necessity, much of our basic knowledge in air pollution research stems from animal experimentation. Humans cannot be manipulated in experiments in the same manner as animals. Moreover, most species of animals and microorganisms have much shorter generation times than man, implying shorter waiting periods to observe the results of long-term exposure experiments. (On the other hand, existence of an adverse health effect following exposure in animals does not necessarily imply a corresponding effect in humans, although effects observed in animals are frequently indicative of the potential harm to humans.) The most dramatic results of this type of investigation show the effects of gaseous air pollutants (most notably SO_2, NO_2, and O_3) on the host animal's resistance to bacterial infections in the respiratory tract. These pollutants impair resistance to infectious disease at concentrations as low as a few tenths of a part-per-million.

Examination of the biochemical interaction of pollutants with the structure and metabolism of tissues and cells (Section 4.3) in the body serves as an indicator that is a step removed from the clinical evaluation of the effects of pollution. However, investigation of health effects at this subclinical level is particularly valuable because the data so obtained are frequently quantitative and can also reveal the biochemical and physiological mechanisms by which clinically observable health effects occur (i.e., the etiology of disease). This information is invaluable for the establishment of standards. It also allows us, in principle, to determine on a fundamental basis whether the successful abatement of one pollutant will ameliorate a prevailing community health effect in the face of other pollutants, and to determine threshold levels for the different clinical and subclinical health effects. (On the other hand, one must take care to remember that not all physiological or metabolic changes which occur in response to pollutant exposure indicate detrimental action. Some responses may occur as part of the body's defense mechanisms against the exposure, or may be merely adaptive.) Typical results of these studies show that SO_2, NO_2, and O_3 all alter the mechanical properties of the lung; all react with cellular constituents such as lipids and proteins; all are known to block the function of or or more essential enzymatic reactions; and all can change the vaibility and appearance of tissue. Because of the relatively precise nature of such data, many of the existing air quality standards are founded on (subclinical) physiological and metabolic effects rather than on epidemiological data. However, information from all of these levels of study is essential and appropriate for their justification.

The effects of specific pollutants

Combination of all the epidemiological, physiological, and biochemical information on health effects of air and water pollutants into an integrated picture is obviously the desired end product of this review. However, many of the pieces of information are so fragmentary, the results so nebulous or tenuous, or the experimental conditions so different from community exposures that it is difficult to establish self-consistent assessments of health effects for any of the pollutants. Except where natural experiments presented themselves, studies have typically utilized only a few risk factors and conclusions have only been tentative. Furthermore, exposure conditions used for a given pollutant in one kind of experiment often differ from other experiments or from real-world conditions by such a vast margin that it is impossible to formulate any consistent view of health effects.

Finally it is difficult to isolate the effect of one pollutant from other pollutants and even other types of factors. Nevertheless, standards and regulations are based on these imperfect, often inconclusive, and anything but definitive studies.

It is not now possible to form a unified view of the health effects of sulfur oxides from existing epidemiological, physiological, and biochemical evidence. Biochemical evidence indicates that SO_2 is detoxified in the body rather efficiently, and that the resulting sulfates are harmless products which are excreted. Physiological experiments have shown that SO_x, and especially sulfates, are potent respiratory irritants which increase one's susceptibility to infections, but only at concentrations which are far above any encountered in routine community or occupational conditions. Yet the bulk of epidemiological research devoted to measuring the health risks of air pollution has associated community mortality and morbidity with the oxides of sulfur. This dichotomy may arise from the fact that epidemological investigations include a varied study population (including the young and the ill) that is subjected to an atmosphere of varied composition; laboratory studies typically expose healthy subjects to a controlled atmosphere, usually with SO_2 added to the air.

The oxides of nitrogen are probably the only pollutants for which the combination of epidemological, physiological, and biochemical data show reasonable agreement on health effects. Nitric oxide has been shown to react with hemoglobin in humans and animals, and the presence of its metabolites, observed in urban populations, might be a factor in cardiovascular stress. Nitrogen dioxide has been shown to react destructively with cell membranes, is a respiratory irritant, and is a suspected causative agent in emphysema and other chronic respiratory diseases. Biochemical and physiological evidence also suggests that NO_2 is a contributing factor in respiratory infections, anemia, and cardiovascular diseases. The relatively meager body of epidemiology on the health effects of NO_2 is consistent with, but neither demonstrates nor disproves, the abnormalities which may be predicted for NO_2 exposures.

At the present time, assembling a unified picture of the health effects of oxidant air pollutants is impossible because epidemiological investigations have thus far been unable to demonstrate any associations with community illnesses or deaths. Yet both the physiological and biochemical studies suggest that oxidants are extremely dangerous. Oxidants react destructively with cell membranes, are respiratory irritants, and are suspected causative agents in emphysema and chronic lung diseases. Furthermore, oxidants are also suspected of contributing to respiratory infections, anemia, and cardiovascular diseases.

Assessment of the health effects of particulates on the basis of epidemiological, physiological, and biochemical evidence is confounded by the absence of any means for comparing the various kinds of studies. Epidemiological investigations attempting to associate community illnesses or deaths with particulates have had mixed results. Sometimes a correlation could be observed, other times not. Invariably, other pollutants including sulfur oxides or nitrogen oxides or their particulate derivatives would be found to co-correlate. In most cases, total suspended particulate mass (ignoring size or composition characteristics) has been the only indicator or particulate pollution used. Physiological studies, on the other hand, have been concerned primarily with the deposition and clearance properties of particulates. These investigations generally explore particulates as respiratory irritants, and have usually been careful to compare the properties of particles on a size-resolved basis. Most of the physiological responses to particulate exposure are independent of their chemical composition. Biochemical studies, to the contrary, necessarily require information on particle composition, and largely disregard size distributions. Most of the existing work has been concerned with how particulate organic compounds cause cancer in humans, and has neglected any of the other possible chemical interactions of particulates. At the present time, the limiting factor in unifying the information on the health effects of particulates is the analytical characterization of particulates (by size and by chemical composition) in epidemiological and laboratory exposure investigations.

The data just summarized have served as the basis for current air quality standards. Although these data have been valuable for the formulation of such standards, they are not comprehensive or precise enough for making quantitative estimates of the health effects caused by power plant emissions. Attempts at such estimates are indicated in section 5.

4.1 Epidemiology

> "It should seem possible, by a set of well adapted experiments, accurately made, to discover what are usually called the occult qualities of the air, and render them manifest to the senses, And if by this means, we come at a tolerable knowledge of the effluvia, salts and other heterogenous matters, wherewith the air at different times, and in different countries is replete, it might give us almost a complete knowledge of the nature of all epidemic diseases that may arise for the future, provided due attention be given at the same time to age, sex, constitution, manner of living and so forth of the patient; all which circumstances being carefully considered and compared together, might probably direct to rational, fixed and effectual methods of cure."
>
> John Swan, M.D.
> London, 1763

Although our scientific achievements have allowed us to be relatively free from great infectious diseases like cholera, smallpox and plague, and have allowed men to live together in large metropolitan areas, some of these achievements have brought new health problems including air pollution and exposure to the byproducts of new energy forms, the magnitude of which could hardly be imagined in 1763. But Swan's suggestion, made over 200 years ago, has provided epidemiologists (consciously or not) with a timeless, basic philosophy for the study of air pollution. Over the years, epidemiology research has concentrated on mortality perturbations during catastrophic episodes, or alternatively on the much more painstaking search for mortality and morbidity effects under continuous "low-level" exposure conditions. We do not attempt to subdivide the following discussions according to pollutant for the simple reason that classification of health effects in a study population in the original studies was not possible. Except for a few remarkable situations, either community or occupational, epidemiological approaches rarely succeed in assigning health effects unambiguously to any single pollutant.

4.1.1 Classic Air Pollution Episodes

A number of acute smog episodes in modern times have been well documented over the past fifty years. All of these incidents have been characterized by a rapid increase in the death rates, attributable to the presence of foul air in the communities.

Meuse River Valley, Belgium, 1930.

The first well-documented air pollution tragedy in this century occurred in the Meuse River Valley, located in Belgium between Liege and Hay[1]. This heavily industrialized area extends for fifteen miles and its valley topography typically lends itself to inversions. A thick, cold fog blanketed the valley in the first week of December, 1930, and, trapped by an inversion, pollutants gathered and stagnated. The episode lasted for five consecutive days, but the human health ramifications were much more long-lasting. Hundreds of people suffered acute respiratory attacks and complained of chest pains, coughing, and shortness of breath. Others experienced heart and circulatory problems. Sixty-three people died on the fourth and fifth days of the episode and while most of these people were already stricken with lung and heart disorders, the number of deaths was much greater than usual (note: no precise, expected number of deaths has been found in the literature so excess mortality was not calculated.) Firket[1], suggested that the SO_2 levels in the air were as high as 8 ppm. He pointed out that other areas in the valley, which experienced the same temperature and fog, but did not have heavy industry, did not witness an increased numbered of deaths. In extrapolation, Firket[1] postulated that if an acute episode such as this one had occurred in a city the size of London, as many as 3,200 deaths would have occurred (see London incident below).

Donora, Pennsylvania, 1948.

Donora, Pennsylvania, another small industrialized town in the Monongahela River Valley south of Pittsburgh was the scene of the next great documented air pollution disaster[2]. In October, 1948, an inversion covered a wide area of the northeastern United States. On Wednesday, October 27, fog set in and the wind ceased. It was reported that "streamers of carbon appeared to hang motionless in the air and that visibility was so poor that even natives of the area became lost." The episode attracted nothing more than conversational comment until Friday when "a marked increase in illness began to take place in the area..." and "the physicans' telephone exchange was flooded with calls for medical aid..." Rain came on Sunday afternoon to clear away the smog, but the damage was already done. Among the population of 14,000, almost 6,000 (42%) fell ill. Instead of the normal 2 deaths expected for the period, the episode produced twenty. Ten percent of the population experienced severe respiratory difficulties, "being unable to breathe easily except in the upright position." Again, the elderly and infirm were hit the hardest -- existing heart or lung disease was a frequent concomitant; one third of the population had a cough during the episode and 12% of the population over age fifty-five were still coughing four months later. Other symptoms included sore throats, chest constriction, headaches, breathlessness, burning and tearing eyes, running nose, vomiting and nausea. From the records of 18 of the people (age 52-84) who died, four had no history of chronic disease. Thus, it was concluded that this smog episode did not merely push chronically ill people "over the edge." Figure 4.1-1 and Table 4.1-1 show the incidence of smog effects among differing age groups and the degree of effect among adults by age and occupation in the Donora area.

London, England, 1952.

Firket's 1936 forecast[1] of the effects of an air pollution episode in a large city was amazingly accurate, for in 1952 London experienced history's most disastrous air pollution incident[3]. Between December 5 and 9, a dense pea soup fog hovered over the city and winds calmed. Thousands of people died during this period. This was no ordinary London fog. Evidently, the combination of massive industrial emissions and the propensity of Londoners to heat their homes with soft coal in their fireplaces was sufficient to kill over 4,000 people during the five-day inversion period[4]. This killer smog, however, was not an isolated incident. There had been earlier episodes in London; six had been recorded between 1873 and 1952, and 2,500 deaths had been attributed to these earlier killer fogs[3,4]. As with the other episodes reported, the elderly and persons with pre-pulmonary or cardiac disease were most susceptible, increased mortality being especially great in those age 45 and over. Another group, the very young, also proved very sensitive. The mortality of new born infants almost doubled, and the mortality of infants one to 12 months old more than doubled. Morbidity reports also swelled during this period. Applications for emergency bed service in London hospitals average about 1000 per week in December. During the 1952 episode, London hospitals received more than 2500 applications and the number did not subside for more than three weeks following the incident[5].

During the episode the maximum daily concentration of SO_2 was about 400 $\mu g/m^3$ (1.6 ppm), recorded on the 3rd and 4th days of the fog. Levels of suspended particulate matter reached almost 4500 $\mu g/m^3$. Lawther[6] concludes that excess mortality is associated with levels of SO_2 at approximately

Table 4.1-1 Incidence of smog affection among adults of indicated age and occupational status in Donora area[2]

Occupational status	Percent of adults of indicated age and occupational status reporting affection from smog															
	All ages				Age in years											
					Under 35				35-54				55 and over			
		Degree of affection				Degree of affection				Degree of affection				Degree of affection		
	Total	Mild	Moderate	Severe	Total	Mild	Moderate	Severe	Total	Mild	Moderate	Severe	Total	Mild	Moderate	Severe
Total (adults)	50.5	16.5	20.4	13.6	39.6	17.0	16.6	6.0	55.7	19.5	23.1	13.1	60.2	11.8	22.2	26.2
Gainfully employed	49.6	15.9	21.1	12.6	38.2	14.7	16.9	6.6	56.4	18.7	25.2	12.5	60.6	13.0	22.5	25.1
Donora steel and zinc plants	52.2	16.1	22.6	13.5	41.0	15.4	18.3	7.3	58.4	17.8	27.1	13.5	60.7	14.1	22.4	24.2
Total employment in Donora area	50.1	16.4	20.9	12.8	39.3	15.5	17.0	6.8	56.0	20.1	24.5	11.4	60.4	11.7	22.6	26.1
Other employment out of Donora area	36.9	13.7	15.0	8.2	29.2	11.8	13.2	4.2	45.3	20.3	15.6	9.4	60.0	8.0	24.0	28.0
Housewife	52.1	18.2	19.7	14.2	43.1	20.4	17.3	5.4	55.3	20.6	20.8	13.9	59.8	11.9	21.5	24.6
Retired	55.1	7.5	21.5	26.1	......	......	......	......	......	......	......	......	55.1	7.5	21.5	26.1
Other	43.5	16.5	14.8	12.2	31.2	16.9	10.4	3.9	41.7	25.0	8.3	8.4	80.8	11.5	30.8	38.5

Table 4.1-2. Numbers of deaths registered in the Greater London Area (population about 8.5 million) from the week ended November 15, 1952 to the week ended January 10, 1953, compared with the annual averages in corresponding weeks of the previous five years.[a]

YEAR	DEATHS IN WEEK ENDED								
	Nov 15	Nov 22	Nov 29	Dec 6	Dec 13	Dec 20	Dec 27	Jan 3	Jan 10
1952	1565	1699	1902	2062	4703	3138	2234	2977	2634
average 1947-1952	1747	1708	1809	1805	1852	1914	1923	2303	2213
difference	-182	-9	+93	+257	+2851	+1234	+311	+674	+421

[a] Taken from ref. 4.

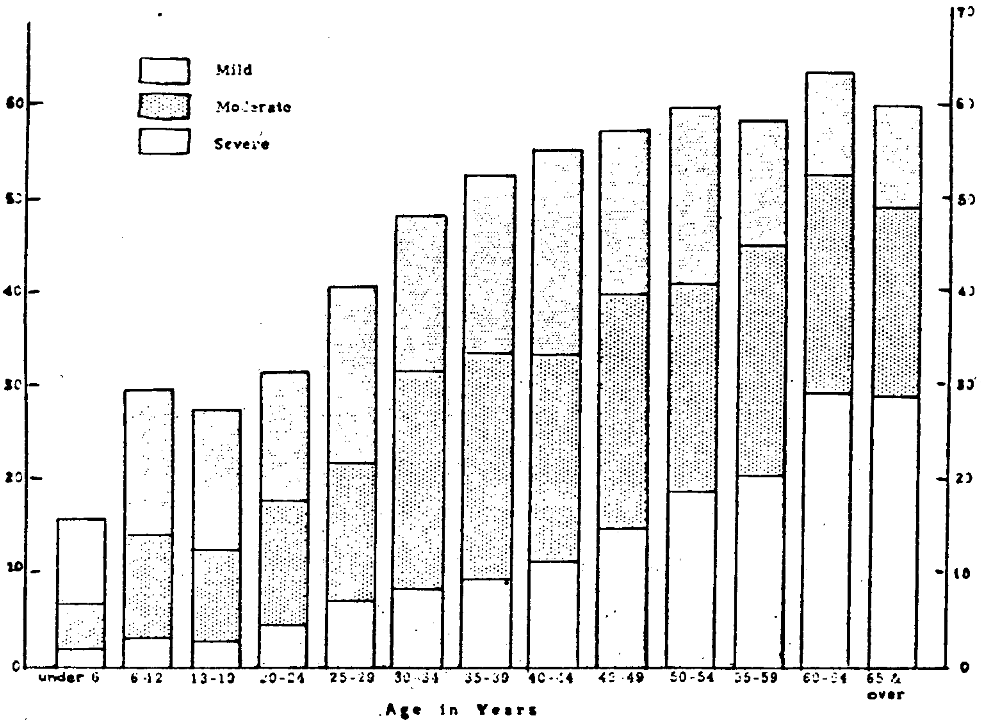

Fig. 4.1-1. Percent of persons in Donora area reporting affection from smog arranged according to age and degree of affection.[2]

715 μg/m^3 (0.27 ppm) and levels of smoke at 750 μg/m^3 (based on the London as well as other episodes).

Table 4.1-2 shows numbers of deaths registered in the Greater London Area (population about 8.5 million) from the week ended November 15, 1952 to the week ended January 10, 1953, compared with the annual averages in corresponding weeks of the previous five years.

New York City, New York, 1963 and 1966

In all of the previously documented disasters -- Meuse Valley, Donora and London -- fog appeared to play a key role in producing pollutant-filled inversions. But episodes in New York City in 1963[7] and 1966[8] have demonstrated that fog is not an essential ingredient in the recipe of an air pollution calamity. In the period from January 29 to February 12, 1963, intense air pollution was noted in the city of New York and 809 deaths were reported in excess of the overall average number for the same fifteen day periods in the years 1961, 1962, 1964, and 1965. If fog was not a factor in this episode, cold weather and influenza certainly were. But they could not explain all of the excess deaths. During a control period in 1958 when cold weather and influenza were present but air pollution was not, it was estimated that 200-400 excess deaths occurred. At the very least then, approximately 400 deaths could be attributed to polluted air. This increase in mortality was significant for the older age groups (greater than 45 years) and for those suffering from influenza/pneumonia, vascular lesions, cardiac and "all others." No significant increase in accidental deaths, homicides, suicides, and deaths of early infancy were found during the fifteen day period in 1963 when compared with the same period in the control years 1961-1965.

Dangerous levels of pollutants again accumulated over New York City during the Thanksgiving holidays, November 23-25, 1966. Although the New York Times reported statements by a city health official and local air pollution researchers that the incident was probably not a serious health hazard, 168 excess deaths were attributed to the episode. This excess occurred in spite of the fact that the inversion occurred during a Thanksgiving weekend when many pollution-producing activities were shut down and strict air pollution restrictions were imposed by the city.

Poza Rica, Mexico, 1950.

A city of 22,000 people, Poza Rica is located approximately 130 miles northeast of Mexico City and is the center of Mexico's leading oil producing region. A gas treatment plant of Petroleos Mexicanos, being constructed to meet Mexico's growing demand for industrial-use sulfur, was partially completed in 1950 when a tragic air pollution incident occurred. Efforts were being made to increase the rate of flow of gas at the sulfur removal Girbotol unit on November 24. At approximately 5:00 a.m. a problem was encountered and gas began surging through the unit. Unburned hydrogen sulfide (H_2S) escaped into the atmosphere. In combination with a low temperature inversion and very slight winds, the H_2S was responsible for an acute exposure of people in immediate geographic proximity to the Girbotol effluent stack. Although the operation was shut down twenty minutes after the difficulty was encountered, 22 deaths and the hospitalization of 320 people were reported. Symptoms, signs and pathological findings were all consistent with H_2S poisoning[9].

Conclusions

Several factors are common to the Meuse, Donora, London, and New York episodes:

1. Effects of the incidents were anatomically localized and generally limited to the cardio-respiratory system.
2. The most vulnerable people were the very young, the very old, and those with pre-existing diseases of the lung and heart.
3. Weather and meteorological conditions played an important role in some manner in all the episodes.
4. Not one, but two or more interacting pollutants were responsible -- oxides of sulfur and sulfuric acid mist, other particulate solids and usually fog as a carrier.

Long term effects were not investigated.

4.1.2 Morbidity and Mortality

The last section treated episodal exposures to high concentrations of pollutants. More broadly based epidemiological studies have elucidated correlations and associations between continuous exposure to air pollution and certain diseases, both acute and chronic. They have yet to direct us to solutions, however. Pollutants, as they have been investigated in epidemiological studies, can only be implicated as indices of general air pollution and, in many cases, cannot be separated from each other. As a result, we cannot ordinarily argue that a specific pollutant from a specific source is harmful to the health of humans. Neither can any pollutant be ruled out as a harmful substance[10]. In the following subsections we review epidemiological studies of the health effects of air pollution.

4.1.2.1 Morbidity Studies of Cardio-Respiratory Diseases

Unlike mortality studies, investigations of pollution-related morbidity concentrate on the ability of pollutants to cause illnesses without specific attention to death rates.

4.1.2.1.1 CHESS

The Environmental Protection Agency (EPA) Community Health and Environmental Surveillance System (CHESS) studies[11-25] are perhaps the best known. The results of studies conducted in CHESS communities in New York[13,15,19,22,24] and the Salt Lake Basin[12,16,20] in 1970-71 as well as in Idaho-Montana[17,21], Chicago[18,23] and Cincinnati[25] are reported. While the reports emphasize the health effects associated with sulfur oxides, various other air pollutants are considered. For long-term pollution effects, health indicators employed in these studies included prevalence of chronic bronchitis in adults, increased acute lower respiratory infections in children, increased acute respiratory illness in families, and subtle decreases in ventilatory function of children. For short-term pollution effects, aggravation of cardiopulmonary symptoms and of asthma were the indicators[11]. The reports often suggest pollutant/disease associations, but the authors acknowledge many unanswered questions. These include: the relative contributions of each pollutant (SO_2, total suspended particulates = TSP, suspended sulfates); the importance of covariates such as socioeconomic status and cigarette smoking; the role of prior exposures in chronic disease prevalence; and the precise threshold value for excess morbidity. Epidemiological studies alone cannot answer these questions and therefore, the conclusions reached in the CHESS studies are not "definitive...[but]...provide one form of data verification required for scientifically defensible air quality standards" (from ref. 11, conclusions and summary). However the usefulness of the CHESS data for predicting health effects has been strongly questioned.

Asthma

In the CHESS asthma studies conducted in the Salt Lake Basin[12] and New York[13], it was observed that asthma attacks consistently correlated with cold outdoor temperatures rather than measured pollutant levels. Therefore, two temperature ranges, 30 to 50°F and greater than 50°F, were used in an analysis of asthma attack rates vs. daily pollutant levels (see Figures 4.1-2 and 4.1-3). In the Salt Lake Basin, no relationship was found between SO_2 and attack rates, but figures reveal that when the effects of total suspended particulates (TSP) and suspended sulfates (SS) were partitioned, attack rates depended strongly on sulfate levels at the higher temperatures (see Figures 4.1-3 and 4.1-4). In New York, daily sulfate levels were also a better indicator of attack rates than either SO_2 or TSP. Attack rates were higher on days with moderate temperatures, i.e., greater than 50°F (Figure 4.1-5). The pollutant threshold for the asthma response was higher in colder temperatures, consistent with the Salt Lake findings. Comparing the temperature effect in the two studies is difficult, however, because the two investigations were carried out during different seasons of the year. In either case, elevated daily sulfate levels were consistently associated with increased asthma attack rates, and the sulfate threshold was higher on colder days.

Cohen and colleagues[14] also studied asthma and air pollution from a coal fueled power plant in New Cumberland, West Virginia. A group of twenty asthmatics reported daily symptoms for over 7 months while local air pollution and weather parameters were monitored. All of the subjects homes were within a 1/2 mile of a power plant which, at the time of the study, had low stacks with no abatement devices and used high ash, high sulfur coal as fuel, therefore emitting relatively large amounts of particulates, SO_2, and oxides of nitrogen. The purpose of the study was to quantify the relationship between short term, relatively high dose pollution exposure and frequency of asthma attacks. Significant correlations (> +0.3, see Table 4.1-3) were found between reported attack rate and temperature and between attack rate and pollution levels after the effects of temperature had been removed from the analysis. The levels of pollution were those commonly found in large cities and appeared greater at moderate than at low temperatures. The correlation coefficients for pollution and weather parameters and attack rate are given below in the table.

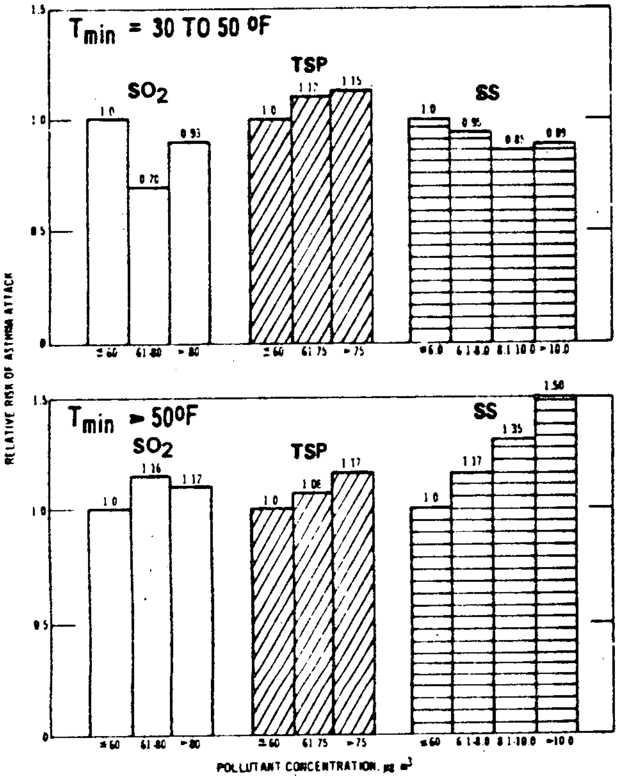

Figure 4.1-2. Relative risk of asthma attack versus sulfur dioxide, total suspended particulate, and suspended sulfate concentrations: Salt Lake area, two minimum temperature ranges.

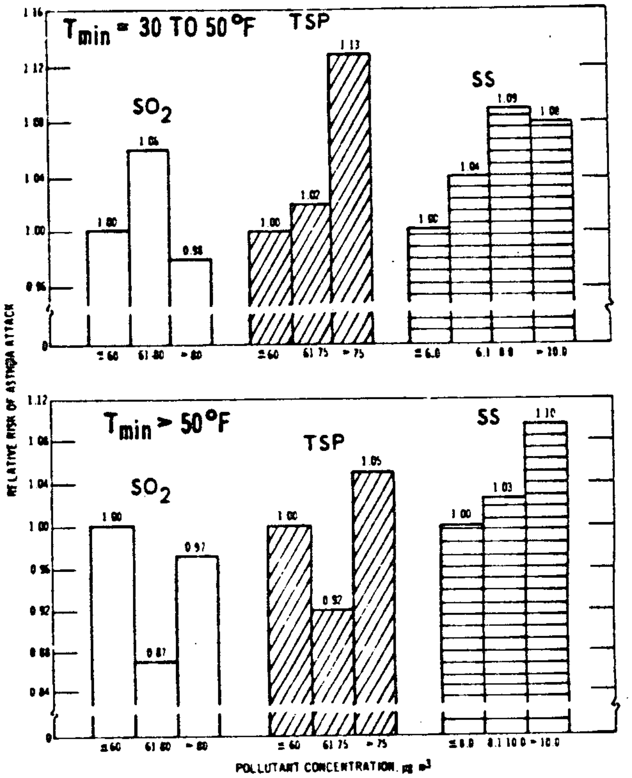

Figure 4.1-3. Relative risk of asthma attack versus sulfur dioxide, total suspended particulate, and suspended sulfate concentrations: New York area, two minimum temperature ranges.

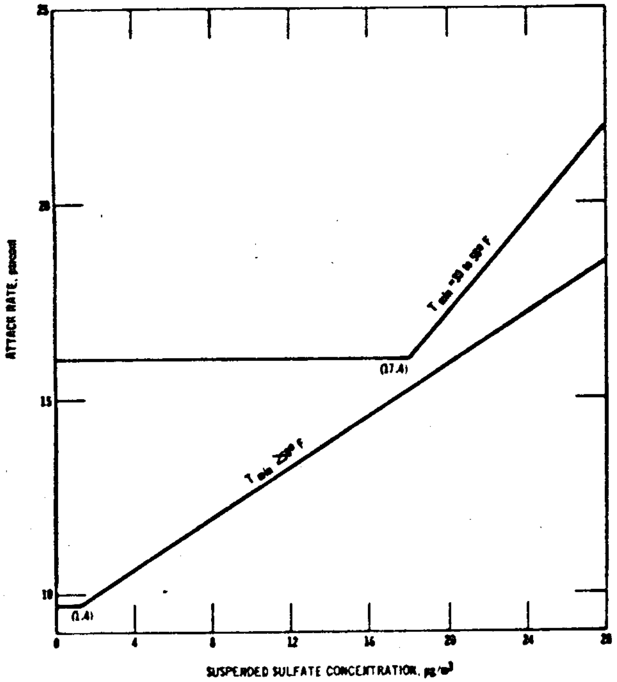

Figure 4.1-4. Effect of minimum daily temperature and suspended sulfates on daily asthma attack rates: Salt Lake area.

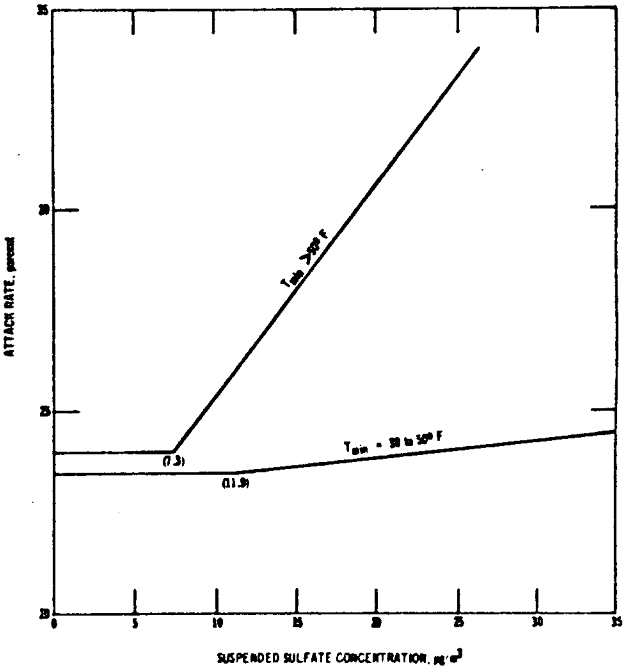

Figure 4.1-5. Effect of minimum daily temperature and suspended sulfates on daily asthma attack rate: New York area.

Results of the CHESS cardiopulmonary panel[15] were similar to those of the CHESS asthma study[12,14] with respect to temperature and pollutants. Cold temperatures were directly related to increased incidence of symptoms in people with existing heart and lung disorders. SO_2 and TSP levels were not associated with aggravated symptoms in the "heart and lung panel" but elevated suspended sulfates were again implicated (Figure 4.1-6).

Chronic Respiratory Diseases

Chronic respiratory diseases were studied in four CHESS locales: The Salt Lake Basin[16], the Rocky Mountain Area[17], Chicago[18] and New York[19]. Prevalence rates for chronic bronchitis, defined by the presence of cough and phlegm on most days for at least three months of the year, are given in Table 4.1-4. A statistically significant difference in chronic bronchitis was found for residents of more polluted areas in all of the study sites. In the Salt Lake Basin, the Rocky Mountain Area and New York, where parents of school children were studied chronic bronchitis rates were much higher among male and female smokers, as would be expected, but smoking did not account for all of the excess. The CHESS authors[16-17] conclude that "the relative contribution of air pollution ranged from one-third to one-seventh as strong as that of cigarette smoking as a determinant of chronic bronchitis prevalence in [the Salt Lake and Rocky Mountain] communities." Air pollution in New York appeared to make a slightly larger contribution than smoking, "a finding which is difficult to accept in light of other evidence." The large differences which smoking and air pollution contribute in each community can be explained by the contrasting pollution profiles and the different smoking patterns in each of the areas. In the Chicago community, where military recruits were studied[18], a smaller excess of chronic bronchitis could be associated with air pollution, and its contribution was much less than that of cigarette smoking. There was still evidence, however, that symptoms were more prevalent among people from more polluted communities.

With the exception of the Salt Lake Basin, where excess chronic bronchitis could reasonably be attributed to SO_2 levels of 92-95 $\mu g/m^3$ (35 ppb) and/or sulfate levels of 15 $\mu g/m^3$, the CHESS investigators judged that the "lowest pollutant concentrations that could reasonably be associated with excess chronic bronchitis were past exposures to 100 to 177 $\mu g/m^3$, SO_2 (40-70 ppb), 80 to 118 $\mu g/m^3$ total suspended particulates and 9 to 14 $\mu g/m^3$

Table 4.1-3. Correlation coefficients for the asthma attack rates as a function of meterological and environmental factors.[14] A strongly positive coefficient indicates direct proportionality, whereas a strongly negative coefficient indicates an inverse relationship.

	Attack rate	Sulfur dioxide	Soiling index	Temperature	Total Suspended particulates	Suspended nitrates	Suspended sulfates
Attack rate							
Sulfur dioxide	+.320†						
Soiling index	+.387†	+.525†					
Temperature	-.427†	-.205†	-.466*				
Total suspended particulates	+.241†	+.537†	+.419†	-.021			
Suspended nitrates	+.169*	+.316†	+.488†	-.084	+.543†		
Suspended sulfates	+.199†	+.349†	+.480†	+.197*	+.567†	+.361†	
Barometric pressure	+.038	-.055	+.122	-.043	+.156*	+.165*	+.107
Windspeed	+.050	+.072	-.290†	-.124	+.033	-.023	+.267†
Humidity	+.112	-.112	+.223	-.162*	-.168*	-.186*	+.089

* P< 05
† P< 01

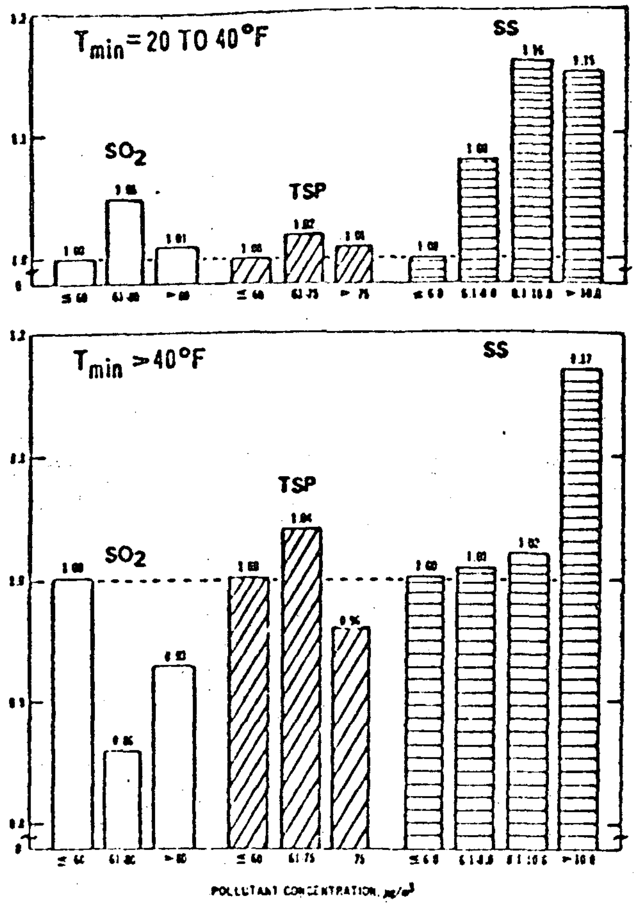

Fig. 4.1-6. Relative risk of symptom aggravation versus sulfur dioxide, total suspended particulate, and suspended sulfate concentrations: New York area, two minimum temperature ranges, "heart and lung" panel.

Table 4.1-4. Smoking and Sex-specific Chronic Bronchitis Prevalence Rates by Community in Four Chess Areas

CHESS area and community	Percent chronic bronchitis					
	Nonsmoker		Exsmoker		Smoker	
	Male	Female	Male	Female	Male	Female
Salt Lake Basin						
Low	3.0	2.3	2.6	5.3	19.9	17.8
Intermediate I	3.6	2.0	3.4	4.0	18.6	14.7
Intermediate II	2.3	4.7	5.4	7.0	20.1	15.3
High	6.8	5.2	6.0	7.1	26.8	22.2
Rocky Mountain						
Pooled Low	1.25	1.08	1.45	3.12	17.05	11.78
Pooled High	3.47	2.54	4.82	2.80	18.63	12.88
Chicago						
Black						
Outstate (Low)	8.8				8.8	
Suburban (High II)	7.8				12.7	
Urban (High I)	9.5				13.0	
White						
Outstate (Low)	4.2				17.6	
Suburban (High II)	5.4				18.8	
Urban (High I)	5.4				17.8	
New York						
Low	4.6	2.0	13.9	3.8	13.9	13.9
Intermediate I	18.0	7.5	18.0	9.0	21.3	19.8
Intermediate II	14.2	4.9	18.7	4.5	22.1	16.6

suspended sulfates. The individual contribution of each pollutant could not be identified[20].

Lower Respiratory Disease

Lower respiratory disease studies of children were conducted in the Salt Lake Basin[20] and the Rocky Mountain[21] CHESS areas. Three findings were reported:

1) Among children whose parents had been residents of their communities for less than three years, no significant association between total respiratory disease and pollution was found, for all combinations of disease and numbers of illness episodes.

2) Among children whose parents had been residents of their communities for three or more years, children of ages 0 to 12 years were reported to have more single and repeated episodes of croup and more repeated episodes of any lower respiratory disease, if they lived in high exposure communities than if they lived in the less polluted communities.

3) No association was found between pollution exposure and pneumonia or number of hospitalizations for lower respiratory diseases for single and repeated illness episodes, regardless of duration of residence.

Larger increases in lower respiratory diseases were observed in the high pollution community of the Salt Lake Basin than in the similar community in the Rocky Mountain area. The mean annual suspended sulfate concentration was greater in the high pollution community in the Salt Lake Basin community than in the Rocky Mountain area, though the opposite was true for SO_2. This suggests that suspended sulfates rather than SO_2 are probably associated with increases in lower respiratory disease frequency.

Many criticisms have been leveled at the lower respiratory disease study. Deficiencies in the data and the test methods have been attributed to the following causes:

1) Recall ability of parents was used in collecting data, and therefore validity can be questioned. However, errors should be fairly random in all of the communities, permitting valid comparisons among them.

2) Differences in diagnostic criteria could exist between physicians of the various communities. On the other hand, none was found when a sample of physicians was asked to diagnose six respiratory syndromes.

3) Since the communities studied were white and middle class, the results can not be applied to other groups in the population.

4) Pollution exposure was estimated from emissions data, and therefore individual exposures are known with very poor precision. Despite these criticisms, the investigators have maintained their stance that a positive association exists between lower respiratory disease frequency in children and pollution exposure at approximately 95 $\mu g/m^3$ (37 ppb) SO_2 and 15 $\mu g/m^3$ suspended sulfates. Total particulates (TSP) were not found to produce adverse health effects in this study.

Acute Respiratory Phenomena

Family members were studied in the New York[22] and Chicago[23] CHESS communities for acute respiratory diseases. With the exception of fathers (who often experience occupational exposures and daily changes of exposure in the workplace different from the rest of the family) a consistent excess acute respiratory disease rate (from 3 to 40%) was reported among those living in more polluted neighborhoods. A conservative estimate was made that exposures to 210 $\mu g/m^3$ (80 ppb) SO_2 with 104 $\mu g/m^3$ total suspended particulates and approximately 16 $\mu g/m^3$ suspended sulfates were associated with a 5-20% excess of acute respiratory illness in family members. A question of the credibility of these results arises because a confounding variable might explain the higher incidence of acute respiratory disease in these areas. Crowding, for example, is known to be a factor in the etiology of acute disease. High pollution levels, however, are often associated with crowded areas; inner city ghettos are a good example. The CHESS Study does not deal with the possible interferences from population density. In this case, only a reproducible association (in the absence of correlating interferents) between increased illness and higher pollution exposures could validate the results. By consistently demonstrating an association between illness and pollution in different parts of the country and in various segments of the population, the CHESS investigators attempted to compensate for the absence of vigorous controls.

Pulmonary Function

The New York[24] CHESS study of pulmonary function was not able to determine the relative importance of specific pollutants in reducing ventilatory function. The Cincinnati[25] CHESS community proved much more enlightening in this regard, however. There, the relative absence of sulfur dioxide (all SO_2 concentrations were at or below the moderate level of 57 $\mu g/m^3$ or 22 ppb) permitted the assessment of health effects due to moderately high levels of suspended sulfates. On the basis of this study, they concluded that one year's exposure to 9 $\mu g/m^3$ of suspended sulfates, in the presence of moderate levels of SO_2 and total suspended particulates, could account for reduced ventilatory function. But the evidence is hardly conclusive because exposure to suspended nitrates happened to correlate with suspended sulfates. While the absolute levels of suspended nitrates were much lower than suspended sulfates, possible effects of the suspended nitrates cannot be ruled out.

Effects Attributed to Nitrogen Dioxide

Epidemiological data on the specific effects of NO_2 are quite meager and exposure to other pollutants, such as ozone, sulfates, metal fumes and aerosols confounds the interpretation of the information collected. But Shy et al.[26,27] have reported on the effects of community exposure to NO_2 in four residential areas in Chattanooga. One area, close to a large TNT plant, had high NO_2 levels and low particulate exposure. In another area, this situation was reversed (low NO_2 and high particulate). The other two areas served as "clean controls". Two health effects, impaired ventilatory function in elementary school children and increased frequency of acute respiratory illness in family groups, were studied over a two year period. Socioeconomic factors such as house value or rent, education of the head of the household, and the number of people in the household were considered also. For children six to eight years old, the respiratory function parameter (forced expiratory volume in 0.75 seconds) was significantly degraded in the high NO_2 area. This area also showed an increased frequency of lower respiratory tract infections in the children exposed two or more years while children exposed one year or less showed no increase. The average NO_2 levels in the high area were 0.10 ppm. Illness incidence rates for families in the high NO_2 area were also consistently and significantly higher than rates in the control areas throughout the study period. In the high NO_2 area and in the high particulate area, excess illness rates occurred in all family segments: children, fathers, and mothers. The relative excess was 18.3% in the high NO_2 area and 10.4% in the high particulate area. These differences could not be explained by family composition, socio-economic level, demographic characteristics, or prevalence of chronic conditions. Parental smoking habits did not appear to influence respiratory disease rates in children.

Pearlman et al.[28] conducted a retrospective study in the same Chattanooga areas and found that exposure to intermediate and high levels of NO_2 in ambient air was associated with a significant increase in the frequency of acute bronchitis. This occurred among infants exposed for three years and school children exposed for two to three years.

The implications of the Chattanooga studies can be cautiously extended to other cities. Direct comparisons among the National Air Surveillance Network (NASN) yearly averages for different cities may be valid if seasonal fluctuations are small. Comparisons with the lower limit values at which health effects were observed in the Chattanooga studies might then be made. Concentrations above 113 $\mu g/m^3$ (0.06 ppm) exceed the Chattanooga study value for the threshold level for health effects. Scrutiny of the NASN reveals that ten percent of cities in the United States with populations of less than 50,000 have a yearly average equal to or exceeding 113 $\mu g/m^3$(0.06 ppm). Fifty-four percent of cities in the 50,000 to 500,000 population range, and eighty-five percent in the over 500,000 population class, equal or exceed the yearly average value of 113 $\mu g/m^3$ (0.06 ppm)[29].

The CHESS* studies[11-28] represent possibly the single most massive air pollution epidemiology program ever conceived. However, they have been the subject of considerable criticism for reasons ranging from non-random study populations to poorly controlled co-correlating variables to primitive methodologies and to inconsistencies in the data.[107-108] Consequently, extreme caution should be exercised in the interpretation of data for regulatory purposes. Thus far, only the studies covering SO_2, TSP, sulfates[11-25] and NO_2[26-28] have been published. However, there are numerous other independent epidemiological investigations in the literature dealing with the health effects of air pollutants. Again, the bulk of these cover SO_2, sulfates, particulates, and to a lesser extent, NO_2.

4.1.2.1.2 Independent Studies

Dohan[30] has found a very high correlation between the mean concentration of "suspended particulate sulfates" in the air of five cities and the incidence rates of respiratory diseases lasting more than seven days in

*This should be interpreted to include the Chattanooga studies.

women employees of the Radio Corporation of America. The suggestion was made that exposure to air pollutants as measured by sulfate levels increases the susceptibility to, or prolongs the duration of, common respiratory infections. Other variables, such as the age distribution of the populations at risk, work conditions, and social and climatic conditions could not account for the variation in incidence of respiratory disease.

Douglas and Waller[31] obtained information on the health of children from their birth in 1946 until they left school in 1961. Of the 3866 children in the study, each was classified into one of four pollution categories, based on residence and domestic coal consumption in 1952. Illness information was based on interviews between the children's mothers and health "visitors" and later, when the children were older, during examinations performed by school doctors. Consistent results were reported: upper respiratory tract infections were not related to the amount of air pollution, but the frequency and severity of lower respiratory tract infections were so related. No difference was found between children in middle class and working class families; and boys and girls were similarly affected. For every age group, the association persisted and chest examinations by school doctors indicated the association exists when the children leave school at the age of fifteen.

Lunn et al[32] gathered data on 919 infant school children living in areas of Sheffield, England with widely varying air pollution levels. The authors found an association between upper and lower respiratory infection rates and high pollution areas, but forced expiratory volume and forced vital capacity, measures used to evaluate pulmonary function, were not significantly affected by pollution levels. The respiratory findings showed no association with area, social class, or number of children in the house or sharing bedrooms.

In 1962 and 1963, Comstock et al.[33] administered cardiorespiratory examinations to men aged 40-64 in various occupations in telephone companies in New York, Washington, D.C., and Baltimore. These examinations were repeated five to six years later on the same groups of employees, and similar examinations were performed on the same types of employees in Tokyo in 1967. These authors found no consistent relationship between present or past residence, birthplace or workplace and respiratory symptoms, although respiratory abnormalities were more frequent with increasing age and increasing numbers of cigarettes smoked per day. Commenting on this finding, they considered whether associations between air pollution and respiratory disease effects might be coincidental rather than causal. According to such a view, positive correlations observed between air pollution and health effects might well have been due to other factors not defined, giving rise to spurious conclusions. Alternatively, negative data such as those reported by Comstock et al.[33] might be observed in spite of positive (and causal) correlation if, for example, people with acute or chronic respiratory symptoms tended to migrate to low pollution areas. Then similar incidence rates of respiratory disease might be found in low and high pollution areas, thus masking a true relationship. In fact, Kelsy et al.[34] presented evidence that such migration does occur. But in the Comstock study,[33] selective migration probably did not occur, because the work location of the subjects changed very little and no positive correlation was found between respiratory symptoms and past residence and birthplace. The authors concluded that their study merely indicates that urban living is not necessarily associated with an increased frequency of respiratory disease. If the.types or concentrations of pollutants changed adversely, positive associations similar to those mentioned above could still occur.

Ferris et al.[35,36] surveyed a random sample of the adult population of Berlin, New Hampshire in 1961 by means of a standard questionnaire and tests of pulmonary function. In 1967, those still living in Berlin were resurveyed using the same techniques. Air pollution levels dropped in the intervening six years. After the effects of aging and cigarette smoking were taken into account, the prevalence of chronic, nonspecific respiratory disease was less in 1967 than in 1961. While the decrease in air pollution might have accounted for the decrease in illness, the authors do not say what the non-response rate was in the initial sample, and they do not state what percentage of the original sample was resurveyed. Sick people might have been likely to participate, thus explaining the alleged association.

Emerson[37] correlated the changes in chronic reversible airways obstruction among 18 patients with the relevant changes in measurements of atmospheric conditions and air pollution in Westminster, a borough of London. Serial spirometric measurements were made in the study subjects at weekly intervals over periods between 12 and 82 weeks. The forced-expiratory-volume-in-one-second test proved to be the most useful, but in only one patient was any significant correlation found with SO_2 levels. In no patient was there any significant correlation with smoke levels. Pulmonary values were correlated with temperature in six patients, with wind speed in four, with humidity in four and with pressure in three. The author attributed the negative results to current low levels of SO_2 in the London area.

4.1.2.2 Cancer Morbidity and Mortality

Numerous researchers have examined the relationship between respiratory system cancer and air pollution. Epidemiological approaches have resulted in four general types of studies: 1) the comparison of urban metropolitan populations with rural populations and an examination of the overall differences in cancer morbidity and mortality (these studies usually do not examine specific etiologic factors); 2) a comparison of cancer rates in migrants with those in their countries of origin and those in the countries to which they migrate (the question of interest here is how a change of environment changes rates of cancer illness and death); 3) a comparison of demographic units, countries, states and cities, and the relationship of various indexes of air pollution to cancer rates (the use of multiple regression techniques allows the separation of environmental and other factors in this type of study); and 4) comparison of the characteristics of cancer cases with corresponding characteristics in those who do not have cancer (obviously, the manner in which the study population is sampled is of critical importance). Such studies, although not conclusive, indicate the following:

Urban dwellers generally suffer a higher rate of lung cancer than people living in rural areas and this result holds true even when normalized for cigarette smoking. Within urban communities the incidence of cancer is greater where more industrial pollution is present. To date, community air pollution has not been proven to be the urban factor responsible for this increase, but high correlations exist between cancer incidence and such urban factors as coal consumption, smoke, and benzo(a)pyrene concentrations.[38-44]

Studies in Buffalo[45] and Nashville[46] reveal that deaths due to stomach cancer are also more frequent in urban areas with higher levels of suspended particulate matter. Analysis of the Buffalo data showed stomach cancer death rates to be twice as high in the most polluted part of the city as in the cleanest areas. Although the Buffalo and Nashville studies controlled for socioeconomic class, they did not control for either occupational exposure or cigarette smoking. However, other investigators have shown that stomach cancer is not strongly associated with smoking[47] and by controlling for economic class, occupation is also partially controlled for, as well.

The results of migrant studies[48-53] are very similar to the results of the urban-rural studies, in that pulmonary cancer rates parallel the general pollution levels of the areas in question. Immigrants tend to have higher rates than people in the country of origin, and lower rates than people in the host countries to which they migrate. Most of these studies, however, lack data regarding the effect of the smoking factor.

Attempts have been made[66] to estimate the effect of pollution on pulmonary cancer death rates from other types of epidemiological studies.[54-65] While existing data suggest that reducing urban air pollution would decrease death from pulmonary cancer, quantitative estimates cannot reliably be made.

While these findings imply involvement of air pollution in the etiology of pulmonary cancer, it is important to consider evidence which does not fit the pattern: 1) Women tend to have much lower rates of lung cancer than men. An explanation for this fact might be that the effects noted in men are due to occupational factors and not urban factors, since the urban environment seems to have relatively little effect on the cancer death rates for women. 2) High pulmonary cancer rates are found in some regions, such as Helsinki, Finland, where pollutant levels are fairly low. Perhaps some special factor(s) account for this incidence (woodsmoke in Finnish saunas), but special factors could probably be found almost anywhere. 3) Finally, it is possible that air pollution is merely highly correlated with some factor (economic status, for instance) that is the real cause of pulmonary cancer. If this is the case, a spurious association exists. Synergism with smoking history should also be explored.

4.1.2.3. Mortality Studies

A number of episodes of extreme air pollution with corresponding increases in the numbers of deaths have been discussed above. Because of the temporal association between the high levels of pollution and excess deaths, it is reasonable to presume that the pollutants have caused the deaths. Much has been written about the great air pollution disasters but many other epidemiological investigators have attempted to link mortality patterns to more routine air pollution situations. In general, these studies have attempted to demonstrate geographical or demographic differences or the trends related to exposure to trends in mortality.

Buechley and coworkers[67] analyzed daily mortality for 422 places in the United States from 1962 to 1966 and provided a consistent set of mortality predictors. In the New York metropolitan area, for example, pollution measurements showed that mortality was 1.5% less than expected on 232 days with SO_2 levels below 30 $\mu g/m^3$ (12 ppb) and 2% greater than expected on 260 days with SO_2 levels above 500 $\mu g/m^3$ (192 ppb) after correcting for other factors. Coefficient of haze correlated with deaths as well as did SO_2. The authors made no conjecture about etiological or causal relationships.

Using multiple regression techniques, Sprague et al.[68] analyzed infant and fetal deaths in Nashville, Tennessee, from 1955 to 1960. Significant positive correlations were found between sulfation and SO_3 and white infant mortality. No relationship was found between SO_2 and mortality. An unsuccessful attempt was made in this study to separate the effects of socioeconomic status from the effects of air pollution.

McCarroll and Bradley[69] showed that periodic peaks in mortality in New York City are associated with periods of high air pollution. These peaks are usually associated with periods of low wind speed and temperature inversions. In these studies, an immediate rise in mortality occurred on the same day as the peaks of pollution. This finding contradicts Greenberg et al.[70] who assumed a three day time lag between pollution peaks and observed increased mortality. Cassell[71] noted this contradiction and added that interpretations by various authors had not accounted for possible influences of environmental factors other than pollutants. In a reanalysis of the New York data he reached three main conclusions: 1) the complex etiology of mortality made it "exceedingly difficult to assign a specific cause and effect role to any one variable." 2) Mortality patterns were "remarkably stable" over time, even though fluctuations could be interpreted differently. 3) The uniformity of the mortality patterns was dependent only on very strong environmental influences.

In a study in 1963, Burn and Pemberton[72] divided the British city of Salford into low, medium, and high pollution areas on the basis of average smoke and SO_2 levels. They found a significant correlation between pollutant level and mortality from bronchitis and lung cancer. But potentially serious methodological considerations were overlooked. The authors neither controlled for socioeconomic status in the study population nor did they identify any other pollutants which may have been present in the environment, and possibly responsible for the results they reported.

A number of studies have been conducted in which respiratory disease mortality was investigated in relation to socioeconomic factors as well as to degree of exposure to air pollutants. In one study by Winkelstein and colleagues[73], a positive association between air pollution level (suspended particulates) and total mortality among white men aged 50-69 is shown when economic factors have been controlled. The relationship is greatly attenuated in white men over the age of 70. The same pattern is also evident in white women. From these data, no association was found between pollution and cancer of the bronchus, trachea, and lung. In a second study, also by Winkelstein and others,[74] total mortality for white men aged 50-69 and for those at least 70 years old showed essentially no association with sulfation (oxides of sulfur) when the relationships were examined within each economic stratum. Nor was there an association between sulfation and cancer of the bronchus, trachea and lung. But a small positive association is revealed between mortality from chronic respiratory disease and sulfation in the lowest economic levels. Finally, Zeidberg et al.[75] demonstrated that with the exception of lung and bronchial cancer, mortality from respiratory disease varied inversely with socioeconomic class when the degree of exposure to air pollution was kept constant. For the middle socioeconomic population, respiratory disease mortality was higher for men than for women, and especially for lung and bronchial cancer mortality. A general criticism has been leveled at all three of these studies[73-75] by Comstock[33], who speculated that the "association of poverty with pollution could create an apparent association of respiratory symptoms with pollution even if, in fact, no association existed."

The preceeding treatment of mortality studies indicates the current controversy among workers in this subject. While many of the publications cited give the impression that mortality data provide clear evidence of association with air pollution, almost all of the authors concede that other factors were operating in the studies they described. When discussing possible health effects of air pollution, cause and effect relationships should be advanced very cautiously. Sir Austin Bradford Hill, in distinguishing between association and causation of disease by environmental factors, stated[76] that a strong association may be evidence of causation but that multicausation of diseases is generally more likely than single causative factors. Hill warned that epidemiological evidence should be judged on its merits independently of the implications for policy decisions. He also said that "all scientific work is incomplete-whether it be observational or experimental."

4.1.2.4 Occupational Exposures

The workplace provides a unique setting for the study of the health effects of isolated air pollutants. Air contaminants tend to interact with one another in the atmosphere with resulting end products which may differ in composition and effect from their individual components. But industrial situations exist in which populations are exposed to high levels of specific pollutants either over a long time period or as the result of a catastrophic fugitive emission. There is, however, one obvious disadvantage in studying occupational exposures. Workers in industrial settings are generally young and healthy and certainly not representative of the entire population. So the absence of a clinically discernible disease in them may not indicate the safety of exposures to a population which includes the elderly, the infirm and other sensitive people who are not so employed.

Because of the wide variety of industrial processes, the number of chemical agents which have been examined as environmental hazards in the workplace is necessarily vast. NIOSH[77,78] has catalogued many of these substances according to their toxic or carcinogenic properties, based on combinations of occupational epidemiology or toxicology studies. However, only a very limited selection of these agents are at all likely to be associated with an electric power generating plant. Occupational epidemiology studies have been reviewed for many of these; of particular interest are the criteria background documents which have been published for SO_2,[79] H_2S,[80] NO_2,[29,81] particulate organic matter,[82] mercury,[83,84] selenium,[85] and arsenic.[86] Most of the epidemiological investigations involved study populations in industrial process plants rather than power plants. However, some of those which are directly translatable to power plant operation are given below.

Occupational Exposures to Sulfur Compounds

In a study of oil refinery workers in South Persia, Anderson[87] compared workers exposed to sulfur dioxide with similar unexposed workers. Daily concentrations ranged from 0 $\mu g/m^3$ to 71,500 $\mu g/m^3$ (25 ppm) with occasional figures as high as 286,000 $\mu g/m^3$ (100 ppm), and exposure periods were from one to nineteen years. No significant differences were found between the two groups in several measures of health including pulmonary function, chest x-rays and clinical examination.

In New Hampshire, Ferris et al.[88] compared a sample of workers in a pulp mill where concentrations of SO_2 ranged from 5,720 to 37,180 $\mu g/m^3$ (2 - 13 ppm) to workers in an adjacent paper mill where occupational exposure to SO_2 was virtually nonexistent. It should be noted that some of the workers in the pulp mill were exposed to chlorine as well as SO_2, and others were exposed to SO_2 alone. Cigarette smoking was controlled for in the analysis of the data. No significant differences in either respiratory diseases or in tests of pulmonary function were found between the workers in the two mills, although men exposed to chlorine had slightly lower respiratory function than workers exposed to SO_2 alone. It should be pointed out that the workers in these two mills had a lower prevalence of respiratory disease than the male population of Berlin, New Hampshire, where the mills are located. This finding suggests that occupational groups may not be representative of the general population.

When Skalpe[89] compared exposed pulp mill workers (levels of SO_2 averaged between 5,720 and 102,960 $\mu g/m^3$ or 2-36 ppm) and unexposed paper mill workers in Norway, he found significantly higher frequencies of cough, expectoration and shortness of breath on exertion among the pulp mill workers, especially those under 50 years of age. It is possible that the older, susceptible workers had already been weeded out of the working population, but even the younger workers had all been employed over one year.

Finally, Kehoe et al.[90] studied refrigeration workers who for 4-12 years had been exposed to concentrations of SO_2 exceeding 28,600 $\mu g/m^3$ (10 ppm). He compared these workers to those who worked in the same plant but who were unexposed. The data revealed an increased shortness of breath, higher incidence of fatigue, abnormal reflexes, and longer duration of "colds" (incidence of colds was not different, however) among the exposed workers.

Few very clear patterns emerge from the occupational exposure studies of SO_2. Workers were frequently found to become acclimated to SO_2[79], so that large segments of the study populations would show no signs of SO_2 toxication while, at the same time, naive workers might be quite sensitive. Significant changes in the resistance of these workers to infectious diseases were sporadically observed; hence, interpretation of the effects is somewhat complicated[79].

Hydrogen sulfide (H_2S) exposures in the workplace have generally occurred as catastrophic occupational accidents[80] principally because the noxious odors can be detected at particularly low concentrations. Incidents of isolated exposures to 20 ppm H_2S have resulted in eye irritation in gas workers[80,91]. Repeated exposures were found to elicit photophobia, blurred vision, eye pain, digestive disturbances, and weight loss, at the same concentrations[80,91]. Prolonged exposure to H_2S at levels higher than 20 ppm resulted in pulmonary edema; incidents of this sort have been extremely rare[91]. Fugitive emissions of H_2S within geothermal power plants may become a potential source of chronic H_2S exposure in the workplace.

Exposures to oxides of nitrogen

Occupational exposures to NO_x have been documented in connection with the use of rocket fuel (nitrogen tetroxide) and dynamite. Other studies include one by McCord[92] who examined production welders at a time when the NO_2 level in the workplace averaged 13 ppm. He showed that methemoglobinemia was established in these workers and in the absence of other sources of methemoglobin, suggested that exposure to nitrous gases may be responsible. Another study by Vigdortschik et al.[93] examined chronic poisoning among etchers in printing shops and men working in sulfuric acid plants who were exposed to nitrogen oxides (2.6 ppm). A conspicuous omission in this paper is a statement of the ambient levels of SO_x to which the sulfuric acid plant workers were exposed and which possibly could confound the results. Nonetheless, the exposed workers were compared with unexposed controls. The authors found differences (the paper does not state whether or not they were statistically significant differences) between the two groups which included more frequent incidence of emphysema, tuberculosis, dental caries, cardiovascular symptoms (hypotonia and bradycardia) and morphological, physical and chemical changes in the blood in the exposed group of workers. This study, although suggestive, points out the need for more carefully conceived and executed research before any of the findings can be confirmed.

Exposures to particulate organic matter

The association between development of cancer and excessive contact with environmental organic matter was first made in 1776 when the British physician Percival Pott noted the high incidence of cancer of the scrotum in the chimney sweeps of London[94]. He correctly attributed the disease to their continual contact with soot[94]. Despite this knowledge almost two hundred years after the first warnings were sounded, chimney sweeps were shown to experience excess scrotal cancer as recently as 1964[95]. Furthermore, wax pressers with prolonged exposure to crude wax have been shown to have increased scrotal cancer rates[96]. Other substances associated with excess skin cancer include tars, shale oil, and cutting oil[97-99].

The illnesses usually related to exposure to particulate organic matter are cancer of the skin and lung. Nearly all the findings have been made in studies of occupational exposure to the combustion products of carboniferous material. In all these studies, concentrations have been very high and exposures prolonged. In most cases, the actual concentrations to which the subjects were exposed were not known, nor could the chemical compounds of the occupational exposure environment be characterized with a high degree of certainty. Of course, in occupational exposure, the dose of particulate organics is far greater than in ambient air. In gas workers, the concentration of benzo(a)pyrene (BaP) has been estimated at 3 $\mu g/m^3$; above coke ovens, it may reach levels of 216 $\mu g/m^3$. In even the most polluted ambient air, the annual average BaP concentration rarely exceeds 0.01 $\mu g/m^3$.[82]

Particulate organic matter is produced mainly by the combustion or volatilization of fossil fuels. Most of the industry-related cancer experiences have been cases involving combustion or distillation of coal products. In gas-works retort houses in England, BaP concentrations of 3 to 216 $\mu g/m^3$ were measured. These concentrations were 100 to 10,000 times higher than the normal BaP level in London[100]. In one study, British gas workers employed for at least 5 years were divided into a high-exposure and a low-exposure group. The lung cancer incidence in the high-exposure group was 69% greater than in the control group. Coke oven workers also have experienced an increase in the incidence of lung cancer[101-103]. Other lung disorders such as pneumoconiosis (black lung disease) and chronic bronchitis have also been encountered[101]. In addition to cancer, other cutaneous disorders have been linked to particulate organic matter. Among these are nonallergic and allergic dermatitis, phototoxic inflammatory reactions, pilosebaceous responses, and pigmentation disorders[104-106].

At the present time, particulate organic emissions from fossil fuel-fired power plants are low relative to other industrial processes. However, in an occupational situation, even these may be significant. Certainly, the introduction of fuel conversion technologies such as coal gasification or coal liquefaction for power plant operation will bring these problems to the forefront.

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4.2 Laboratory Studies; Physiological and Cellular Effects

In the assessment of the health risks of air pollutant exposure, one alternative to the epidemiological approach, which is basically a field investigation under conditions which cannot be controlled, is the examination of discernible health effects under laboratory-controlled conditions. The principle advantage of laboratory studies is flexibility. Exposure conditions can be manipulated at will, in order to optimize both positive and negative controls. Ideally, the exposure conditions should mimic "real-world" pollution levels. In practice, however, pollutant exposures are usually at concentrations high enough to elicit the health effect of interest to the investigator. Exposure atmospheres are generally simple and may consist of a known quantity of a single pollutant. In laboratory experiments, the subjects are usually animals rather than human volunteers, since time scale requirements and moral restrictions are less stringent. This section examines the literature on the physiological and cellular level health effects of combustion-type pollutant on humans and animals, on a pollutant-by-pollutant basis. Metabolic effects at the biochemical level are examined in Section 4.3.

Most pollutants enter the body by one of two routes, either inhalation into the lungs and respiratory tract or ingestion through the gastro-intestinal tract. For emissions into air, the first route is normally the more important. Understanding the processes of respiration and absorption is essential to understanding the physiological mechanisms by which fossil fuel emissions exert their toxicity.

During breathing, air enters the nasal passages and passes through the nasal passages, larnyx, trachea, bronchi and bonchioles, through the terminal bronchioles, the respiratory bronchioles, and alveolar ducts into the air sacs or alveoli. (See Figure 4.2-1). One of the normal functions of the respiratory system is to exchange CO_2 in the blood for oxygen in the air. At the alveoli, oxygen/CO_2 exchange takes place through a thin cell layer which separates the air from the pulmonary blood stream. Ordinarily, the surface system is kept in balance with pulmonary surfactant fluid, a mixture of lipids which maintains the proper surface forces in the alveoli during inhalation and exhalation to keep the airways open. One should keep in mind that lung tissue contains some 42 morphologically distinct[1] cell types, whose functions include metabolism of toxins,synthesis of surfactant, clearance of particles, gas exchange, control of blood flow, control of air flow, etc.

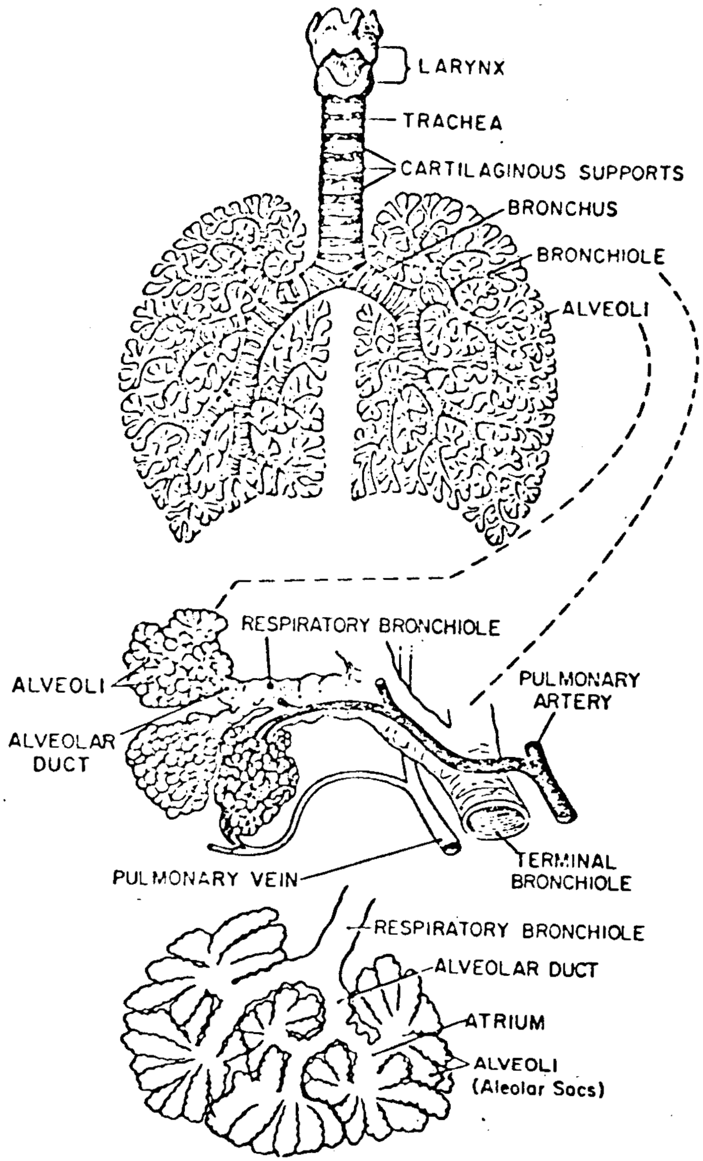

Fig. 4.2-1. The lungs and the pulmonary alveoli. Top panel modified from W. W. Tuttle and B. A. Schottelius, Textbook of Physiology, ed. 15, C. V. Mosby, St. Louis, 1965. Lower panels modified from S. Grollman, The Human Body. The Macmillan Co., New York, 1964.

This system is protected against the invasion of particles, toxic gases and aerosols, bacteria, viruses and other foreign bodies by a host of defense mechanisms which cleanse the air as it travels its course. These mechanisms include coarse hairs in the nose which remove large particles, mucous membranes in the nasal passages, and a specialized cell layer called the ciliated epithelium which lines the inner surface of the trachea and smaller tubes to trap particles (2-10 μm in size) via a combination of beating cilia and a surface blanket of mucus. In the bronchioles and alveolar regions, alveolar macrophages engulf, metabolize and transport into the lymphatic system airborne pollutants. Pollutants which escape the macrophages will penetrate "type II" alveolar cells (this cell type carries out most of the energy metabolism, drug and toxin metabolism, and hormone and surfactant synthesis) where they can either be detoxified or interfere directly with gas exchange in the blood. Alternatively, they may directly enter the blood or lymph systems and interact with tissues in other parts of the body (systemically).

Ingestion via the gastro-intestinal tract represents a second major route for the introduction of pollutants into the body. Most water-borne pollutants enter exclusively by this route. Air pollutants which have been cleared from the respiratory tract but swallowed may also enter the body via this route. Most absorption in the gastro-intestinal tract is accomplished by the epithelial mucosal cells which line the luminal surface of the small intestine.[2] The permeability of the intestinal epithelium to particles varies over a factor of a trillion (10^{12}); the major determinant is particle size. In the absence of a vehicle such as lipids or other fatty materials to dissolve the particles, any substance with particle diameter greater than 0.003 μm will not be transported into the blood stream.[2] While lipid solubility of mineral particles may not be sufficient to allow absorption, it is very likely that absorption through the gastrointestinal tract may be an important route of entry for organic pollutants.

For certain pollutants, particular adverse health effects may only begin to occur at a concentration threshold governed by the rate at which body defense mechanisms can remove the pollutant either by metabolic activity or physical clearance. When pollutant levels exceed the threshold, biochemical, physiological, cytological, and immunological changes can take place which place susceptible individuals in jeopardy. However, for other pollutants or resulting health effects, there may be no threshold. Adverse effects may be induced, with some probability, at arbitrarily low concentrations.

4.2.1 Sulfur Oxides

The physiological effects of SO_2 and H_2SO_4 have been studied very extensively by a number of workers, in both humans and animals. In 1965, Cooper[3] compiled a bibliography of 994 studies on the effects of sulfur oxides, and many more since that time have been published. Review of this data uncovers many apparent inconsistencies, due presumably to dissimilarities in exposure conditions, animal species, or measurement techniques. Most of the work has approached the problem of SO_x toxicology at the level of effects on respiratory-pulmonary mechanics and on cell populations and activities. Of the findings which are relatively self-consistent, we can generally conclude that: 1) H_2SO_4 is a more toxic aerosol than is SO_2; 2) guinea pigs are the most susceptible laboratory animal employed, but concentrations of H_2SO_4 mist which this animal can withstand would often be intolerable to man, and 3) compared to ambient air pollution levels, relatively higher levels of SO_2 and H_2SO_4 are required to produce lung pathology or mortality in animals. However, the literature on sulfur oxide effects is fraught with disagreements among different studies.

Sulfur dioxide produces a bronchoconstriction with subsequent pulmonary flow resistance common to various other respiratory irritants. This response has been shown in the guinea pig, the dog, and the cat and can be elicited by exposing only the upper airways to SO_2. Sulfuric acid and some, but not all, particulate sulfates also produce bronchoconstriction. This response has been shown repeatedly in the guinea pig, and is highly dependent on particle size, with the smallest particles (< 1 µm) showing the greatest irritant potency because of their ability to penetrate more deeply into the respiratory system and irritate tissues in the alveolar region of the lung to a much greater extent than larger particles. These effects have been reviewed by EPRI,[4] the EPA,[65,69] the ARB,[66] NIOSH,[67] Snodderly,[68] and others.[70-72]

Human experimentation has shown that SO_2 and H_2SO_4 aerosols both have a bronchoconstrictor effect in man, most likely mediated by a parasympathetic reflex. In these studies, techniques which measure the resistance to the flow of the respiratory gases by the pulmonary airways have been used on "healthy adults," that is, those least susceptible to adverse effects. Figures 4.2-2 and 4.2-3 illustrate the airway resistance effects of SO_2 and H_2SO_4 in humans and animal.

Bushtueva[54] reported that the minimum concentration of H_2SO_4 mist detectable by 10 healthy human subjects averaged 750 $\mu g/m^3$ with a range of 600-850

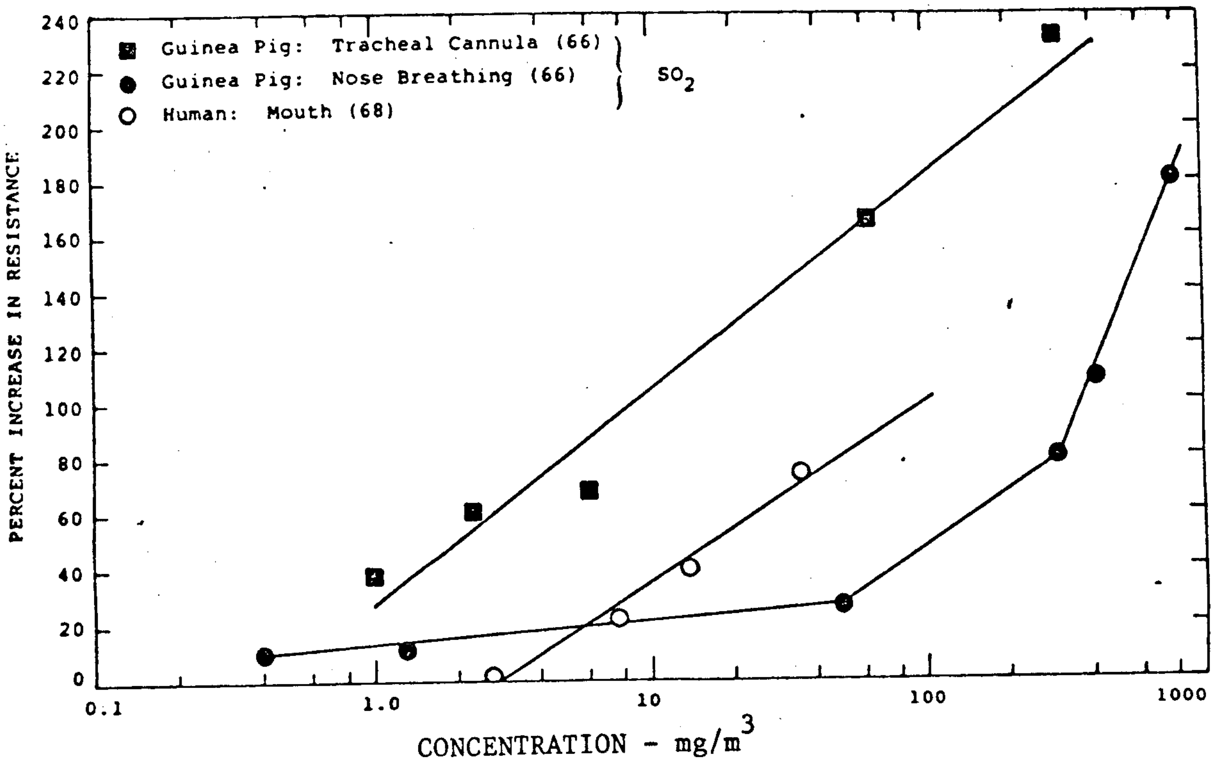

Figure 4.2-2: Airway resistance effects of SO_2 (32, 52, 53)

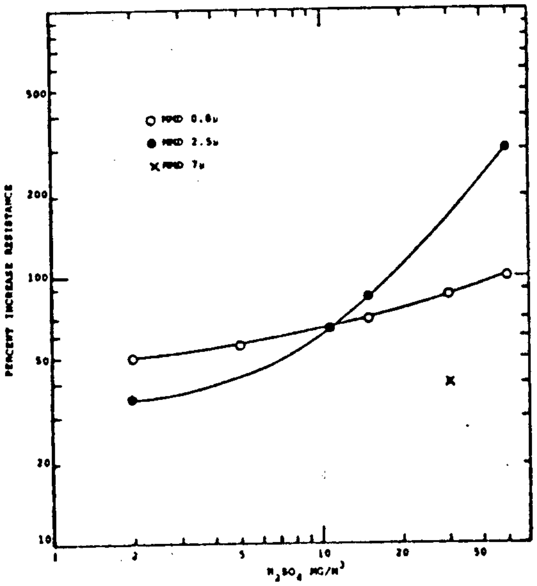

Figure 4.2-3: Dose-response curves for a one-hour exposure to sulfuric acid mist (Admur 15, 16, 27).

$\mu g/m^3$, but this study used physiological responses of the central nervous system rather than changes in respiratory function as measured of the effects of the aerosol.

Sim and Pattle[55] exposed healthy males 18-45 years old to sulfuric acid mist, sulfur dioxide and various aldehydes for periods up to sixty minutes. The main effects of SO_2 and sulfuric acid mist were an increase in airway resistance and the appearance of rales. Two subjects exposed to H_2SO_4 mist developed long-lasting bronchitic symptoms. When steam was added to the H_2SO_4 mist, causing the particles to enlarge and thus simulate periods of high humidity, the irritant effects were intensified.

Amdur and colleagues[56] subjected normal human subjects to concentrations of sulfuric acid mist from 0.35 to 5 mg/m^3. By means of a pneumotachograph, all changes in respiration were observed and measured. Retention of inhaled acid mist averaged 77%. Marked effects upon respiration were always noted in normal men who had no regular exposure or adaptation to sulfuric acid; changes of a purely reflex nature (not under the control of the subject since he was unable to detect the presence of acid mist) occurred at concentrations as low as 0.35 mg/m^3. These changes were indicated by shallower, more rapid breathing. At a high concentration of acid mist, 5 mg/m^3, easily detected by all subjects, very marked reactions were demonstrated by some of the subjects. The greatest effect at this concentration was a decrease in minute volume in two subjects: 11.7 to 9.3 liters/minute in one and 9.2 to 7 liters/minute in the other.

Frank et al.[52] exposed eleven healthy male adults on separate occasions to levels of SO_2 of 1, 5, and 13 ppm. The exposures lasted 10 to 30 minutes and were spaced one month apart for each subject. At the lowest concentration of gas, only one subject showed a significant increase in air flow resistance. At both 5 and 13 ppm SO_2, however, flow resistance was elevated in all subjects, the change being greatest at 13 ppm. Increased resistance usually occurred within 1 minute of exposure, increased after 5 minutes, but, on the average, showed no further change after 10 minutes. No consistent changes were found in pulmonary compliance, tidal volume, breathing frequency or pulse rate, but functional residual capacity increased slightly during exposure to 13 ppm.

Findings qualitatively similar to Frank et al.[52] were presented in a study by Snell and Luchsinger.[57] Since urban concentrations of SO_2 are generally well below 5.0 ppm, this study observed the acute effects of SO_2 exposure in the 0.5 to 5.0 ppm range. Following 15 minute inhalation by mouth of 1 ppm SO_2 in air, a small but significant decrease in flow rates was observed; at 5 ppm a further decrease occurred, but the addition of a saline aerosol to the gas did not accentuate the effect. This result conflicts with the work of Amdur in guinea pigs (see below) in which combinations of SO_2 gas and NaCl aerosol exert a synergistic effect and do accentuate the response. In order for this to happen, two possible theories are advanced: 1) the salt must catalyze the conversion of SO_2 (or SO_3) to a toxic sulfate compound, or 2) particles must deposit in the lower airways. Snell and Luchsinger[57] believed the data support the second theory, and argue that because relatively large diameter particles are produced by ultrasonic generation of the saline mist, deposition in the lower airways is slight (protective mechanisms would keep large particles out) and retention in the upper respiratory tract great. Since both the Amdur study[56] and the Snell-Luchsinger investigation[57] present presumably valid experimental data, the discrepancy between the two sets of results points out the necessity to distinguish between and avoid generalizations in animal and human experimentation which might lead to erroneous extrapolations.

Burton and colleagues,[58] in a study of response of healthy men to gas-aerosol mixtures, report findings which support the above work.[52,57] In this study, gas-aerosol synergism for SO_2 (less than 3 ppm) and inert aerosols at concentrations approximating those in urban atmospheres could not be demonstrated. The authors conceded that gas-aerosol synergism may yet prove to be an important toxologic mechanism in man, however, and that testing pulmonary mechanics studies may not be the best approach to problems of acute-effect air pollution toxicology in man.

Sulfur oxides have also been shown to cause alterations in cell populations and activities in the lung and respiratory tract.[59-63] Short-term exposure to SO_2 concentrations in excess of 10 ppm has been reported to damage the ciliated epithelial cells in the trachea (responsible for mechanically removing bacteria, dusts, and other large particulate masses). This effect could alter the size-dependence of particle deposition in the lung, allowing the larger particles to deposit in alveolar spaces following SO_2 exposure.[59] Exposure to very high concentrations (50 ppm and above) for varying periods of time can alter the local populations of cells in the lung and respiratory tract. As Figure 4.2-4 reveals, high SO_2 exposure causes the mucus-secreting goblet cells normally found in the trachea to migrate into the bronchioli.[61] Presumably, the cells in the trachea are initially overstimulated, then killed.[61]

Further exposure results in the eventual migration of mucus-secreting cells into alveoli.[62] These changes can be extremely harmful, even fatal.

Ordinarily, mucus secreted by other cells, as well as particulate matter, are removed from the alveolar spaces by alveolar macrophages. Their activity is quite sensitive to sulfur oxides exposure.[61-63] The ability of macrophages to keep the alveolar airways open may determine the extent and dose dependence of the bronchial responses characteristics of SO_x. The viability of alveolar macrophages may determine also the host organism's resistance to infections diseases.

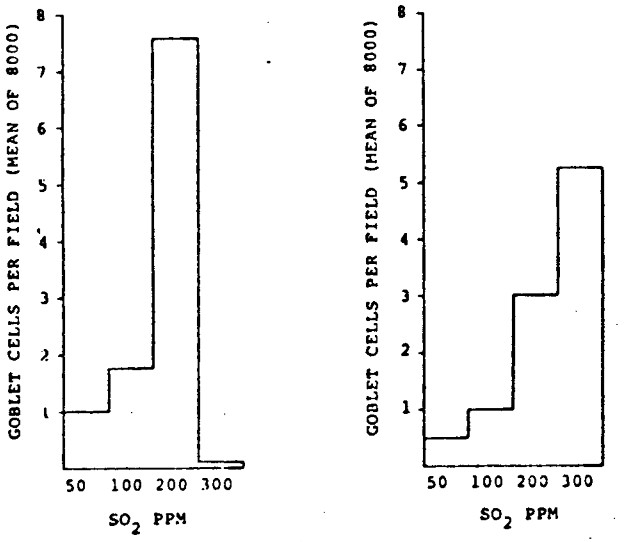

Fig. 4.2-4 The effects of various levels of sulfur dioxide on the rat tracnea (left) and bronchiolus (right). (61)

Continued exposure to very high levels of SO_2 eventually leads to a complete changeover in the relative populations of the various cell types in the lung and respiratory tract. The sequence of airway epithelial changes after exposure to non-fatal doses of sulfur dioxide is first dilation and destruction of ciliated cells, followed by replacement of ciliated cells by goblet cells, Later, goblet cells disappear and are replaced by squamous cells in the epithelium.[4,61,62,63,39,64]

One should remember that the functional disorders which appear during acute exposure to SO_2 occur at concentrations which are at least 3-4 orders of magnitude higher than typical ambient air levels. In addition, none of these effects has yet been traced to any particular reaction of SO_2 with biochemical and cellular constituents (Section 4.3.1).

Similar studies with SO_3 and H_2SO_4 mists suggest that particulate sulfates may be much more irritating than SO_2. Figure 4.2-3 shows this effect clearly. Morphological evidence[4,69,74] suggests that either SO_2 or H_2SO_4 exposure results in the formation of necrotic zones (areas of dead tissues) in the trachea and possibly in the bronchi. Hence, H_2SO_4 may have many of the same effects on cell populations, even though the chemistry of its reactions with cellular constituents is very different from SO_2 effects (see Section 4.3.1).

The ability of atmospheric sulfur oxides to cause illness may stem from toxic effects on tissues in the respiratory tract whose normal function is to combat infections. Other disease states of a more primary or secondary nature have been attributed to SO_x as well. However, it is not so clear that sulfur oxides are actually responsible for all of the conditions. The effects of chronic exposure to low levels to sulfur oxides have been studied[15,75,76,79] in animals, with the principal manifestation of harm being a reduction in the rate at which foreign bodies are cleared from the respiratory tract. Several investigators[36,77-79] have suggested that chronic exposure to sulfur oxides alters the antibody defense mechanism of the lung against airborne bacteria in the lung and throughout the body, and may therefore impair resistance to infectious diseases.

One can summarize threshold concentrations for the acute interactions of SO_x in humans as follows:

	SO_2	Sulfates
(Standards:	0.03 ppm (1 yr) or 0.5 ppm (1 hr)	25 μg/m^3)
Taste/Odor:	0.3 ppm	700 μg/m^3
Irritation:	> 3 ppm	350-2,000 μg/m^3
Causes illness:	> 1 - 10 ppm	10-3,000 μg/m^3
Lethal dose:	> 400 ppm	?

4.2.2 Nitrogen Oxides

Nitric Oxide

Of the oxides of nitrogen commonly encountered in occupational and community air, only nitrogen dioxide (NO_2) has received any significant attention from biomedical scientists investigating the health effects of combustion-generated pollutants. There are two major reasons for the emphasis on NO_2. First, at high concentrations, nitric oxide (NO) reacts readily with oxygen to form NO_2 (see Section 3.3.3.3), so that it becomes difficult to maintain NO in a laboratory exposure experiment. Second, no cases of human poisoning attributed strictly to NO have ever been reported in the literature. In animals, extremely high concentrations of NO produced central nervous system paralysis and convulsions. Mice exposed to 3,075 mg/m^3 (2,500 ppm) were narcotized (in 6 to 7 minutes) and died within 12 minutes, but when the narcotized animals were returned to fresh air after 4 to 6 minutes of exposure, they rapidly recovered.[80] In experiments on guinea pigs, the data indicated no effect on pulmonary function from 4 hour exposures to concentrations of 19.7 to 94.0 mg/m^3 (16-50 ppm).[81] NO, therefore, does not elicit any obvious physiological changes in the lung. However, recent biochemical evidence (see Section 4.3.3) suggests that NO may behave like carbon monoxide in its effects on cardiovascular physiology (see Section 4.2.5).

Nitrogen Dioxide

NO_2 exposure elicits a range of effects in the lung which include changes in pulmonary function mechanics, changes in cell populations and growth patterns, changes in tissue morphology, and depression of resistance to disease. Additional metabolic changes are discussed in Section (4.3.3), although some of the physiological effects of NO_2 can be traced directly to specific biochemical lesions. Typical health effects of nitrogen oxides exposure, either chronic or acute, include symptoms which appear immediately (early responses), those which appear throughout the exposure period but remit during a subsequent recovery period, and those which are apparently irreversible (persistent responses) or from which the animal recovers very slowly.[82-88]

Early responses may include:

bronchiolar inflammation;
loss of cilia in terminal bronchioles;
Type I alveolar epithelial cell replacement by Type II or Type II mitosis stimulation;
tachypnea, tidal volume decrease, increase flow resistance;
hematologic indicator changes;
eye and nasal irritation;
delayed septation of air spaces (alveolar maturation);
mucociliary transport rates delay;
mortality.

Exposure duration responses include:

tachypnea (some species);
reduced resistance to respiratory infection;
macrophage dysfunction;
peroxidation of lung lipids;
reduced weight gain;
elevated urinary protein levels.

Persistent responses include:

alveolar distension;
septal wall thinning;
emphysema;
surfactant surface tension degradation;
peripheral organ involvement;
mortality (due to pulmonary edema).

Responses to acute exposures of NO_2 do not differ qualitatively from those of chronic exposures. Acute exposures are most often used to simulate episodic conditions and to develop a refined understanding of mechanisms. NO_2 exerts its primary toxic effect on the lungs. Concentrations greater than 188 mg/m^3 (100 ppm) are lethal to most animal species, and 90% of the deaths are attributed to pulmonary edema. The mortality rate may be modified by varying the duration or dose of the exposure to NO_2, the temperature, and the presence of other irritants (88).

Short-term exposures to NO_2 increase pulmonary flow resistance (89,90) and can reduce the rate of diffusion of gases into the bloodstream (91). These effects seem to combine additively with those induced by sulfur oxides (84,88), so that the simultaneous presence of NO_x and SO_x results in neither synergism nor overlap of effects on pulmonary function. This independence of the respiratory effects of the two gases from one another may stem in part from the fact that SO_2 is primarily an upper respiratory tract irritant, while NO_2 is large a deep-lung irritant (4,15,65,82-88).

In studies of pulmonary function, one experiment by Rokaw et al[92] utilized six normal subjects and four with "moderate to marked" pulmonary disease. On exposure to concentrations of 940 to 5,640 ug/m^3 (0.47 to 2.8 ppm) NO_2 for two to three hours at a time, no consistent changes in airway resistance, pulse rate, respiratory rate or subjective complaints were observed. These parameters were measured before, during, and after exposure when the subjects were either resting or exercising; smokers were included in the study but were required to abstain from smoking for eight hours prior to exposure.

In a study of the additive effects on pulmonary function of NO_2 and SO_2 by Abe,[93] five healthy males (ages 21-40), judged to be free from respiratory disease, were exposed on separate occasions to 7.5 to 9.4 mg/m^3 (4-5 ppm) NO_2 and 10.5 to 13.1 mg/m^3 (4-5 ppm) SO_2. Each exposure was for 10 minutes with two week intervals between exposures. Inspiratory and expiratory flow resistance and pulmonary compliance were measured before, during, and after exposure. One second forced expiratory volume, maximal mid-expiratory flow rate, and peak flow rate were measured prior to and 30 minutes after exposure. Inhalation of NO_2 alone did not significantly change lung volumes and peak flow rates, but did cause an increase in both expiratory and inspiratory flow resistance; mean pulmonary compliance decreased slightly 30 minutes after exposure (significant at $p < 0.10$ but not at $p < 0.05$) SO_2 inhalation also caused an increase in inspiratory and expiratory flow resistance which was maximal immediately after exposure. Exposure to a mixture of 4.7 mg/m^3 (2.5 ppm) NO_2 and 6.6 mg/m^3 (2.5 ppm) SO_2 produced a bimodal increase in both inspiratory and expiratory flow resistance which corresponded to an immediate reflex increase due to SO_2 and a delayed increase due to NO_2. As mentioned before, SO_2 is known to cause an immediate reflex along parasympathetic pathways. The mechanism by which NO_2 induces resistance is unknown, but probably different from that of SO_2.

Smidt and von Nieding[94] exposed patients with chronic, non-specific lung disease to a range of concentrations of NO_2 from 1-10 ppm. Above 2 ppm, there was a significant increase in airway resistance reported in 63 patients. Another study by von Nieding et al.[91] among normal males 18-35 years old also demonstrated increased airway resistance and the effect was proportional to NO_2 concentration (range of 1.5 to 5 ppm; no effect below 1.5 ppm). Decreased diffusion capacity was also noted.

In experiments in which healthy male volunteers, 20-35 years old, were exposed to varying concentrations of NO_2, Henschler et al.[80] measured olfactory perception. At 225 $\mu g/m^3$ (0.12 ppm) only a few subjects perceived the odor. At 415 g/m^3 (0.22 ppm) over half perceived odor and at higher concentrations, beginning with 835 $\mu g/m^3$ (0.42 ppm), all subjects immediately recognized the odor. Another study by Shalamberidze[81] demonstrated that the olfactory perception of NO_2 and SO_2 was additive, that is, when both gases were presented simultaneously, lower concentrations of each gas led to odor perception.

Exposure to NO_2 under either acute or chronic situations can elicit morphological changes in lung tissue structures. Direct microscopic examination of exposed tissues usually reveals significant damage within a short period following onset. Ill effects of NO_2 seem to reach their worst extent after about 4 hours, after which general recovery takes place even during continued exposure.[97-99] One of these which persists long after NO_2 exposure is the change in the appearance of connective tissue in the lung.[95] These morphological changes, however aesthetically displeasing, cannot always be correlated with impairment of lung function. On the other hand, these changes have obviously occurred in situations in which NO_2 exposure causes alveolar wall disruption and the loss of ciliar activity in the air passages,[96] or in which lung function has been impaired.[91] One can argue that morphological changes are due to the increased level of proteolytic activity in the lung during the initial stages of exposure, and that the apparent recovery of lung structure is due to subsequent falloff in proteolytic activity.[97-99]

In addition to these effects, inhaled NO_2 alters cellular populations and growth characteristics of several lung cell types. Most notable is the ability of NO_2 to induce the proliferation of Type II alveolar wall cells.[100,101] Whether other types of cells in the alveolar blood-gas barrier are affected by the sudden expansion of the Type II cells is not clear,[102,103] mainly because the roles of these other cell types in the alveolar have not been well established.

Exposure to NO_2 results in the loss of ciliar activity,[96] and in a decrease in the ability to remove foreign objects from the respiratory tract. Hence, the result for a population at risk is an increased susceptibility to respiratory infections. Indeed, the incidence of respiratory infections in animals under controlled laboratory conditions increases during exposure to NO_2.[96,103-108] Attempts to correlate NO_2 exposure with emphysema and related chronic lung diseases have resulted in considerable controversy. The possibility of direct air pollutant participation in the etiology of emphysema became apparent in 1964 when Gross et al.[109] demonstrated that treatment of lung with (digestive) proteolytic enzymes could produce symptoms of emphysema in animals artifically. Since then, several workers[110-116] have presented evidence that NO_2 is a causative agent in emphysema. The work of Freeman et al.[95,98,99,110,111] suggests that emphysema-like symptoms are the result of NO_2-induced structural degradiation in lung due to proteolysis. The fact that leakage of proteins into the lung lavage fluids[95,97,100,102,115,116] occurs would confirm this view. Alternatively, Balchum and co-workers[113,114] have observed the formation of anti-lung antibodies in serum in response to NO_2 attack. The presence of antibodies against lung tissue has frequently been considered diagnostic of emphysema.[113] On the other hand, Kleinerman[97,102] has observed no visible symptoms of emphysema in guinea pigs following exposure to NO_2, even though protein leakage may have occurred. Apparently, proteolytic activity in the lung induced by NO_2 can be at least partially countered by protease inhibitors in the blood.[97]

These studies suggest that NO_2 exposure may subject an occupational or community population to an increased risk of infectious respiratory diseases, emphysema, and increased difficulty with breathing. The primary and secondary effects of NO_2 on the cardiovascular system have not generally been deduced from pulmonary function or respiratory disease studies, but instead, from more direct biochemical observations (see Section 4.3.2). While the incidence of respiratory diseases in a community can be determined fairly easily by epidemiological approaches, it would be difficult to separate the influences of other pollutants known to elicit similar symptoms (see Section 4.1.2.1). Emphysema, which is apparently specific to pollutants such as NO_2 and ozone (see 4.2.3), is a relatively difficult disease to diagnose. It is clear that studies of the types described above could prove immensely helpful in directing epidemiology studies of the health effects of NO_2 exposure.

From the studies discussed above, we can conclude that levels between 1 and 3 ppm (2,000-6,000 $\mu g/m^3$) of NO_2 are likely to produce injurious effects in man. Even though some of these effects are reversible, we should not assume that they constitute an acceptable risk, especially for susceptible individuals. In addition, it is difficult to translate from effective dose in a laboratory animal species to _Homo sapiens_. For example, adult humans are some 50 times more sensitive to the effects of NO on hemoglobin than most laboratory animals.[117] Similar variations for the effect of NO_2 on humans and animals are apparent from Figures 4.2-5 and 4.2-6.[88] One is _not_ justified in assuming that the comparable harm levels in humans are the same as in Figure 4.2-6 for animals. Typically, evidence of morphological changes in the lung are visible at 0.5 ppm NO_2; however, other symptoms of chronic disorders for which these changes are supposed to be indicative do not appear until NO_2 levels exceed several ppm. Depressed resistance to respiratory infections may become detectable at NO_2 concentrations as low as 0.2 ppm (Figures 4.2-5, 4.2-6); however, most studies of disease resistance have utilized level > 1 ppm (2000 $\mu g/m^3$).

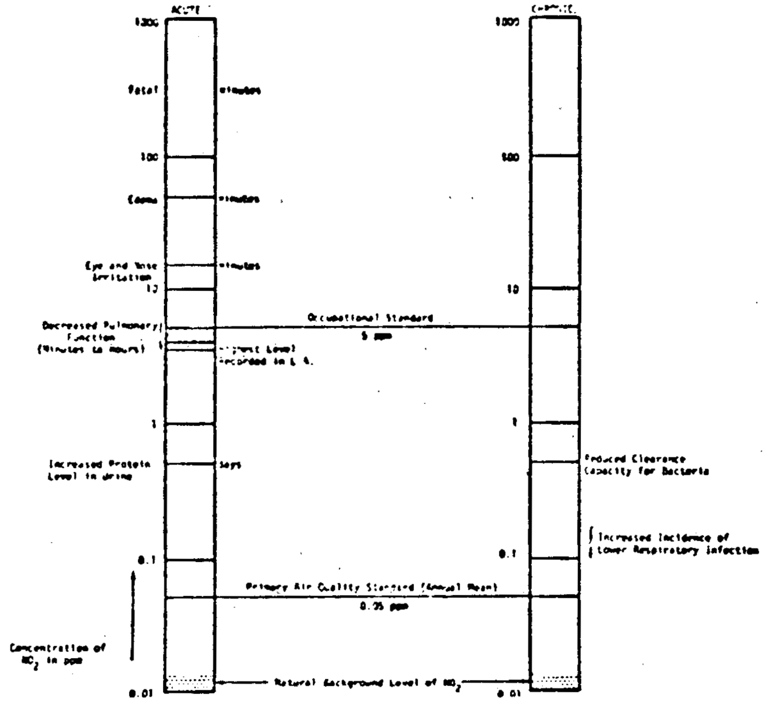

Fig. 4.2-5. Observed effects of NO_2 on humans.

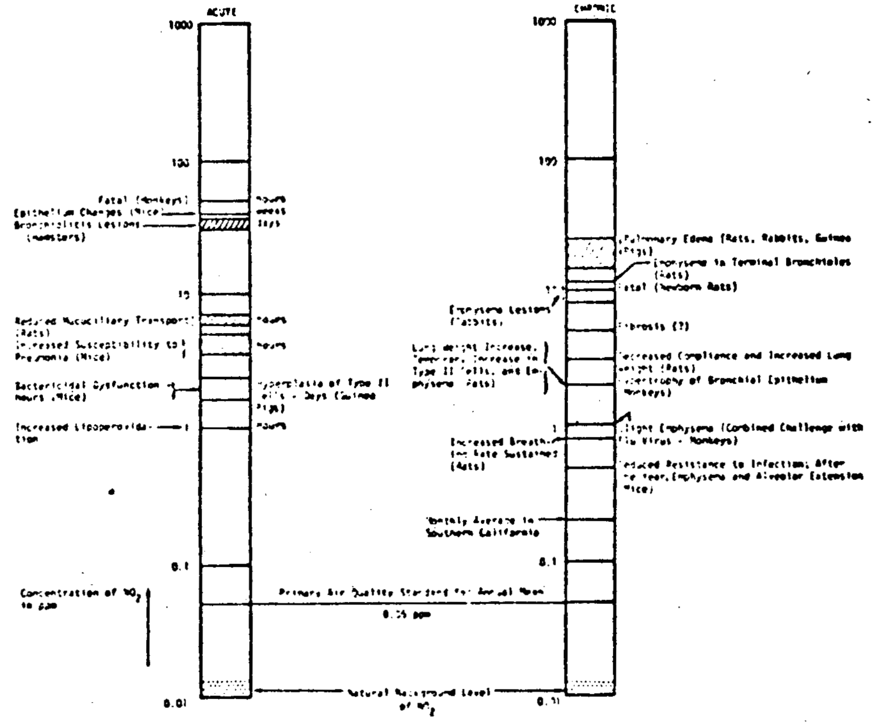

Fig. 4.2-6. Observed effects of NO_2 on animals.

One general criticism of the studies cited above is that they may not be relevant to us because levels of compounds used were higher than normally found in ambient air. The recent (1975) average daily concentrations of NO_x and oxidants in U.S. cities ranged from 0.01 and 0.17 ppm.[87]

The existing air quality standards for NO_2 are based quite correctly on known symptoms of acute inhalation toxicity. No reliable estimate of the margin of safety built into these standards, however, can be made because of the large differences in NO_2 sensitivity between humans and animals. Accordingly, the EPA established an annual average standard of 0.05 ppm presumably based on the premise that chronic effects usually require lower concentrations of pollutant than more acute effects, again with an undefined safety margin.[82] The ARB standard of 0.25 ppm for a 1 hour exposure is based on lung function data from normal and bronchitic adults, and contains a factor of 2 safety margin.[83-84] Neither standard takes into account the possibility of a "detoxification mechanism" in the lung for NO_x, and no information presently exists on the potential of a threshold level at which NO_2 can begin to elicit adverse health effects.

One can summarize the known and suspected effects of NO_2 in humans as follows:
(Standards: 0.05 ppm (annual average), 0.25 ppm (1-hr, California)
5 ppm (8-hr, occupational))
Taste/Odor Threshold: 1-3 ppm
Irritation: 1-4 ppm
Causes Illness: 0.2-0.5 ppm (increased risk of respiratory infection)
Lethal Dose: 50-300 ppm

4.2.3 Ozone

As indicated earlier (Section 3.3.3.1), the principal component of photochemical oxidants is ozone. Other constituents are sufficiently unstable to preclude their routine use in laboratory exposures. Ozone and its derivatives are generally highly reactive with cellular and tissue components, and the health consequences of exposures to even low levels of the oxidant can be damaging. As a result of its chemical reactions with biological materials (Section 4.3.3), the health effects of ozone include lung tissue destruction, emphysema, increased susceptibility to respiratory infections, increased difficulty with breathing, etc. These are summarized in a semi-quantitative manner for animals (Table 4.2-1) and for humans (Table 4.2-2; Ref. 68).

TABLE 4.2-1. *Ozone Dose-Response Chart*[a] *in Animals (68)*

Concentration		Duration	Effect	Species	Ref.
1	ppm	6 hours/day 5 days/week for 62 weeks	Terminal airways distorted, thickened, and fibrous; mild to moderate degree of emphysema	Rat, guinea pig, hamster, mouse	*136*
1	ppm	3 hours	Increased susceptibility to bacterial pneumonia	Hamster, mouse	*133*
1	ppm	1 hour	Formation of carbonyl groups in lung collagen; modification of lung carbohydrates	Rabbit	*130*
0.6-1.3	ppm	7 hours	Disruption of membranes of cells lining lung capillaries; occasionally blood-air barrier completely broken	Mouse	*129*
0.4-0.7	ppm	4 hours	Peroxidation of lung fats	Mouse	*128*
0.5	ppm	6 hours	Suppression of DNA synthesis in alveolar cells	Mouse	*132*
0.5	ppm	6 weeks	Changes in composition of lung fats; edema of lungs; especially severe in Vitamin E-depleted animals	Rat	*68*
0.4	ppm	6 hours/day 5 days/week for 10 months	Walls of small arteries thickened and inner diameter reduced; moderate degree of emphysema; increase in blood factor related to breakdown of proteins	Rabbit	*134, 135*
0.3	ppm	3-5 hours	30% decrease in rate of diffusion of gas from air into blood in the lung	Mouse	*68*
0.2	ppm	1 hour	Release of chemicals (serotonin) from blood cells (platelets)	Rabbit, frog	*137*
0.08	ppm	3 hours	Increased susceptibility to infection with streptococcus (a bacterium)	Mouse	*131*

TABLE 4.2-2. *Ozone Dose-Response Chart in Humans (68)*

Concentration	Duration	Effect	Species	Ref.
1 ppm	30 minutes or longer	Headaches in most individuals	Man	*124*
1 ppm	10 minutes	Rate at which oxygen is transferred from blood to tissue is drastically reduced	Man	*125*
0.6-0.8 ppm	2 hours	Impaired rate of diffusion of gas from air into blood in lung; decreased vital capacity and forced expiratory volume; large individual differences between persons	Man	*123*
0.5 ppm	3 hours/day 6 days/week for 12 weeks	Forced expiratory volume decreased during last 6 weeks; mean decrease of 25% in 6 subjects; interpreted as indicating obstruction of terminal bronchioles and bronchi	Man	*122*
0.3-0.8 ppm	Working day	Subjective complaints of chest constriction and throat irritation	Man	*126*
0.35-0.5 ppm	Two 3-hour exposures separated by 1 hour of rest	Subjective complaints of eye irritation, tightness of facial skin as after prolonged sunbathing, tiredness and difficulty concentrating; feeling of lethargy often persisted for a day or two after exposure	Man	*127*
0.1 ppm	--	Dryness of nasal mucous membranes	Man	*124*
0.1 ppm	1 hour	Airway resistance increased in 2 of 4 subjects	Man	*121*
0.1 ppm	8 hours	RECOMMENDED LIMIT FOR INDUSTRIAL EXPOSURE 1970	Man	
0.05 ppm	--	Irritation of nose and throat in sensitive individuals	Man	*124*
0.02-0.05 ppm	--	Odor threshold	Man	*124*

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[a] Los Angeles air contains approximately the range of ozone concentrations covered by this chart (74).

Ozone is known to increase the specific airway resistance in the lung and respiratory tract, and other changes in respiratory mechanics typical of noxious pollutant irritation[68,118-121] have been reported for ozone at levels below 1 ppm (2000 $\mu g/m^3$). These effects, however, are not identical to those elicited by other pollutants, since the simultaneous presence of other agents (SO_2 or NO_2) continue to elicit superimposable bronchial responses during administration of O_3.[66] However, the operational criteria in these tests show that exposure to ozone, like SO_2 or NO_2, decreases the efficiency of respiration.

Morphological evidence of ozone-induced damage to cellular and subcellular structures in the lung and respiratory tract are quite striking, even in the absence of measured metabolic changes. The work of Coffin and colleagues[138,139] indicates that ozone at very low concentrations (~0.1 ppm) destroys alveolar macrophages. Other investigators have noted significant ultrastructural alterations in the lung tissues of mice exposed to oxidants,[140] changes in ciliated epithelial cells,[138] slight destruction of Type I alveolar wall cells,[141] but no more than temporary harm to Type II alveolar wall cells.[141] These results suggest that ozone (O_3) increases the toxicity of other pollutants by destroying the biological mechanisms for removing other foreign objects, hence, increased susceptibility to infection. Evidently, O_3 does not permanently damage the metabolic machinery in lung. Lungs from animals breathing ozone appear visually to be heavily pitted during the first 48 hours of exposure, but subsequently begin to recover a more or less normal appearance (G. D. Case, et al., unpublished observations).

Oxidants also hinder the exchange of O_2 and CO_2 across the air-blood barrier in the lung. Whether this occurs because of thickening of the gas exchange barrier[42] or its rupture,[129] it is measurable after short duration ($<$ 2 hours) exposures to O_3 levels no more than 1 ppm.[120,123] Knowing that ozone attacks the lung and retards the transfer of oxygen to the body tissues,[68] it is not surprising to find that the toxicity of ozone is aggravated by exercise.[119] Sedentary rats exposed to 1 ppm ozone show no acute symptoms, but the animals die if forced to exercise for a few minutes each hour.[118] It is thus disturbing to realize that athletes complain of chest discomfort after exercising in the Los Angeles area on days with high oxidant levels.[143] Individuals with subclinical or preclinical cardiovascular conditions might be expected to suffer a relatively greater health risk in the presence of oxidants at concentrations lower than ambient levels. Acute exposure to sufficient ozone results in death by pulmonary edema.[68] The concentration at which (fatal) edema occurs can vary --

depending on diet, prior exposure and acclimatization, level of exercise, etc. -- from 0.5 ppm to 50 ppm.[68] Since ambient oxidant levels in the South Coast Air Basin have been known to exceed 0.5 ppm, the acute poisoning aspects of ozone pollution cannot be neglected for community exposure.

The principal long-term problem with ozone stems from its ability to cause diseases in humans. Evidence that O_3 attacks cell structures in the lung[113,115,114,116,144,146] suggests its role as a causative agent in emphysema. Unlike NO_2, however, O_3 concentrations in ambient California air are frequently high enough to trigger such responses. The ability of O_3 to destroy alveolar macrophages marks this pollutant as an increased risk factor in infectious diseases. O_3 has been shown to depress the anti-bacterial defense mechanism in the lung and respiratory tract,[133,139,144,146,147] decreasing the rate at which foreign bodies are removed from the lung and increasing the incidence of pneumonia. Thus far, however, these exposure symptoms have not yet been reported in the morbidity and mortality (epidemiology) statistics of "high oxidant" areas. Epidemiological studies have not established the detailed relationship between photochemical oxidant exposure and health effects. Some associations between oxidant exposure and health effects such as asthma, pulmonary function, and athletic performance have been suggested.

Oxidants are one class of pollutant, therefore, for which existing ambient air quality standards are based largely on biochemical and histological criteria. The current EPA and ARB standards of 0.08 ppm O_3 represent a threshold concentration at which adverse biochemical and histological changes can be observed.[144] There is no margin of safety factor employed in the case of O_3 -- as there is with other pollutants such as SO_2, NO_2 and sulfates -- because any safety margin factor greater than 1.5 - 2.0 would push the O_3 standard below the global natural background ambient O_3 concentration (0.05 ppm). Consequently, there is no real hope of making the air totally safe to breathe from the point of view of oxidant effects on health. However, in view of the acute toxicity effects which emerge from exposures to O_3 in the 0.1 - 0.5 ppm range, oxidant control is quite rightly an area of primary concern.

In summary, one can express the effects of O_3 on humans in the following terms:

(Standards: 0.08 ppm (1-hour exposure))
Taste/Odor Threshold: 0.02 - 0.05 ppm
Irritation: 0.4 - 1.0 ppm
Causes Illness: 0.1 - 0.5 ppm (increased risk of respiratory infection)
Lethal Dose: 1.0 - 40 ppm.

The rather wide ranges for irritation, illness, and mortality reflect variety in sensitivity due to exercise, pre-exposure history, etc. The absence of a reasonable margin of safety factor can be interpreted to be adequate for any pollutant and the frequency of ambient concentrations of O_3 in the 0.2-0.6 ppm range--especially in California--point out the extent of the danger of oxidants to community health.

4.2.4 Particulates

Airborne particulate matter can enter the body either directly, by deposition in lung and respiratory tract, or indirectly by absorption in food and water supplies. Because of the physical and chemical complexity of particulates, it would be difficult to assess in any general way the effects on human health by either mode of ingestion. Since the effects of waterborne particulates would be expected to arise strictly from the toxic behavior of specific substances which have to be individually examined, we shall be concerned with effects of inhalation of airborne particles on human health.

Atmospheric aerosols can stimulate responses in the body which are due either to the physical deposition of particles in the respiratory tract, or to the chemical interactions of substances contained in or on the particles with cell structures. There are, in essence, health effects which are independent of the chemical composition of the deposited particles, as opposed to health effects due to toxic substances contained therein. The latter are discussed more fully in Section (4.3.4). The composition-independent health effects are generally observed as changes in foreign body clearance rates or in pulmonary mechanics.[148]

In order for any kind of particulate matter to affect the health of an individual, particles must be deposited. Figure 4.2-7 shows typical size-distribution curves for particles deposited in the upper respiratory tract and those which collect in the lung.[148] Total particle deposition for particles larger than 5 μm MMD (mass median diameter, see Section 3.1.1.3.1) is nearly 100 per cent, nearly all of which is trapped in the upper tract. As the particle size drops below 1μm MMD (respirable size range), very few of the particles are trapped in the nose and throat, and considerably more reach the lung spaces. However, deposition in the lung is far from complete, since the fraction of particulate matter retained in the pulmonary regions range from about 15% (1 μm MMD) to 70-80% at 0.01μm MMD.[148] Evidently, a large fraction of the fine particulate matter can be exhaled[148,149] without impaction. Desaedeleer and

Winchester[149] have shown that the size at which maximum exhalation occurs lies between 0.25 μm and 0.5 μm MMD.

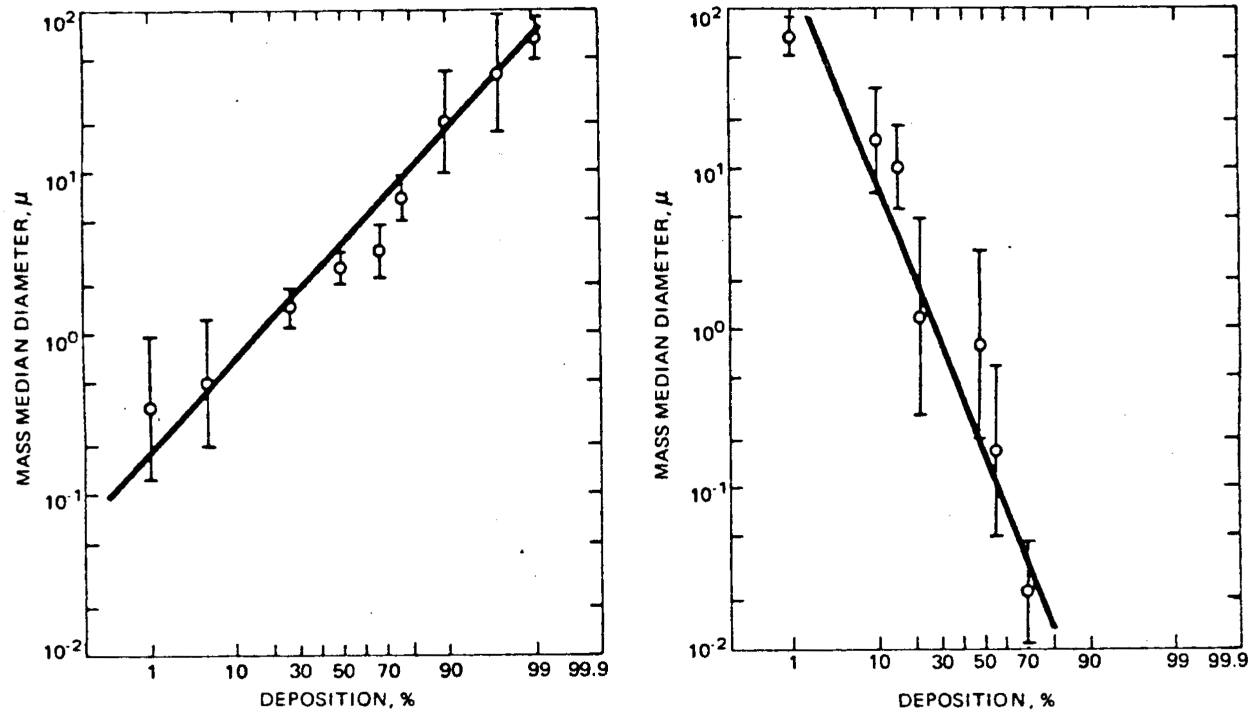

Fig. 4.2-7 Particle deposition in the Naso-Pharyngeal Compartment (Left) and in the Pulmonary Compartment (Right) as a function of a particle volume. Data are plotted as a Log-Probabitity Function (Ref. 148).

One should keep in mind that particle deposition in the airways depends heavily on the degree of obstruction. If a portion of the respiratory-pulmonary tract is blocked, as in chronic lung or respiratory disease or in cases of severe irritation due to other pollutants, subsequent particle deposition will occur preferentially in regions that are still free of obstruction.[150] This means that continuing exposure to atmospheric aerosols will result in a uniform blanket of particles in healthy lungs, but in a disproportionately aggravated deposition burden in lungs with partially obstructed air passages.[150,152] Further, in cases of existing constriction, more of the particles, regardless of size, reach the alveolar spaces.[152] Consequently, the effects of particulate air pollution on diseased individuals should be much more dramatic than effects on healthy specimens, irrespective of the chemical composition of the aerosol.

The primary physical effect of any airborne particle landing in the lung or respiratory tract is to stimulate coughing to clear out foreign matter. In many respects, this is an irritant response,[151] and is very much like that associated with other irritating air pollutants. There is evidence that pathologic alterations in the airway "sensitize" the nerve receptors responsible for bronchoconstriction responses, so that discharge occurs at a lower threshold.[151] In addition, particulates often elicit an inflammatory response which results in the entrapment of a particle within a fibratic network. This occurs with most of the biologically active particulates.

Several cleansing mechanisms operate to clear out the deposited particles. These include a) absorption into the lymphatic system, b) ejection into the throat by ciliary propulsion, c) engulfment by alveolar macrophages and d) solubilization; and are reviewed more extensively by Morrow,[153] Green,[154] and the EPA.[148] The prevailing mode of clearance depends on the solubilities of the substances entrained in the lung and the respiratory tract, the disposition site, and particle size.[148,153,154] Sulfates, nitrates, and ammonium species are generally sufficiently soluble to be taken up into cells for metabolism, or into the bloodstream.[66] Lead and carbon, on the other hand, typically accumulate in the lymph system.[36,155] Particles smaller than 0.01μm diameter can pass directly through the air-blood barrier in the lung and into the bloodstream.[1]

The site of deposition and the mechanism for clearing trapped aerosol particles govern the rate at which particulates can be removed from the lung and respiratory tract.[148] As a rule, clearance of particles is rapid from the pharyngeal region, requiring only minutes to a few hours.[155-157] Clearance from smaller airways is definitely slower.[151,158,159] Material in bronchioles only clears after several days or weeks, but material deposited in alveoli may show no evidence of clearance even after 18 months.[151,153,154,156,157] Smoking, and other pollutant exposure, can drastically retard particle removal.[157]

For substances of approximately similar size and solubility, clearance rates from the various portions of the airways are surprisingly independent of particle composition.[148] This is relfected in the good agreement obtained by numerous workers on the particle deposition curves for different types of test aerosols.[27,36,148,149,151,153,154,156-161] Small differences in clearance rates for similar-sized particles containing carbon versus those containing lead have been reported;[159] however, the present data base is insufficient to distinguish the different removal kinetics for more than a few laboratory test aerosols. Virtually no studies involving real-life urban particulates of known composition have as yet been attempted.[161]

Existing air quality standards for particulates are based rather tentatively on mass deposition loading in the respiratory tract and the poorly known rates of particular clearance.[148] The sole criteria for particulates outlined in both the EPA and California standards[148] is total suspended mass. No provision is made in any of the regulations for particle size or chemical composition (except for lead and sulfates) or particle origin.[148] While deposition and clearance of aerosols may be independent of particle compositon, they are strongly affected by particle size. Furthermore, the toxic properties of airborne particulates -- especially their carcinogenicity -- are obviously highly dependent on chemical composition as well as particle size and surface distribution of the constituents. With the information presently available on size distributions and chemical composition of atmospheric aerosols, scant as it is, regulatory agencies concerned with air quality are becoming able to promulgate particulate standards more directly related to health effects of the various kinds of aerosols. However, neither the EPA nor the ARB has advanced in this direction, in spite of data available from the California ACHEX program (see Section 3.1.1.3).

4.2.5 Carbon Monoxide

Biochemical evidence (Section 4.3.5) indicates that both CO and NO should have virtually identical health effects. While fossil-fuel-fired power plants emit rather insignificant amounts of CO, they produce substantial NO emissions (Section 3.1.1). However virtually no physiological data exist for NO in either humans or animals, so that the existing body of knowledge of health effects for CO serves as a basis for understanding the effects of NO.

The "health effect" of CO (and presumably NO) arises from its ability to displace oxygen from hemoglobin in the blood. In order to prevent acute tissue hypoxia from occurring during exposure, the cardiovascular system must compensate by increasing the rate of blood circulation. This places an added stress or burden on the cardiovascular system. The more serious health effects begin when the circulatory system starts to fail (see Ref. 68,162-167 for review). Table 4.2-3 summarizes the various accessory symptoms which can be traced to the action of CO on the cardiovascular system. The studies cited[68] show that when the carboxyhemoglobin levels exceed 2% of the total hemoglobin, there are already signs of insufficient oxygen delivery to the tissues.

Existing ambient air quality standards for CO have been promulgated by the EPA[162] on the basis that a body burden of 2% carboxyhemoglobin is unacceptable. The occupational standard[164] is based on a threshold limit of 5% for the maximum acceptable threshold. The concept of body burden analysis is described in Section 4.3.5.

4.2.6 Hydrogen Sulfide

Hydrogen sulfide (H_2S) is an important emission from geothermal steam areas, but is not a significant by-product of large-scale fossil fuel combustion. Studies of its toxicity to humans and animals are limited primarily to occupational exposures to or unusual community episodes.[175] H_2S is a foul-smelling gas which can be detected in the air by humans at concentrations on the order of a few parts per billion (ppb), and is toxic at much higher levels.[175] Its characteristics can be summarized as follows:[175,176]

(Standards: 0.03 ppm (1-hour California)
10 ppm (8-hour occupational))
Taste/Odor threshold: 0.03
Sensitivity to light: 0.003 - 0.004 ppm
Irritation: 10 - 40 ppm
Causes illness: see below
Lethal dose: 100 - 800 ppm

Ambient air seldom contains more than 0.1 ppm H_2S and even during severe episodes, 0.3 ppm is a high level.[175] The summary of health effects given above considers only the acute interactions of the pollutant. The only well-documented study of the health effects of H_2S[177] is the result of an episode which occurred in Terre Haute, Indiana in May and June 1964. There, H_2S evolving from an industrial waste treatment lagoon generated ambient air concentrations of the pollutant between 22 and 300 ppb H_2S. Predictably, citizens in the area began complaining of nausea, shortness of breath, headaches and insomnia.[177] No deaths during this period were attributed to the H_2S exposure and no etiology of these symptoms could be elucidated.

H_2S can be detoxified in the body by the same metabolic pathway as SO_2, by means of the lung or liver sulfite oxidase-rhodanese systems as shown in Figure 4.3-1 of Section (4.3.1).[178] No reliable assessment of the total H_2S

Table 4.2-3. Carbon Monoxide Dose-Response Chart (68)

Concentration	Duration	% COHb	Effect	Species	Ref.
300-400 ppm	Several hours or more depending on activity	30-40[a]	Severe headache, weakness, dim vision, nausea, collapse	Man	68
200-300 ppm	Several hours or more depending on activity	20-30[a]	Headache, throbbing in temple	Man	68
80-200 ppm	Several hours or more depending on activity	10-20[a]	Possible slight headache, dilation of skin blood vessels	Man	68
110 ppm	1-2 hours	4-7	Reduced vigilance for visual task	Man	172
100 ppm	Short exposure	5-10	Impaired performance on psychological tests such as arithmetic	Man	68
			Effects may occur at still lower levels of COHb, but there is some uncertainty about the exact COHb levels	Man	168,162
100 ppm	11 minutes or longer	Unknown	Impairment in judgment of time intervals	Rat	170
50 ppm	8 hours	7-8 (calculated)	RECOMMENDED LIMIT FOR INDUSTRIAL EXPOSURE 1970	Man	
Brief doses of high concentration		4 and higher	Rise in visual increment threshold, the ability to detect a dim light superimposed on a uniform field	Man	173,171
50 ppm	49 minutes	3	Rise in visual increment threshold	Man	169
50 ppm	27 minutes	3	Reduced visual acuity	Man	169
50 ppm	75 minutes or longer	1.5-2.5 (Calculated)	Impaired judgment of time intervals in nonsmokers	Man	168
50 ppm	1 hour or longer	Unknown	Alterations in electrical responses of visual nervous system	Rat	174
0 ppm		0.4	Level of COHb normally maintained in blood by metabolism of hemoglobin	Man	168
			In disorders of hemoglobin and red blood cell metabolism this baseline value can be much higher	Man	166

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[a] Equilibrium values given in Goldsmith and Landaw (1968).

burden which can be safely handled by the body is presently available. Unmetabolized H_2S can cleave the disulfide bridges of proteins, thus altering their structure.[178] In addition, H_2S can react with hemoglobin[179] resulting in a decrease in the oxygen-carrying capacity of blood. H_2S has also recently been shown to combine with cytochrome oxidase (an essential enzyme in respiratory energy conservation), in a manner which is nearly identical to that for hydrogen cyanide.[180,181] Hence its toxic reaction is the same as for HCN. H_2S is also known to combine with several enzyme-bound metals such as zinc and copper, as well as the more toxic metals Cd, Hg, Ag, and Pb. The extent to which reaction of H_2S with metal proteins in the body contributes to the symptoms of the H_2S toxicity has not been thoroughly characterized.

The Terre Haute H_2S episode of 1964 indicates a potential danger in the disposal of sludge from fossil fuel and geothermal power plant flue gas treatment systems. Both types of sludge are rich in sulfur compounds, and the introduction of any organic matter would create an ideal medium for the evolution of H_2S either by direct chemical or bacterial action. Methods for preventing the emission of H_2S from sludge ponds, either by chemical or biological[182] regulation, are available and inexpensive.

Currently existing air quality standards for H_2S include an 8-hour occupational standard (10 ppm), which is based on the threshold concentrations for acute eye and lung irritation.[175,176] In addition, the California Air Resources Board has promulgated an ambient air quality standard of 30 ppb (0.03 ppm) for H_2S, based primarily on the odor and public nuisance threshold for humans. In view of the public complaints and chronic poisoning cases reported during the Terre Haute episode,[177] one could also reasonably justify the California standard on the basis of documented long-term health effects observed at 0.3 ppm and incorporating a margin-of-safety factor of 2 - 10 fold. In view of the ability of the human body to detoxify H_2S (at least in the liver), a factor of 10 margin-of-safety may not be necessary. However, it would probably be unwise to relax the existing standard to a level beyond 0.06 ppm H_2S, since the threshold for adverse chronic health effects due to H_2S has not been well defined.

It should be noted that while the present standards reflect the traditional values for the threshold for H_2S effects, the data underlying these standards has become controversial. If one assumes that the standard should be set at the threshold for odor perception (which was the past criterion) then the standard should be lowered by a factor of 3 to 5 to the more recently accepted value for the odor perception threshold. These ambient air quality standards are presently being reconsidered (see Ref. 183 for a more complete discussion).

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4.3 Biochemical and Genetic Interactions

It is a central tenet of toxicology that a substance is poisonous if and only if it interferes with an essential biochemical function in living organisms. Understanding how metabolic processes may be altered by pollutants is basic to understanding their health effects and, possibly, to determining standards and controls. While all of the interactions described in this section are necessarily biochemical in origin, we emphasize genetic effects such as carcinogenesis, teratogenesis (induction of malformations such as birth defects), and mutagenesis because of the fundamental manner in which environmental agents may be involved. Ordinarily most pollutants which affect a specific metabolic reaction in the body elicit characteristic observable health effects (such as discussed in section 4.2) shortly after the onset of exposure. Alternatively or additionally the pollutant may react with the cell's genetic material in such a way that no detectable malfunction takes place until the next cell division (which may be days, weeks, or years later). A third possible fate for a pollutant is detoxification into harmless products; keeping metabolic processes intact in the face of pollutant exposures may be a fruitful and important area for future medical research.

According to biochemical criteria, the concentration of a pollutant at which adverse health effects begin to occur, the threshold limit value, is determined by the rate at which body defense mechanisms can remove the pollutant either by metabolic detoxification or physical clearance. When pollutant levels exceed the threshold, biochemical, physiological, cytological (cellular), and immunological changes can occur which place susceptible individuals in jeopardy. Hence, biochemical information can be used reliably, in conjunction with supporting physiological or epidemiological evidence, in the formulation of standards.

4.3.1 Sulfur Oxides

The effects of sulfur oxides (SO_x, composed of SO_2, SO_3, H_2SO_4, and their salts) on public health and the physiological function of respiration have been reviewed quite extensively (esp. refs. 1-7; see section 4.2.1). However, somewhat less attention has been devoted to the study of their effects at the biochemical level. Two routes of entry into the body exist for the oxides of sulfur: absorption of sulfites and sulfates by the gastro-intestinal tract; and inhalation of SO_2 gas and SO_3, sulfuric acid (H_2SO_4) mist, and sulfate aerosols into the respiratory tract and lungs. Vastly different effects are observed for the two modes of entry[8-11]. Once in the bloodstream and body tissues, sulfate ($SO_4^=$) is generally harmless, and is readily excreted[11]. In fact, the EPA water quality standard for sulfate was dropped because the evidence for any health effects for ingested sulfates was insufficient to warrant regulation. Adverse effects resulting from inhalation of sulfates might be attributable to locally high acidity or salinity rather than from any metabolic action of sulfate, since chemical reaction of the sulfate itself has never been observed.

SO_2 and sulfites, on the other hand, react quite readily with many cellular constituents. These include derivatives containing thiamine[12,13], epinephrine (adrenalin, ref. 14), vitamin K[15], riboflavin[16,17], folic acid[18], and niacin[19-20]. Of these reactions with SO_2, only the breakdown of the vitamin thiamine is important[10] in the mechanism of SO_2-aggravated cell destruction. Evidence of thiamine destruction in cells of the respiratory tract and the lung should appear as acute alteration in carhohydrate metabolism, as observed by Lamb and Reid[21,22]. None of these reactions is likely to be important in any other bodily system.

Once SO_2 or sulfite enters the bloodstream, it is immediately incorporated into the antibody protein α-globulin as its thiosulfate ($R\text{-}SSO_3^-$) ester.[11] (Reaction 1, Fig. 4.3.1). Interestingly, no incorporation into red blood cells or other blood proteins is detected[11]. The thiosulfate ester ($R\text{-}SSO_3^-$) is eventually metabolized according to the enzymatic reaction scheme shown in Figure 4.3-1[10]. At least 85% of the total inhaled SO_2 which enters the bloodstream is oxidized to inert sulfate by this process[10,11,23,23]. The key enzyme in this chain is sulfite oxidase (Reaction 7 of Fig. 4.3-1) which serves to directly oxidize sulfite to sulfate in cells and tissues[24]. Mudd et al.[25] have reported that a genetic deficiency in sulfite oxidase leads to neurological disorders and death in humans. There is sufficient sulfite oxidase activity in the liver and other body organs to detoxify up to about 40 grams (1.4 ounces) of sulfite per 100 kilo-grams (220 pounds) of body weight[25,26], which is far more than the amount of sulfite absorbed during inhalation of 600 ppm SO_2. Consequently, the toxic effects of inhaled sulfur oxides should be confined to the lung and the respiratory tract of humans and animals. Sulfite oxidase activity has been detected in the lung[27] and in various cells of the respiratory tract[21,28], so that the toxicity of SO_2 is governed by the existing levels and rate of synthesis of sulfite oxidase in the various cell types which are present. Any SO_2 (as sulfite) which is not metabolized can remain to kill cells. Therefore, because a detoxification system exists for SO_2 and sulfites, chronic exposures to low-level SO_2 in the air should not elicit health effects comparable to a brief acute exposure to high SO_2 concentrations, and one is not justified in extrapolating from one case to the other.

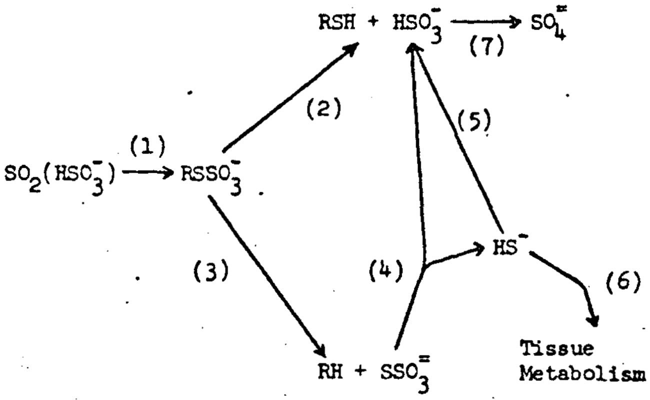


Fig. 4.3-1 *SO_2 and sulfite metabolism in the body. Reaction (2) requires reduced nicotinamide adenine dinucleotide phosphate, and Reactions (5) and (7) require oxdizing equivalents. Reactions (2) - (7) are enzyme-catalyzed. From Petering and Shih (Ref. 10).*

An additional biochemical reaction of SO_2 with implications for health effects is its ability to deaminate cytosine.[29] Several workers[8, 29-31] have suggested on this basis that SO_2 is a mutagen, and that community exposure to this substance may be carcinogenic in humans. However, the mutagenic potency of sulfites under physiological conditions is quite low,[10] and the ability of SO_2 to cause cancer in humans has never been established. (See bibliography of refs. 32-33.)

SO_x exposures used in "chronic" physiological studies (section 4.2.1) are higher than those ordinarily experience by most urban populations over the course of a year, and total integrated doses higher than exposures during "smog episodes".[3] Chronic effects of even lower SO_x levels on humans and animals would be still more difficult to detect, especially if the sulfite detoxification mechanism[10,11,23-28] fixes a threshold concentration below which there cannot possibly be any adverse health effects.

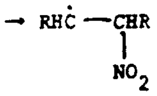
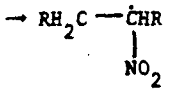
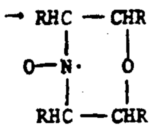
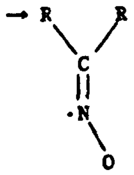
Existing ambient air standards for SO_2[1] and sulfates[2,6] are based on the results of epidemiological surveys and also on the physiological effects of both pollutants on respiratory mechanics. Clearly, no biochemical basis presently exists for any of these standards. Most of the epidemiological data cited by the EPA as its justification for SO_2 standards[14] has recently been thought to have implicated sulfates (as H_2SO_4) as the causative agent in mortality and morbidity[2,5,6,7,8,9]. The California sulfate standard of 25 $\mu g/m^3$ is based on the premise that ambient sulfate levesl a factor of 10 below the threshold concentration for measurable changes in respiratory function are a safe limit for the general population. The data base has been used to establish this H_2SO_4 health effects threshold in the vicinity of 300 $\mu g/m^3$, and to justify the factor of 10 safety margin as reasonable.[2] The SO_2 standard was originally also predicated on a factor of 10 or so margin of safety.[1] However, in view of difficulties in resolving health effects due to SO_2 from those due to other accompanying pollutants this standard probably should be reexamined.

4.3.2 Nitrogenous Pollutants

The oxides of nitrogen are relatively strong oxidants, and their reactions in the body largely reflect this fact. Two routes of entry into the body exist for the oxides of nitrogen: absorption of nitrites (NO_2^-) and nitrates (NO_3^-) by the gastro-intestinal tract; and inhalation of NO, NO_2, and nitrate (HNO_3) aerosols. Because a large number of interconversions among the types of nitrogen oxides can occur in the body, the fact that a single class of biochemical reactions occurs with all of the NO_x species does not mean that their health effects are similar. Several other processes may also occur (Table 4.3-1).

The most obvious and easily detectable biochemical reaction of NO_x is the oxidation of hemoglobin or oxyhemoglobin from the ferrous form to the ferric (methemoglobin). The clinical consequences of hemoglobin oxdidation include cardiovascular stress and possibly other symptoms of tissue hypoxia, similar to those described for carbon monoxide (section 4.2.5). This reaction occurs during exposure to either NO[34-42] or NO_2[38-42] in the presence of air. Oxidation of hemoglobin by NO and NO_2 in the air has been studied in humans under occupational hazard conditions, and has resulted in the current OSHA standards for both NO (25 ppm) and NO_2 (5 ppm)[41] in the workplace[41-43]. Oxidation

Table 4.3-1. Reactions of Nitrogen Oxides in the Body.

	Reaction	Site	Health Burden	Reference
a)	$NO\cdot + \text{Hemoglobin} \xrightarrow{O_2} \text{Methemoglobin}$	Blood	Hypoxia-induced-cancer	(34-42)
b)	$NO_2\cdot + \text{Hemoglobin} \rightarrow \text{Methemoglobin}$	Blood	Cardiovascular burden	(38-42)
c)	$NO_2^- + \text{Hemoglobin} \rightarrow \text{Methemoglobin}$	Blood	Cardiovascular burden	(43,44)
d)	$NO_2^- + H^+ + \text{Amines} \rightarrow \text{Nitrosamines}$	Tissues	Cancer	(46,47)
e)	$2NO_2 \xrightarrow{H_2O} NO_2^- + NO_3^-$	Universal	See above	
f)	$NO\cdot + NO_2\cdot \underset{H^+}{\overset{H_2O}{\rightleftharpoons}} 2\ NO_2^-$	Universal	See above	
g)	$NO_3^- \rightarrow NO_2^-$	Intestines	Bacterial action	(46,47)
h)	$NO_2\cdot + \text{Olefins } (RHC{=}CHR)$			
i)	 $\rightarrow RH\dot{C}-\underset{NO_2}{\underset{\vert}{CHR}}$	Lung, lipids	Respiratory disease	(53,54)
ii)	 $\rightarrow RH_2C-\underset{NO_2}{\underset{\vert}{\dot{C}HR}}$	Lung, lipids	Respiratory disease	(53,54)
iii)		Lung, lipids	Respiratory disease	(53,54)
iv)		Lung, lipids	Respiratory disease	(53,54)

of hemoglobin also occurs following the ingestion of nitrites[43,44] and nitrates, which are reduced to nitrites by intestinal bacteria[43,44]. This phenomenon accounts for the acute toxicity of nitrites, and is a major criterion for existing food and drinking water quality standards for nitrites and nitrates[44]. In addition, nitrites can react with endogenous amines in foods to form nitrosamines -- which are carcinogens. This factor is responsible for regulation of these agents in cured meats. However, it is possible to generate nitrosamines in the body from NO_x derivatives, and nitrosamines have been detected in community air in many urban areas of the U.S.[46,47].

Only recently has the role of community exposure to NO and NO_2 in urban ambient air received any significant attention with regard to the direct reactions with hemoglobin[45]. Methemoglobin burdens in school children have been found to range between 2.0 and 5.2 per cent of the total hemoglobin in several urban communities[48,49], as opposed to the 0.2-0.7 per cent range for a background level in humans[39,43]. NO_x in the atmosphere was implicated as a major causative factor for methemoglobin burdens in these studies[48,49]. The work of Case et al[39,40] indicates that NO may elevate the methemoglobin burden, regardless of the presence of NO_2, so that either gas may have been responsible for the results of the epidemiological studies[48,49]. One should note that most routine monitoring of NO_x in urban areas equates NO_x with NO_2 and neglects NO. Consequently, the promulgation of an air quality standard at 3 ppm (3.75 mg/m^3) for NO, and a monitoring program for NO, based on the known effects of CO on hemoglobin and human health[50], may be justifiable[39,40]. NO is not known to elicit any other direct health effects, although its metabolites may be involved in carcinogenesis.

Nitrogen oxides, however, are generally considered dangerous pollutants in the ambient air not because of their reactivity with hemoglobin <u>per se</u>, but rather because of specific effects on the lungs and respiratory tract[51,52]. These are due strictly to NO_2, whose reactions with lung lipids are given in Table 4.3-1.[53,54] and whose effects are generally confined to the respiratory system. These are "pseudo-oxidation" reactions, and characteristically result in the destruction of cell membranes[30,33], frequently called lipid peroxidation in spite of the fact that peroxides are not involved. Most sensitive to NO_2 exposure are the alveolar macrophages and type II alveolar cells, which are responsible for foreign body removal and drug/hormone metabolism in the lung[55]. Not surprisingly, a number of histological, physiological, and pathological changes occur in the lung as a result of acute or chronic exposures to NO_2. These have been extensively documented and are reviewed in section (4.2.2).

NO_2 exposures between 0.1 ppm and 10 ppm (180 - 18,000 $\mu g/m^3$) are also believed to be responsible for a number of enzymatic alterations. NO_2 stimulates the activity of glutathione peroxidase and glucose-6-phosphate dehydrogenase (both essential for preserving membrane integrity, and for carrying out detoxification). On the other hand, NO_2 increases the leakage of lysozyme (a serum protein) into lung fluids[56,57] and oxidizes substrates in lung and blood cells[58]. Most importantly, NO_2 attacks the lung cells which produce prostaglandin-type hormones[55,59], with the result that the prostaglandin precursors accumulate in the alveolar fluids and alter the surface tension of the surfactant[55,59,60]. While it is not yet clear what immediate implications a change in specific enzyme levels in lung due to NO_x exposure have for human health, the appearance of proteins and lipids in the lung lavage fluid means that cells are being killed. There is evidence that hemolytic anemia may be one manifestation of these enzyme function alterations[56,59,63,64].

One can view the accumulation of unsaturated fatty acids either as an indicator of a poisoned metabolic process or as a physiological defense mechanism against further NO_2-induced cell destruction, since unsaturated lipids serve as an NO_2 trap[53,54]. In any case, the production of enough lipid matter in the lavage fluid results in the thickening of the air-blood exchange barrier[61], and eventually in pulmonary edema[4,45,51,52,62,63,64] which is frequently fatal. The effect of a subclinical form of pulmonary edema caused by chronic exposure to ambient levels of NO_2 on the cardiovascular burden has not been investigated. Any adverse effects due to the action of NO_2 on the air-blood barrier in the lung would, of course, compound the stresses due to the reactions of NO and NO_2 with hemoglobin. Hence, the possible involvement of NO_x in the etiology of cardiovascular disease ought to be examined more closely.

A fact that mitigates the association of biochemical reactions of NO_2 with specific health effects is that few of the measurable changes are permanent. Ill effects of NO_2 seems to reach their worst extent after about 24 hours exposure. Subsequently, recovery processes take over, even during continued exposure[71-73].

While neither NO nor NO_2 is thought to cause cancer per se, metabolic derivatives of these two pollutants can be very potent mutagens and carcinogens. Nitrite ion (NO_2^-) may be formed during the metabolism of NO in the blood[40], and its formation during the dismutation of NO_2 in water is well known (Table 4.3-1). And, of course, there exist ample supplies of nitrites in food and water for exposure. The acid form of nitrite (HNO_2) was one of the first chemical mutagens ever used in experimental genetics[65,66], and alters genetic information by substitution in the genetic code (HNO_2 deaminates cytosine and adenine in DNA). While HNO_2 is weakly mutagenic in microorganisms[32,33], it is reported to be only a "moderate" carcinogen in humans and animals[32,33,67]. (???)

In addition, many organic amines, which may be formed by soot-catalzed reactions of NO[69,70], are known to be carcinogens[32,33,67]. Further reaction of HNO_2 with organic amines, either in the air or in the body, gives rise to nitrosamines[46,47] which are mutagens and among most potent carcinogens known[32,33,67]. Tumors triggered by nitrosamine exposure are relatively nonspecific, and may be distributed among every cell type in the body[46]. Hence, one might expect mortality rates from nitrosamine-induced cancers to be higher than for other kinds. The detection of nitrosamines in many urban atmospheres[46] has rejuvenated interest in the question of why cancer morbidity and mortality rates are higher in urbanized areas of the U.S.[68]. Clearly, since most work with nitrites and nitrosamines as mutagens and carcinogens has been qualitative, dose-response data are scant.

Biochemical and genetic evidence, although somewhat fragmentary, are sufficient to point out a clear warning on the dangers of nitrogen oxides in the environment. However, there has been insufficient examination, at the biochemical level, of the threshold concentrations of NO and NO_2 for changes in metabolic function. Consequently, existing standards are predicated largely on the basis of physiological and histopathological studies. No support for a biochemical detoxification mechanism has appeared for either NO or NO_2, as opposed to the case of SO_2. NO and NO_2 may, in turn, adversely affect the detoxification of other air pollutants. Some synergisms may be explained on this basis. The threshold concentrations at which these adverse changes begin to occur has never been defined.

4.3.3 Oxidants

Oxidants are operationally defined as a class of compounds, excluding the nitrogen oxides, whose common feature is the ability to oxidize potassium iodide[74]. By far, the most prevalent constituent of "oxidants" in the atmosphere is ozone (O_3); however, other substances such as peroxyacetyl nitrates (PAN), hydrogen peroxide (H_2O_2), hydroxyl radical (OH) are also present. Most of these compounds are either free radicals themselves or are free radical precursors, and are therefore extremely reactive and relatively unstable. As a result, oxidants may enter the body through inhalation, but are unlikely to be fixed in ingested liquids or solids. Most of this discussion concerns itself with ozone, since the relatively few investigations of other oxidants[75] suggest that their health effects are similar.

Ozone is most reactive with olefins (unsaturated organic hydrocarbons and fatty acids, designated RCH=CHR), and generates the corresponding ozonides in non-aqueous solvents[76-77]. Mechanisms such as Figure 4.3-2 have been proposed for this class of reactions.

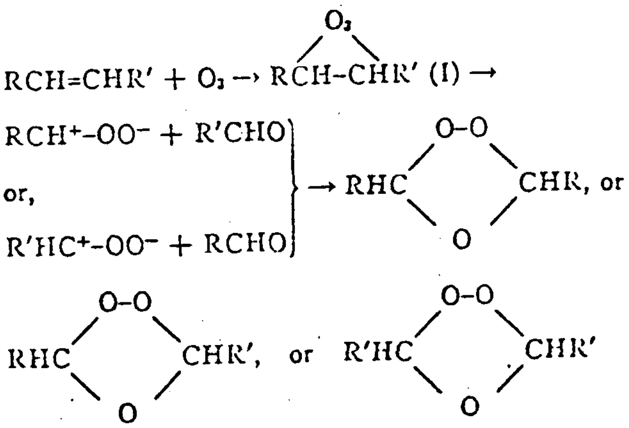


Fig. 4.3-2. Reaction of O_3 with olefins.

The ozonides can decompose to free radical species (RO_x) and hydroperoxides (R-O-OH), but the ultimate products of the reaction are aldehydes (R-CHO), organic peroxyacids and hydrogen peroxide. Ozone also attacks other classes of organic compounds[76], and cross-links proteins. In water, O_3 can also decompose into hydroxyl radical (OH), which reacts vigorously with any organic compound, and into the somewhat milder oxidant superoxide ($O_2^{\cdot-}$). All of these reactions of O_3 render it useful as a bacteriocidal agent in water purification, such as in situations where organic contamination precludes the use of chlorine[78].

The biochemical significance of these reactions is obvious. Lung surfactant fluid is rich in olefins (unsaturated fatty acids) as are the lipids of all cell membrances. That O_3 attacks these systems is now well established[74,76,79]. Hydrolysis of O_3 gives rise to the following scheme of reactions[76-84]:

$$O_3 + H_2O \xrightarrow{OH} OH\cdot + O_z^{\overline{\cdot}}$$

$$O_2^{\overline{\cdot}} + \text{superoxide dismutase} \longrightarrow O_2 + H_2O_2$$

$$H_2O_2 + O_2^{\overline{\cdot}} \longrightarrow OH\cdot + O_2$$

$$OH\cdot + R \longrightarrow R\text{-}OH$$

While no one has as yet demonstrated the simultaneous occurrence of all four reactions, individual reagents have been mapped in the body[76-85]. Some of these are important for essential metabolic processes such as bacteriocidal activity[85].

Inhalation of O_3 at levels between 0.2 ppm and 0.5 ppm (380 - 950 $\mu g/m^3$) elicits measureable alterations in selected enzyme functions in humans[86] and animals[56]. These studies agree that O_3 depresses glutathione, glutathione reductase, and enhances glucose-6-phosphate dehydrogenase activities. While these activities are involved with cell repair mechanisms, the significance of the changes observed (± 10-50%) is difficult to ascertain in the absence of information on the cell groups in which these changes occur[55].

The direct reactions of ozone with lung lipids and surfactant represent the primary point of attack in O_3 toxicity[98]. Investigators have named this process "lipid peroxidation"[80,87], although the principal products are fatty acid ozonides, and not peroxides[76,88,89,90]. As one would expect[76-85], O_3 attack results in the accumulation of harmful aldehydes in the lung lavage fluid[86]. In addition, the content of unreacted unsaturated lipids increases during O_3 exposure[59,86,91-94]. On the other hand, the accumulation of lipids in the surfactant also mirrors the destruction of prostaglandin (hormone) synthesis in the lung[59]. The fact that vitamin E, an antioxidant reputed to bolster the body's defenses against oxidant attack[74,87,89,91,93,97] fails to retard the secretion of unsaturated lipids into the surfactant[94] suggests that the O_3 induced secretions may actually serve as a defense or detoxification mechanism[95].

Several related studies[86,89,90] have suggested that the toxic effects of O_3 are not confined to the lung. O_3 has been shown to sensitize red blood cells to rupture in humans[86] and in drawn blood[89,90]. This condition is partially prevented by the presence of sufficient vitamin E[89] in vitro. The formation of "Heinz bodies" in blood during O_3 exposure has been attributed to the O_3-induced oxidation, peroxidation, and cross-linking of hemoglobin[89,90,96]. However, the O_3 concentrations used in some of the exposures[89,90] were on the order of several thousand ppm, which is 3-5 orders of magnitude greater than O_3 levels ordinarily encountered during community air pollution episodes (see section 3.3.1). Case et al.[40] have observed no such effects upon either in vivo or in vitro exposure of blood to 1 ppm levels of O_3 in mice. Unlike the oxides of nitrogen, O_3 does not oxidize hemoglobin to methemoglobin, nor does it generate any detectable free radicals or peroxides (Figure 4.3-3, also refs. 39,40). As Figure 4.3-3 shows[40], O_3 exposure depresses the level of iron-transferrin in blood, such that transport of iron to the blood cells is inhibited.

Predicted clinical manifestations of O_3 reactions with blood suggest that O_3 may be a causative factor in one or more kinds of anemia. If, as Menzel et al.[89,90] suggest, ozone exposure sensitizes blood cells to rupture, hemolytic anemia should result. Furthermore, existing hemolytic anemia in individuals with a genetic deficiency in the enzyme glucose-6-phosphate dehydrogenase (a syndrome whose incidence is much higher among black races than among whites) should be aggravated by exposure to oxidants. On the other hand, hemolysis rates in the presence of 2 ppm O_3 were found to be no different from those obtained in pure air[40]. Prolonged depression of transferrin[40] should give rise to iron-deficiency anemia. No information is presently available on the incidence of either kind of anemia in urban populations, in response to exposure to photochemical oxidants. Hence, health risks due to O_3 effects on blood cannot be assessed at the present time.

Other effects of O_3 which are attributed to cell damage include the leakage of plasma proteins into alveolar spaces[99], the formation of unusual antibodies[100], and the release of neuro-transmitter substances[55]. Several reports have demonstrated the abnormal appearance of both lung and plasma

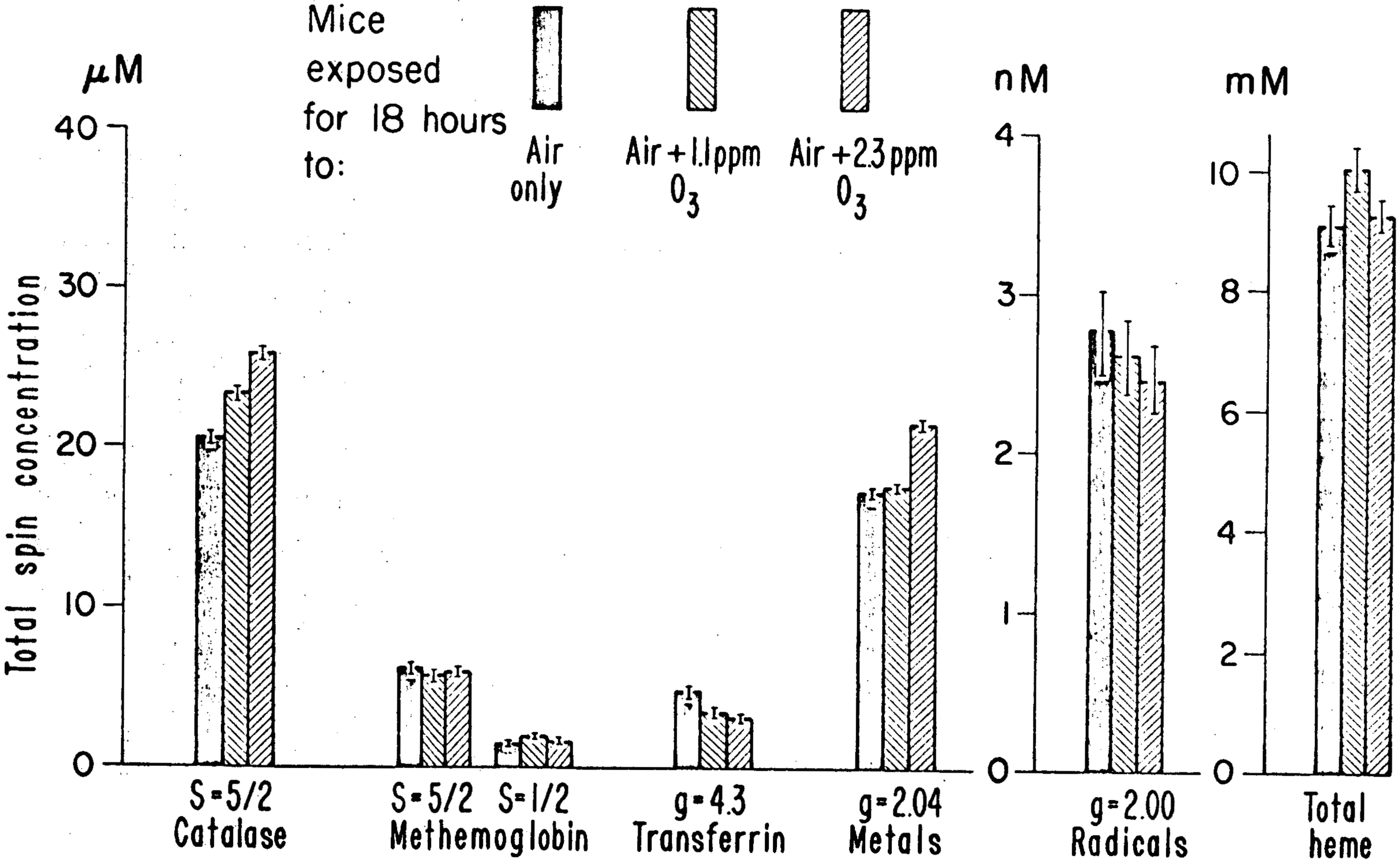


Fig. 4.3-3. Effect of an *in vivo* ozone exposure on mouse blood proteins. Catalase is an iron protein responsible for decomposing H_2O_2 in blood. Transferrin is the iron-carrying protein in blood. The metals which give rise to the g=2.04 signal are Cu and Fe in unidentified proteins, and "g=2" radicals are organic species.

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proteins[56,74,99,101], in the alveoli occurring in response to O_3 levels as low as 0.25 ppm. These effects are analogous to those which follow NO_2 exposure, except that the dose of O_3 required is 1-2 orders of magnitude lower than for NO_2 (see sections 4.2.2 and 4.3.3). Acute exposure to 6 ppm (11.2 mg/m^3) O_3 stimulates the release of serotonin, a bronchial constriction regulating substance and also a very potent central nervous system agent[55,102]. Predictably, ozone has a very noticeable effect on the metabolism of neurotransmitters in the brain[102], which is manifested clinically in the onset of headaches and lethargy during exposure. Therefore, one can conclude that oxidants can interfere with normal brain function at certain levels, and may even affect behavior.

The ability of O_3 to retard O_2 exchange across the air-blood barrier in the lung (due to a "subclinical" form of pulmonary edema, for example) and O_2 distribution to the body tissues also raises the possibility that ozone may, like CO and NO, increase cardiovascular stress[103]. In this event, O_3 could aggravate the risks from cardiovascular diseases among the populations exposed (see sections 4.2.5 and 4.3.5). These effects may occur at sub-ppm O_3 concentrations, which are periodically reached in California urban areas. Any forms of anemia which are predicted to follow O_3 exposure should further aggrevate the symptoms of partial cardiovascular failure in the community. These effects of O_3 have not yet been investigated.

Several studies[74,104,105,106] have suggested that O_3 may participate in carcinogenesis in humans. The evidence, however, is very indirect and not at all conclusive in this regard. Merz et al.[104] and Zelac et al.[105] have reported that O_3 can cause mutations in human or animal lymphocytes. The mutations apparently occur as unrepaired breaks in chromosomes rather than as substitution[65,66] or frameshift[107] mutations. Other workers, however, have failed to reproduce the work of Zelac.[161] Whether this form of mutagenesis is similar to that observed for hypoxia,[108] or is a real threat to human health should be studied further. At the present time, there is no concrete evidence in humans or in animals that ozone can cause malignant tumors.[74]

Therefore, on the basis of fragmentary biochemical and physiological evidence, four types of health problems--emphysema and chronic lung disease, respiratory infections, anemia, and cardiovascular disease--may increase in areas with high oxidant concentrations, such as Southern California. Of these, increases, acute respiratory symptoms are best documented.

4.3.4. Particulates and Carbonaceous Matter

Apart from their physical effects on respiratory-pulmonary mechanics and on the biological mechanisms for foreign body clearance (see section 4.2.4), airborne particulates may elicit health effects by virtue of their detailed chemical composition. Similar effects are expected for ingested (food-borne or waterborne particulates) with the exception that the primary target organ is more likely to be the liver than the lung. Chemical constituents of particulates which have received attention include sulfates (discussed in sections 4.2.1 and 4.3.1), trace metals[109-111], and organic compounds[112-115].

The principal heavy elements found in urban aerosols, and associated with fossil-fuel combustion, are iron, nickel, vanadium, manganese, and lead[109-111]. Lead in the atmosphere is associated almost solely with motor vehicle emissions and is not a particularly important product of steam electric generation,[109] although power plant emissions do contribute to the atmospheric loading of particulate level. The health effects of lead have been reviewed previously[117] and include inhibition of hemoglobin synthesis, liver and kidney cell destruction, mental retardation symptoms, abnormalities in fertility, and higher risks of cardiovascular diseases. Inhalation appears to be the dominent route of entry[117], except for cases of acute poisoning. The existing California standard for ambient air lead (1.5 $\mu g/m^3$ over 30 days) is predicated on a body burden analysis of not more than 5% depression in hemoglobin synthesis, and utilizes purely biochemical criteria for exposure.

The health effects of other important metals found in particulate emissions from fossil-fuel power plants have generally been extrapolated from investigations of catastrophic occupational episodes. Manganese is considered to be "the least toxic of all metals to humans and animals"[116,118]; however, virtually no data exist on the effects of chronic low-level exposures[119]. Vanadium is reportedly a strong respiratory irritant, but is toxic only in very high doses -- no data on chronic vanadium poisoning on health effects exist [41]. Particulate emissions from coal-fired power plants are rich in iron, with relatively insignificant proportions of manganese, vanadium, and nickel[130]. Most of the iron exists as complexes of ferric oxide[130]. Relatively little information exists on the toxicology of ferric iron, largely because ingested ferric iron is not absorbed by the gastro-intestinal tract[131]. Inhalation of ferric iron in fly ash and dusts would therefore appear to be the only way in which iron could enter the body. Inhaled "ferric iron is thought to be relatively non-toxic"[109]. Nickel compounds have been demonstrated as carcinogens[120]; however, levels required to induce tumors in animals are as much as 6 orders of magnitude higher than typical urban ambient air concentrations[121]. Nickel is also a potent respiratory irritant[121] at high concentrations. In studies of accident victims in New York, the only metals accumulated in the tissues of urban residents in concentrations significantly higher than those from their non-urban counterparts were lead and nickel[109]. Whether the excess nickel found in lungs, lymph and kidney of the city dwellers[109] is enough to contribute to the increased incidence of cancer in urban areas[68] may not be known for many years to come. As discussed below, there are many other known and suspected organic carcinogens in urban ambient air, which may also be responsible.

Relatively little is known about the health consequences of carbonaceous matter in particulates, except for their ability to cause cancer (see Table 4.3-2). The demonstrated ability of carbon particles to catalyze some very noxious atmospheric reactions (see sections 3.1.1.3.2.3, and 3.3.3) has not yet led biomedical investigators to probe the possibility of direct destructive cellular reactions facilitated by carbonaceous matter in the lung and respiratory tract. Carcinogenicity, on the other hand, has been thoroughly studied for a host of organic compounds[67,122]. Table 4.3-2 presents an up-to-date compilation of carcinogenicity[67,122] and mutagenicity[32,33] indices for organic compounds typically found in urban air[46,47,112-115,115a].

Table 4.3-2. Carcinogenic Activity of Organic Particulates in the Atmosphere.

Atmospheric Contaminant	Observed Concentration (picogram/m^3)	Mutation Frequency (revertants[e] nmole)	Carcinogenicity Index[f] (NIOSH, PHS)
Paraffins	500,000[a]	<0.006	-,N.L.
Fatty Acids	400,000[a]	<0.001	-,N.L.
Biphenyl	320[a]	---	N.L.
Biphenyl	62.7[b]		
Binaphthyl	480[a]	---	N.L.
Binaphthyl	788[b]		
Naphthalene	<160[a]	<0.09	±0
Anthracene	350[b]	<0.01	±0
Anthracene }	320[a]		
Phenanthrene }			
Phenanthrene	407[b]	<0.25	N.L.
Fluoranthene	3,200[a]	---	N.L.
Fluoranthene	10,500[b]		
Fluorene	16.1[b]	---	—
Pyrene	2,400[a]	<0.02	±0
Pyrene	11,260[b]		
Chrysene	6,240[a]	38	+
Benzo(a)Anthracene	27,960[b]	11	+
Benzo(c)phenanthrene	800[a]	---	±0
Benzo(c)phenanthrene	6,515[b]		
Benzo(b)fluoranthene }	13,300[a]	---	+
Benzo(k)fluoranthene }	21,840[b]	---	+
Benzo(ghi)fluoranthene	480[a]	---	N.L.
Benzo(ghi)fluoranthene	2,840[b]		
Benzo(j)fluoranthene	1,295[b]	---	+
Benzo(a)fluorene	480[a]	---	N.L.
Benzo(a)fluorene	1,704[b]		
Benzo(b)fluorene }	3,050[b]	---	N.L.
Benzo(c)fluorene }			
Benzo(c)fluorene	480[a]	---	N.L.
Benzo(a)pyrene }	8,160[a]	121	+
Benzo(e)pyrene }	9,996[b]	0.60	+
Perylene	800[a]	---	N.L.
Perylene	1,444[b]		
O-Phenylene-fluoranthene	104[b]	---	N.L.
Benzo(b)chrysene }	2,720[a]	---	N.L.
O-Phenylene pyrene }	4,395[b]	---	+
Picene }	480[a]	---	N.L.
Benzo(c)tetraphene }	65.6[b]	---	N.L.
Benzo(ghi)perylene	1,920[a]	---	±0
Anthanthrene	2,540[b]	---	N.L.
Dibenz(a,c)anthracene	890[b]	175	+
Dibenz(a,c)anthracene }	480[a]		
Dibenz(a,h)anthracene }		11	+
Dibenz(a,h)anthracene	980[b]		
Dibenz(a,h)pyrene }	320[a]	---	*
Dibenz(a,i)pyrene }	907[b]	20	+
Dibenz(a,l)pyrene }			
Coronene	833[b]	---	N.L.
Methyl-biphenyl	22.8[b]	---	N.L.
Methyl-anthracene	160[a]	---	+
Methyl-anthracene	399[b]		
Methyl-phenanthrene	160[a]	---	N.L.
Methyl-phenanthrene	388[b]		

Atmospheric Contaminant	Observed Concentration (picogram/m^3)	Mutation Frequency (revertants[e] nmole)	Carcinogenicity Index[f] (NIOSH, PHS)
Methyl-fluorenes	74.5[b]	---	N.L.
Methyl-fluoranthene	320[a]	---	+
Methyl-fluoranthene	1,450[b]		
Methyl-pyrenes	320[a]	---	N.L.
Methyl-pyrenes	1,683[b]		
Methyl-benzo(a)anthracene	480[a]	22	+
Methyl-benzo(a)anthracene	953[b]		
Methyl-β,β'-Binaphthyl	611[b]	---	N.L.
Methyl-triphenylene	264[b]	---	N.L.
Methyl-chrysene	480[a]	---	+
Methyl-chrysene	4,125[b]		
Methyl-benzo(b)fluoranthene }	480[b]	---	N.L.
Methyl-benzo(k)fluoranthene }	1,168[b]	---	N.L.
Methyl-benzo(a)pyrene	480[a]	---	+
Methyl-benzo(e)pyrene	584[b]	---	+
3-Methyl-cholanthrene	544[b]	58	+
Higher-order methyl-subsituted polynuclear aromatic hydrocarbons	497[b]	---	+
Ethyl anthracene	160[a]	---	N.L.
Ethyl anthracene }	696[b]	---	N.L.
Dimethyl anthracene }			
Ethyl-phenanthrene	160[a]	---	N.L.
Ethyl-phenanthrene }	579[b]	---	N.L.
Dimethyl-phenanthrene }			
Trimethyl-fluoranthene }	430[b]	---	N.L.
Trimethyl-pyrene }			
Dimethyl-benzo(a)anthracene	64.3[b]	19	+
Dimethyl-chrysene	75.7[b]	---	+
Dimethyl-benzo(b)flouranthene }	218[b]	---	N.L.
Dimethyl-benzo(k)fluoranthene }		---	N.L.
Dimethyl-benzo(a)pyrene	444[b]	---	+
Dimethyl-benzo(e)pyrene		---	+
Dihydro-anthracene	20.3[b]	---	N.L.
Dihydro-phenanthrene	37.0[b]	---	N.L.
Dihydro-fluoranthene	12.2[b]	---	N.L.
Dihydro-pyrene	78.0[b]	---	N.L.
Dihydro-benzo(a)fluorene }	1,573[b]	---	N.L.
Dihydro-benzo(b)fluorene }		---	N.L.
Dihydro-benzo(c)fluorene	387[b]	---	N.L.
Dihydro-benzo(c)phenanthrene	343[b]	---	N.L.
Dihydro-benzo(a)anthracene }	1,603[b]	---	N.L.*
Dihydro-chrysene }		---	N.L.*
Dihydro-triphenylene }		---	N.L.*
Dihydro-methyl-benzo-(ghi)fluoranthene	705[b]	---	N.L.*
Dihydro-methyl-benzo-(b)fluoranthene }	1,083[b]	---	+*
Dihydro-methyl-benzo-(k)fluoranthene }		---	N.L.*
Dihydro-methyl-benzo-(a,e)pyrenes }		---	N.L.*
Dihydrobenzo(a)pyrene	<10[a,b]	20	+

Table 4.3-2. Carcinogenic Activity of Organic Particulates in the Atmosphere. (Continued)

Atomspheric Contaminant	Observed Concentration (picogram/m^{3})	**Mutation Frequency** (revertants^{e} nmole)	Carcinogenicity Index^{f} (NIOSH, PHS)
Tetrahydro-methyl-benzo-(a)anthracene	654^{b}	---	N.L
Hexahydro-chrysene		---	N.L.
Octahydro-fluoranthene	19.6^{b}	---	N.L.
Octahydro-anthracene	10.9^{b}	---	N.L.
Octahydro-phenanthrene			
Octahydro-pyrene	54.2^{b}	---	N.L.
Hydroxynaphthalene	<10^{b}	<0.01	-,N.L.
Hydroxy-anthracene	320^{a}	---	N.L.
Hydroxy-phenanthrene		---	N.L.
Tetrachlorophenol	3,200^{a}	---	-,N.L.
Pentachlorophenol	12,000^{a}	<0.32	-,N.L.
Anthraquinone	2,400^{a}	---	+
Benz(d,e)anthracene-7-one	800^{a}	---	N.L.
Diethyl phthalate	40,000^{a}	---	-,N.L.
Di-n-butyl phthalate	51,200^{a}	---	-,N.L.†
Benzyl butyl phthalate	12,800^{a}	---	N.L.
Bis-(2-ethylhexyl) phthalate	115,200^{a}	---	N.L.
Benzoic acid	1,440^{a}	<0.009	-,N.L.
Salicylic acid	960^{a}	<0.02	-,N.L.
m,p-Hydroxy-benzoic	12,800^{a}	---	N.L.
Naphthalene carboxylic acids	2,800^{a}	---	N.L.
Anthracene carboxylic acids	6,720^{a}	---	N.L.
Phenanthrene carboxylic acids	2,080^{a}	---	N.L.
Pyrene carboxylic acids	480^{a}	---	N.L.
Phthalic acid	4,000^{a}	---	N.L.
Isophthalic acid	4,000^{a}	---	N.L.
Terephthalic acid	24,000^{a}	---	N.L.
Methyl phthalic acid	480^{a}	---	N.L.
Dimethyl nitrosamine	3,900,000^{c} 70,000^{d} 800,000^{d}	0.02	+
Diisopropyl nitrosamine	656,000^{c}	0.08	+
Fluorene carbonitrile	90^{b}	---	N.L.
Benzidine	18.5^{b}	1.4	+
Quinoline	70^{a}	0.78	+
Isoquinoline		---	N.L.
Acridine	900^{a}	0.02	±0,N.L.
Acridine	450^{b}		
Alkyl-substituted quinolines	688^{a}	---	N.L.
Benzo-quinoline	480^{a}	---	N.L.
Benzo-quinoline	460^{b}		
Alkyl-substituted benzo-quinolines	1,120^{a}	---	N.L.
Aza-fluoranthenes	2,560^{a}	---	N.L.
Aza-pyrenes			
Benz acridine	2,560^{a}	---	N.L.
Aza-chrysenes		---	N.L.
Dibenzo quinolines		---	N.L.
Dibenzo isoquinolines		---	N.L.
Dibenz(a,h)acridine	640^{a}	---	+
Dibenz(a,i)acridine		2.0	+
Dibenz(a,j)acridine		18	+
Methyl benzacridines	480^{a}	---	+
Methyl benzophenanthridines		---	N.L.
Methyl dibenzo quinolines		---	N.L.
Methyl dibenzo isoquinolines		---	N.L.
Aza-benzo pyrenes	1,440^{a}	---	N.L.
Aza-benzo fluoranthenes			N.L.

(a) W. Cautrells and K. Van Cauwenberghe (1976) Atmos. Environ. 10, 447-457. Total suspended particulate mass was 160 μg/m^{3} for these samples. Air samples collected in Antwerp, Belgium air basin.

(b) R. C. Lao, R. S. Thomas, H. Oja, and L. DuBois (1973) Anal. Chem. 45, 909-915. *Total suspended particulate mass was not stated.* Air samples collected in the Ottawa, Canada air basin.

(c) D. H. Fine, C. P. Rounbehler, N. M. Belcher, and S. S. Epstein (1975) in Proc. Int. Conf. Environ. Sensing Assess., Vol. 2, paper 30 7, Las Vegas, NV, September 14-19 (avail IEEE, New York). Gaseous and particulate nitro-samines were not *discriminated in these measurements. Samples collected in Baltimore,* Maryland.

(d) D. Shapley (1976) Science 191, 268-269. Nitrosamines in U. S. air.

(e) J. McCann, E. Choi, E. Yamasaki, and B. N. Ames (1975) Proc. Nat. Acad. Sci. U. S. 72, 5135-5139. Some data are also taken from unpublished observations of J. McCann and B. N. Ames as well as from J. McCann, personal communications. Mutagenicity numbers expressed as "revertants per nmole of suspected mutagen," *based on the* Salmonella-microsome test. The precise strain used as well as the concentration and types of microsome preparations are indicated in the ref. Substitution of either testor strain or microsomal preparation can change the mutagenicity index by 2-3 orders of magnitude. The number given is the highest value observed for any of the testor strains.

(f) Carcinogenicity data are taken from:
National Institute of Occupational Safety and Health "(1975)" Suspected Carcinogens: A Subfile of the NIOSH Toxic Substances List," Center for Disease Control, Public Health Service, U. S. Department of Health, Education, and Welfare, Rockville, Maryland 20852;

P. Shubik and J. L. Hartwell (1973) *"Survey of Compounds Which Have Been Tested for Carcinogenic Activity,"* Publication 149-4, Public Health Service, U. S. Department of Health, Education, and Welfare, Washington, DC.

"+" indicates a proven carcinogen (ref. e or f). "-" indicates a demonstrated non-carcinogen (refs. e-g). "±0" indicates a very weak or questionable carcinogen, which may or may not be suspected of causing cancer in humans. *"N.L." indicates that substance is not listed in the NIOSH register (ref. f).*

● Alkyl-substituted derivatives are suspected carcinogens.

† Acutely toxic.

Most of the compounds in urban air which have been examined as either carcinogens[67,122] or mutagens[32,33] are polynuclear aromatic hydrocarbons (PAH compounds). Very few PAH compounds are directly mutagenic, themselves. Biochemical activation is apparently required before these substances can interact with the genetic material DNA[107,123,124]. Grover and Sims[125] first demonstrated that PAH compounds become covalently bound to DNA only if microsomal aryl hydrocarbon hydroxylase enzymes and cofactors are present, indicating a need for metabolic activation. Furthermore, unless aryl hydrocarbon hydroxylase enzyme activity is present (by addition of microsomes), the bacterial mutagenesis test[32,33,137] fails to detect mutations due to PAH compounds. This supports the view that covalent binding of a PAH derivative to DNA is required for mutagenesis or carcinogenesis, and that the parent compounds themselves do not bind[125]. The suspected metabolites which do bind to DNA are the PAH epoxides[107,125,126]. These epoxides presumably cause frameshift mutations and single- or double-strand breaks in the genes[107,125,126]. The ability of PAH compounds to cause mutations depends not only on their conversion to epoxides, but also on the rate at which these epoxides can be inactivated. Pathways for inactivation include rearrangement to phenols, coupling with glutathione, or hydrolysis to the corresponding diols[127.128,129,125,126]. Figure 4.3-4 summarizes the biochemical conversions of PAH compounds[123-129].

The ability of a PAH compound to cause cancer, therefore, is connected with the balance among the metabolic reactions in Figure 4.3-4. Changes in any of the pathways, such as might result from PAH-stimulated induction of enzyme synthesis or enzyme inhibition by an accompanying pollutant may dramatically alter the carcinogenic potential of a PAH substance. Organs in which PAH metabolism has been detected, and which are therefore targets for PAH-induced cancer, include liver, lung, intestine, kidney, skin, placenta, adrenal glands, and testis[125,132-136].

Three very important implications are evident from the information given above. First, only a limited variety of cancers can be caused by PAH compounds. This is so because most cell and tissue types do not metabolize PAH compounds. In lung, nearly all of the PAH metabolic activity is found in one cell group type II alveolar epithelial cells[55,123]. Other types of carcinogens are probably not so selective about their target cells. Therefore, it should be theoretically possible to pinpoint the chemical carcinogens

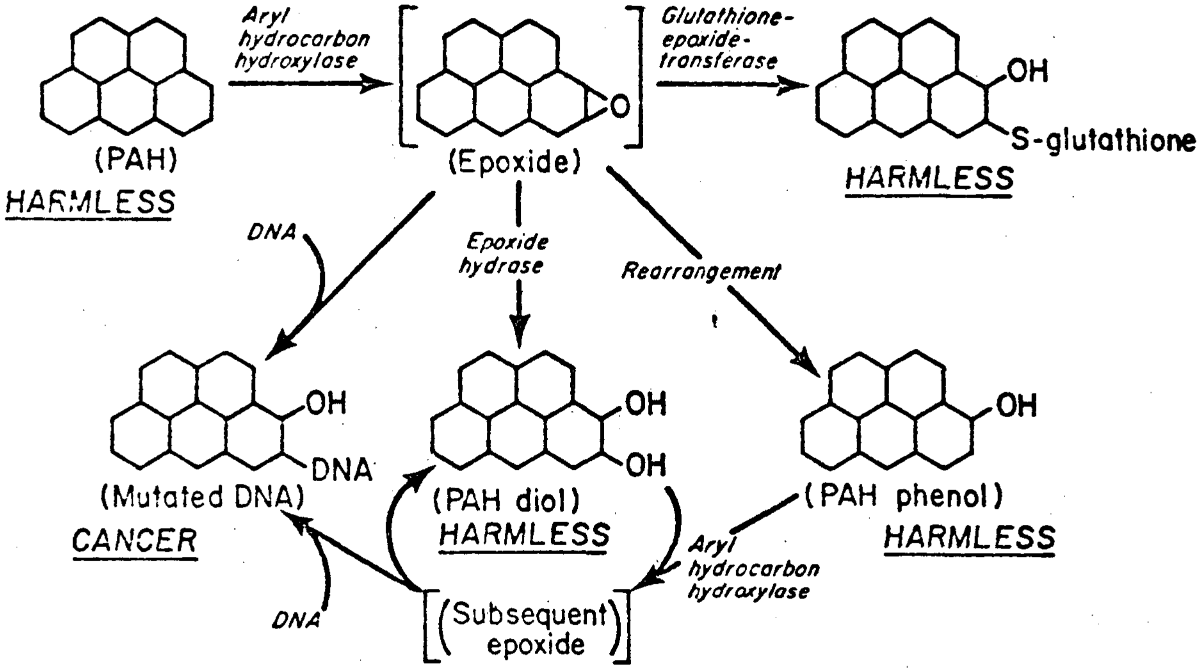

Figure 4.3-4. Metabolism of Bensopyrene.

responsible for triggering lung cancer cases in the populations. This same factor may also explain why soot causes cancer of the scrotum in chimney sweeps (see section 4.1.2.2). Cigarette smoking, for example, may be a factor in cancers in liver and intestine as well as lung, for the same reason[138].

Second, the requirement for metabolic activation undoubtedly plays a role in the high degree of variability in the mutagenic and carcinogenic potential of PAH compounds (see Table 4.3-2). Aryl hydrocarbon hydroxylase and epoxide hydrase enzymes, for example, surely exhibit some degree of specificity for substrates. This fact has to be the reason that benzo(a)pyrene is such a strong mutagen and carcinogen, while the chemically similar compound pyrene is neither[32,33]. Furthermore, substrate specificities are certain to differ from organ to organ and from animal species to animal species[55].

The microsomes routinely used in the bacterial mutagensis test[32,33,137] are derived from rodent liver and not from human lung. For this, and many other reasons, the mutagenicity data of Table 4.3-2 cannot be considered quantitative.

Finally, other pollutants may affect the activity level of PAH metabolism in lung. Nitric oxide, ozone, and carbon monoxide, for example, both react with aryl hydrocarbon hydroxylase[127,132,142] in a manner which suggests inhibition. NO_2, on the other hand, triggers the uncontrolled proliferation of type II alveolar epithelial cells[55,140], and might therefore increase PAH metabolic activity. These competing interactions should be explored more completely.

At the present time, there are no air quality standards or emission standards for either particulate metals in fly ash or particulate organic matter, except for the all-encompassing ARB and EPA standards for total particulate mass. The EPA has recently released a criteria document on emissions, urban air concentrations, and health effects of polycyclic aromatic hydrocarbons[141], and a recommendation of standards for PAH compounds is likely to be made public in the near future. At the present time, little quantitative information on dose requirements of PAH for cancer in humans exists, so that any standards which are promulgated will be predicated on an extrapolation from tumorigenesis data in animals, perhaps supported by mutagenesis data.

4.3.5 Carbon Monoxide

As indicated in section (4.2.5), while CO emissions from power plants are not an important contribution to ambient CO in urban air, a discussion of its health effects is warranted for extrapolation to the effects of NO, which is a major power plant emission. All of the characterized health effects of CO are due to its binding to hemoglobin during exposure (see Figure 4.3-5, also ref. 143), just as the effects of NO exposure are attributable to accumulation of nitroxyhemoglobin and methemoglobin[35-42,144].

The existing ambient air and occupational standards for CO[143,145] are predicated on a body burden analysis. That is, the maximum allowable concentration in the air is determined by the amount of pollutant required to generate a given threshold concentration of a biochemical metabolite (in this case, carboxyhemoglobin) which more accurately reflects observed physiological and health effects (see section 4.2.5). The advantage of a body burden analysis is that the dose-response characteristics of given pathological responses are

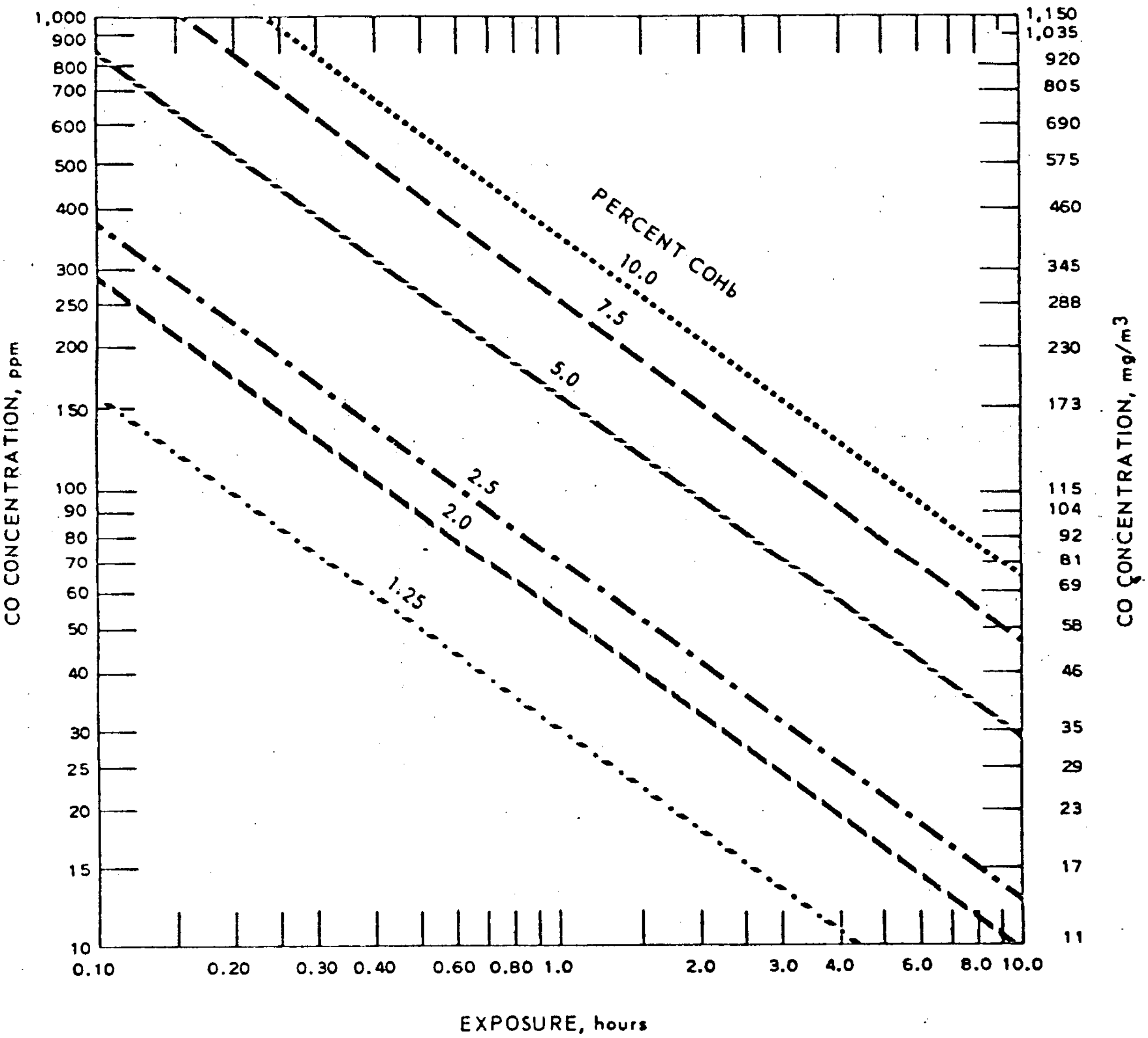

Fig. 4.3-5. Concentration and duration of continuous CO exposure required to produce blood COHb concentrations of 1.25, 2.0, 2.5, 5.0, 7.5, and 10 percent in healthy male subjects engaging in sedentary activity. (143)

accurately known. No extrapolation from ambient air concentrations is necessary, so that errors due to uncertainty in measuring the actual exposure level to the body are eliminated. At the present time, methods for body burden analysis are available for CO[143,145], No[39,40,48], lead[117], and cadmium[146].

4.3.6 Hazardous Metal Vapors

Mercury and selenium are two minor but very hazardous pollutant emissions from fossil fuel-fired power plants about which relatively little is known at the level of community health effects. Hg is a very potent sulphydryl chelating agent, and therefore reacts with nearly every kind of protein in the body[147]. Se, on the other hand, would appear to mimic sulfur in the body, presumably by incorporating into and being metabolized with sulfur compounds in the body -- with disastrous results[148].

Man generally absorbs 75 to 85% inhaled mercury vapor at concentrations between 50 and 350 $\mu g/m^3$.[151] Experiments, however, have shown that some individuals can have nearly complete absorption at concentrations between 60 and 250 $\mu g/m^3$.[150] Reports regarding the respiratory intake of mercury other than elemental vapor are scarce, but inorganic and organic compounds are known to be absorbed[149,153]. Elemental and especially organic mercury is also absorbed through the skin.

Inorganic mercury compounds, phenyl-mercury, and methoxyethylmercury are converted in the blood to soluble inorganic mercury salts[149,150]. Carried by the blood plasma, the mercury is widely distributed in all tissues, but accumulates primarily in the kidneys and liver prior to excretion[149,150]. Some accumulation of the mercury salts also occurs in the brain, spleen, and alimentary tract[150]. Nonalkyl mercury might, to a limited extent, be transformed into methylmercury within the liver[149,152]. In general, those compounds which are, or readily form, water-soluble inorganic salts are among the least toxic of the mercury compounds.

Elemental mercury has transport and retention properties resembling both inorganic and alkyl mercury compounds. Converted to mercury salts, it is partially transported in the blood plasma. While able to penetrate all body tissues, it accumulates in the brain, other nervous tissue, intestinal tract, and salivary glands[149]. Having characteristics intermediate between inorganic and alkyl mercury, elemental mercury is somewhat more toxic than the former but far less toxic than the latter.

The toxicity of mercury is attributed to its high affinity for sulfur-containing compounds and its lesser affinity for organic ligands[150]. Interference by mercury in the synthesis and function of enzymes and other proteins can result in a variety of adverse effects[150].

The present threshold limit standard for Hg in ambient air of 1 $\mu g/m^3$ is predicated on a maximum safe level of uptake of 20 μg/day for an average individual, and assumes that no additional Hg from food or water sources is ingested at the same time[150]. The estimated contribution of a 870 MW power plant to the concentration of mercury in the atmosphere is on the order of 0.05 $\mu g/m^3$ [154], which is well within current standards.

Chronic mercury poisoning can result from inhalation of inorganic mercury at concentrations as low as 100 $\mu g/m^3$. Slight anemia, hypothyroidism, and increased excitability may result from occupational exposures as low as 10 to 30 $\mu g/m^3$ elemental mercury[149]. Among 642 workers in the chlor-alkali industry, low-level exposures averaging from < 50 to 270 $\mu g/m^3$ elemental mercury have been strongly correlated with loss of appetite and weight[149]. Chronic poisoning by inorganic mercury affects primarily the nervous system. There may arise anxiety, insomnia, muscular tremor, and other psychological disturbances. Other possible symptoms are erethism, inflammation of the gums, gastrointestinal disturbances, weakness, and other symptoms similar to those in acute poisoning[149,150,153].

Acute mercury poisoning can result from inhalation of inorganic mercury at concentrations from 1,200 to 8,500 $\mu g/m^3$ [150]. The kidneys and intestinal tract are primarily involved. Symptoms are metallic taste, nausea, abdominal pain, vomiting, diarrhea, headache, salivation, and anuria[150,153]. The stomach, gums, and salivary glands may become inflamed. Acute exposure to elemental mercury can also cause pulmonary irritation and neural damage. Chronic symptoms such as muscular tremor may persist in some cases. Extreme cases may lead to hemolysis, insomnia, delirium, and ultimate death from exhaustion[149,150].

Considerably less is known about the effects of airborne selenium on human health, especially at ambient air levels. There is amazingly little information on typical community exposures to Se, or on the relative contributions of airborne, waterborne, and foodborne Se to the total body insult among the population[148]. Under industrial exposure conditions, selenium as SeO_2 was found to be a highly irritating and toxic vapor to workers[155], resulting in respiratory tract irritation, eye irritation, and pulmonary edema at high concentrations. Trace amounts of selenium are apparently required as dietary nutrients in humans and animals[4], but is extremely toxic biochemically at higher concentrations[156,157,158]. Selenium has been described as both a carcinogen and an anticarcinogen[148]; the dual nature is probably due to complex synergistic effects in addition to basic dose level differences. The implications of the biochemical reactions of Se on physiological function in humans and animals are also not clear[148]. Selenium inhalation studies on the laboratory scale are virtually nonexistent. According to the National Academy of Sciences[159], "little quantitative information is available regarding the absorption of Se through the lungs or skin." Accordingly, the present maximum allowable concentration of Se in air has been tentatively set at 100 $\mu g/m^3$, corresponding to a daily intake of 2000 μg per individual[160]. As of the present time, best estimates of the total inhaled dose above normal dietary levels are on the order of 50-150 μg/day[160]. Considerably more study should be devoted to determining whether Se emissions from power plants (presumably a major source of Se emissions in the future) represent a real or potential threat to human health. As of now, almost nothing is known about this problem.

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5. DIFFICULTIES WITH EXISTING DATA -- THE NEED FOR FURTHER INFORMATION

The existing body of information on the emissions, dispersion, and health effects of air pollutants from fossil fuel and geothermal power plants is -- as demonstrated in this review -- incomplete and tenuous. A good deal of regulatory planning can be and has been carried out on the basis of existing data. However, the efficiency and economy of regulation and power plant operation is impaired where the lack of correct or precise information results in safety margins that are later proven to be unnecessary or too stringent or where insufficient controls are imposed on harmful pollutants.

Many investigations have employed methods which were too crude for the precision and accuracy demanded in the studies. In addition, many crucial questions regarding various aspects of pollutant emissions dispersion, and health effects have gone unanswered either because the investigative tools necessary for experiments were unavailable or because workers dealing with these questions failed to execute their investigations correctly. Some of the more important of these problems are discussed below, in Sections 5.1, 5.2, and 5.3. The extent of our ability to actually assess the human health impacts of conventional emissions from fossil-fuel and geothermal power plants is summarized in Section 5.4.

5.1 Deficiencies in Existing Data

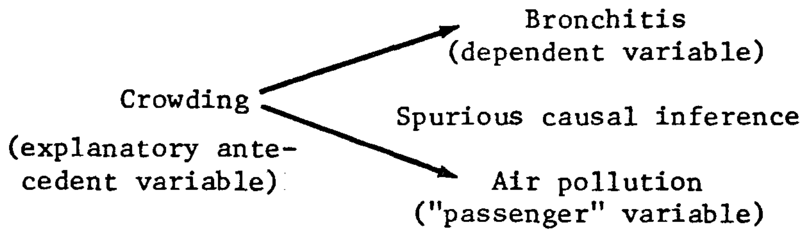
Assimilation of the existing body of information on pollutant emissions and their effects on health has been hampered by some rather basic problems. Most studies have examined effects which could be measured by means readily available to the investigator, regardless of the actual pollutant concentrations typically observed in environmental media; as a result, health effects studies on various levels (epidemiological, physiological, and biochemical) are often not comparable among themselves. Moreover, many epidemiological studies have relied uncritically on crude analytical data, without regard to its relevance to the study population; these data have often been gathered on the basis of expediency, rather than on pertinence as judged by fundamental biochemical understanding. Finally, because of the small overlap in training and expertise of investigators engaged in the primary analyses of air quality and those involved in assessing the health and biomedical effects of pollution, the work performed by one of these groups is often not as helpful to the other as it might be. With these difficulties in mind, Section 5.1.1 summarizes the problems in carrying out valid, reliable, and unambiguous epidemiological studies, attempting to relate changes in the state of public health to air pollution; Section 5.1.2 treats problems in air pollutant monitoring; Section 5.1.3 surveys the problems associated with physiological and biomedical measurements of the effects of air pollutants.

5.1.1. Problems with Control Variables

In Section 4 of this report, we discussed the hypothetical causal independent variable, air pollution (specifically from fossil fuel sources) and its association with the dependent variable, health. In good experimental design, the aim is to isolate the effect of the independent variable (in this case air pollution) from all the other possible independent variables. The latter are called control variables if they meet two conditions: 1) they have a potential effect on the dependent variable and 2) they are subject to control by analysis. Uncontrolled variables, on the other hand, have not been brought under control by the analysis and should not be related to the hypothetical causal variable. However, in many epidemiological studies, and especially in air pollution research, we find independent variables which are related to the hypothetical causal variable and which are uncontrolled. These are appropriately named confounding variables and present particular problems in analysing data. Confounding variables typically include such factors as social-economic status, crowding, age distributions, mobility, education, etc. It is self-evident that in an urban population, uniform or random mixtures or samples of these variables are difficult, if not impossible, to achieve. Susser[1] presents a very lucid example of confounding variables and the manner in which epidemiologists are often misled when these variables are uncontrolled:

> In the example of the association of air pollution with bronchitis, air pollution will be found to vary systematically and directly with the density of urban settlement (so much so that researchers have used this density as an index of pollution). Pollution will also vary with the overcrowding of homes and consequent respiratory infection and with the social and economic levels of residential areas. The causal model for the association of air pollution with bronchitis, then, would be as follows:
>
> Air pollution ⟶ Bronchitis
>
> (independent variable) (dependent variable)

> But the truth could as well be that the overcrowding and high population density so regularly found with the urban poverty complex confound the association. These factors could cause bronchitis by facilitating the spread of infection, on the one hand; on the other hand, quite independently of bronchitis, they could cause air pollution by a concentration of the use of domestic and industrial fuels and motor transport. In that case crowding would be a confounding variable: air pollution and bronchitis would be in a symmetrical relationship with each other as part of a complex of factors, and the causal inference would be spurious.
>
> The variable wrongly designated as cause that leads to the spurious inference in such an association might fittingly be called a "passenger" variable. It "rides" with the dependent variable just as a passenger virus rides with a cancer without causing it. Thus a passenger variable varies systematically with the dependent variable under study without being causally related to it (most often because a particular causal factor can give rise to both).



The difficulty in carrying out well-controlled epidemiological studies has — as is clear in Section 4.1 — decreased their potential value in establishing the relationships between pollutants and health effects.

5.1.2 Analytical Measurements of Pollutants

Difficulties in the qualitative and quantitative analyses of air pollutants have plagued researchers in a wide diversity of disciplines in identifying the effects of air pollutants on the general population. Errors and deficiencies in pollutant analysis have had a profound effect on the assessment of the health effects of air pollutants on study populations, on the incidence of declarations of air pollution episodes, on the actions of regulatory agencies in response to air pollution, and on the economic development of whole communities. A study of the record in this regard reveals considerable room for improvement, especially along the lines indicated below, where difficulties which may not have been evident in Section 3 and

4 are emphasized.

5.1.2.1 Insufficient Distribution of Monitoring Stations

One of the critical choices which a regulatory agency or investigative team can make in regard to studies of the effects of air pollution lies in the selection of air monitoring stations. The U.S. Environmental Protection Agency (EPA) the California Air Resources Board (ARB), and most of the local Air Quality Control Districts (AQCD's) rely very heavily on central station type monitoring.[2,3] That is, one site in an area such as a large city or suburb is selected as a permanent and stationary air pollution monitoring facility. Concentrations of pollutants determined at this central station are by implication assumed to be quantitatively representative of the entire community. In fact, the kind of site which is usually chosen is the rooftop of a government-owned building, irrespective of neighborhood of that site. A classic example of analytical errors due to monitoring site selection is found in the erroneously high CO and hydrocarbon measurements in Berkeley, California during the 1973-1974 "fuel crisis".[4] The central monitoring station happened to lie above a service station in downtown Berkeley at which long lines of idling automobiles waited their turns at the gasoline pumps.

In addition, the ARB also maintains a small fleet of mobile (i.e. truck-mounted) monitoring stations which are intended to survey air quality over a wide area of an air basin.[3] This method is a definite improvement over fixed-station minitoring, but since motor vehicles are generally confined to city streets, open roads, and freeways, measurements from these sites may show a decided vehicular bias.

Since people spend relatively little of their time on roof tops or in automobiles, air quality measurements from these fixed or mobile stations may be poor indicators of the pollutants which are actually breathed. A more broadly distributed monitoring system would be suitable.

5.1.2.2 Imprecision and Inaccuracy in Monitoring

The air quality monitoring program is also deficient from in its selection of pollutants to be monitored and in the manner of their measurement. The selection of pollutants is discussed in the next section. However, for nearly every pollutant which is now widely monitored, there are a variety of analytical physical and chemical measurement techniques for an monitoring, which vary in sensitivity, precision, accuracy, and sampling time.[5] Most agency monitoring stations employ the least expensive analytical methods instead of ones which provide more suitable information.

One example of this is the analytical technique outlined by the ARB for ambient air sulfate measurements.[6] Turbidimetric analysis for sulfates is suitable for order-of-magnitude determinations, but is subject to interference from any coprecitating or turbid species, and is precise only to within a factor of about 2.[5] In addition, the sensitivity of this technique is inadequate for the ambient air measurement of sulfates in most parts of California. Several other wet chemical methods for sulfate are more sensitive and accurate, and some emerging physical techniques are proving to be even better.[5]

As a second example, errors associated with the use of an inferior analytical procedure for oxidant monitoring have been reported in California, and have had embarassing results. For years, oxidant concentrations have been monitored by both the ARB and the Los Angeles County Air Pollution Control District, using different wet chemical methods, with substantial disagreement. Finally, it was resolved[3] that the ARB methods gave results which were too high by some 20 per cent, and that the Los Angeles County APCD data were more accurate. Several oxidant smog episodes in the South Coast Air Basin during the period 1965-1974 were therefore overrated and some abatement procedures may therefore have been ordered needlessly and mistakenly. There is now widespread agreement that spectrometric or chemiluminescence methods for oxidant monitoring are not only more sensitive, more accurate, and more reliable than any wet chemical techniques used by regulatory agencies, but are faster and easier to carry out.[5]

5.1.2.3 Lack of Resolution Among Possible Pollutants

5.1.2.3.1 Uncontrolled Interference

Many analytical techniques used in routine air quality monitoring, especially wet chemical methods, do not discriminate among classes of pollutants as well as would be useful. An example is the potassium iodide method for oxidants, which -- in addition to sensing oxidants -- measures NO_2, SO_2, H_2S, and halogens.[5] Any such substance, which an analytical method detects other than the pollutant of interest, is an interferent and introduces an uncontrolled error into the air quality measurements. In the absence of special sample treatment procedures designed to remove interference, all of the wet chemical analytical methods are susceptible to this difficulty.[5] See reference 5 for further information.

5.1.2.3.2 Qualitative Differentiation of Pollutants

Obviously epidemiological and biomedical studies of the health effects of air pollutants are hampered when community air monitoring data fail to distinguish among critical kinds of pollutants. One example is the discrepancy between the analytical definition of oxidants (as anything that oxidizes iodide to molecular iodine) and the biomedical definition (ozone). This disparity is actually not as serious as those for some other pollutants. The most common analytical procedures for sulfates, for example, do not discriminate among H_2SO_4, ammonium sulfates, sodium sulfates, metal sulfates, or -- for that matter -- sulfites.[5] The health effects of these sulfur species differ by orders of magnitude (see Refs. 5 and 6 and Sections 3.1.1.1, 4.2.1, and 4.3.1 of this report).

The most serious instance of lack of resolution occurs with particulate monitoring. Both the EPA and ARB methods call for high-volume sampling of air for total particulate mass, a procedure which does not allow for sampling or analysis of particles by size or chemical composition. Hence, a great deal of extremely valuable air quality information is lost during collection. It is now well known that the health effects of particulates depend heavily on particle size and composition (see Ref. 7 and previous sections in this report), of these, relatively less is known about the direct influence of particle composition. Until more refined information regarding urban aerosol size distribution and chemical composition is available in the air monitoring programs, epidemiological surveys of urban populations for the health and welfare effects of particulates will have severely diminished value, if any at all.

5.1.3 Physiological Biomedical Measurements

Most presently available information on the direct biological effects of air pollutants can be classed into five categories: a) measurements of respiratory-pulmonary mechanics; b) morphological evidence; c) biochemical analyses of certain enzymes in certain cell types; d) the chemical state of hemoglobin; and e) measurements of foreign body clearance in the lung. In terms of measuring health effects as experienced in the population, these approaches all differ in their sensitivity, reliability, and significance.

For example, measurements of respiratory mechanics (pulmonary flow resistance, forced expiratory volume, etc.) are good indicators of airway obstruction in the relatively wide passages such as the bronchi and the upper tracts. They are less sensitive to changes in the deep lung spaces such as the alveoli, where the air passages are small and where greatest pollutant damage is likely to occur. Not too surprisingly, therefore, increases in airway resistance observed during pollutant exposures do not occur except at concentrations far above those needed to elicit other kinds of pathological responses. Even so, changes in breathing mechanics are frequently small (~10-20 per cent) except at pollutant exposures which are some 1 to 4 orders of magnitude above ambient air quality standards.

Observable changes in the physical appearance of lung and respiratory tract tissues are often accurate and sensitive indices of physiological damage wrought by air pollutants. Morphological evidence of this type is usually manifested as changes in the abundance of cell debris, in connective tissues, in populations of different kinds of cells, or in subcellular structures such as mitochondria or lysosomes. Physical changes in the lung are evident as the result of subclinical exposures to NO_2 or oxidant air pollutants, and are always present in situations where other types of effects are detectable. The major deficiency with most studies that have examined morphological changes in the lung and respiratory tract is the failure of the investigators to correlate these structural alterations with deterioration in lung or respiratory functions. Only structural information, valuable as it is, is available from this approach. Interpretation of structural data in terms that relate to health effects, however, requires additional types of information.

Biochemical analyses of the effects of air pollution to examine the root causes of any health effects which may result from exposure. Usually, these are carried out by the investigation of the cellular or tissue distribution of selected proteins and enzymes. Examples include measurements of lysozyme or protease in the lung lavage fluids; and studies of specific metabolic enzyme activities such as lactic acid dehydrogenase, glutathione peroxidase, or oxidative phosphorylation. The magnitude of biochemical change in response to pollutant exposure depends on the purity of the cell or tissue preparation studied. For example, studies which examine crude tissue preparations are likely to be more insensitive to damage due to pollutant exposure than are investigations using fractionated or pure individual cell types. On the other hand, yield losses during the further purification steps may reduce the total enzyme signal below the detection limits. Therefore, although 10-50 per cent changes in enzyme activity usually do not affect cell function, one should not interpret enzyme changes of this magnitude in crude lung preparations as insignificant with respect to health effects. Air pollution does not attack all cells equally.

One additional aspect of biochemical analyses deserves comment. There are conservatively at least 1000 different types of enzymes in living cells, which are involved with metabolism, cell transport, cell structure, and cell growth. Selection of enzymes in most of the current biochemical studies is based at least as much on the ease of analysis as it is on the importance to cell function. Studies which examine only a few (< 5) types of enzyme activities, and this includes nearly every one in the literature, may overlook lesions in cell metabolic activity (points at which an enzyme has been "killed") induced by air pollutants. Substrate accumulations are often a better indicator of metabolic lesions than enzyme activities for those pathways in which one enzyme somewhere suffers a real "hit" (> 80-90 per cent enzyme loss or > 2-fold accumulation of a metabolic intermediate) upon exposure. Therefore, biochemical changes are extremely important, sensitive, and direct indices of health effects. Logical extrapolations can usually be made from a known metabolic lesion to a characterized disorder. Examples include Parkinson's disease and schizophrenia, both of which are caused by environmentally induced point lesions in amino acid metabolism. Most studies, however, have not clearly demonstrated enzymatic "hits". An important metabolic activity which has not been scrutinized thoroughly is the direct detoxification of air pollutants. The clearest example is sulfite oxidase, in the lung, which detoxifies SO_2 with an efficiency which is relatively unknown at present.

Perhaps the best characterized indicator of effect of air pollutant exposure is the chemical state of hemoglobin. Historically, hemoglobin (Hb) reactions have been measured with O_2, CO, NO, NO_2, and H_2S, largely because of this ferroprotein's strong visible absorption spectrum. Because of this, it is possible to detect Hb-CO, Hb-NO, methemoglobin, etc., at levels on the order of 2 per cent of the total hemoglobin in whole blood. One should note that the current ambient and occupational air quality standards for CO are based on blood levels of Hb-CO equal to 2.0 and 5.0 per cent, respectively. Both numbers approach the lower detection limit of spectrophotometric methods, now used almost universally for body burden analysis (see Section 4.3.5) of pollutant exposure.[5,8] Hence, the threshold for health effects of CO is obscured due to resolution limitations. The same lower detection limit also applies to measurements of Hb-NO, methemoglobin, and sulfohemoglobin in blood, if visible spectrometric methods are used.[8]

On the other hand, better methods are now available for the measurement of Hb-CO, Hb-NO, and methemoglobin. Chance and his colleagues[9] have successfully applied flash photolysis spectrometry to the analysis of Hb-CO, under a variety of conditions. Bright light drives off CO from the Hb complex without affecting any other form of Hb, so that the large Hb background is eliminated. The sensitivity of the method is therefore 100 times better than for other existing analytical methods. Likewise, both Hb-NO and methemogobin can be studied in blood by electron paramagnetic resonance spectroscopy, without interference from other forms of Hb, in which case the sensitivity is 1000 times greater than for existing visible spectrometric methods.[8] Epidemiological studies in which Hb-CO or methemoglobin body burdens have been or are being investigation in order to assess pollution related health risks, should therefore be reexamined to determine whether the body burden levels are actually greater than zero. The connection of "inactive" hemoglobin (Hb-CO, met-Hb, etc.) body burdens with cardiovascular and neurological disorders is direct and well-characterized, so that no ambiguity exists in the interpretation of this type of data regarding the health effects of CO or NO_x.

Investigation of <u>foreign body clearance</u> is one of the most sensitive and reliable indicators of the effects of pollutants on humans and animals. Unfortunately, not many of these studies have been performed. Most studies of this sort examine the rate at which test particles, usually either bacteria or some inert aerosol, are removed from the lung and respiratory tract. If bacteria are used, there are two possible indices: a) test bacteria which are exhaled or cleared in mucus transport can be analyzed directly; b) bacteria which are not cleared cause the test animals to become ill or die. In the latter case increases in the incidence of respiratory infection are the final result. Since people do breathe polluted air and contract respiratory infections from time to time, data obtained from these kinds of studies can be translated directly to health effects. Frequently, changes in the incidence of respiratory infections are observed at pollutant doses up to an order of magnitude lower than those required to elicit changes in respiratory function or even lung morphology. However, this approach examines only one kind of pathological change. It does not deal with the etiology of changes in disease-resistance; it completely ignores changes in lung and respiratory systems which give rise to chronic illnesses such as cancer, emphysema, cardiovascular disorders, subclinical or preclinical edema, or metabolic changes. On the other hand, particle clearance studies do offer some insight into how one pollutant affects the disposition of other pollutants in the lung, or how "synergisms" in health effects might arise from combinations of two or more pollutants. Particle clearance should therefore be investigated in conjunction with other experimental approaches in order to obtain a more comprehensive and uniform assessment of the health effects of pollution.

5.2 Possible future studies

Substantial gaps exist in our information base on pollutants and their health effects, not only because many previous studies were carried out imprecisely or incompletely, but also because many of the most important questions have not been investigated properly by anyone. Section 5.1 has indicated areas in which previous studies have been deficient and has suggested how this might be remedied; in view of the remaining uncertainties, as discussed in that section and in section 4, we presume that epidemiological, physiological, and biochemical studies will continue on a broad and large scale. The present section offers some possibilities for more precise and, in some cases, more basic work to determine the health impacts of air pollution from fossil-fuel and geothermal facilities. This listing of future studies is not complete or exhaustive in any sense. However, it broadly notes those areas which require a change in effort.

5.2.1 Biochemical Analyses

An understanding of the biochemical reactions of air pollutants with living systems is important and desirable for determining the etiology of pollution related health effects, and for pointing out target illnesses for epidemiological research. While some efforts in this direction have been reported, the vastness of the range of possible interactions is such that considerable additional study should be encouraged. The fruits of successful investigations here could lead to the development of preventive and/or therapeutic measures for the abatement of air pollution-related health effects at the level of the exposed individual. The sections below suggest some areas of future endeavor which might become the most productive in this regard.

5.2.1.1 Characterization of Detoxification and Metabolic Alterations

The interactions of air pollutants with the drug and toxin metabolizing systems of lung tissues are presently not understood. Little is known about the lung's ability to detoxify air pollutants, or about the capacity of pollutants to aggravate the toxic effects of other foreign chemicals or microorganisms. Future work should be directed toward learning the fates of foreign substances, drugs, and hormones in the presence of the air pollution products of fossil-fuel combustion. The implications of these interactions for lung structure and function resistance to infections, behavior, and stresses on other body organs are obvious.

5.2.1.2 Correlations with Suspected Physiological Effects

As suggested above, there should exist an underlying biochemical cause for the observed physiological, pathological, morphological, and epidemiological effect of combustion-generated air pollutants. Finding the metabolic lesions responsible for the more gross effects would make possible effective efforts for control and treatment. Future investigations should attempt to examine metabolic activities in individual cell populations, so that real "hits" do not become diluted into relatively small changes in enzyme activities or substrate/intermediate concentrations.

5.2.1.3 Biochemical Surveys Among Human Populations

Body burden analysis of air pollutant exposure is essentially a biochemical indicator (see Section 4.3.5) which can be related to other kinds of health effects. As an index of pollutant exposure itself, body burden analysis is preferable to central station air monitoring, because the burden levels (Hb-CO, etc.) reflect the pollutants concentrations which the individual subjects actually breathe. Body burden analysis has been used for many years for monitoring the population exposures and health effects of CO (as Hb-CO) and lead. Recently, methemoglobin body burden analysis has been applied to study populations as an indicator of exposure and health risks to NO and NO_2. This approach should be extended to as many pollutants as can be studied in this manner, because the use of pollutant body burden measurements (as opposed to central station air monitoring) eliminates a major source of uncertainty and error in epidemiological surveys. Ultimately, of course, the affect of ambient pollutant levels must be ascertained; however, using body burdens as the causal variable may serve to break down the epidemiological approach into tractable portions.

5.2.2 Pollutant Monitoring

5.2.2.1 Qualitative and Quantitative Characterizations

A great deal can and should be done in the near future to improve the resolution, precision, and accuracy of air pollution monitoring systems.

Improvement in the quality of existing instrumentation is clearly called for and to some extent is occurring. In some cases, development and acceptance of existing analytical procedures which are capable of quantitively determining ambient pollutant concentrations on a real time basis would be sufficient. In other cases, however, new techniques for qualitative resolution of undefined or unidentified species are necessary.

Particulates are one class of pollutants for which both qualitative and quantitative analytical capabilities need to be improved. No one has successfully elucidated the complete chemical composition of combustion-generated particulates. Previous attempts have results in the nearly complete characterization of carbonaceous species, but only for a solvent extraction technique which is known to account for perhaps 30 per cent of the total carbon mass. Other, more exhaustive procedures for analyzing carbon in aerosols have not been sufficient to resolve the organic species into more than 3 to 4 very general and operational classifications. Additional methods are now available which should allow investigators to determine in greater detail which carbonaceous species are present in particles as well as to give information on their surface distributions. While trace elements have been more thoroughly characterized in particulates than has carbon, little information on surface properties is available for these substances either.

The surface properties of particulates are important, not only because these are the sites for heterogeneous catalysis of atmospheric reactions, but also because any direct reactions with body tissues would occur with these constituents. Dependence of reactivity on surface properties desperately needs to be investigated. Additional effort to widen the distribution of air monitoring sites capable of aerosol size-sorting should be made, as well. This would allow a critical assessment of respirable aerosol concentrations in the atmosphere and would also provide community-wide information on the catalytic or reactive surfaces that are present.

Because sulfates have now been implicated as dangerous air pollutants, their characterization deserves some attention. It is well known that all sulfates are not alike, either in terms of their health effects or in terms of their presence in the air. Consequently, techniques for measuring sulfates in the air or in power plant plumes should determine their chemical form. Furthermore, analytical methods for air monitoring should be upgraded so that it is possible to measure a 5 $\mu g/m^3$ sulfate level meaningfully. The present wet chemical methods do not allow this, but other more physical techniques have demonstrated promise in this area.

Nitrogeneous pollutants represent another area of difficulty in air monitoring. Very little information is presently available on the effects of air-borne nitrates or air-borne ammonia on human health. Relatively little is known about how these species are formed in the atmosphere, and prevalent (wet chemical) analytical techniques are generally insufficient to monitor the atmosphere accurately on a real time basis. New procedures now exist which extend the NH_3 and nitrate measurement capabilities so that reliable area-wide measurements can be made in the future. Organic nitrogen compounds represent a much more difficult analytical problem, although recent breakthroughs in nitrosamine (organic N-nitroso-amine) monitoring should allow for the first time a wide scale measurement of these carcinogens. In view of the relation between urban population density and cancer rates, nitrosamine measurements should definitely be carried out to find out: a) how much is present in urban air, b) how these are formed in the air. In addition, since NO may play role in community risks of cardiovascular disease, routine area-wide monitoring programs should be measuring NO concentrations (as well as NO_2). This is not presently being done on a wide scale in California.

5.2.2.2 Personal Dosimetry

In instances for which body burden analysis of air pollutant exposure is not possible, the next best alternative for epidemiological studies is personal dosimetry. In these situations, the subjects of the study are themselves the monitoring stations for air pollutant analysis. This procedure is now routinely used in occupational monitoring, especially for mine workers and others in hazardous occupations. In order for personal dosimetry to be effective in ambient air applications, existing air monitoring systems would have to be miniaturized and improved in sensitivity and interference control. This task presumably would require several years of analytical method development, but should definitely be pursued. Once accomplished, specialized epidemiological studies using personal monitors would be possible.

5.2.3 Interactions Among Pollutants in the Atmosphere

Many of the pollutants emitted from stationary fossil-fuel combustion sources are dangerous to urban populations not so much because of their primary toxicity, but rather because the reaction products of these pollutants in the atmosphere are far more hazardous. This is certainly true for NO and SO_2, and probably also for combustion particulate emissions.

Because of recently burgeoning interest in atmospheric sulfates as a health hazard, the problem of how sulfates are produced in the air certainly deserves close attention. However, existing data on sulfate formation are presently in a state of flux and conflict with regard to atmospheric sulfur chemistry. Competing SO_2 oxidation mechanisms such as photochemistry, metal catalysis, and carbon catalysis obviously bear on the types of SO_2 and particulate control measures which would be desirable to incorporate into a power plant. Further analytical chemistry data on SO_2 and sulfate reactions in the air are sorely needed in order to identify the co-pollutants responsible.

Several investigations have alluded to the possibility that SO_2 (or H_2SO_4 or some other sulfurous pollutant) participates actively in the formation of photochemical oxidants. However, there presently are virtually no hard data in support of this claim. Elucidation of sulfur compounds as catalysts in oxidant formation probably will require artifical smog chamber experiments, since the ubiquitous co-presence of nitrogen oxides would undoubtedly obscure any results from field studies.

Perhaps the greatest question of analytical environmental chemistry at this point is the role of combustion generated particulates in secondary reactions in the atmosphere. This question has largely been ignored in the past because particulate pollutants are much more difficult to characterize and define than are the gases. Smog chamber-type studies, using controlled combustion conditions to give predictable but "real-life" aerosols and doping the plume with test gases, will probably provide the most reliable information in this area. However, the improved ambient monitoring capabilities discussed in Section 5.2.2 will be necessary to characterize more fully the atmospheric pollutant mix and resulting human exposures.

5.3. Deficiencies in Existing Standards

5.3.1 Ambient Air Quality Standards

Ambient air quality standards are derived for the purpose of protecting the health and welfare of people in a community from the harmful effects of pollutant exposure. Three factors are necessarily defined in an ambient air quality standard: 1) a maximum allowable pollutant concentration; 2) an averaging time over which concentration measurements are to be taken; and 3) a prescribed method for measuring the pollutant. This section is not concerned with deficiencies in the analytical and health studies on which the existing standards are based, but rather on flaws in the standards as formulated.

Sulfur Dioxide

The principal difficulty with existing SO_2 and sulfate standards is the limitation on the averaging time posed by the analytical method. The EPA reference method for SO_2 requires a sampling (and analysis) time on the order of 1-2 hours for an individual measurement in order to give reliable data. Hence, it is not realistic for the EPA to promulgate a one-hour standard for SO_2, even if one is needed, using its reference method. In addition, recent EPA surveys have found that data obtained from the pararosaniline reference method by the majority of public and commercial analytical laboratories are not accurate and reliable. The EPA has promulgated a formal procedure for certifying alternative analytical procedures as equivalent methods for SO_2, and many of these operate on a nearly real-time basis, so that truly continuous monitoring of SO_2 can be carried out.

The California standards for SO_2 prescribe the use of a conductimetric method for analysis. Unfortunately, conductimetry measures all acid-formings, including H_2SO_4, NO_2, and CO_2, and interference control is difficult. While no formal method now exists for the certification of equivalent methods for SO_2 analysis by the ARB, there is an informal procedure which stipulates that; "any equivalent procedure which can be shown to the satisfaction of the Air Resources Board to give equivalent results at or near the level of the air quality standard may be used." This procedure does not allow substitution of other methods on the basis that reference method data would be erroneous. Because of the large discrepancy between the EPA and ARB SO_2 standards, for the same (24 hour) averaging time, a reexamination of the criteria on which both sets of standards were promulgated is warranted.

Sulfates

There are two major drawbacks with the existing ARB standard for sulfates. The first is the apparent absence of discrimination in the standard itself. Sodium sulfate, which arises mostly from natural background sources and which is neither toxic nor irritating, is included by the regulations in the total atmospheric sulfate burden. The standard does not, for example, specify airborne combinations of metal sulfates, sulfuric acid, and ammonium sulfates as substances to be regulated. Therefore, to be consistent with the results of the criteria studies, the standard should either be redefined to specify which sulfates are to be regulated, or be raised by 4-5 $\mu g/m^3$ to account for the natural coastal background.

The ARB reference method for analysis of sulfates is a turbidimetric procedure which follows a high-volume particle collection. Besides being subject to interferences from other co-precipitating agents, the turbidimetric procedure is not a particularly sensitive or accurate method for sulfate analysis. Analytical data obtained in this manner should be treated as ± 5 $\mu g/m^3$ at best. Other methods for sulfate analysis which are more accurate, precise, and which discriminate among different forms of sulfates are available and should be considered.

Nitric Oxide

Ambient air quality standards for NO do not presently exist. Previous associations of the oxidation rate of NO to NO_2 may have been too high in some cases. Recent biomedical evidence points to similarities in its health effects to those of CO. Given that information, an 8-12 hour standard of 3-5 ppm would seem justified, even though this level is rarely reached in open areas. Analytical methods for NO are rather limited in number, but chemiluminescence appears to be a promising candidate as a NO reference method, just as it is for NO_2.

Nitrogen Dioxide

The only drawback associated with (California) NO_2 standards at the present time is selection of a wet chemical reference method. The Saltzman reaction requires short sampling times and minimal delay between sampling and analysis. This factor limits the distribution of monitoring sites to those which are quickly accessible to an analytical facility on a routine basis. Provision for a continuous monitoring technique, such as chemiluminescence, as an alternative reference method or an equivalent method is strongly recommended.

Oxidants

Existing EPA and ARB standards for oxidants both equate oxidant levels in the atmosphere with ozone concentrations. This is a practical equivalence since both reference methods are specific for ozone and largely ignore other oxidants, such as peroxyacetyl nitrates (PAN). While this is justifiable in most circumstances, under episode conditions concentrations of PAN, nitric acid, and other non-ozone oxidants may be quite high, and should be monitored separately or by difference methods. While both the ARB (ultraviolet photometry) and the EPA (chemiluminescence) reference methods are sensitive and precise, some question exists concerning the accuracy of the EPA method and concerning interferences with the ARB method. To avoid a repetition of embarrassing past errors on ozone concentrations in California air basins, provision for additional reference and equivalent methods, combined with better coordination with EPA, is strongly recommended.

5.3.2 Occupational Standards

Air quality standards in the workplace exist in order to protect employees from the health hazards due to pollutants produced at the plant. These standards are invariably not as stringent as ambient air standards because workers are assumed to be in generally better health than the community population as a whole, because workers are exposed inside the plant for only 40 hours per week, and because of the presumption that workers accept a higher level of risk. The diversity of specific substances whose occupational concentrations are subject to regulation is much greater than for ambient air. Occupational standards do not specify or recommend reference or equivalent methods for the measurement of pollutants in the workplace. Consequently, routine monitoring is usually carried out by means of relatively inexpensive methods which may, in fact, be only semi-quantitative or reliable only to within an order of magnitude of the actual pollutant concentrations. For many occupational situations, improved quality assurance mechanisms might be desirable.

5.3.3. Emission Standards

Existing source performance standards are predictated on the capabilities of current pollution control technologies. Most of State and Federal regulations limit the amount of a specific pollutant emitted into the air on the basis of input (fuel) consumed. It would be much more desirable to limit emissions on the basis of output (power) produced, because under present regulations, there is no incentive to reduce emissions by improving the energy-efficiency of the plant. For similar reasons, regulations limiting fuel sulfur, for example, might be based on output power rather than on input fuel consumption.

On the other hand, in order to be consistent with their mission to maintain acceptable air quality, local regulatory agencies might emphasize emissions standards or goals based on impact on ambient air quality rather than on capabilities of existing technology. In order to do this correctly, information is needed on source emission strengths, plume dispersion maps, and secondary reaction chemistry. With some difficulty, this kind of information can be assembled for many California air basins. It could be used to formulate a consistent basis for the new source review process.

Particulates

Present EPA and ARB standards for airborne particulate matter consider only the total mass of suspended particles collected by high-volume sampling. These regulations are qualitatively and quantitatively deficient in information content. All existing studies of the health effects of particulates point to the need to monitor and regulate aerosols according to size and chemical composition. No such regulatory program now exists. The total mass regulations do not make exception for airborne soil dust or sea salts, whose health effects are obviously very different from each other and from man-made particulates.

Furthermore, no standards presently exist for specific chemical substances in airborne particulates whose toxicological properties are known, with the exception of lead and sulfates in California. Air quality standards for particulate matter should be redefined in order to account for the differences due to size, chemical composition, and particle origin.

In addition, the reference method for particulates should be revised accordingly. High-volume sampling allows the determination of total mass and the chemical analysis of a limited range of substances; all size data are lost on the collection filters. Several methods now exist for particle size analysis which offer the choice of non-destructive measurement or size-resolved collection. These should be considered in the revision of a particulate standard.

5.4 Assessment of Human Impacts from New Sources

Given sufficient information on the emissions, dispersion,and health effects of conventional air pollutants, it would be possible to determine the community health impacts of new fossil-fuel and geothermal power plants. At the present time, however, no reliable estimates can be made. Although the emissions from power plants may be characterized reasonably well in principle, the details of their dispersion and interaction in the atmosphere and especially the manner and extent of their resulting effects on human health are too poorly known to permit an overall assessment of the health impact of the introduction of a new source into a specified region. Nevertheless, numerous attempts have been made to estimate the impacts of power plants and their associated support facilities on human health. The discussion in the body of this report offers plentiful reason for discounting any precise estimate of this sort. However, in order to demonstrate the range of quantitative estimates, we briefly mention a number of representative estimates, which -- as will be seen -- often differ by orders of magnitude. Many such estimates are summarized in a recent article by Comar and Sagan.[1]

The usefulness of these estimates should be considered in light of their individual purposes, the pollutants which they considered, and the type of health effects considered, as well as the specific health-effects basis of the estimates. For example, a recent estimate arose as part of a "quantitative framework" used for making judgments on stationary source emission controls by the National Academy of Sciences - National Academy of Engineering - National Research Council. Their 1975 report offered health effects estimates (due to fossil-fuel plants) based solely on alteration of ambient sulfate concentrations due to uncontrolled sulfur dioxide emissions. The health effects were stated in terms of "premature deaths", cases of children's lower respiratory disease, asthma attacks, person-days of aggravated heart-lung disease symptoms, and cases of chronic respiratory disease. It is difficult to compare these differing types of health effects. However, in terms of the valuation used in their report,[2] the last two categories dominate the total health effect, and it is difficult to see how the relatively small number of premature deaths estimated could be considered to be as harmful, overall, as the much larger number of lesser health effects. It should be emphasized again that the numbers we will now quote were used as part of a judgmental framework and not as an independent estimate of health effects. The numbers are very uncertain and include a factor of 20 uncertainty from the estimated health effects of a given increase in the ambient sulfate concentration.

For a 600 MWe power plant burning 3% sulfur fuel without sulfur emission control, reference 11 estimated the increase in average annual ambient sulfate concentration to be 0.145 $\mu g/m^3$, with a population at risk of 50 million, for a remotely sited plant, and 1.86 $\mu g/m^3$, with a population at risk of 11.5 million, for an urban sited plant. The estimated health effects are:

	Remote	Urban
Cases of chronic respiratory disease	25,600	75,500
Person-days of aggravated heart-lung disease symptoms	256,000	755,000
Asthma attacks	53,000	156,000
Cases of children's respiratory disease	6,200	18,400
Premature deaths	14	42

(All these results assumed a background ambient concentration of 16 $\mu g/m^3$.)

These results are cited, not because they are accurate, but because they are instructive. They were calculated to provide a framework for the formulation of sulfur control strategies. Similar estimates have been made for other purposes. For example, Lave and Freeburg[12] attempt to estimate health effects from oil, coal, and nuclear fuel on a comparative basis, concluding that routinely operating nuclear power plants have smaller public impacts than coal-fired plants, but that a similar comparison with oil-fired plants yields less conclusive results. This is the same conclusion that one would draw, roughly, from Table 5.4-1 (reproduced from Ref. 11), where the number of premature deaths to workers and to members of the general public from routine operation of various portions of nuclear and fossil fuel cycles are compared. Restricting our attention to the public impacts of the power plant itself ("general public, conversion"), we would conclude that nuclear offers less risk to the public than coal or oil. This conclusion would be strengthened, considering the fact that the major impact of fossil-fuel combustion comes through less severe health effects than death (see above), but the same is not considered to be true of radioactive emissions. However, it should be noted that the uncertainties for fossil-fuel impacts are 2 or 3 orders of magnitude, most of which arises from uncertainties in the dose-response relationship. Similar technological comparisons have been attempted in other reports, cited in reference 10.

Table 5.4-1 Premature deaths per year associated with operation of a 1000-MWe power plant (values are lowest and highest estimates from cited references)[a]

	Coal	Oil	Natural Gas	Nuclear
Occupational				
Extraction				
Accident	0.45–0.99 (15, 17, 18, 21, 22)	0.06–0.21 (15–18, 22)	0.021–0.21 (15–18, 22)	0.05–0.2 (15, 17, 18, 20, 22)
Disease	0–3.5 (17)	--	—	0.002–0.1 (17, 19, 20, 22)
Transport				
Accident	0.055–0.4 (15, 17, 18, 22)	0.03–0.1 (15–17, 22)	0.02–0.024 (15, 17, 18, 22)	0.002 (15, 18, 22)
Processing				
Accident	0.02–0.04 (17, 18)	0.04–1 (15–18, 22)	0.006–0.01 (15, 17, 18, 22)	0.003–0.2 (15, 17, 18, 20, 22)
Disease	--		--	0.013–0.33 (17, 19, 20, 22)
Conversion				
Accident	0.01–0.03 (15–18, 22)	0.01–0.037 (15–18, 22)	0.01–0.037 (15–18, 22)	0.01 (15, 17, 18, 22)
Disease	—	—	—	0.024 (20)
Subtotals				
Accident	0.54–1.5	0.14–1.3	0.057–0.28	0.065–0.41
Disease	0–3.5	--	—	0.039–0.45
Total	0.54–5.0	0.14–1.3	0.057–0.28	0.10–0.86
General Public				
Transport	0.55–1.3 (15, 17, 21, 22)		--	—
Processing	1–10 (17)	--	—	—
Conversion	0.067–100 (17, 21)	1–100 (17)	--	0.01–0.16[b] (15, 17, 19, 20, 22)
Total	1.6–111	1–100		0.01–0.16
Total Occupational and Public	2–116	1.1–101	0.057–0.28	0.11–1.0

[a] Note: Dashes indicate no data found; effects, if any, are presumably too low to be observed; and no theoretical basis for prediction.

[b] For processing and conversion.

In view of the large uncertainties, no basis presently exists for making quantitative estimates of the health effects of conventional emissions into air. The one pollutant for which such attempts are often made, as might be inferred from the discussion above, is sulfates. Workers at Brookhaven National Laboratory are attempting to assemble a quantitative framework for health-effects assessment,[3] beginning, as above, by concentrating on the health impacts of sulfates. In view of the importance of other pollutants in California air basins, it is unlikely that such a limited assessment, even if successful, would be appropriate for the California situation.

For specific siting decisions, one might consider the advisability of a somewhat less ambitious approach, i.e., to establish exposure categories, calculate the associated populations at risk, and use this information for comparing sites. Note that the calculation performed in reference 11 for sulfates established a single exposure category, i.e., average annual increase in ambient sulfate concentration, and calculated health effects from that on the basis of a linear dose-response with a threshold (which was exceeded by the "background" ambient concentration). In view of the lack of dose-response relationships for many pollutants, site-specific assessments can retreat one step, relying directly on the size of the population at risk for specific exposure categories. However, in view of the uncertainties in atmospheric dispersion and transformation and in health effects associated with various pollutants, establishment of this type of assessment framework would necessarily be extremely tentative. As more reliable and detailed information is developed, its value and dependability would substantially increase. Establishment of such assessment frameworks and of the broader but less detailed type of framework discussed in Ref. 13 would serve as a useful background for the much more extensive and detailed effort which needs to be devoted to the qualitative and quantitative elucidation of fundamental dispersion, transformation, and health-effects phenomena.

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Appendix A - Air Pollution Control District Rules and Regulations

(taken from the updated ERCDC staff compilation; auxiliary tables not included in this appendix, but supplied with the updated compilation to the ERCDC staff)

TABLE III-1 DISTRICT AIR POLLUTION RULES AND REGULATIONS

AIR BASINS	GREAT BASIN VALLEYS AIR BASIN	LAKE COUNTY AIR BASIN	LAKE TAHOE AIR BASIN	
AIR POLLUTION CONTROL DISTRICTS	Great Basin Unified APCD Alpine, Inyo, Mono Counties	Lake County APCD	El Dorado County APCD	Placer County *Plan accepted by Lake Tahoe Air Basin Control Council on 8/25/76. To be ratified.*
SULFUR				
Sulfur Compounds	*0.2% (max.) by dry volume, SO_2*	1,000 ppm (max.) SO_2	0.2% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2
Sulfur Content of Fuels				
Fuel Burning Equipment			New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2
Totally Reduced Sulfur			Pending Further Investigation	Pending Further Investigation
OXIDES OF NITROGEN				
Fuel Burning Equipment	New Equipment Limited to 140 lbs/hr (max.) NO_2 Max. Heat input > 1.5 x 10^9 Btu/hr Gross Gaseous fuel, 3% O_2 125 ppm NO_2 Liquid/Solid, 3% O_2 225 ppm NO_2		New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2
CARBON MONOXIDE				
Carbon Monoxide				
PARTICULATE MATTER				
Particulate Matter	0.3 grains/scf. (max.)		0.1 grains/scf (max.)	0.1 grains/scf (max.)
Process Weight Dust and Fumes	See Table 2 40.0 lbs/hr max. for process weight $\geq$ 60,000 lbs/hr		See Table 6 46.8 lbs/hr max. for process weight $\geq 1 \times 10^6$ lb/hr	See Table 6 46.8 lbs/hr (max.) for process weight $\geq 1 \times 10^6$ lbs/hr
Combustion Contaminants		0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2	0.1 grains/scf (max.) @ 12% CO_2
Fuel Burning Equipment			New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants
Visible Emissions	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *
NEW SOURCE PERFORMANCE STANDARDS				

TABLE III-1 (continued)

AIR BASINS	MOUNTAIN COUNTIES AIR BASIN				
AIR POLLUTION CONTROL DISTRICTS	Amador County APCD	Calaveras County APCD	El Dorado County APCD	Mariposa County APCD	Nevada County APCD
SULFUR					
Sulfur Compounds	0.20% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2	0.2% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2	0.2% (max.) by dry volume SO_2
Sulfur Content of Fuels					
Fuel Burning Equipment	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2
Totally Reduced Sulfur	Pending Further Investigation	Pending Further Investigation	Pending Further Investigation	Pending Further Investigation	Pending Further Investigation
OXIDES OF NITROGEN					
Fuel Burning Equipment	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)
Process Weight Dust and Fumes	See Table 6 46.8 lbs/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 6 46.8 lbs/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 6 46.8 lbs/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 6 46.8 lbs/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 6 46.8 lbs/hr max. for process weight ≥ 1 x 10^6 lb/hr
Combustion Contaminants	0.1 grain/scf (max.) @ 12% CO_2		0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2
Fuel Burning Equipment	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants
Visible Emissions	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	*Ringlemann No. 2 (max) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *
NEW SOURCE PERFORMANCE STANDARDS					

TABLE III-1 (continued)

AIR BASINS	MOUNTAIN COUNTIES AIR BASIN				NORTH CENTRAL COAST AIR BASIN
AIR POLLUTION CONTROL DISTRICTS	Placer County	Plumas County	Sierra County	Tuolumne County	Monterey Bay Unified APCD Santa Cruz, San Benito, Monterey Counties *Being revised*
SULFUR					
Sulfur Compounds	0.20% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2	0.20% (max.) by dry volume SO_2
Sulfur Content of Fuels					50 grains/100 ft^3 (gaseous fuel) H_2S std. 0.5% by weight (liquid or solid fuel)
Fuel Burning Equipment	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	
Totally Reduced Sulfur	Pending Further Investigation	Pending Further Investigation	Pending Further Investigation	Pending Further Investigation	
OXIDES OF NITROGEN					
Fuel Burning Equipment	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs./hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	140 lbs/hr (max.) NO_2. *For Gross Thermal Input > 1.5×10^9 Btu/hr Natural Gas, Liquid, or Solid fuel, at 3% O_2, 225ppm (max)*
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.15 grains/scf (max.)
Process Weight Dust and Fumes	See Table 6 46.8 lbs/hr (max.) for process weight ≥ 1 x 10^6 lbs/hr	See Table 6 46.8 lbs/hr (max.) for process weight ≥ 1 x 10^6 lbs/hr	See Table 6 46.8 lbs/hr (max) for process weight ≥ 1 x 10^6 lbs/hr	See Table 6 46.8 lbs/hr (max.) for process weight ≥ 1 x 10^6 lbs/hr	*See Table 4* *40.0 lbs/hr (max.) for process weight ≥60,000 lbs/hr*
Combustion Contaminants	0.1 grains/scf (max.) @ 12% CO_2	0.1 grains/scf (max.) @ 12% CO_2	0.1 grains/scf (max.) @ 12% CO_2	0.1 grains/scf (max.) @ 12% CO_2	
Fuel Burning Equipment	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	
Visible Emissions	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour.	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*
NEW SOURCE PERFORMANCE STANDARDS					*Yes*

TABLE III-1 (continued)

AIR BASINS	NORTH COAST AIR BASIN				
AIR POLLUTION CONTROL DISTRICTS	Del Norte County	Humboldt County	Mendocino County APCD	Northern Sonoma County APCD	Trinity County APCD
SULFUR					
Sulfur Compounds	1,000 ppm (max.) SO_2	1,000 ppm (max.) SO_2. Maximum allowable SO_2 Conc. Grn. Level 0.5 ppm - 1 hour 0.04 ppm - 24 hrs. avg.	1,000 ppm (max.) SO_2. Maximum allowable SO_2 Conc. Grn. Level 0.5 ppm - 1 hour 0.04 ppm - 24 hrs. avg. (2 ppm at any time)	1,000 ppm (max.) SO_2. Max. allowable SO_2 Conc. grd.-level 0.5 ppm - 1 hr., 0.04 ppm - 24-hr. avg. (or 2 ppm at any time)	1,000 ppm (max.) SO_2
Sulfur Content of Fuels					
Fuel Burning Equipment					
Totally Reduced Sulfur	*≤ 10% H_2S produced or 0.4 lbs/hr/MW 24 hr average, not to exceed 80 lbs/hr/max. See Table 12*	*≤ 10% H_2S produced or 0.4 lbs/hr/MW 24 hr average, not to exceed 80 lbs/hr/max. See Table 12*	*≤ 10% H_2S produced or 0.4 lbs/hr/MW 24 hr average, not to exceed 80 lbs/hr/max. See Table 12*	*≤ 10% H_2S prod.or 0.4 lbs/hr/MW 24 hr average, not to exceed 80 lbs/hr (max), except Zone 1, see Fig. 2 and Table 12*	*≤ 10% H_2S produced or 0.4 lbs/hr/MW 24 hr average, not to exceed 80 lbs/hr/max. See Table 12*
OXIDES OF NITROGEN					
Fuel Burning Equipment					
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	*0.1 grains/scf (max).*	*0.1 grains/scf (max.)*	*0.1 grains/scf (max).*	*0.1 grains/scf (max).*	*0.1 grains/scf (max).*
Process Weight Dust and Fumes	*See Table 4 40.0 lbs/hr (max.) for process weight ≥60,000 lbs/hr*	*See Table 4 40.0 lbs/hr (max.) for process wieght ≥60,000 lbs/hr*	*See Table 4 40.0 lbs/hr (max.) for process wieght ≥60,000 lbs/hr*	*See Table 4 40.0 lbs/hr (max.) for process wieght ≥60,000 lbs/hr*	*See Table 4 40.0 lbs/hr (max.) for process weight ≥60,000 lbs/hr*
Combustion Contaminants	*0.1 grains/scf (max.) @ 50% air or 12% CO_2*	0.1 grains/scf (max.) @ 12% CO_2	*0.1 grains/scf (max.) @ 12% CO_2*	*0.1 grains/scf (max.) @ 12% CO_2*	*0.1 grains/scf (max.) @ 50% air or 12% CO_2*
Fuel Burning Equipment					
Visible Emissions	Ringlemann No. 2 (max.) 3 minutes in any 1 hour	Ringlemann No. 2 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	*Ringlemann No. 2 (max.) 3 minutes in any 1 hour*	Ringlemann No. 2 (max.) 3 minutes in any 1 hour
NEW SOURCE PERFORMANCE STANDARDS	Yes	Yes	Yes	Yes	Yes

TABLE III-1 (continued)

AIR BASINS	NORTH EAST PLATEAU AIR BASIN			
AIR POLLUTION CONTROL DISTRICTS	Lassen County APCD	Modoc County APCD	Shasta County APCD *Also in Sacramento Valley Air Basin*	Siskiyou County APCD
SULFUR				
Sulfur Compounds	0.2% by volume (max.) SO_2	0.20% by volume (max.) SO_2	1,000 ppm (max.) SO_2	0.20% by volume (max.) SO_2
Sulfur Content of Fuels	50 grains/100 ft^3 of gaseous fuel (H_2S) 0.5% by weight liquid/solid	50 grains/100 ft^3 of gaseous fuel (H_2S) 0.5% by weight for liquid/solid		
Fuel Burning Equipment				
Totally Reduced Sulfur			*17.5 ppm as H_2S for new sources*	60 ppm by dry volume (max.) *(sulfides)*
OXIDES OF NITROGEN				
Fuel Burning Equipment				New Equipment Limited to 140 lbs/hr (max.) NO_2
CARBON MONOXIDE				
Carbon Monoxide				
PARTICULATE MATTER				
Particulate Matter	0.3 grains/scf (max.)	0.3 grain/scf (max.)	0.1 grain/scf (max.) existing Δ source < 1000 ft & New Sources 0.2 grain/scf (max.) Existing source > 1000 ft	0.3 grain/scf (max.)
Process Weight Dust and Fumes	See Table 9 69.0 lbs/hr (max.) for process weight ≥ 1 x 10^6 lbs/hr	See Table 8 92.7 lbs/hr (max.) for process process weight ≥ 8 x 10^6 lbs/hr	See Table 4 40.0 lbs/hr (max.) for process weight ≥ 60,000 lbs/hr	See Table 2 40.0 lbs/hr (max.) for process weight ≥ 60,000 lbs/hr
Combustion Contaminants	0.3 grains/scf (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2	0.15 grains/scf (max.) existing source < 1000 ft. New & source 0.2 grain/scf existing source > 1000ft @ 12% CO_2	
Fuel Burning Equipment				
Visible Emissions	Ringlemann No. 2 (max.) 3 minutes in any 1 hour *	Ringlemann No. 2 (max.) 3 minutes in any 1 hour *	Ringlemann No. 2 (max.) 3 minutes in any 1 hour	Ringlemann No. 2 (max.) 3 minutes in any 1 hour *
NEW SOURCE PERFORMANCE STANDARDS				*after 1/30/???*

Δ Existing Source refers to prior 6/1/72

TABLE III-1 (continued)

AIR BASINS	← SACRAMENTO VALLEY AIR BASIN →			
AIR POLLUTION CONTROL DISTRICTS	Butte County APCD	Colusa County APCD	Glenn County APCD	Sacramento County APCD
SULFUR				
Sulfur Compounds	0.20% (2,000 ppm) by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2
Sulfur Content of Fuels				*11 grams/m^3 sulfur compounds calculated as H_2S (gas.) 0.5% by wt liq./sol.*
Fuel Burning Equipment				
Totally Reduced Sulfur	0.03 ppm for 60 min. period Ground Level Emissions *expressed as H_2S*		0.03 ppm for 60 minute period Ground Level Emissions *expressed as H_2S*	
OXIDES OF NITROGEN				
Fuel Burning Equipment				
CARBON MONOXIDE				
Carbon Monoxide				
PARTICULATE MATTER				
Particulate Matter	0.3 grains/scf (max.)	0.3 grains/scf (max.)	0.3 grains/scf (max.)	0.3 grains/scf (max.)
Process Weight Dust and Fumes	See Table 6 92.7 lbs/hr max for process weight $\geq 6 \times 10^6$ lbs/hr	See Table 6 92.7 lbs/hr max. for process weight $\geq 6 \times 10^6$ lbs/hr	See Table 6 92.7 lbs/hr max. for process weight $\geq 6 \times 10^6$ lbs/hr	See Table 2 40.0 lbs/hr max. for process weight $\geq$ 60,000 lbs/hr
Combustion Contaminants	0.3 grains/scf. (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2
Fuel Burning Equipment				
Visible Emissions	Ringlemann No. 2 (max.) 3 minutes in any 1 hour *	Ringlemann No. 2 (max.) 3 minutes in any 1 hour *	Ringlemann No. 2 (max.) 3 minutes in any 1 hour	Ringlemann No. 2 (max.) 3 minutes in any 1 hour *
NEW SOURCE PERFORMANCE STANDARDS			Yes	

TABLE III-1 (continued)

AIR BASINS	SACRAMENTO VALLEY AIR BASIN		SACRAMENTO VALLEY AIR BASIN		
AIR POLLUTION CONTROL DISTRICTS	Shasta County APCD *Also in Northeast Plateau Air Basin*	Sutter County APCD	Tehama County APCD	Yolo-Solano County APCD Yolo County Northeast Solano County	Yuba County APCD
SULFUR					
Sulfur Compounds	1000 ppm by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2
Sulfur Content of Fuels			50 grains/100 ft^3 std gaseous (H_2S) fuel - 0.5% by weight liquid/solid		
Fuel Burning Equipment		New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	
Totally Reduced Sulfur					
OXIDES OF NITROGEN					
Fuel Burning Equipment		New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment limited to 140 lbs/hr. (max.) NO_2. For Gross Thermal Input > 1.775 x 10^9 Btu/hr. Natural Gas 3% O_2, 125 ppm; Liquid/Solid Fuel 3% O_2, 225 ppm.	New Equipment Limited To 140 lbs/hr (max.) NO_2	
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	0.1 grain/scf (max.) existing source < 1000 ft. New Source 0.2 grain/scf (max.) Existing source > 1000 ft.	*0.1 grains/scf (max).*	0.3 grains/scf (max.)	0.3 grains/scf (max.)	0.3 grains/scf (max.)
Process Weight Dust and Fumes	See Table 4 40.0 lbs/hr max. for process weight ≥ 60,000 lbs/hr	See Table 8 92.7 lbs/hr max. for process weight ≥ 6 x 10^6 lbs/hr	See Table 8 92.7 lbs/hr max. for process weight ≥ 6 x 10^6 lbs/hr	See Table 7 40.0 lbs/hr (max.) for process weight ≥ 58,300 lbs/hr	See Table 8 92.7 lbs/hr (max.) for process weight ≥ 6 x 10^6 lbs/hr
Combustion Contaminants	0.15 grain/scf (max.) existing source < 1000 ft. New Source 0.2 grain/scf (max.) existing Source > 1000 ft @ 12% CO_2	*0.1 grains/scf (max.) @ 12% CO_2*	0.3 grains/scf (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2
Fuel Burning Equipment		New Equipment Limited to 10 lbs/hr Combustion Contaminants	New Equipment Limited to 10 lbs/hr Combustion Contaminants	New Equipment Limited to 40 lbs/hr Combustion Particulates	
Visible Emissions	Ringlemann No. 2 (max.) 3 minutes in any 1 hour	*Ringlemann, No. 1 (max) 3 minutes in any 1 hour*	Ringlemann No. 2 (max.) 3 minutes in any 1 hour	Ringlemann No. 2 (max.) 3 minutes in any 1 hour*	Ringlemann No. 2 (max.) 3 minutes in any 1 hour
NEW SOURCE PERFORMANCE STANDARDS				*Soon?*	

TABLE III-1 (continued)

AIR BASINS	SAN DIEGO AIR BASIN	SAN JOAQUIN VALLEY AIR BASIN	SAN JOAQUIN VALLEY AIR BASIN		
AIR POLLUTION CONTROL DISTRICTS	San Diego County APCD *Also in Southeast Desert Air Basin*	Fresno County APCD	Kern County APCD Valley - Basin *Also in Southeast Desert Air Basin*	Kings County APCD	Madera County APCD
SULFUR					
Sulfur Compounds	0.05% by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2	0.20% by volume (max.) SO_2
Sulfur Content of Fuels	10 grains/100 ft^3 Gaseous fuel (H_2S) 0.5% by weight liquid/Solid				
Fuel Burning Equipment		New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2
Totally Reduced Sulfur					
OXIDES OF NITROGEN					
Fuel Burning Equipment	For Maximum Heat Input ≥ 50 x 10^6 Btu/hr natural Gas, 3% O_2 125 ppm NO_2 Liquid/Solid Fuel, 3% O_2 225 ppm NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2. For Gross thermal inputs ≥ 1.775 x 10^9 Btu/hr Natural Gas 3% O_2 125 ppm NO_2. Liquid/Solid 3% O_2 225 ppm NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2. For gross thermal input 1.775 x 10^9 Btu/hr Natural Gas, 3% O_2 125 ppm NO_2. Liquid/Solid 3% O_2 225 ppm NO_2
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)	0.1 grains/scf (max.)
Process Weight Dust and Fumes	See Table 2 40.0 lbs./hr (max.) for process weight ≥ 60,000 lbs/hr	*See Table 5* *46.72 lbs/hr (max.) for process weight ≥ 1 x 10^6 lbs/hr*	*See Table 5-1* *46.79 lbs/hr (max). for process weight ≥ 1x10^6 lb/hr.*	See Table 5 46.72 lbs/hr max. for process with ≥ 1 x 10^6 lbs/hr	See Table 5 46.72 lbs/hr max. for process weight ≥ 1 x 10^6 lbs/hr
Combustion Contaminants	0.1 grain/scf (max.). @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2
Fuel Burning Equipment		New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants
Visible Emissions	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*
NEW SOURCE PERFORMANCE STANDARDS	*Soon?*	*Yes*	Yes		Yes

TABLE III-1 (continued)

AIR BASINS	←——SAN JOAQUIN VALLEY AIR BASIN——→		←—— SAN JOAQUIN VALLEY AIR BASIN ——→		SAN FRANCISCO BAY AREA AIR BASIN
AIR POLLUTION CONTROL DISTRICTS	Merced County APCD	San Joaquin County APCD	Stanislaus County APCD	Tulare County APCD	San Francisco, San Mateo, Santa Clara, Alameda, Contra Costa, Marin, Napa, and part of Sonoma (southeast) and part of Solano (southwest) counties.
SULFUR					
Sulfur Compounds	0.2% by volume (max.) SO_2	0.2% by volume (max.) SO_2	0.2% by volume (max.) SO_2	0.2% by volume (max.) SO_2	Ground Level Concentrations 0.5 ppm (vol.) 3 consecutive minutes; 0.5 ppm (vol.) avg. 60 consecutive min.; 0.04 ppm (vol.) avg. 24 hours
Sulfur Content of Fuels					*0.6% by weight liquid or solid fuel*
Fuel Burning Equipment	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	
Totally Reduced Sulfur					Ground Level Concentrations H_2S 0.06 ppm (vol.) 3 cons. min. 0.03 ppm (vol.) avg. 60 cons. min. in 24 hr period See Table 11.
OXIDES OF NITROGEN					
Fuel Burning Equipment	New Equipment Limited to 140 lbs/hr (max.) NO_2 for max. heat input >1.775 x 10^9 Btu/hr gaseous fuel 3% O_2 125 ppm NO_2 Solid/liquid 3% O_2 225 ppm NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2 for max. heat input > 1.775 x 10^9 Btu/hr gaseous fuel 3% O_2 125 ppm NO_2 Liquid/Solid 3% O_2 225 ppm NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2 for max. heat input > 1.775 x 10^9 Btu/hr Gaseous fuel 3% O_2 125 ppm NO_2 Liquid/Solid 3% O_2 225 ppm NO_2	New equipment > 250 x 10^6 BTU/hr heat input limited to emission of 125 ppm (gaseous fuel) and 225 ppm (liquid fuel). Any heat transfer operation > 1.75 x 10^9 BTU/hr heat input limited to 175 ppm (gaseous fuel) and 300 ppm (liquid fuel)
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	0.1 grain/scf (max.)	0.1 grain/scf (max.)	0.1 grain/scf (max.)	0.1 grain/scf (max.)	0.15 grain/scf (max.)
Process Weight Dust and Fumes	See Table 5 46.72 lb/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 5 46.72 lb/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 5 46.72 lb/hr max. for process weight ≥ 1 x 10^6 lb/hr	See Table 5 46.72 lb/hr max. for process weight ≥ 1 x 10^6 lb/hr	*See Table 6* *40.0 lbs/hr (max.) for process weight ≥60,000 lbs/hr*
Combustion Contaminants	0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2 *At point of discharge*	0.1 grain/scf (max.) @ 12% CO_2	0.1 grain/scf (max.) @ 12% CO_2	0.15 grain/scf (max.) @ 6% O_2
Fuel Burning Equipment	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	
Visible Emissions	Ringlemann No. 1 (Max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *
NEW SOURCE PERFORMANCE STANDARDS		Yes		*soon?*	Yes

TABLE III-1 (continued)

AIR BASINS	SOUTH CENTRAL COAST AIR BASIN			SOUTH COAST AIR BASIN	
AIR POLLUTION CONTROL DISTRICTS	San Luis Obispo County APCD	Santa Barbara County APCD *Also in South Coast Air Basin*	Ventura County APCD *Now in South Central Air Basin since 9-1-76*	Southern California APCD Los Angeles, Riverside (West Central) San Bernardino, Orange Counties	Santa Barbara (South) APCD *Also in South Central Coast Air Basin*
SULFUR					
Sulfur Compounds	0.2% by volume (max.) SO_2	0.2% by volume (max.) SO_2	300 ppm by volume (max.) SO_2 liquid/gaseous fuel *600 ppm solid*		deleted 5/30/72
Sulfur Content of Fuels	*60 grains/100 ft^3 (max.) calc. as H_2S, gaseous fuels 0.5% by weight, liquid and solid fuels*	50 grains/100 ft^3 (max.) H_2S gaseous fuel 0.5% by weight liquid/solid fuel	50 grains/100 ft^3 std H_2S Gaseous fuel (15 grains/100 ft^3) Natural gas 0.5% by weight liquid/Solid	*600 ppm calc as SO_2 (max.) 16 min.*	*800 ppm H_2S gaseous fuel, 3 days: 0.5% liq./sol. by weight*
Fuel Burning Equipment	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2	New Equipment Limited to 200 lbs/hr (max.) SO_2
Totally Reduced Sulfur	0.005 ppm by volume (max.) avg. 60-min. period. Ground Level, H_2S		10 ppm by volume (max.) H_2S		Maximum Odorous Sulfur (H_2S) .03 ppm 3 min. avg. .06 ppm 24 hour avg.
OXIDES OF NITROGEN					
Fuel Burning Equipment	*New Equipment limited to 140 lbs/hr (max.) NO_2. For max. heat input >1.775×10^9 Btu/hr (gross) @ 3% O_2; gaseous fuel 225 ppm NO_2; liquid or solid fuel 350 ppm NO_2, new sources after 1-1-70 330 ppm NO_2.*	New Equipment Limited to 140 lbs/hr (max.) NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2. For Max. heat input > 2.5 x 10^9 Btu/hr Gaseous Fuel @ 3% O_2 125 ppm NO_2 Liquid/Solid @ 3% O_2 225 ppm NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2 for Max. heat Input > 1.775 x 10^9 Btu/hr gaseous fuel @ 3% O_2 125 ppm NO_2 Liquid/Solid @ 3% O_2 225 ppm NO_2	For Maximum heat Input > 1.775 x 10^9 Btu/hr gaseous fuel @ 3% O_2 125 ppm NO_2 Liquid/Solid @ 3% O_2 225 ppm NO_2
CARBON MONOXIDE					
Carbon Monoxide			2000 ppm by volume (max.) CO	*8000 ppm CO (max.) av. over 16 min.*	2000 ppm by volume (max.) CO
PARTICULATE MATTER					
Particulate Matter	0.3 grain/scf (max.)	0.3 grain/scf (max.)	0.2 grains/scf (max.) ≤ 1000 scf max.	*450 mg/m^3 (0.196 grains/hr) (max.), except liq. 5 av. over 1 hr.*	0.2 grains/scf (max.) ≤ 1000 scfm
Process Weight Dust and Fumes	*See Table 3* *40.0 lbs/hr (max.) for process wieght ≥60,000 lbs/hr*	*See Table 2* *40.0 lbs/hr (max.) for process wieght ≥60,000 lbs/hr*	See Table 3 30.0 lbs/hr max. for process weight ≥ 1 x 10^6 lbs/hr	See Table 3 30.0 lbs/hr max. for process weight ≥ 1 x 10^6 lbs/hr	See Table 3 30.0 lbs/hr max. for process weight ≥ 1 x 10^6 lbs/hr
Combustion Contaminants	*0.3 grains/scf (max.) @ 12% CO_2*	0.3 grains/scf (max.) @ 12% CO_2 *at point of discharge*	0.1 grain/scf (max.) @ 12% CO_2	*0.1 grains/scf (max.) @ 12% CO_2 av. over 15 min.*	0.1 grains/scf (max.) @ 12% CO_2
Fuel Burning Equipment	*New Equipment limited to 10 lbs/hr (max.) Combustion contaminants*	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants
Visible Emissions	Ringlemann No. 2 (max.) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour*	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour
NEW SOURCE PERFORMANCE STANDARDS		*Yes*		*soon?*	*Yes*

TABLE III-1 (continued)

AIR BASINS	←SOUTHEAST DESERT AIR BASIN→		←SOUTHEAST DESERT AIR BASIN→		
AIR POLLUTION CONTROL DISTRICTS	Imperial County	Kern County APCD *Also in San Joaquin Air Basin*	Los Angeles County APCD *So. Cal APCD until 2/1/77*	Riverside County APCD *So. Cal APCD until 2/1/77* That part not included in South Coast.	San Bernardino County APCD *So. Cal APCD until 2/1/77*
SULFUR					
Sulfur Compounds	0.2% by volume (max.) SO_2	0.2% by volume (max.) SO_2		0.15% by volume (max.) SO_2	0.1% by volume SO_2; Liquid or Gaseous 500 ppm SO_2 by volume
Sulfur Content of Fuels	50 grains/100 ft^3 gaseous fuel H_2S 0.5% by weight liquid/Solid fuel		50 grains/100 ft^3 std gaseous fuel H_2S 0.5% by weight liquid/solid fuel	50 grains/100 ft^3 std gaseous fuel H_2S 15 grains/100 ft^3 std Natural gas - 0.5% by volume liquid solid	50 grains/100 ft^3 std. Gaseous Fuel H_2S (800 ppm) 15 grains/100 ft^3 Natural Gas 0.5% by weight liquid/solid
Fuel Burning Equipment	New Equipment Limited to 200 lbs/hr (max.) SO_2	EPA Standards of Performance	New Equipment Limited to 200 lbs/hr (max.) SO_2		New Equipment Limited to 200 lbs/hr (max.) SO_2
Totally Reduced Sulfur					
OXIDES OF NITROGEN					
Fuel Burning Equipment	New Equipment Limited to 140 lbs/hr (max.) NO_2	EPA Standards of Performance	New Equipment Limited to 140 lbs/hr (max.) NO_2 for max. heat input ≥ 1.775 x 10^9 Btu/hr Gaseous fuel 3% O_2 125 ppm Liquid/Solid Fuel 3% O_2 225 ppm	For Maximum heat input ≥ 1.775 x 10^9 Btu/hr Gaseous Fuel 3% O_2 125 ppm NO_2; Liquid/Solid Fuel 3% O_2, 225 ppm NO_2	New Equipment Limited to 140 lbs/hr (max.) NO_2 Max. heat input ≥ 1.775 x 10^9 Btu/hr Gaseous Fuel, 3% O_2 125 ppm Liquid/Solid Fuel 3% O_2 225 ppm NO_2
CARBON MONOXIDE					
Carbon Monoxide			0.2% by volume (max.) CO	0.2% by volume (max.) CO	2000 ppm (max.) CO
PARTICULATE MATTER					
Particulate Matter	0.2 grains/scf (max.)	0.2 grains/scf (max.) *New Sources after 3-10-74 0.1 grains/scf (max.)*		0.2 grains/scf (max.)	0.3 grains/scf (max.)
Process Weight Dust and Fumes	See Table 3 40.0 lbs/hr Max. for process weight ≥ 60,000 lbs/hr	*See Table 3* *40.0 lbs/hr (max.) for process wieght ≥60,000 lbs/hr*	See Table 3 30.0 lbs/hr max. for process weight _ 1 x 10^6 lbs/hr	0.5 lbs/ton of process weight fed/hour (max.)	See Table 3 30.0 lbs/hr (max.) for process weight ≥ 1 x 10^6 lbs/hr
Combustion Contaminants	0.2 grains/scf (max.) @ 12% CO_2	0.1 grains/scf (max.) @ 12% CO_2	0.3 grain/scf (max.) @ 12% CO_2	0.1 lb/scf (max.) @ 12% CO_2	0.3 grains/scf (max.) @ 12% CO_2
Fuel Burning Equipment	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants	EPA Standards of Performance	New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants		New Equipment Limited to 10 lbs/hr (max.) Combustion Contaminants
Visible Emissions	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour *	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour	Ringlemann No. 1 (max.) 3 minutes in any 1 hour
NEW SOURCE PERFORMANCE STANDARDS		Yes			

TABLE III-1 (continued)

AIR BASINS	SOUTHEAST DESERT AIR BASIN				
AIR POLLUTION CONTROL DISTRICTS	San Diego County APCD *Also in San Diego Air Basin*				
SULFUR					
Sulfur Compounds	0.05% by volume (max.) SO_2				
Sulfur Content of Fuels	10 grains/100 ft^3 std (max.) H_2S gaseous fuel; 0.5% by weight liquid/solid fuel				
Fuel Burning Equipment					
Totally Reduced Sulfur					
OXIDES OF NITROGEN					
Fuel Burning Equipment	Max. Heat input $\geq 50 \times 10^6$ Btu/hr. Gaseous fuel, 3% O_2, 125 ppm NO_2; Liquid/Solid, 3% O_2, 225 ppm NO_2				
CARBON MONOXIDE					
Carbon Monoxide					
PARTICULATE MATTER					
Particulate Matter	0.1 grains/scf (max.)				
Process Weight Dust and Fumes	See Table 2 40.0 lbs/hr Max. for process weight $\geq$ 60,000 lbs/hr				
Combustion Contaminants	0.1 grain/ scf (max.) @ 12% CO_2				
Fuel Burning Equipment					
Visible Emissions	Ringlemann No. 1 (max.) 3 minutes in any 1 hour				
NEW SOURCE PERFORMANCE STANDARDS	*soon?*				