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ACID RAIN: COMMENTARY ON CONTROVERSIAL ISSUES AND OBSERVATIONS ON THE ROLE OF FUEL BURNING

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March 1982

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PEDCo Environmental, Inc.
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and

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CONCLUSIONS

Even though much information has been accumulated on the subject of acid precipitation, lack of knowledge in certain technical areas precludes an adequate understanding of 1) how serious the acid precipitation problem really is and 2) what effect controlling sources of acid precipitation precursors would have in reducing acidification. It is nevertheless possible to draw some broad conclusions regarding the problem and to ascertain the direction that the required further work should take.

Occurrence of Acid Precipitation

Although acid precipitation seems to be a worldwide phenomenon, such precipitation is most common and most acidic in highly industrialized countries. It appears to have become perceived as a problem in the 1950's, but its origins are not well documented. It is believed to be worsening and spreading, but substantiating data are not conclusive. Evidence suggests, however, that acidic precipitation is associated with pollution from industrialization; thus, it is logical to assume that increased industrialization in the world has probably been responsible for an increase in acidic precipitation.

Effects of Acidic Precipitation

Understanding of the effects of acidic precipitation is poor. It appears to have produced adverse effects on aquatic life in northeastern United States and in Scandanavia, mostly in high-altitude lakes. It also has been implicated in materials damage, and it may play a role in general pollution-associated damage. There is, however, no evidence of adverse health effects from acidic precipitation per se, and studies of its effects on plants and soils are inconclusive. Estimates of the cost of the impacts of acid precipitation are not available; hence it is not possible to judge their economic importance at this time.

Sources of Acid Precipitation

Natural sources may contribute to worldwide acidic precipitation; however, man's contribution to pollution (mainly SO_2 and NO_x from combustion of fossil fuels) are by far the most important sources of acid precipitation precursor pollutants in areas of the world where the environment is believed to be threatened. The amount of fuel burned is a function of the degree of industrialization and population density; hence acid precipitation generated by man's activities is linked to these factors.

Transport, Transformation, and Deposition

A good understanding of the ways in which precursor pollutants are transformed into acidic pollutants and deposited so that they contribute to acidification is also lacking. Sulfur compounds are believed to play an important role, and they have received the most study. On the other hand, nitrogen compounds, which can also play an important role, have received little study. Photochemical reactions and hydrocarbons are known to be involved. Again, information on where the hydrocarbons come from and how they participate is unclear. Atmospheric catalysis is also believed to make important contributions to the formation of acidic components, but the extent of its role is controversial. Even the manner in which acidic components are removed from the atmosphere and deposited is not clearly understood. Given this state of our knowledge, it currently is not possible, even with our most sophisticated computer simulation models, to show definitive cause-and-effect relationships for specific sources of pollution and the occurrence of acid rain.

Fuel Trends Analysis

An analysis of fuel-use trends provides another insight into the difficulty in defining the cause-and-effect relationships for acid precipitation. Two highly significant changes in worldwide fuel consumption patterns have taken place in the post-World War II period when acid precipitation was first perceived to be a problem, and during which time we developed our present perception of the situation. First, the use of coal (whose production has, until recently, remained fairly constant for many decades) has changed dramatically. Its use in locomotives and home heating has been virtually discontinued, whereas its use by electric utilities has increased dramatically. Second, the use of petroleum-derived products (principally motor fuels and liquid fuels for boilers and furnaces) also has increased greatly. These trends are apparent in varying degrees in different areas of the industrialized world but are most pronounced in the United States. It appears that acid precipitation in such industrial areas is primarily attributable to a multiplicity of sources associated with heavily populated industrial areas -- mostly sources burning fossil-derived fuels. The logistics and timing of the changes indicate that both coal combustion and oil burning are contributing to the current levels of acid precipitation in the northeastern United States.

Further Research

Acid precipitation is a specific manifestation of the pollution resulting from our continued industrial growth and our increasing use of fossil fuels, and all aspects of this problem need further research.

The following are specific areas that need to be addressed:

- Monitoring of acidic precipitation should be continued and expanded as necessary to reach an accurate definition of the limits and intensity of acidic precipitation.

- Work on the definition of the mechanisms of transport, transformation, and deposition of pollutants should be expanded to consider all important precursor compounds, including NO_x and HC as well as SO_x.
- Work should be undertaken to inventory the location and amount of precursor pollutants produced by all combustion sources that can be contributing to acid rain.

Concurrent with the above activities a control strategy that considers all combustion sources, including motor vehicles and liquid fuels in boilers and furnaces as well as coal burning sources, should be developed.

INTRODUCTION

COMMENT ON THE STUDY

This study began as an investigation of the various issues associated with acid rain and an objective assessment of the quality of the information supporting the many strong (and often conflicting) statements on these issues. These statements, which have appeared in both the technical literature and the popular media, concern the causes of acid rain, the seriousness of its impacts, and the urgency of the need for action for its mitigation. Midway into the study it became apparent that firm answers were not available to many of the basic questions. For example, some people are convinced that acid rain is worsening every year, whereas others believe that the data do not support this theory.

At this point, the study took a different turn. The search for further information was deemphasized. Instead, an attempt was made to identify the key issues and to examine both sides of the controversial questions with the aim of defining the consensus.

Also present in the early stages of the study was the suspicion that there might be a previously unappreciated connection between the highly acidic rain in the Northeastern United States and the high incidence of oil burning in that region. This usage of oil in combustors had been established in previous industrial and utility boiler studies that were unrelated to acid rain. Investigation of emission testing showed that oil burning does indeed produce primary sulfates that could participate directly in acidification of precipitation. Further investigation revealed that others had pointed to increases in oil burning as one of the changes in fuel burning patterns in recent decades that could have contributed to increased acid rain. The discovery of these events that had never been seriously explored led to the redirection of this study toward further examination of this possibility.

The major result of the adjustments made to accommodate changing perceptions of the meaning of the accumulated data is the evolvement of the final report into a document made up of two distinctly different parts. Part 1 attempts to interpret expert opinion and describe what is known about the occurrence of acid rain, the possible contributing sources of precursor compounds, and how these compounds become important constituents of acidic rain. No attempt is made to interpret basic data; this is left to the experts in their respective fields. Neither has any attempt been made to present a comprehensive compendium of the results of all the latest and most relevent studies. Instead, treatment is intended 1) to convey a perception of the state of the art that presumably will be useful to a nonexpert, and 2) to set the stage for Part 2, which discusses possible contributions to acid rain.

Part 2 presents the results of an analysis of the production of precursor pollutants by local sources (particularly those burning oil products) in various industrialized areas where acid rain is a problem. No attempt has been made to prove a quantitative connection between oil burning and acid rain by defining the mechanisms of transport and transformation. The intent is simply to point to what is considered a remarkable coincidence between historical oil burning patterns and the occurrence and severity of acid rain. For comparison purposes, data are also presented on the production of precursor pollutants associated with coal burning.

Further, no attempt has been made to balance the discussion of remote sources and the long-range transport of pollution from coal-burning in utility boilers with that of pollution from oil burning in local sources. To repeat all the previously raised arguments concerning coal burning seemed unnecessary in light of the intent of this study, which is merely to point up the need for local sources, particularly those that burn petroleum products, to be given more consideration than they have received in past assessments of acid precipitation.

Neither has an attempt been made to vindicate coal burning plants of contributing to acid rain. To the contrary, an attempt has been made to present the circumstantial evidence linking coal burning in the Midwest with acid rain in the Northeast. On the other hand, no attempt has been made to indict oil burning as the sole culprit. The evidence linking oil burning to acid rain in industrialized areas of the world is as circumstantial as that linking remote coal burning, and no claim has been made regarding the relative contribution of either to the acidification of the environment in Northeastern United States.

BACKGROUND

Within the past decade much technical effort has been directed toward identifying the origin, causes, and effects of air pollution. Although acknowledged more than a century ago, the term "acid rain" was coined relatively recently to describe how gaseous pollutants discharged into the air return with precipitation to man's terrestrial environment.

Since the emergence of acid rain as a problem in the 1950's, the questions of what is causing it and the extent of the damage it may inflict on the environment have become controversial issues. The problem is now an international concern because it involves man's activities in all industrialized nations and the impacts of those activities can cross political borders.

Some aspects of the acid rain issue are seemingly well established, whereas others remain controversial. The relatively few well-established issues are:

- Acid rain is occurring.
- It has gained significant attention since the 1950's.
- It is derived from sulfur oxides (SO_x), nitrogen oxides (NO_x), chlorides, and possibly other pollutants in the air.
- It is caused primarily by manmade activities in industrialized areas.
- Fuel burning is the most important manmade activity contributing to acid rain.

Some controversy and legitimate uncertainty exist regarding other aspects of the acid rain issue, especially those pertaining to sources, formation, effects, and control. Following are some examples:

- Whether acid rain is increasing and/or spreading to new areas
- The relative importance of sources burning petroleum fuels compared with those burning coal
- The importance of large, coal-burning, electric power plants
- The role of natural sources and the natural acidity of rain
- Atmospheric transport, transformation, and deposition mechanisms leading to formation of acids from precursor pollutants
- Whether acid rain is a global phenomenon, in the sense that the release of precursor pollutants in industrialized areas of the world can contribute to acid rain in areas very remote from all sources of manmade pollution
- Accuracy of the methods for measurement of acid rain, and adequacy of data for documentation of acid precipitation
- The effects of acid rain on public health, the environment, and property
- Methods of controlling acid rain and mitigating its effects

Resolving these uncertainties will require much more information than is now available regarding acid rain formation and transport phenomena, as well as substantial improvements in monitoring, data collection, and data analysis. In terms of technical progress, investigations of acid rain, which date back only a few years, are still in the developmental stage.

REPORT CONTENT

The principal focus of this report is on possible contributing sources of acid rain. In view of the information deficiencies just cited, the report obviously cannot provide definitive answers to the question of who contributes what to the acid rain problem; however, it does attempt to define what we do and do not know on this subject. Also, it casts doubt on some of the prevalent thinking regarding the major contributors.

The report is in three parts; the first provides general background on acid precipitation, the second discusses the relative contributions of natural and manmade sources, and the third summarizes important findings and their implications. In Part 1, the first section gives an overview of the occurrence of acid rain in various parts of the world and outlines the knowns and unknowns regarding its environmental effects. Section 2 discusses the sources of precursor pollutants, both natural and manmade. Section 3 briefly outlines the formation, transport, and deposition mechanisms. Section 4 describes the measurement of rainfall acidity and current monitoring efforts. Each of these discussions focuses on the state of the investigative art.

Part 2 of the report addresses the role of manmade sources. It discusses the work that has been done in the development of simulation models to evaluate the contribution of various source types to acidification of precipitation (Section 5), worldwide fuel trends and the occurrence of acid rain (Section 6), and a series of case studies of areas where acid rain is occurring (Section 7).

The contents of Part 2 represent a blend of evaluation and specific findings about source contributions because examination of the methods that are and can be used in tracing probable sources led the investigators to new information, particularly regarding the influences of local sources in areas subjected to acid rain. The importance of local fuel consumption patterns is indicated in Sections 6 and 7.

Part 3 summarizes the principal findings, discusses their implications, and offers recommendations for continued study of the acid rain phenomenon.

Throughout this report two terms are used in reference to sources of acid rain. The term "remote" indicates sources distantly located with respect to an area receiving acid rain. The definition of the term "local" varies with the geographical area being examined. For example, in the context of the northeastern United States "local" indicates sources located less than about 200 miles from the Adirondack Mountains, the so-called center of the acid rain problem in that area. In Florida, the area of local influence also extends for about 200 miles around the northern part of the State. In California, there are two local areas of impact, one centering on San Francisco and the other around Los Angeles. Thus, local sources are defined here as those located within an area where acid rain is occurring that have potential for contributing precursor compounds to the acidification process.

PART 1

BACKGROUND

Part 1 of this report, which is intended as a brief overview of some basic aspects of acid rain issues, addresses such questions as: Where does it occur? What are its effects? From what sources does it arise and by what mechanisms? How is it measured? This is not an exhaustive presentation, but rather provides background for the later discussions of contributing manmade sources of acid precipitation precursors.

1. OCCURRENCE AND EFFECTS OF ACID RAIN

OCCURRENCE* OF ACID RAIN

Although the term "acid rain" was introduced to describe acidic precipitation observed before the turn of the century, it was not until the 1950's that acidic precipitation came to be perceived as a potentially serious environmental threat. It was recognized at that time in Norway and Sweden where the initial reaction to reports of of acid rain, depletion of aquatic life, fish kills, and black snow in southern Scandanavia was that there was a direct causal relationship between the acid rain and emissions of sulfur dioxide (SO_2) from tall stacks in some upwind industrialized European countries. This reaction was emotionally charged and widely publicized. Subsequent years of study have since shown that the situation is far more complex than was originally thought. One particularly significant point that has emerged is that "low level (elevation) emissions are acknowledged to be almost as important as tall stack sources" (Barnes 1979). Thus, local sources with shorter emission heights are also now considered important contributors to acid rain in industrialized areas.

Today, acid rain has been reported worldwide. Figure 1-1 depicts a global map, showing pH values of rainfall as indicated by currently available data. The three values in the Atlantic Ocean are from shipboard measurements representing single precipitation events. The values for Iran, Tasmania, Point Barrow, Hawaii, Samoa, Amsterdam Island, Poker Flat, Venezuela, and Bermuda are from NOAA stations. The Hawaii values represent hundreds of samples covering a 5-year period, whereas those for the other NOAA sites generally represent sampling over just a few months.

Notwithstanding the diversity of sampling modes represented in the figure, the global prevalence of acid rain is indicated. In addition to the European nations shown on the map (Scandanavia, France, Germany, Italy), acid rain is known to occur in The Netherlands, Hungary, Czechoslovakia, and Great Britain. The average annual pH level of rain in these European countries often lies between 4 and 5, depending on location.

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* The occurrence of acid rain is determined most often by measuring the pH level of collected precipitation. The pH value is the negative logarithm of hydrogen ion concentration. Thus, pure water, with a hydrogen ion concentration of 1×10^{-7} moles per liter, has a pH value of 7. This value lies at the midpoint of the pH scale, which ranges from 0 to 14. Values below 7 are on the acidic side of the scale; those above 7 are considered basic or "alkaline."

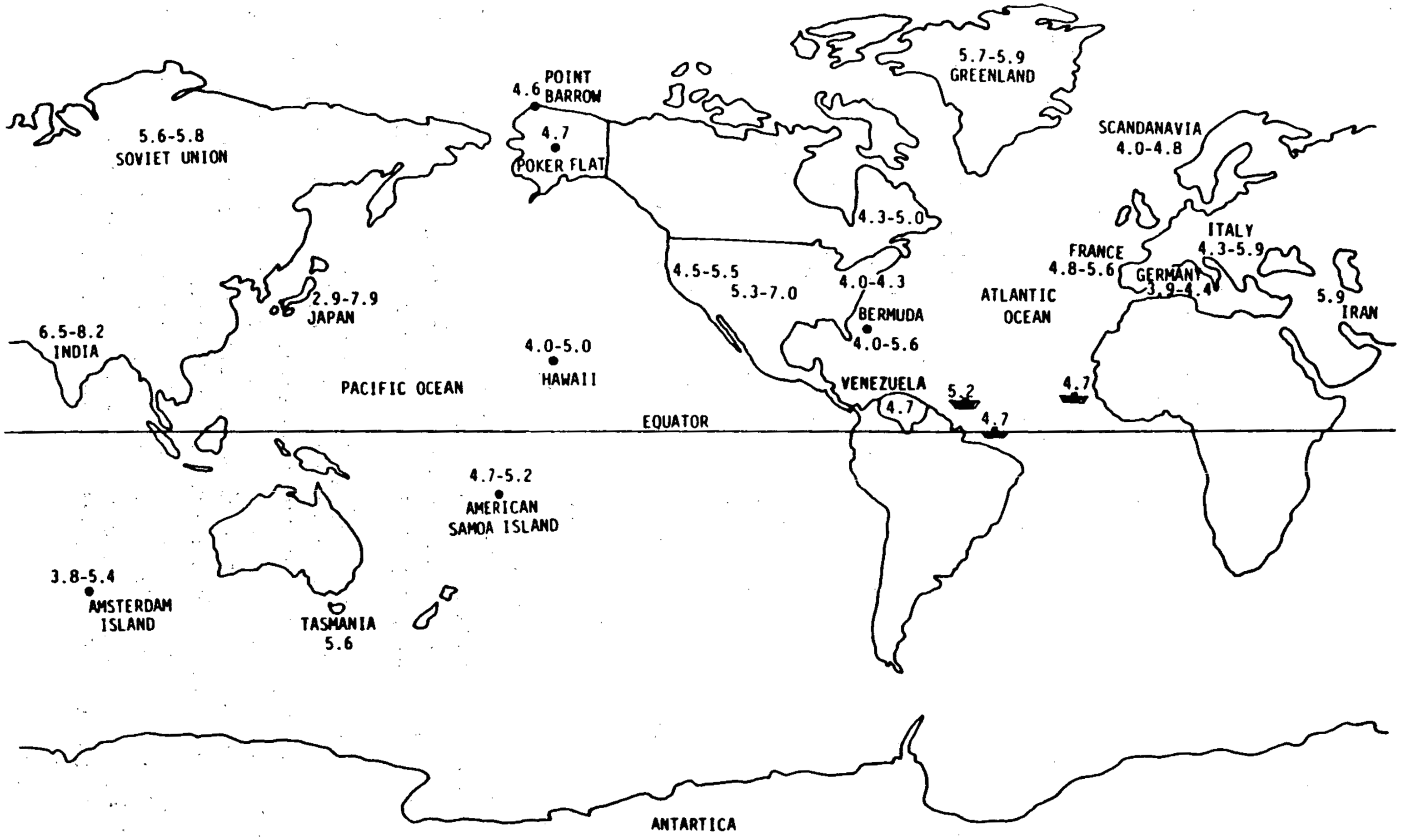

Figure 1-1. Global map showing range of rainfall pH values. The Atlantic Ocean, Point Barrow, Hawaii, Samoa, Amsterdam Island, Poker Flat, Venezuela, Iran, Tasmania, and Bermuda values are courtesy of John H. Miller, NOAA, Silver Springs, MD., 1980. Values for Soviet Union, India, Canada, France, Germany, Greenland, and Italy are from 1976-77 World Monitoring Organization data (Environmental Data and Information Service, 1977.) Values for Japan were observed at various urban and rural sites between 1974 and 1977. Values for the U.S. are from Henderson et al. 1981 and Cooper, Demo, and Lopez 1976.

Figure 1-1 indicates also that some parts of the world apparently do not receive acid rain. The values for India, Greenland, the Soviet Union, and the central United States, for example, show pH levels typically between 5 and 7. The reason for the higher pH values of rainfall in these areas is not known. It may reflect the absence of industrial activity or partial neutralization effects by entrained alkaline soil particles.

In the United States, acid rain is occurring across the entire eastern half of the country, as shown in Figure 1-2. Rain is most acidic in the corridor extending from Indiana, Ohio, and Kentucky through Pennsylvania to New York, New Jersey, Rhode Island, Connecticut, and Massachusetts; the annual average pH of rainfall in this area is 4.1-4.2. The southern and western coastal states are also experiencing acid rain, although it is less acidic than in the Ohio Valley and northeastern states. Average pH values in Virginia and the Carolinas range from 4.2 to 4.6, in Florida, from 4.7 to 5.2, and in California and Washington, from 4.2 to 5.3.

Low-pH rain has often been reported to occur in cities or urban areas, and near large point sources of pollutants considered to be acid rain precursors (sulfur oxides, nitrogen oxides, chlorides). Precipitation with pH less than 4 has occurred in New York, Chicago, Philadelphia, Louisville, Evansville, Birmingham, Providence, and Boston (Wolff et al. 1978; National Academy of Science 1975). The mean pH of rain during the winter rainy season in Los Angeles and Long Beach is 4.5 (Morgan and Liljestrand 1980). A similar situation exists in the San Francisco area, where at San Jose the seasonal mean pH is 4.4, and at Berkeley, 4.6 (McColl 1980). In Colorado the rain and snow in the mountains near Boulder and Denver are also slightly acid, with annual average pH values centering on 5.0 (Lewis and Grant 1980).

The operations of a metal smelter or a power plant can influence the local acidity of precipitation. For example, the rain in the vicinity of a copper smelter at Tacoma, Washington, and a copper and nickel smelter at Sudbury, Ontario, has pH levels below 4 (Larson et al. 1975; Nisbet 1975; Freedman and Hutchinson 1980a). Near the Chalk Point power plant in Maryland, the rain pH levels range from 3.0 to 5.7 (Li and Landsberg 1975). Emissions from the Douglas copper smelter in southeast Arizona appear to be influencing the acidity of local precipitation (refer to Figure 1-2).

Neutralization is another apparently localized phenomenon leading to higher rainfall pH values in areas near sources of alkalinity (Larson et al. 1975; Semonin 1976). This localized neutralization phenomenon is slowly becoming recognized as a primary factor in the variability of pH level with location. Neutralization processes can skew the data on pH trends if monitoring sites, sampling methods, and emissions are not held constant during the time frame of interest. Data may suggest a shift or spread in the occurrence of acid rain over time when, in fact, the measured values reflect changes or differences in localized rainfall neutralization patterns. For example, it has been suggested that the variability of precipitation acidity may result from variations in atmospheric levels of alkaline soil particles and/or ammonia from natural sources (Frohliger 1980).

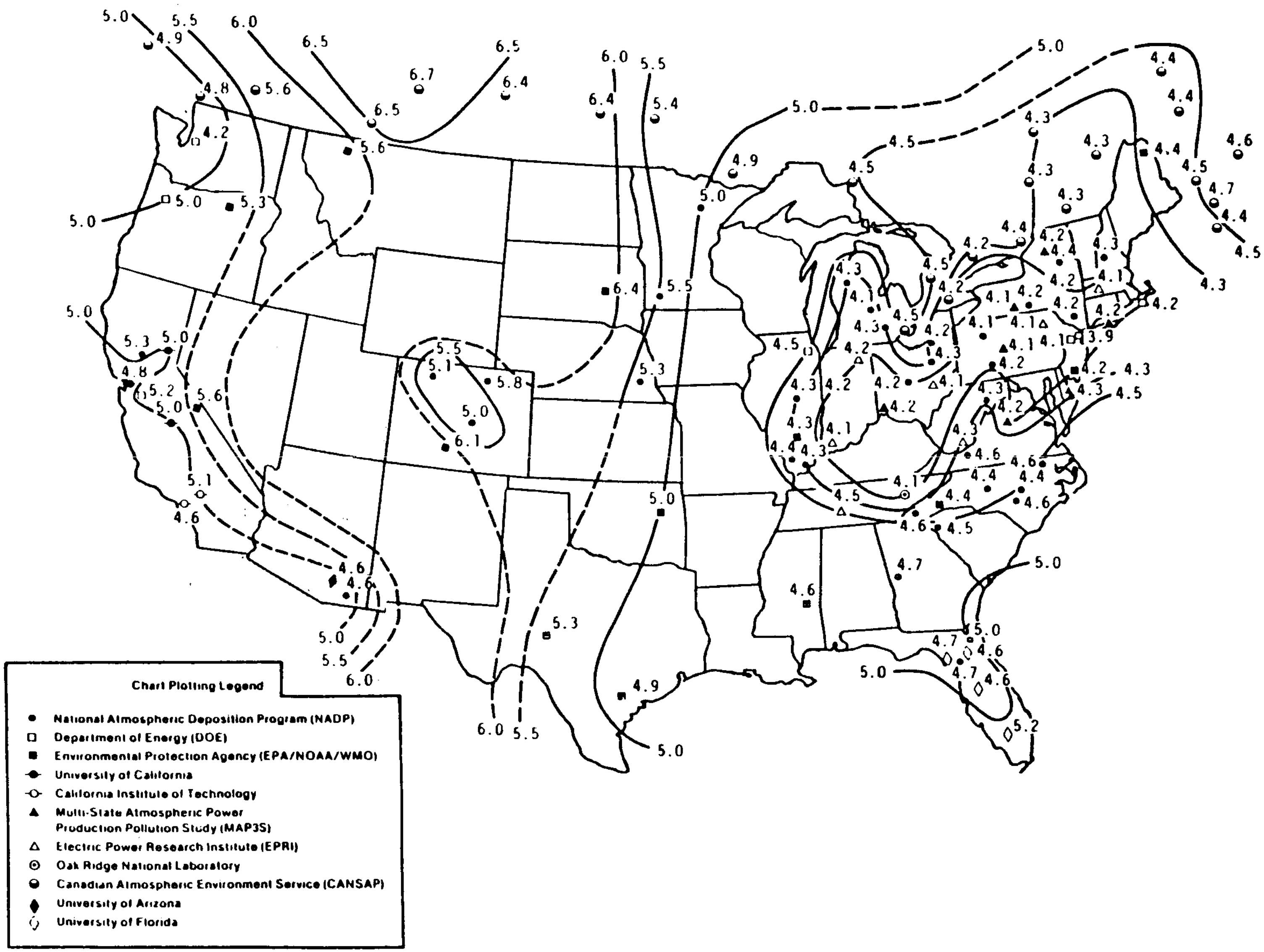

Figure 1-2. Weighted mean pH of precipitation in United States, 1976-79 (Henderson et al. 1981).

Another approach to describing acid deposition is to present the data in terms of wet hydrogen ion deposition. The pH values are converted to simple hydrogen ion concentrations, which are multiplied by the volume of rainfall to give total wet hydrogen ion deposition. This approach was taken in developing hydrogen ion deposition isopleths for the United States for the combined years 1976-79, as shown in Figure 1-3. This arithmetic approach eliminates the confusion commonly associated with comparing logarithmic pH values. All unit values are of equal weight; that is, a change from 0.1 to 0.2 has exactly the same weight or value as a change from 0.2 to 0.3.

By depicting the arithmetic hydrogen ion deposition pattern in the United States, Figure 1-3 gives added perspective on U.S. acid deposition patterns that is not apparent in similar isopleths based on pH values. Most significantly, the figure indicates that the mean annual hydrogen ion deposition in precipitation is greatest in the eastern Pennsylvania, New Jersey, and New York City area, not in the Adirondacks. Annual hydrogen ion deposition in the Adirondacks is only half that of the eastern tri-state region, and is equal to that deposited in Ohio, Indiana, Illinois, and other mid-to-south central states. Another important observation is that although acid rain is known to be occurring in California, the magnitude of the total annual hydrogen ion deposition is only a fraction (10 to 20 percent) of that observed in the midwest and east. Farther up the Pacific coast, however, near Seattle and Puget Sound, much higher values of wet hydrogen ion deposition are occurring than would be indicated by rainfall pH values (compare with Figure 1-2).

Hydrogen deposition isopleth maps, as in Figure 1-3, are valuable and can be used in conjunction with pH measurements and isopleths to provide additional insights on acid rain patterns. Unfortunately, historical data are too fragmented to allow development of similar isopleths for purposes of identifying past trends.

In summary, several general comments can be made relative to the occurrence of acidic precipitation. First, limited data suggest that to some degree the acidity of rainfall in remote areas can be acidic. Second, it appears that large pollution sources can contribute to the acidification of rain that falls in their vicinity. Third, it appears that the high levels of pollution associated with activities in large cities can contribute to acidification of rain in the surrounding area. Finally, as will be discussed later, acid rain appears to be most prevalent and most severe within and downwind of regions of heavy industrialization.

EFFECTS OF ACID RAIN

The effects of acid rain, like the occurrence, vary in degree and extent. Assessment of the effects is substantially more difficult because only a small amount of information is available from which to relate estimates of the acidity of rain to some observed effect that is believed to result from that acidity. Not all areas experiencing acid rain are equally

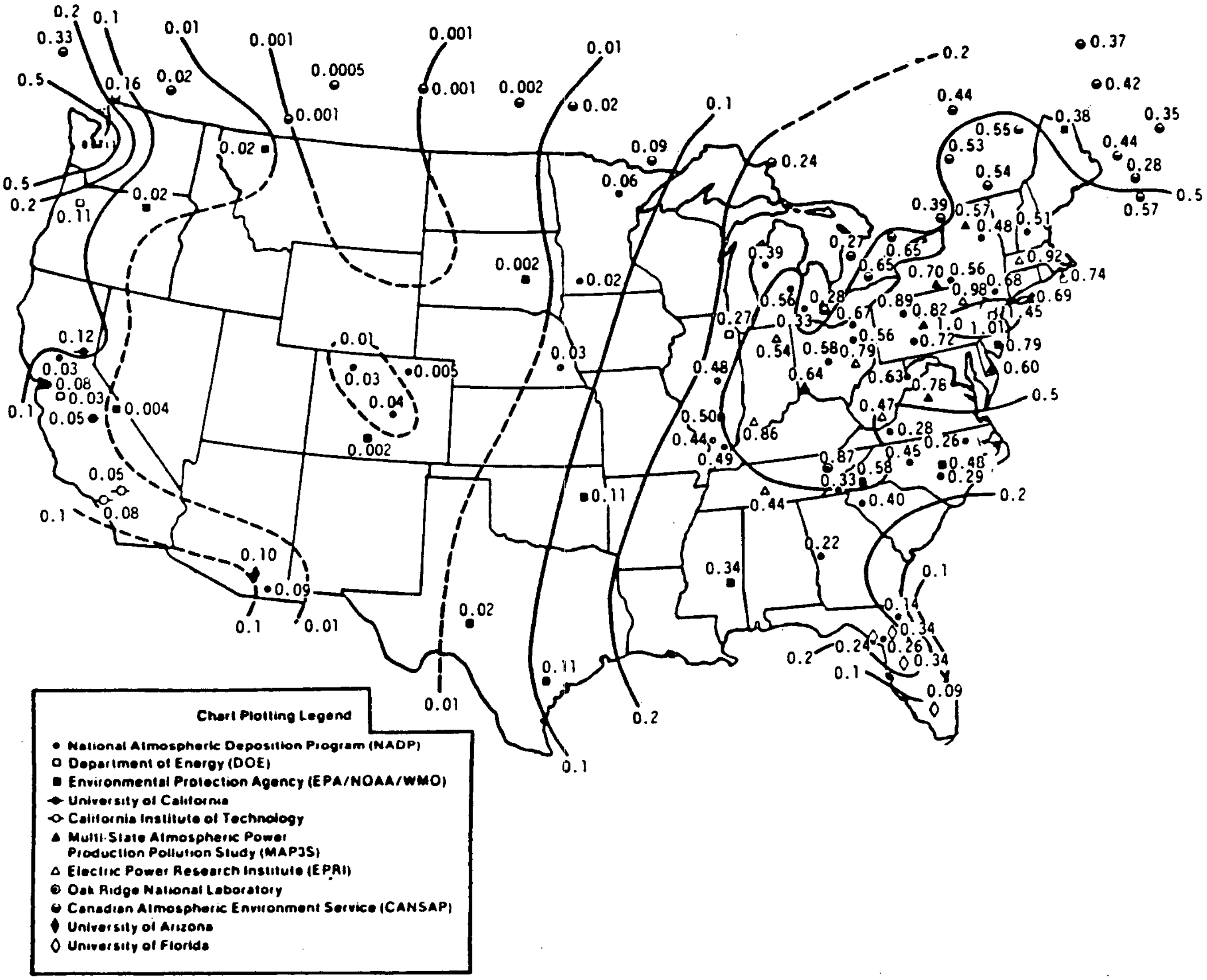

Figure 1-3. Mean annual hydrogen ion deposition in precipitation, 1976-1979 (kg ha^{-1} yr^{-1}), estimated from weighted mean pH and mean annual precipitation (Henderson et al. 1981).

affected. Some areas are more sensitive because the local ecosystems cannot counterbalance acid deposition with neutralizing alkaline materials. Mountainous and other areas of high elevation are especially susceptible because their soils are thin.

This subsection briefly addresses the reported effects of acid rain in the continental United States. The acidification of lakewaters and effects on aquatic life are discussed first since these are the items about which most information is available. The possible effects of acid rain on human health, drinking water supplies, soils and plant life, and structures and materials are also discussed briefly.

Aquatic Effects

Figure 1-4 shows the U.S. areas believed to be most vulnerable to acid rain. Vulnerable areas are often mountainous, with thin soils on granite rock bases. Lakewaters in these areas are typically of low alkalinity.

Attention has focused on the impact of acid rain in the Northeast, especially in the Adirondack mountain region, because the area has many ponds and lakes, the environment is considered susceptible, and the rain is especially acid. Atmospheric acid deposition is believed to be causing the acidification of some Adirondack lakewaters, with accompanying losses of fish populations. Although these impacts are not yet completely defined, some citizens are concerned that results may be irreversible and are exerting considerable pressure for relief and remedy. Information is currently lacking on (1) the total extent (both temporal and spatial) of the acidification of northeastern lakewaters and stream headwaters; (2) the overall economic impact of current and continued acidification; and (3) what to do to remedy the situation.

The Adirondack region of New York State contains some 2877 individual lakes and ponds* (Figure 1-5) covering more than 282,000 surface acres (Pfeiffer and Festa 1980b). The average lake size is almost 100 acres, although sizes range from less than one to several thousand acres.

Adirondack lakes that now exhibit low pH and loss of fish populations are primarily at high elevations (>2000 ft), as shown in Figure 1-6. Today the average pH level is 5 or less in 90 percent of the lake acreage at elevations of 2500 ft or more and in 40 percent of the lake acreage at 2000 to 2499 ft. These acid lakes are usually small, with surface areas under 100 acres (Pfeiffer and Festa 1980b). Losses of fish populations have been linked to both the low pH values and to toxic effects from aluminum solubilized from feldspars in the rocky-bottomed lakes.

Information on the current water quality of lakes and streams in the Adirondacks and throughout the Northeast is being developed, but there is little historical information with which to compare present values, and what

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* Lake Placid is excluded because of its size.

Figure 1-4. Areas of North America considered sensitive to acid precipitation. Shaded areas have igneous or metamorphic bedrock geology and for this reason are expected to have low buffering capacities (i.e., alkalinities <0.5 meq HCO_3^-/liter). Unshaded areas have calcerous or sedimentary bedrock geology and therefore have higher alkalinities (Galloway and Cowling 1978).

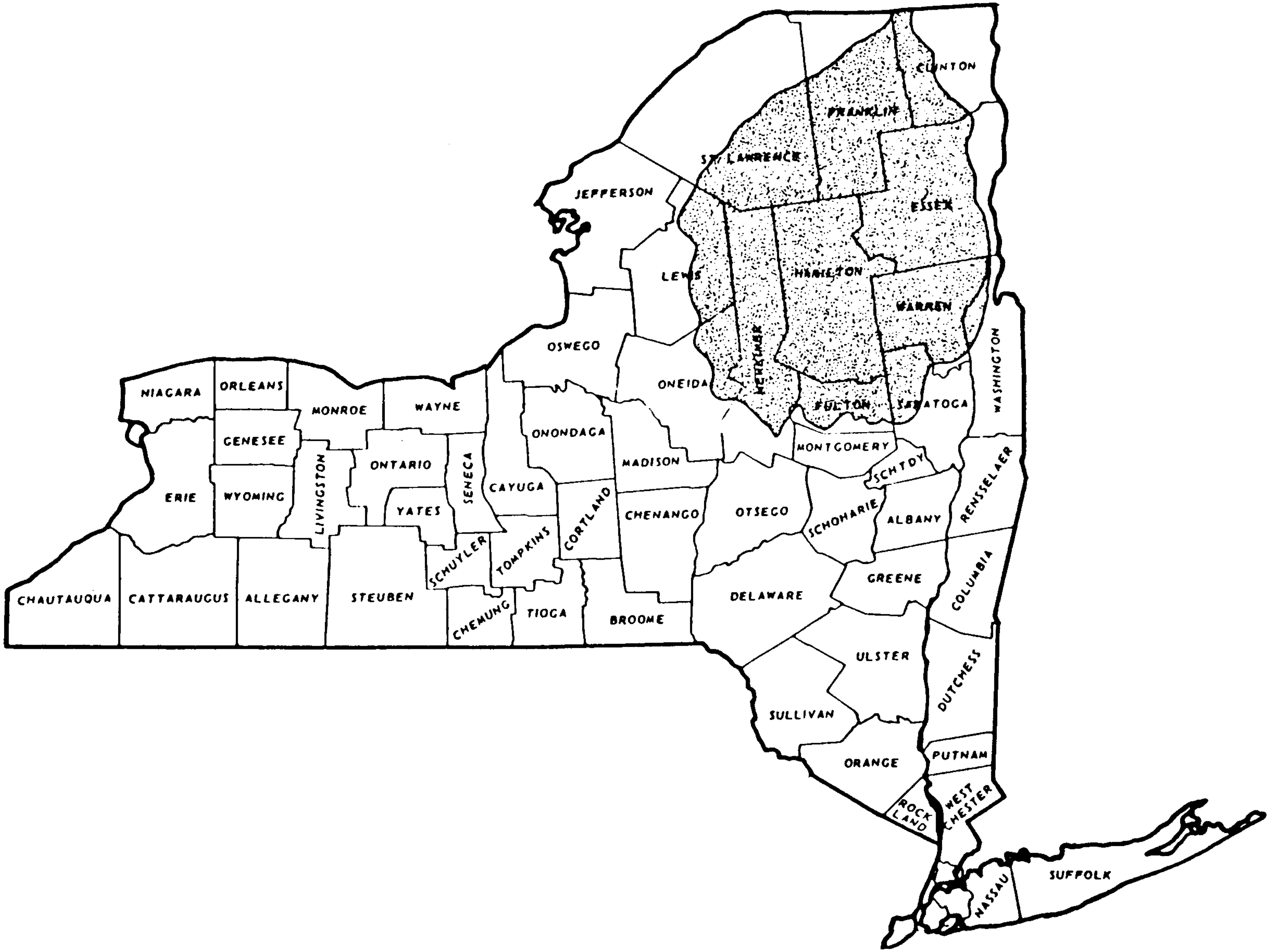


Figure 1-5. Boundary of Adirondack ecological zone containing over 2800 individual lakes and ponds (Pfeiffer and Festa 1980b).

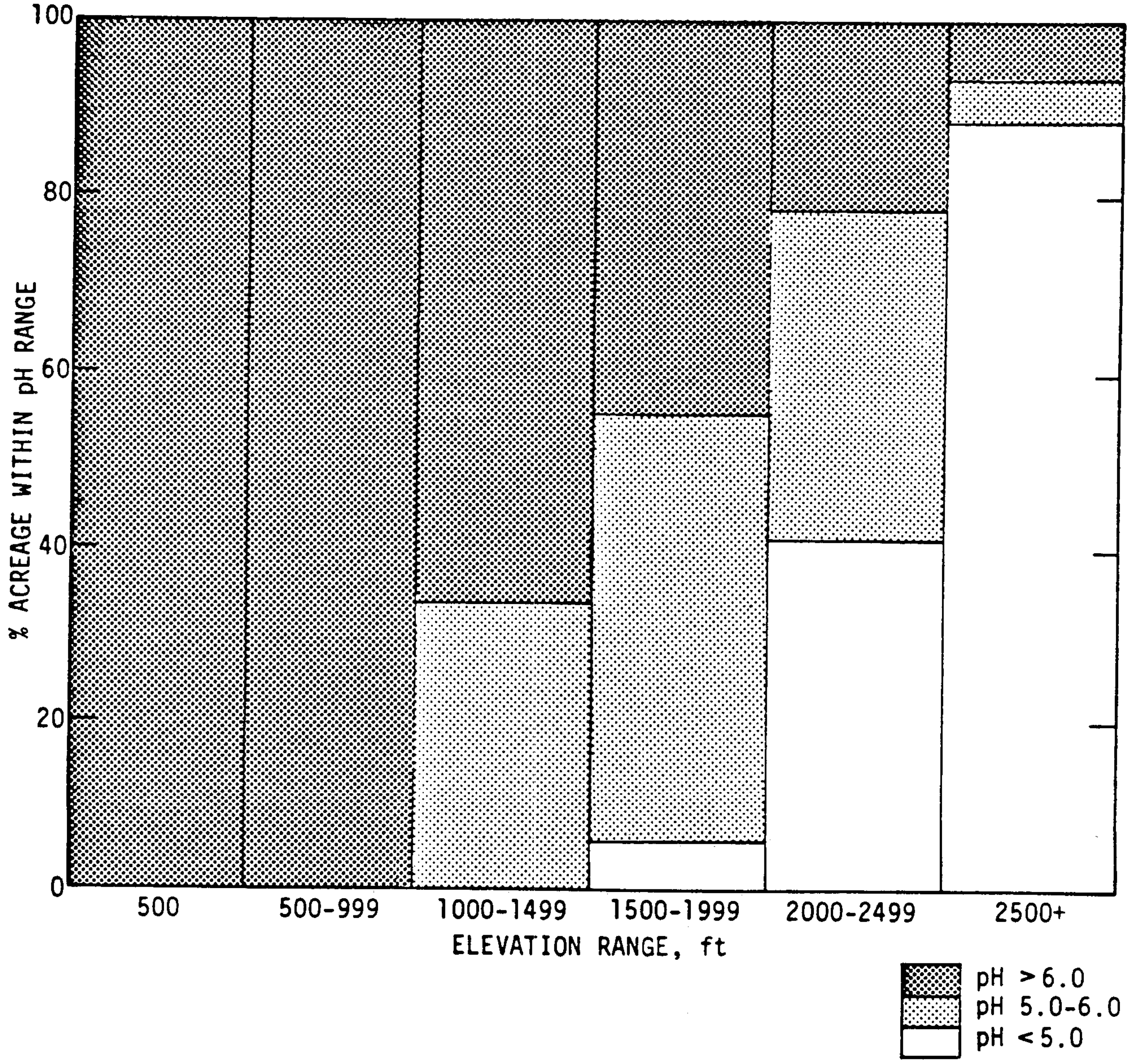


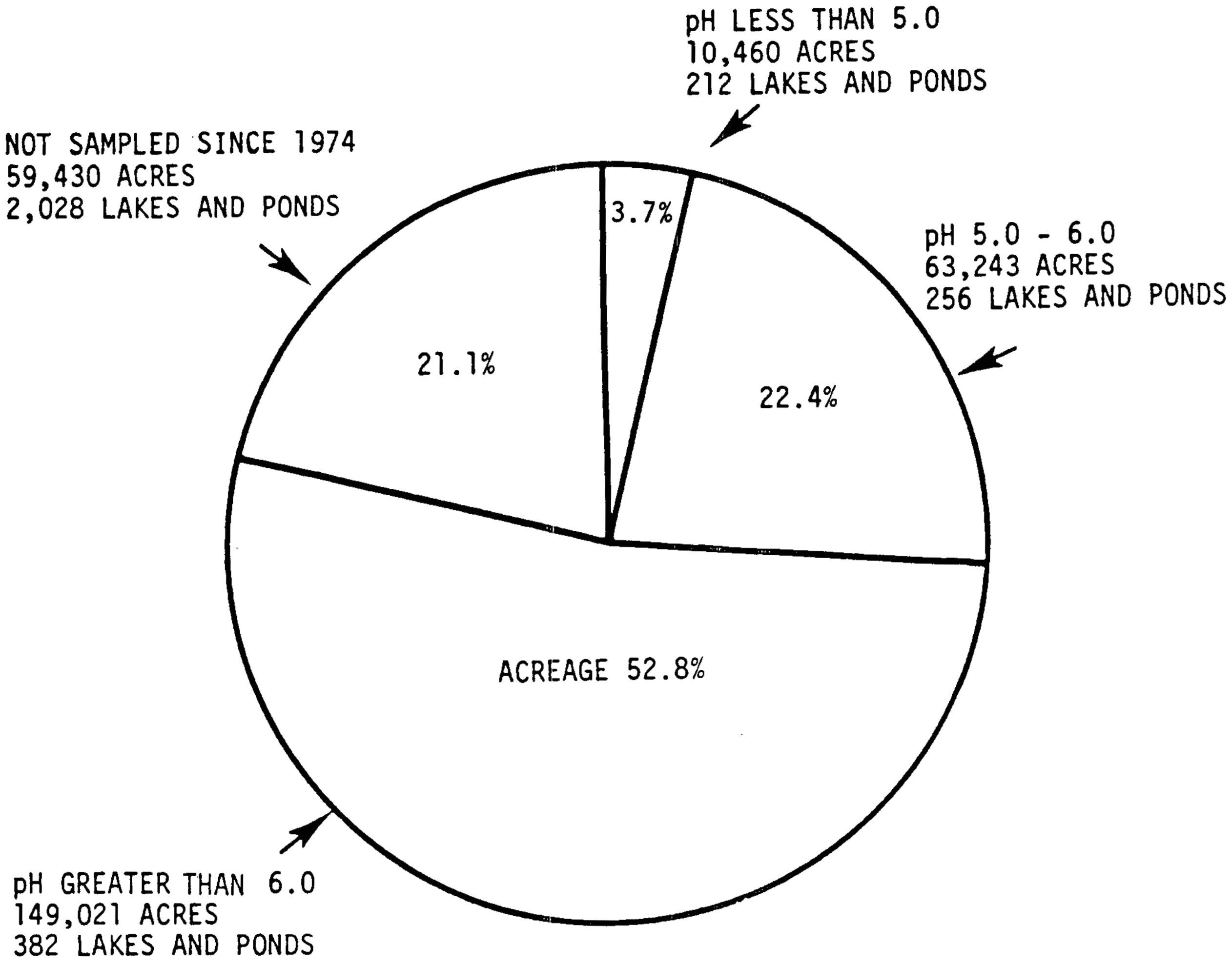
Figure 1-6. Occurrence by elevation of Adirondack waters in various pH categories (Pfeiffer and Festa 1980b).

is available is of questionable validity. For example, there is concern that the acidity of the high Adirondack lakes has increased in recent years. Schofield reports that in the 1930's the waters of 40 high-elevation Adirondack lakes had pH values centering on pH 6.5 to 7.5, but by 1975 these values had shifted in the mean to less than pH 5 (Schofield 1976). The historical data indicate that in the 1930's only 4 percent of the high-elevation lakes had pH values of 5 or less and were fishless, whereas by 1975, 51 percent of the high-elevation lakes had pH values below 5, and 90 percent of these had no fish (Schofield 1976).

Schofield's comparison of early and recent pH values may somewhat overstate the apparent acidification that has occurred during the past 40 to 50 years. This is because the comparison appears to be based on different methods of pH measurement. In the 1930's, pH was measured colorimetrically, whereas today a more accurate electrometric method is used (i.e., measurement with glass electrode and voltage meter). A recent comparison of values obtained by the two methods on Adirondack lakewater samples taken in 1979 shows that the values obtained electrometrically are very often 1 to 1-1/2 pH units lower (10 to 30 times more acid) than values obtained from the same samples by the older colorimetric method (Pfeiffer and Festa 1980a, 1980b). The implication of this finding with respect to Schofield's work is that pH values of the 1930's samples may have been at least 1 to 1-1/2 units lower than was reported. Therefore, the earlier distribution of pH values might have centered more on pH 5 to 6 or 5.5 to 6.5 instead of 6.5 to 7.5. Had the measurement methods been the same, the pH differences observed over time might have been lower making the association between the increased incidence of fishless lakes, cited above, and changes in acidity of the lakes less apparent.

The acid quality of high-elevation lakes in the Adirondacks may not be due entirely to anthropogenic pollution. Naturally occurring acid lakes and bogs have been known in the United States for more than a century (since 1860) (Patrick, Birnette, and Halterman 1981). They are typically small, weakly buffered, silacious lakes and ponds with natural organic accumulations, and they are often located at high elevations. One would therefore expect at least some of the high-altitude Adirondack lakes to be, at least to some degree, acidified naturally, regardless of man's activities. However, no studies to determine the importance of this phenomenon have been made.

Additional perspective may be gained by considering the total population of Adirondack lakes. Figure 1-7 shows the present acidity status of all Adirondack ponded waters. Of the total population of 2877 lakes and ponds, the pH levels are below 5 in 212, which cover 4 percent of all Adirondack lake acreage (Pfeiffer and Festa 1980b). Another 256 lakes and ponds, covering 22 percent of the ponded acreage, are considered endangered because the pH values range from 5 to 6, a range considered borderline for successful reproduction of many desirable fish species. More than half of the lakewater acreage in the Adirondacks has a pH of 6 or higher and is not now considered endangered. The remaining 21 percent of the ponded acreage contains many small lakes that have not been sampled recently and may or may not be at risk.



TOTAL ACREAGE: 282,154

TOTAL NUMBER LAKES AND PONDS: 2,877

Figure 1-7. Acidity status of Adirondack ponded waters (Pfeiffer and Festa 1980b).

Pfeiffer and Festa have recently developed evidence of a slight trend toward increasing lakewater acidity at all elevations of the Adirondacks (as opposed to only the high-elevation lakes) (Pfeiffer and Festa 1980b). These investigators studied the historical pH of 138 lakes using a single pH measurement method--the older Helligel colorimetric comparator method. Results of their study indicate that a slight, though not dramatic, shift toward increasing acidity occurred between the 1930's and 1979. This trend is demonstrated by the shift in the frequency and distribution of pH values for the 138 lakes, as shown in Figure 1-8. The median (50 percentile) pH value decreased from 6.75 to 6.51 during the 40- to 50-year study period, and the frequency of values below pH 6 increased from 6.5 percent to 19.6 percent.

Lakes in close proximity to each other presumably receive equal exposure to acid rain yet often react differently. For example, variations of 2 or more units in pH have been observed in three Adirondack lakes closely located to each other. The pH of Panther Lake is 7.0, the pH of Sagamore Lake from 5.5 to 7.0, and the pH of Woods Lake ranges from 4.5 to 5.5. Researchers believe that these differences are due to variations in the depth of soil (and therefore in the neutralizing capability) immediately surrounding each lake [Electric Power Research Institute (EPRI) 1980].

Vegetative cover can change the impact of rainfall passing through it on surface waters. For example, the pH level of the runoff streamwater below the forest canopy at Hubbard Brook, New Hampshire, (deciduous canopy) consistently averages about pH 5, while the pH of rainfall there averages 4.1. In other words, rainfall below the forest canopy is about one pH unit higher, or 10 times less acid, than rainfall above the canopy (Hornbeck, Likens, and Eaton 1977). Thus, the forested ecosystem at Hubbard Brook appears to moderate the impact of acid precipitation.

Economic Losses

The extent of economic losses to the Adirondack region is not yet known. A number of lakes have lost their trout and small-mouth bass populations in recent years (Whelpdale 1978; Pfeiffer and Festa 1980b). Reproductive failures associated with increased acidity are suspected (Pfeiffer and Festa 1980b). Examples of the Adirondack lakes which have lost their bass population are Woodhull, Big Moose, and Canada Lakes. Cranberry and Tupper Lakes, which have waters of marginal pH for bass (pH 5 to 6), are also suffering marked population declines. New York State estimates Adirondack fishing losses due to atmospheric acidification at 22,000 pounds per year (Pfeiffer and Festa 1980b). This is roughly $66,000 annually (based on $3/lb). The economic impact associated with this loss or possible future losses and related losses of recreational opportunity and tourist trade is not known. New York State has spent $15 to $30 per acre per year since the 1950's in remedial efforts to lime 51 ponds in the Adirondacks (Davis 1980). The total cost presumably is in the neighborhood of $125,000 per year. The exact costs and effects of this project are not reported.

Pennsylvania has relatively few lakes but many mountain streams that are aesthetically and economically treasured for their trout fishing. A

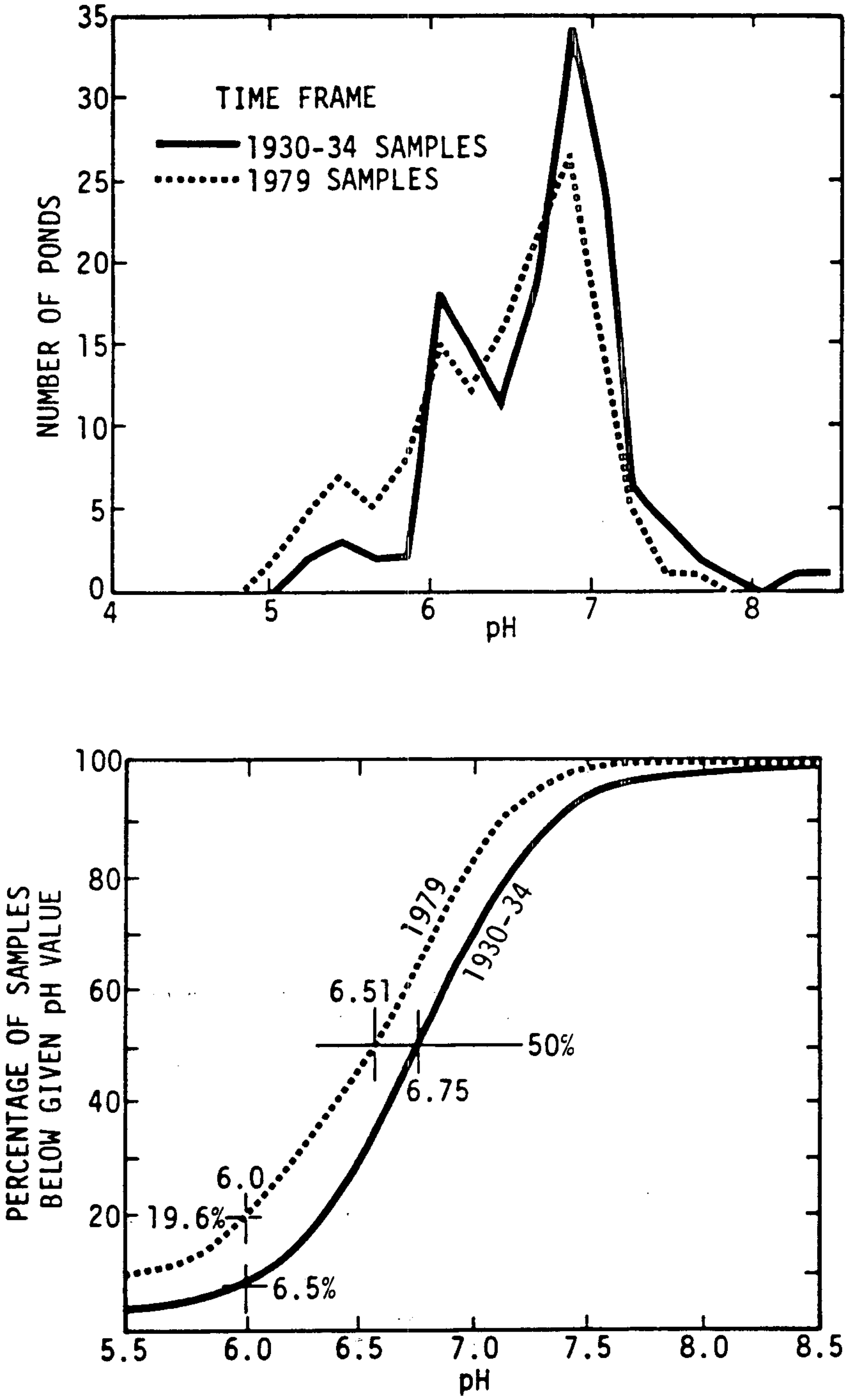


Figure 1-8. Distribution of historic and recent colorimetric pH readings for a set of 138 Adirondack ponds (Pfeiffer and Festa 1980b).

trend toward lower pH in some of Pennsylvania's stream headwaters has been reported and accompanied by observations of decreases in streamwater alkalinity and species diversities (Arnold 1980).

Acid precipitation is also believed to be causing minor ecological effects on poorly buffered lakes in the northern part of Florida. The pH of some lakes has dropped, and shifts in algal population have been observed (Crisman and Brezonik 1980). Losses of fish populations, however, are not yet a problem, presumably because toxicity from aluminum leaching is not occurring.

Investigators do not believe that acid rain is causing detrimental environmental effects in most parts of California at this time. Areas such as San Francisco and Los Angeles have few lakes, and soils tend to be well-buffered. A few mountain lakes at 4000- to 5000-ft elevation have been monitored, and all have a pH of 6 or more; average pH of rainfall to these lakes is 4.9.* The continued pH stability of lakes at higher elevations is of some concern because they tend to have lower pH levels, to be granite-based, and to be poorly buffered (Tonnessen and Harte 1981). Recent fish deaths in Sequoia National Park lakes are speculated to be due in part to either acid rain or melting acid snow (Washington Post 1981).

Other Possible Effects

The remainder of this section discusses possible health and ecological effects of acid rain. Information in this area is both sketchy and speculative, and the reported effects often are not firmly linked to acid rain.

Health Effects--

Acid fogs and drizzles have been reported to adversely affect public health and property in Japan on several occasions since 1973 (Chemical Abstracts 1981). The episodes have caused eye and skin irritations among hundreds of exposed people, and also have caused injuries to vegetation. Rainwater associated with these episodes was always very acid, with a pH of about 3. Nitric acid vapor formed photochemically and incorporated into the droplets is believed responsible for the very low pH. Chlorinated alkenes such as trichloroethylene and perchloroethylene found in samples of the drizzle water droplets also may have been partially responsible for the adverse effects.

There are no similar reports of adverse health effects from acid fogs in the United States or Europe although heavily polluted London fogs of the past may have been a related phenomenon. Some reports indicate that cloud waters are often very acid (pH 3-4.5), and if this is so, it would be reasonable to expect that fogs and mists are sometimes very acidic also. Additional research on potential health effects seems needed.

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* Personal communication from K. Tonnessen of Lawrence Berkeley Laboratory, University of California, on December 10, 1980.

Drinking Water--

There has been some speculation that acid rain could have indirect health effects by increasing the leaching of heavy metals from copper pipes and lead solder into catchment-type drinking water supplies. Actual data, however, are very limited. Some results that would appear to support the speculation include the following. In Amsterdam, New York, the reservoir from which the population's drinking water is pumped has become acidified; it is reported that lead from the solder and copper from the water pipes dissolve and accumulate in the lines overnight (Davis 1980). Similarly, observers in a few small towns in the Adirondacks and parts of New England state that acid rain water collected in cisterns and shallow well systems has leached copper from the pipes and lead from the solder (Sharpe, Young and Hershey 1980). In some areas, the lead levels in water that had laid overnight in the pipes were 5 times the recommended EPA maximum for drinking water, and the tap water in one household had copper concentrations of 7 times the Federal secondary standard of 1.0 mg/liter (LaBastille 1979). In Clarion County, Pennsylvania, a survey of cistern-equipped homes showed that the water in 5 out of 35 (14 percent) had more than the maximum allowable lead level (50 µg/liter), and residents have been advised not to drink the water (Davis 1980; Science News 1980). Rainwater collected in these cisterns has a pH of about 4.0, which means it is potentially quite corrosive.

While these results could be indicative of indirect effects of acid rain, they could also be the result of pollutants such as lead from auto exhaust being co-collected with the rainfall in the catchment system. Decomposition of organic material collected with the rainwater runoff also could account for increased acidity. Thus, the correct cause of the observed effects remains uncertain. More information should be collected both on pH and on the metals content of water in these types of collection systems. The extent to which acidification is due to natural decay versus precipitation should also be determined.

Materials Damage--

Because of the generally corrosive nature of acid rain, it might be expected to contribute to the material damage process by accelerating deterioration of painted surfaces, limestone, concrete, copper, and other metals. Data to support or refute the contribution of acid rain to material damage is very limited. One example is a researcher's suggestion that acid rain is responsible for the corrosion that has turned Boston's bronze statues green (Adams 1980). In fact, the degree of damage to public and private property from acid rain cannot be established because of the lack of reliable data.

Plants and Soils--

Research is underway to determine whether acid precipitation could ultimately lead to a permanent reduction in tree growth, food crop production, and soil quality. Some experts fear this could be happening if useful soil microorganisms are being eliminated and potentially toxic soil elements such as aluminum and maganese are being brought into solution to exercise deleterious effects on plant roots and nutrient absorption. Such a cause and effect relationship has not yet been demonstrated in the Northeast or in other areas experiencing acid rain. Controlled field studies have generally shown that application of acid solutions having pH values of 3 to trees or crop plants reduces growth rate and/or damages foliage. At higher pH values, little or no effect is usually seen. The acid solutions tested are usually only sulfuric acid in water; dilute mixtures containing sulfuric and nitric acids, ammonia, and other trace materials normally found in rain water have not been studied.

In summary, the limited assessments to date of adverse effects of acid rain on the environment suggest that some damage to health and property could be occurring. It is not clear, however, whether the damage is serious, or likely to become serious, from the standpoint of health or economic impacts.

2. NATURAL AND MANMADE SOURCES OF ACID RAIN PRECURSORS

Acidity of rain is attributed primarily to the atmospheric conversion of the oxides of sulfur (SO_x) and the oxides of nitrogen (NO_x) to sulfuric (H_2SO_4) and nitric (HNO_3) acids; direct emissions of primary sulfates, however, are also an important source of acid rain. Investigators speak of SO_x and NO_x compounds as acid rain "precursors" because their presence in the atmosphere is believed to precede the occurrence of acid rain. The sources of SO_x and NO_x are both natural and manmade, the latter being generally accepted as the most important contributors to acid rain. The manmade activity of dominant importance in production of SO_x and NO_x is the burning of fossil fuels (coal, petroleum products, and natural gas). Other industrial sources of SO_x and NO_x emissions can be important in some situations. The following discussion begins with a brief consideration of the acidity of natural rain, followed by a review of the natural and manmade sources of precursor compounds.

NATURAL UNPOLLUTED RAINFALL ACIDITY

The pH of natural, unpolluted rainfall is still a matter of some uncertainty. One hypothesis regarding the pH of natural rainfall is frequently cited in the literature. This hypothesis, called the CO_2 theory, states that the pH of natural rain is expected to be 5.6 to 5.7, which is the pH of distilled water in equilibrium with atmospheric carbon dioxide (CO_2). However, even in the absence of any man-made activity natural rain would not consist of pure water and CO_2. Natural precipitation would still contain a wide range of chemical components derived from natural sources. Those which have been widely discussed include sea salts, earthen and volcanic dusts, ammonia and sulfur compounds from decaying plants and animal matter, etc. Hence it is generally accepted that the pH of natural rainfall, devoid of manmade pollutants, could be higher or lower than the hypothetical value of pH 5.6 to 5.7.

One investigation has suggested that precipitation pH would probably depend upon local conditions. In marine areas where there is little alkaline earth dust, the pH might naturally be below 5.7. Over large, nonforested, continental land masses, the pH might naturally be higher than 5.7 because of entrainment of alkaline soil particles (GCA Corporation 1981).

There is preliminary evidence of naturally acid precipitation (pH 3.8 to 5.4) in remote marine areas of the world such as off the coast of South

America or Africa, and on Amsterdam Island. (Refer to Figure 1-1.*) Other evidence to this effect is apparent in analyses of ice core samples from remote areas, as shown in Table 2-1. Some of these samples are as much as 350 years old, well before the age of industrialization. Sulfate values are low, as expected, yet so are the pH values. This evidence is limited and preliminary, but it suggests that rain and snow can be naturally more acid than would be expected from the CO_2 theory.

TABLE 2-1. ACIDITY OF REMOTE SNOW AND ICE CORE SAMPLES

Source	Number of samples	Approximate age of ice	Mean pH	Sulfate content	Reference
Antarctica	80	Up to 350 years	4.8-5.0	low[a]	Lynch (1980)
Himalaya Mts.	250	Up to 30 years	5.1[b]	-	Lynch (1980)
Cascade Mts., USA	-	Glacier ice	5.6	-	Vermeulen (1980)

[a] The low sulfate levels were interpreted as meaning not much influence on pH from fossil fuel pollution.

[b] Freshly fallen snow had pH of 5.1, which is more acid than CO_2 theory predicts. Also, the pH readings in some 30-year-old ice core samples were constant from bottom to top, indicating that the acid content had not changed in recent years.

NATURAL SOURCES

Numerous efforts have been made to estimate global emissions of sulfur and nitrogen compounds produced by natural sources. Such estimates are necessarily based on some very uncertain assumptions, and results are highly variable. The tonnages of estimated global emissions are substantial, however, and the evaluations are summarized briefly here.

Figure 2-1 depicts the atmospheric sulfur cycle as it is currently understood. Natural sources of sulfur compounds in the atmosphere include biogenic emissions from the ocean, marshes, and land of reduced sulfur

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* Hawaii, American Samoa, and Point Barrow, Alaska, cannot be considered truly remote because they have permanent populations that rely on oil as their principal combustion fuel.

compounds such as hydrogen sulfide (H_2S), dimethyl sulfate ($[CH_3]_2S$), carbonyl sulfide (COS), and carbon disulfide (CS_2). Nonbiogenic sources include sea spray emissions of neutral sulfate ($SO_4^{=}$) salts and volcanic emissions of both reduced and oxidized sulfur such as hydrogen sulfide, SO_2, and sulfate.

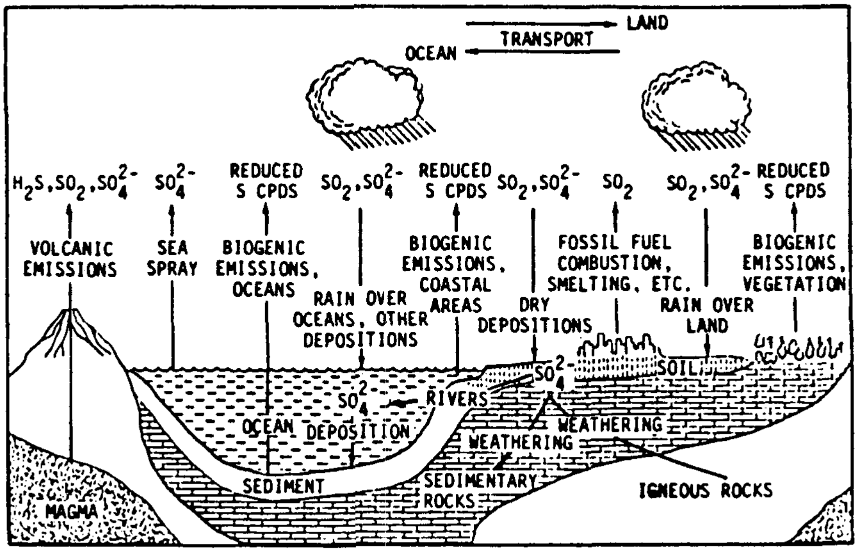


Figure 2-1. The atmospheric sulfur cycle (Cullis and Hirschler 1980).

Table 2-2 summarizes data from several attempts to estimate the global magnitude of the various sources of sulfur emissions. The estimates of natural emissions (first four columns) show that those from biogenic sulfur sources are most uncertain; they probably account for one-half to two-thirds of the total natural contribution. Estimates of sea spray and volcanic emissions are more certain.

Information on the natural sources of nitrogen oxides (NO_x) in the atmosphere is much less complete than that for sulfur oxides. Nitrogen is naturally emitted from the earth (land and sea) in reduced form as ammonia or NH_3, some of which is subsequently oxidized to NO_x in the atmosphere. Nitrogen oxides are also formed in the atmosphere from molecular nitrogen and oxygen in the presence of lightning. Nitric acid (HNO_3) is formed by the conversion of NO_x to HNO_3.

Global emission estimates are variable and incomplete, as shown in Table 2-3. Estimates of the ratio of atmospheric nitrogen from natural sources to that from man's activities have ranged from 15:1 to as low as 1:1. Most of the nitrogen from natural sources appears to be emitted in the form of NH_3, although emissions of NO_x are also large.

TABLE 2-2. ESTIMATES OF GLOBAL ATMOSPHERIC SULFUR EMISSIONS FROM NATURAL AND MANMADE SOURCES, 10^6 METRIC TONS SULFUR PER YEAR[a]

Natural				Natural total	Manmade	Total manmade plus natural	Relative manmade contribution		Reference
Biogenic		Sea spray	Volcanoes				% of total	% of natural	
Land	Sea								
70	160	45		275	40[b]	315	13	15	Junge (1963)[a]
110	170	45		325	40[b]	365	11	12	Eriksson (1963)
70	30	44		144	76[c]	220	35	53	Robinson and Robbins (1968)
71	18	44	1	134	50[c]	184	27	37	Kellogg et al. (1972)
58	48	44	2	152	65[c]	217	30	43	Friend (1973)
3	28	44	3	178	65[c]	143	45	37	Bolin and Charlson (1976)
3	34	44	3	84	65[c]	149	44	77	Hallberg (1976)
5	27	44	3	79	65[c]	144	45	82	Granat (1976)
106	46	44	-	196	70[c]	266	26	36	Garland (1977)
60	26	44	10	140	60[c]	200	30	43	Davey (1978)
48	50	44	5	147	86[d]	233	37	59	Cullis and Hirschler (1980)
48	50	44	5	147	93[e]	240	39	63	Cullis and Hirschler (1980)
48	50	44	5	147	104[f]	251	41	71	Cullis and Hirschler (1980)

[a] Modified from Cullis and Hirschler (1980).

[b] Based on 1956 emission data.

[c] Based on emission data from the mid-1960's.

[d] Based on 1970 emission data.

[e] Based on 1974 emission data.

[f] Based on 1976 emission data.

TABLE 2-3. ESTIMATES OF GLOBAL EMISSIONS OF OXIDES OF NITROGEN AND RELATED COMPOUNDS

(10^6 metric tons nitrogen/yr)

	Emissions	Reference
NO_x emissions from land to atmosphere	40-108	Soderlund and Svensson (1976)
NO_x emissions from land and sea (as NO)	210	Robinson and Robbins (1975)
NO_x formed by combustion	15	Burn and Hardy (1975)
	19	Soderlund and Svensson (1976)
	15	Robinson and Robbins (1975)
NO_x formed by industrial processes	30	Delwiche (1970)
	30	Burn and Hardy (1975)
	36	Soderlund and Svensson (1976)
	40	Liu et al. (1977)
Atmospheric NH_3 transformation to NO_x	30	Burn and Hardy (1975)
	3-8	Burn and Hardy (1975)
NH_3 emissions to atmosphere	165 (land and sea)	Burn and Hardy (1975)
	113-244 (land)	Soderlund and Svensson (1976)
	870 (land and sea)	Robinson and Robbins (1975)
Atmosphere production of NO_x by lightning	10	Burn and Hardy (1975)
	30-40	Chameides et al. (1977)

[a] Source: GCA Corporation (1981).

MANMADE SOURCES

Most manmade emissions of SO_x and NO_x come from the burning of fossil fuels (coal, petroleum products, and natural gas) to satisfy man's energy needs. Other important sources include the industrial processes in which major raw materials such as metallic ores and phosphate rock are converted to primary metals or large-volume chemicals. The relative importance of the major U.S. sources of SO_x and NO_x in terms of national annual emissions is shown in Table 2-4.

The estimated emissions shown in Table 2-4 for mobile sources are produced principally by motor vehicles burning gasoline or diesel fuels. The emissions from stationary fuel consumption comes largely from utility boilers producing electricity; the balance comes from combustion in boilers and furnaces used to produce steam for industrial processes or for space heat. The total emissions from industrial processes are small by comparison with other categories. The largest industrial process source, from the roasting of sulfide metal ores, was estimated to produce only 2.4 million metric tons of SO_x in 1977. Industrial processes are thus of secondary importance as large tonnage sources of acid rain precursors. Only about 15 percent of the total annual emissions of SO_x and 3 percent of the NO_x come from industrial processes. Most of this is associated with smelting of ores for metal production or with petroleum refining. Other industries with potential for contribution to acid rain are sulfuric and nitric acid plants, phosphate and nitrate fertilizer plants, and pulp mills. Emissions from these industrial processes are small in the United States and generally should be even smaller in other industrialized areas experiencing acid rain because emissions are often more closely controlled. For example, copper smelters, which produce most of the SO_x from industrial processes in the United States, are controlled to high levels of efficiency in Japan and in some European countries. These processes are identified here because industries are implicated in some occurrences of acid precipitation. Also, some of these noncombustion sources can be very large; for example, the Sudbury smelter in Canada is the world's largest source of SO_2, emitting 2 to 3 percent of all the manmade emissions in the world.

RELATIVE CONTRIBUTIONS OF NATURAL AND MANMADE SOURCES

Early estimates of the relative contribution of natural and manmade sources suggested large global emissions of sulfur in the 1960's (about 60% of the total) compared with those from manmade sources. More recent comparisons are based on more refined estimates of natural emissions and more current figures on manmade emissions. These data suggest that natural emissions now make up only 30 to 40 percent of the total, and it has been predicted that man will be emitting far more sulfur than nature by the year 2000 if the present growth in manmade emissions (2.2% per year) continues (Cullis and Hirschler 1980) and natural emissions remain constant.

Although it has been shown that natural sulfur and nitrogen emissions contribute significantly to the total sulfur and nitrogen budgets, they are not believed to be important contributors to acid rain in industrialized

TABLE 2-4. 1977 U.S. NATIONAL SO_x AND NO_x EMISSIONS ESTIMATES (10^6 metric tons)[a]

	SO_x	NO_x
Mobile source fuel combustion	0.8	9.2
Highway vehicles	0.4	6.7
Non-highway vehicles	0.4	2.5
Stationary source fuel combustion	22.4	13.0
Electric utilities	17.6	7.1
Industrial	3.2	5.0
Residential, commercial, and institutional	1.6	0.9
Industrial processes	4.2	0.7
Chemicals	0.2	0.2
Petroleum refining	0.8	0.4
Oil/gas production and marketing	0.1	0
Metals	2.4	0
Mineral products	0.6	0.1
Other industrial processes	0.1	0
Miscellaneous	0	0.3
Total	27.4	23.1

[a] U.S. EPA (1978b).

areas of the world. In these areas the manmade emissions are highly concentrated and probably exceed those from natural sources by a large margin. For example, one investigator estimates that 90 percent or more of the sulfur emissions in eastern North America are manmade (Galloway and Whelpdale 1980). In Canada, manmade sulfur emissions are at least 5 times greater than natural emissions (Environment Canada 1980). Studies of SO_x emissions in Europe have reached similar conclusions. Furthermore, manmade emissions of sulfur and nitrogen occur mostly in oxidized form, whereas natural emissions of sulfur and nitrogen are most often in reduced forms, which must undergo oxidation before they can be considered acid rain precursors. Although sea sulfates are in oxidized form, they are emitted as neutral salts and are not, therefore, considered as acid rain precursors. Collectively, these facts diminish the seemingly great potential of natural sources for production of acid rain, especially in industrialized areas.

In industrial areas, fossil fuel burning is the most important source of precursor emissions. While emission patterns would vary among different parts of the industrialized world where acid rain is most prevalent, all areas have one thing in common. Combustion of coal, petroleum products, and natural gas is the dominant source of manmade NO_x and SO_x discharged to the atmosphere. The major fuels consumed in industrialized areas since the turn of the century have been coal, petroleum products (gasoline, distillate fuel oils, residual fuel oils), and natural gas. Sulfur-containing fuels are thought to have greater potential for participating in acid rain formation because of the emission of SO_2 and sulfate pollutants. Coal and residual oil are potentially the greatest contributors. Distillate oils and gasoline are quite low in sulfur content, but they may also contribute to formation of atmospheric sulfuric acid in regions where they are burned in large quantities.

3. FORMATION, TRANSPORT, AND DEPOSITION

Over the past 5 to 10 years researchers have generated a considerable amount of information on the occurrence of sulfates and nitrates in the atmosphere. The primary purpose of some of these studies was to further our understanding of acid rain. Although other studies were more general or conducted for other reasons they uncovered clues that are useful in the study of the causes and mechanisms that lead to the occurrence of acidic precipitation. Unfortunately the complexity of the problem is such that information on chemistry of formation and mode of deposition is incomplete, as are other background data on the production, transport, and transformation of precursor pollutants into acid precipitation.

The discussion that follows attempts to provide a general review of some perceptions of the physical and chemical processes associated with acid precipitation.

CHEMISTRY OF ATMOSPHERIC ACID FORMATION

Rainfall contains both strong and weak acids. The weak acids are often organic compounds having low ionization (dissociation) constants. For this reason, they exhibit relatively little free hydrogen ion activity or free acidity. Examples are carbonic, acetic, and propanoic acids. Weak acids are not believed to be important in acid rain formation in the northeast United States but they may have greater importance in other parts of the world.

Strong acids, in contrast, are usually inorganic compounds that completely (or near completely) ionize in water and provide relatively high free hydrogen ion activity or free acidity. Examples are sulfuric (H_2SO_4), nitric (HNO_3), and hydrochloric (HCl) acids. These strong inorganic acids are believed to have the major impact on the acidity of rainfall; thus, the sulfur oxides (SO_x), nitrogen oxides (NO_x), and chlorides are considered the principal precursors to acid rain formation.

The chemistry of strong acid formation in the atmosphere is not well understood. Complex chemical transformation and deposition processes are believed to be involved. While SO_x and NO_x precursor gases are being emitted and transported over distance and time, some are being converted to acid sulfates or nitrates. This conversion is thought to occur by several mechanisms, the most important of which are photochemical and catalytic oxidation. See Figure 3-1.

The rate of atmospheric oxidation of precursor gases is apparently quite variable, depending upon whether the oxidation occurs in the gaseous, liquid, or solid state. High humidity favors the oxidation process, as do sunlight and high temperatures. Metal catalysts, carbon, ozone, and ammonia are also thought to be important rate-controlling factors.

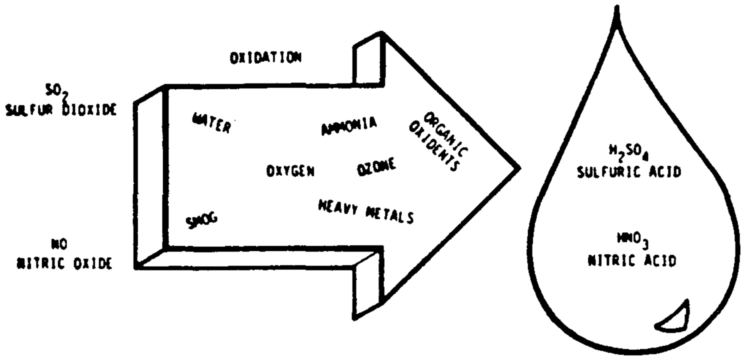


Figure 3-1. Simplified diagram showing formation of acid rain from NO and SO_2 precursor gases (U.S. EPA 1979).

More is known about oxidation of SO_2 than of NO_x. At present it is generally accepted that homogeneous, gas-phase, photochemical conversion of SO_2 to SO_3 by reaction with OH, HO_2, RO, and RO_2 is an important source of ambient sulfates (Eliassen and Saltbones 1978). Also, many have come to accept that the liquid-phase conversion of SO_2 and SO_3 in clouds and ambient aerosol is an important mechanism for the generation of sulfates. On the other hand, experts do not appear to agree as to which reaction routes are most important or what the controlling factors are.

Photochemical oxidation of SO_2 requires sunlight and therefore depends on latitude, season, altitude, and time of day. Direct photochemical oxidation of SO_2 to sulfate in pure air is believed to be negligible. If it occurs at all, the rate is probably less than 0.03 percent per hour (GCA 1981). In polluted atmospheres where photochemical oxidation is already occurring because of hydrocarbon (HC) and NO_x emissions, SO_2 is oxidized at a much higher rate. Rates of oxidation of SO_2 to sulfate in the presence of oxidizing radicals have been estimated to range from 1 to 10 percent per hour, depending on HC and NO_x emission rates, temperature, dewpoint, solar radiation, and absolute concentration of reactive pollutants (GCA 1981). Once formed, the sulfur trioxide quickly hydrolyzes to sulfuric acid in the presence of high humidity or rainfall.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In contrast to the photolytic process, catalytic oxidation of SO_2 involves water and oxygen in the presence of a catalyst (Cheng, Corn, and Frohliger 1971). Laboratory measurements implicate particulate carbon (soot) and a number of metals and metal oxides such as vanadium, manganese, nickel, iron, vanadium pentoxide, and ferric oxide as active catalysts in the oxidation of sulfur (Penkett et al. 1979; Cheng, Corn, and Frohliger 1971; Chang 1980). These chemicals are suspected of promoting the oxidation of SO_2 to sulfate both during combustion and/or after emission within the plume. Concentrations of NO_x and NH_3 also are important in catalytic oxidation of SO_2.

The role of catalysis in promoting oxidation of SO_2 and NO_x is poorly understood and controversial. Nevertheless, one researcher, after reviewing the data, presented the following qualitative conclusions (Larson 1980):

1. The important component in aqueous-phase reactions can be metal ion (manganese), carbon, ozone, or oxygen, depending on prevailing conditions.

2. At low pH (less than 5) and high concentrations of liquid water (as in clouds over polluted areas), ozone is the controlling component.

3. At low pH (less than 5) and low liquid concentration characteristics of acid aerosols, carbon-catalyzed reactions are most important.

4. At higher pH (more than 5) in aerosols, metal ion catalysis is the important mechanism.

5. At higher pH (more than 5) and higher concentrations of liquid (as in clouds in a clean atmosphere), oxygen may be important. The rates for catalytic oxidation of SO_2 in the atmosphere are not known.

As with sulfur, the chemical mechanisms by which NO_x is converted to HNO_3 are complicated and not well understood. One proposed route is the hydrolysis of N_2O_5 (Drake and Barrager 1979).

$$H_2O + N_2O_5 \rightarrow 2HNO_3$$

Another proposed mechanism is the combination of NO_2 with the OH radical (Drake and Barrager 1979).

$$NO_2 + OH \rightarrow HNO_3$$

The rates of these reactions in the atmosphere are not known.

Once formed, atmospheric acids may be neutralized by alkaline materials in the air such as smoke solids and fly ash, soil and cement dusts, or ammonia. Neutralization of sulfuric and nitric acids by calcium carbonate or ammonia results in the formation of calcium and ammonium sulfate or nitrate salts, which are either washed from the air during a rainfall, or become part of the total dry deposition that falls to the ground between rainstorms.

TRANSPORT AND DEPOSITION OF ATMOSPHERIC ACIDS

The amount of acid impacting a given area from the atmosphere is dependent upon transport and deposition factors, which provide the key to identification of the sources of emissions contributing to acid rain in any given location. The following discussion highlights the complexity and variability these important factors--meteorological and climatological influences--on transport of acidic pollutants and the wet and dry deposition processes.

Meteorological and Climatological Influences

Both small- and large-scale meteorological factors contribute to the transport and dispersion of acidic precursors and influence their transformation and final deposition through precipitation events. Meteorological factors that influence the pollutant pathway from the moment of release to eventual deposition include:

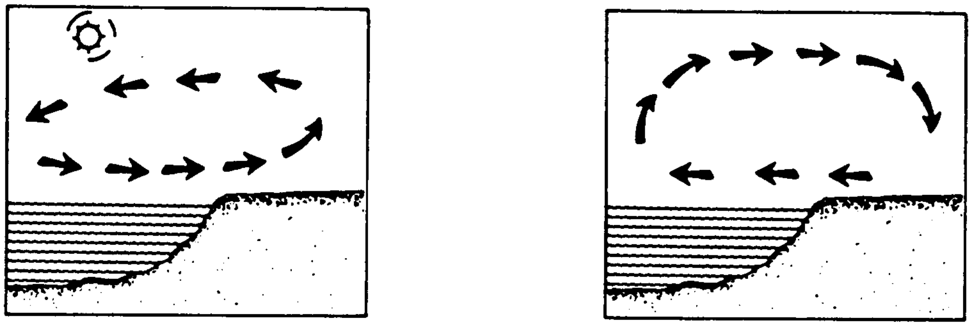
- wind: speed, direction, variation with height
- turbulence: thermal and mechanical
- convection: vertical transport
- thermal layers: inversions of temperature
- precipitation: frequency and type
- orographic and water body influences
- temperature and humidity

The meteorological factors of a particular weather event govern the transport and diffusion of emissions on either a local, mid-range, or long-range scale. The initial transport winds carry the plume downwind from the source. As the plume moves from the area, the thermal structure of the atmosphere determines the effects of convective mixing and turbulence. In daytime, with strong solar surface heating, the plume may mix rapidly throughout the atmosphere (up to the mixing height). In a stable air mass, however, the effluents released within the inversion layer may be trapped and their dispersion and transport severely limited, whereas those released above the inversion may be transported by winds aloft.

Thermal turbulence may be enhanced or modified by mechanical turbulence induced by complex terrain, water bodies, or urban effects. Figure 3-2 demonstrates one such regime involving wind influences and turbulence structure near a body of water. In this case, the general transport winds and atmospheric dispersion mechanisms are significantly influenced by the interaction of the two air masses over the land and sea (Schroeder and Buck 1970).

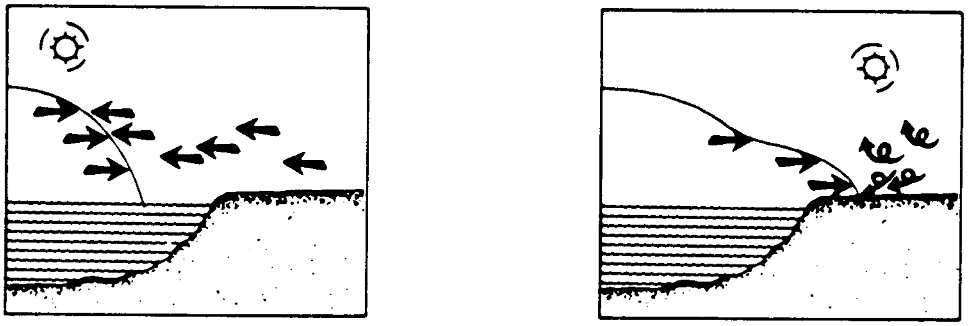
In addition to these transport and dispersion influences, precipitation affects the fate of pollutants. Higher amounts of wet deposition of acidic precipitation generally correspond to a higher frequency of precipitation. Thus, areas of higher humidities and more frequent precipitation events may undergo more acid rain events. As clouds are formed, they lift great air masses from the surface, effecting a net vertical transport of pollutant emissions high into the troposphere and making these pollutants available for incorporation into the vapor and liquid states of the cloud.

Larger-scale weather systems also can strongly affect transport and dispersion of pollutants. Cyclonic (low-pressure) systems are usually



AS LAND SURFACES BECOME WARMER THAN ADJACENT WATER SURFACES DURING THE DAYTIME, AND AIR OVER THE LAND BECOMES WARM AND BUOYANT, THE DENSER SEA BREEZE BEGINS TO FLOW INLAND FROM OVER THE WATER AND FORCES THE LESS-DENSE AIR UPWARD.

AT NIGHT, LAND SURFACES COOL MORE QUICKLY THAN WATER SURFACES. AIR IN CONTACT WITH THE LAND BECOMES COOL AND FLOWS OUT OVER THE WATER AS A LAND BREEZE, DISPLACING THE WARMER AIR.



A GENERAL WIND BLOWING TOWARD THE SEA OPERATES AGAINST THE SEA BREEZE AND, IF STRONG ENOUGH, MAY BLOCK THE SEA BREEZE ENTIRELY.

IF MARINE AIR HAS BEEN PILED UP OVER THE WATER BY AN OFFSHORE WIND, IT MAY RUSH INLAND LIKE A SMALL-SCALE COLD FRONT WHEN THE LOCAL PRESSURE DIFFERENCE BECOMES GREAT ENOUGH.

Figure 3-2. Sea-land breeze circulations (Schroeder and Buck 1970).

associated with strong winds, storms, precipitation, overcast skies, frontal mixing and turbulence, and an unstable to neutral atmosphere. In contrast, the anticyclonic (high-pressure) systems are characterized by light, disorganized winds, abundant sunshine, low humidities, and stable air layers. The layers may be formed aloft by cold subsiding air or at the surface by radiational cooling of the air near the earth's surface at night. In any case, stagnating air is very often related to anticyclones, especially on the eastern side of high-pressure systems. Figures 3-3 and 3-4 display the average tracks of cyclone and anticyclonic systems across the contiguous United States (Klein 1957).

Of special note in these figures is the tendency of both systems to follow the prevailing westerly winds. As they approach eastern United States, cyclones follow the Appalachian Mountains and move northeast toward Canada. This pattern of movement of low- and high-pressure systems is particularly important in the areas of high pollutant emissions and frequent precipitation because of possible cumulative entrainment and deposition of emissions as the air is transported through each region.

A study of anticyclones by Korshover shows the frequency of occurrence of atmospheric stagnation (i.e., stagnation for 4 days or more) (Korshover 1971). The study focuses on the monthly distribution of stagnating anticyclones east of the Rocky Mountains from 1936 to 1970. Figure 3-5 shows the summer distribution of such episodes, the most frequent cases occurring in the southeastern United States. The importance of such studies is the probability that pollutants may remain in stagnating systems that are conducive to oxidation and slow dilution. The southeastern portions of the country are also subject to frequent precipitation events, and thus the combination of stagnation, and slow dilution followed by precipitation could lead to the occurrence of acid rain, especially in the presence of high pollutant emissions.

The primary cause of precipitation is the forced ascent of air from the lower atmosphere, resulting in condensation and precipitation of water as rain or in a frozen form. Certainly the primary mechanisms of cloud formation in the atmosphere can contribute to the transport and dispersion of pollutants from the surface into the air loft. These mechanisms include frontal, orographic, and convective formation. A frontal zone is the demarcation between two major air masses of significantly different temperatures, humidity, and density. As one air mass displaces another, clouds are formed and precipitation occurs along the frontal boundary. Orographic precipitation occurs when an air mass is forced up and over a topographic feature and cooled to the condensation point of the water. Much of this precipitation falls in mountainous regions and, if the air mass is polluted, may lead to significant acid deposition. Convective cloud formation occurs in the presence of strong surface heating, leading to buoyant air. In the presence of sufficient moisture, clouds and precipitation may form, carrying pollutants into the upper air and making them available for longer-range transport and deposition (Schroeder and Buck 1970; Galloway and Likens 1978).

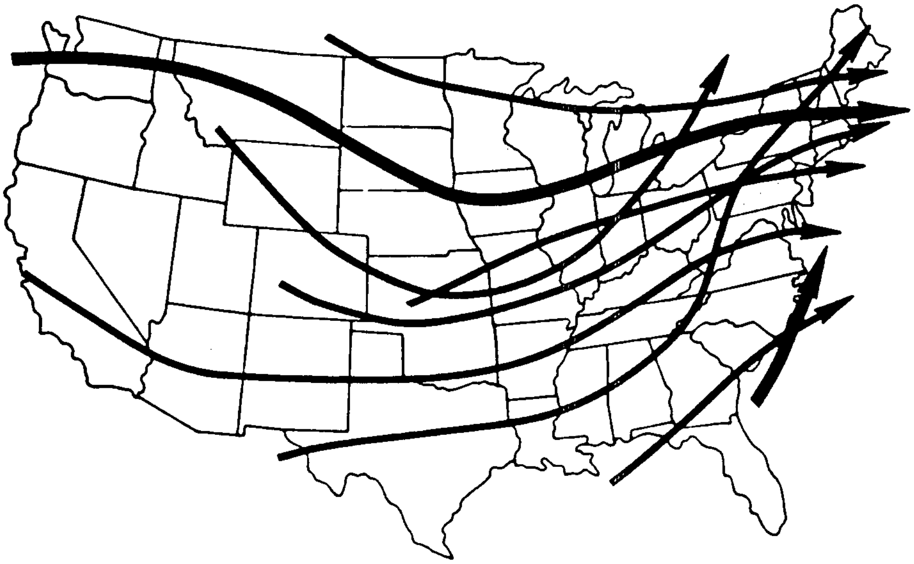


Figure 3-3. Average tracks of cyclones (Klein 1957).

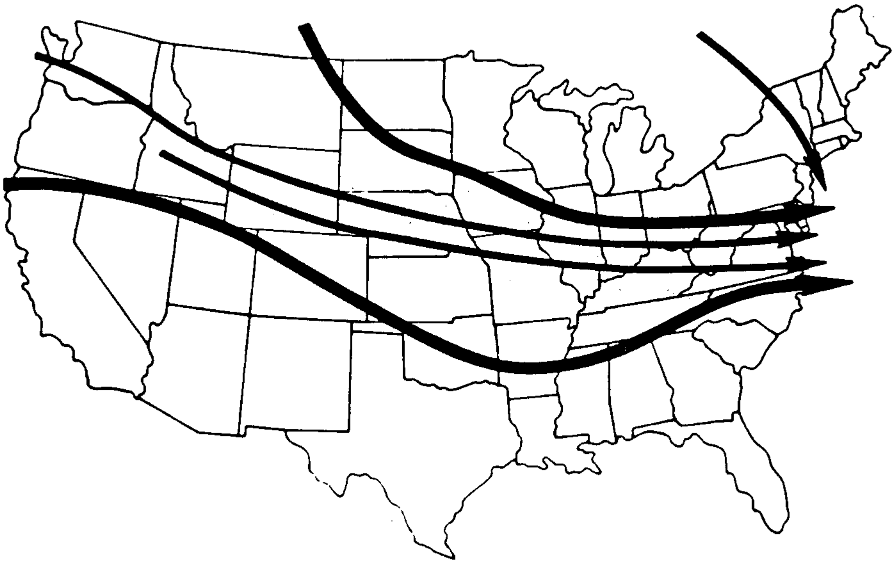


Figure 3-4. Average tracks of anticyclones (Klein 1957).

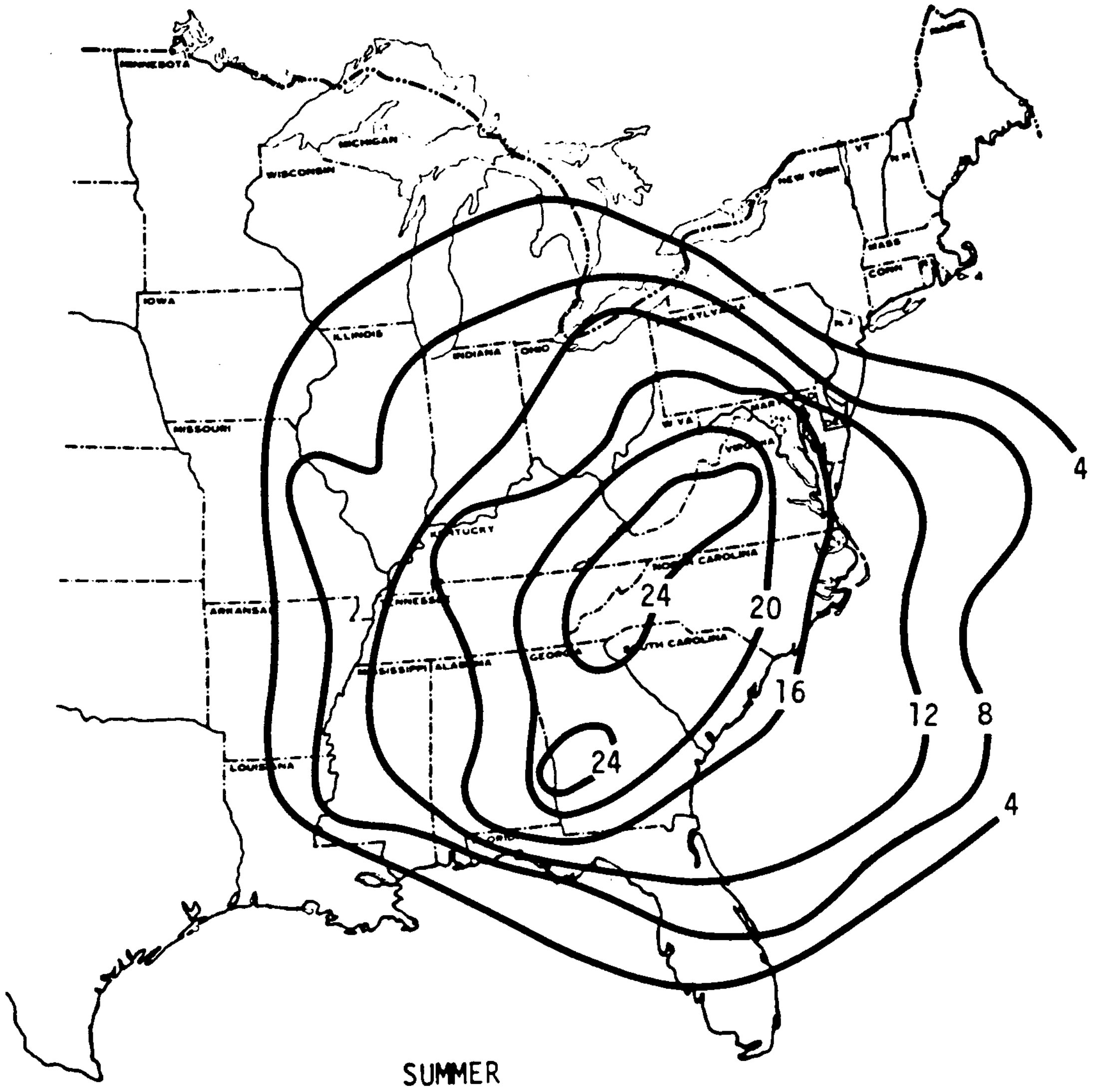


Figure 3-5. Summer distribution of atmospheric stagnation occurrences (four days or more), 1936-1970 (Korshover 1971).

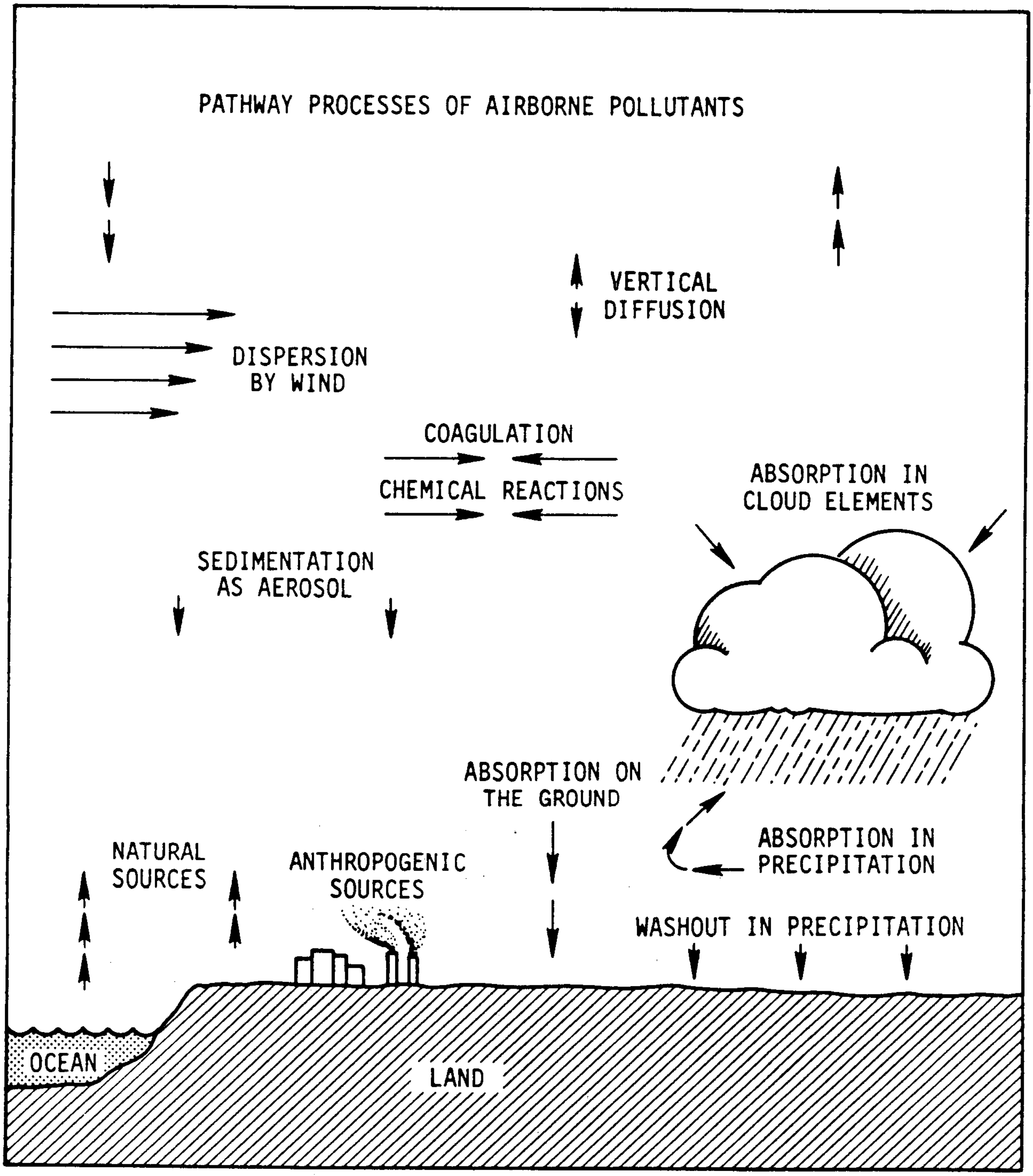


Figure 3-6. A schematic of the pathway process of airborne pollutants (Drake and Barrager 1979).

Deposition Processes

Acidic materials are removed from the air through wet and dry deposition, the former occurring during fogs and precipitation events. Figure 3-6 shows schematically the combined effects of the potential pathways and processes affecting the precursors of acid deposition.

The term "dry deposition" as applied to acid rain denotes acid materials or precursors that are deposited from the atmosphere in the absence of water. It includes gravitational dry fall, impaction, absorption, and adsorption of gases, aerosols, and particulate matter from the atmosphere.

The rate of dry deposition of a gas is determined by the affinity of the receiving surface (vegetation, soil, water) for the gas and the rate of transport to that surface. The presence of moisture, such as dew on vegetation, greatly increases the deposition rate of SO_2. Similar relationships are thought to be true for dry deposition of gaseous nitrogen dioxide and nitric acid. The rates of dry deposition of particles such as sulfates and nitrates, which are products of the chemical conversion of SO_2 and NO_x, depend primarily on particle size.

Mechanisms for deposition include impaction and gravitational force. Once deposited, particles may be returned to the atmosphere by wind or surface disturbance before they are wetted by precipitation.

Wet deposition properly includes all forms of water that condense from the atmosphere. Wet deposition may occur through two processes: rainout and washout. The incorporation of gases or particles into cloud droplets prior to their descent as raindrops is called rainout. The removal of gases and particles by the raindrop as it falls through the atmosphere is known as washout.

In rainout, particulate materials in a cloud act as condensation nuclei. In addition, particulate matter may be captured by cloud droplets through impaction and interception. The water solubility and atmospheric concentration of a gas are important factors in rainout efficiency. The pH of the rain is also a factor, in that the more acidic rain limits the solubility of gases like SO_2.

In washout, the air mass through which the precipitation falls is cleansed as the precipitation captures pollutants in the atmosphere. The surface area of the raindrop and the ambient concentrations of pollutants are the main factors affecting washout of gases. The washout of particulate matter occurs primarily through impaction and interception by falling rain drops.

The wet events most often associated with the wet deposition process are rain and snow. Other potentially important wet events have received only minimal attention in the literature by comparison. These include dew, frost, fog, hail, sleet, and mist. Because these events usually occur in very finely divided particle or droplet form, they have large surface areas upon which wet chemical reactions can take place. For this reason, they have the potential to be especially acidic. Evidence to this effect has appeared in the literature. Several investigators have noted that the slower the rainfall rate (and therefore the smaller the droplet size), the more acid the pH. In Japan between 1973 and 1975, several episodes of acid fogs and mists were recorded (Chemical Abstracts 1981). High elevation studies of cloud water droplets in New York, Washington, D.C., Japan, and Hawaii have shown very acid values (Chemical Abstracts 1981; Miller 1980).

The relative acid contributions of wet and dry deposition or of special wet events are not known. On the basis of model calculations of wet and dry sulfur deposition values, (GCA 1981), some believe that wet and dry acid deposition are of near equal importance. This hypothesis cannot yet be verified in the field because suitable techniques for dry deposition sampling are not available. Bulk sampling and wet/dry sampling are not the most highly recommended methods, and also capture only some fraction of gravitational dry fall. The best sampling method available today for studying precipitation chemistry, is use of wet only sample collectors, and this method does not account for any of the various dry deposition processes taking place in nature.

4. MEASUREMENT AND MONITORING

Measurement of rain acidity and precursors in the ambient air is a critical step in the determination of relative source contributions to acid rain. Analysis and interpretation of these data are complicated by the variations that can occur in the measurement process and the method of interpretation.

Data obtained from sampling of both precipitation and ambient air pollutants by a variety of techniques are used to study long-term trends, geographical distributions, and the cumulative impacts of pollution exposure. In terms of both rain acidity and precursor concentrations, there is a need for firm "baseline" data in areas where changes are believed to be occurring.

Precipitation monitoring was first undertaken on a very limited basis in the 1950's, but was later virtually abandoned because of measurement difficulties and lack of support. A resurgence of interest in precipitation monitoring has arisen from the widespread concern with the acid rain problem. The lack of historical precipitation monitoring data has hampered efforts to define the impacts of acid rain on ecological processes in the northeastern United States and to document trends in acidification. Four major monitoring networks consisting of over 150 monitoring stations are currently operational in the United States and Canada. In addition, monitoring work is being or has been conducted by a number of universities and EPA regions. These efforts will add to the accumulation of available data.

PRECIPITATION SAMPLING AND ANALYSIS

Selection of rainfall parameters to be measured depends on the purpose of the measurement study. Some of the common parameters measured in rainfall studies are summarized below:

- Acidity, pH
- Conductivity
- Precipitation Amount
- Sulfate
- Nitrate
- Ammonium
- Chloride
- Metal Ions (Ca, Mg, Na, K)
- Alkalinity

These parameters allow the determination of commonly occurring major species and major free acid contributors; they also enable the analyst to conduct some quality control checks. Other parameters (e.g., sulfite, nitrite, and organics heavy metals) are sometimes measured depending on the purpose of the study.

Sample Collection

Collection of precipitation samples for analysis is probably the most critical aspect of the measurement process. A number of investigators have considered the problems involved in sample collection. Some of the more important ones are discussed here. The five major factors to be considered in sample collection are (1) collector type (wet, dry, bulk), (2) the material of which the collector is fabricated, (3) the reliability and efficiency of the collector, (4) the collection site, and (5) the collection period.

The three basic types of collectors are bulk, wet, and wet/dry. A bulk collector is an open vessel that collects both precipitation and dry deposition, mainly dry fallout. A wet collector is equipped with a moisture sensor, which opens the collection vessel only during periods of rain or snow. A wet/dry collector has one vessel to collect rain or snow and another to collect dry deposition. A moisture sensor exposes the appropriate vessel (Galloway and Likens 1978).

Of the three types, the wet collector gives the best-defined samples. A disadvantage, however, is that the sensor may not always open the collector immediately when precipitation begins, and this may affect the measured pH value, because early rainfall can be more or less acid than the later rainfall in any given precipitation event.

A bulk or dry sample is less well-defined. Dry deposition occurs by fallout, impaction, adsorption, and absorption, but the dry collection vessel does not collect materials deposited by all of these modes. The material trapped in the dry collector consists mostly of gravitational fallout and possibly some material deposited by impaction or adsorption. The representativeness of the dry sample in relationship to actual dry deposition in the environment is believed to be very poor (Galloway and Likens 1978).

In a bulk collector the measurement of dry deposition suffers the same limitations, with additional problems of evaporation and possible absorption in the wet sample. Data presented by Galloway and Likens (1976) show that differences in collector design can lead to significant differences in the measured chemical composition of dry deposition or of bulk samples. For the above reasons, wet sample collectors are currently recommended for the study of precipitation chemistry (Galloway and Likens 1978). The current estimate is that wet and dry deposition contribute about equally. If this is true, there is a real need for methods of measuring the contributions made by dry fallout, impaction, adsorption, and absorption.

The materials used in the collection vessel can significantly influence the measured composition of precipitation. The use of acid-washed plastic containers for inorganic species and glass for organic species is recommended for both collection and storage of samples (Galloway and Likens 1978; Topal et al. 1981).

Reliability and efficiency are obviously important considerations, both in obtaining the required samples and in ensuring cost-effectiveness. The efficiency of a collector is determined by comparing the volume collected with that collected by a standard rain gauge. Published data indicate varying degrees of reliability and efficiency among different brands of collectors (Galloway and Likens 1976).

A precipitation collector must be located so as to provide representative samples. The recommended location is a wind-sheltered site on flat or gently sloping terrain, free from the influence of local sources of contamination such as roads, smoke stacks, and cultivated fields.

Duration of the sampling period also influences the precipitation measurement. Galloway and Likens (1978) have studied the effect of sampling time on the chemistry of bulk collectors. Their data compare measurements of samples collected on a per-event basis with values of a composite sample collected over a series of three to eight storms. The variability of these data is much greater than that expected among adjacent collectors. Therefore the recommended procedure calls for collection of samples on an event basis or over weekly intervals at most.

Two additional considerations are important in sample collection. First, the volume of sample must be sufficient for the required analyses. For example, a collector with 100 percent efficiency relative to a standard rain gauge must have a 12-inch opening in order to collect 175 ml of precipitation from a 0.1-inch rainfall. Second, some means must be provided to protect the integrity of the collected sample. The samples are easily contaminated; they must be sealed against dry deposition when closed and protected against splash from the cover or sampler housing when open. Galloway and Likens (1976) have evaluated different automatic samplers in regard to this design feature.

Factors relating to sampling can also significantly affect the pH values in measurements of stream and lakewater acidity. For example, samples collected at the surface are generally more alkaline than those at lower depths, except after a rainfall (Pfeiffer and Festa 1980b). Seasonal variations such as snow melt can also dramatically alter the measured pH of lakewater. These influences should be factored into every stream and lakewater monitoring program.

Sample Analysis

The dilute nature of precipitation samples requires that analytical techniques be selected with care to ensure the necessary sensitivity. Sensitivities of the techniques in current use range from about 0.005 to 0.1 milligram per liter.

Before the advent of the modern glass electrode in the 1960's, colorimetric methods were used to determine the pH of aqueous solutions. Comparison of pH measurements by electrode with those obtained by colorimetric titration reveals substantial differences, as shown in Figure 4-1. This comparison of the two types of methods indicates that the Helligel colorimetric method used in the 1930's to measure the pH of Adirondack lakewaters may have been in error on the alkaline side by as much as 1 pH unit, or a factor of 10 in hydrogen ion concentration (Pfeiffer and Festa 1980a, 1980b). The error may have been even greater (as much as 1.5 pH units), in the range of pH 4 to 5.5. Because of this substantial error factor, only pH data derived by identical methods should be acceptable for comparison and for use in acidification trend studies.

Major Acid Precipitation Monitoring Systems

Table 4-1 lists the major acid rain monitoring programs that are collecting wet precipitation throughout the world. The sites in North America are located primarily in the United States and Canada. Monitoring sites are located throughout Europe, concentrated most heavily in Scandanavia. One monitoring program collects data on a global basis. All of the networks listed in Table 4-1 collect separate wet precipitation samples, although other types of collection are also performed at some sites. The major programs are described briefly in the following paragraphs.

National Atmospheric Deposition Program--

The main object of the National Atmospheric Deposition Program (NADP) is to provide data on pollutant deposition and its effects on the environment (Galloway et al. 1978). Approximately 80 sites are located throughout the United States. Precipitation samples have been taken weekly at some sites since July 1978. Additional sites have been established since that time.

World Meteorological Organization (WMO)--

The WMO network was established in 1974 to analyze precipitation samples throughout the world. The WMO network in the United States is coordinated by the U.S. Environmental Protection Agency (EPA) and NOAA. Samples are taken on a monthly basis. The network consists of approximately 130 sites throughout the world, 12 of which are in the U.S. The U.S. sites are now operated under the NADP system.

University of California--

The University of California's monitoring program was undertaken to determine the chemical composition of rain by collecting precipitation at eight sites in northern California. Data were collected from November 1978 to May 1979 on an event basis (McColl 1980).

California Institute of Technology--

In the monitoring program of the California Institute of Technology, nine stations collected data during the fall-spring season of 1978-79. Precipitation samples were taken on an event basis. The result of this monitoring program was determination of the chemical composition of precipitation in the Los Angeles basin (Morgan and Liljestrand 1980).

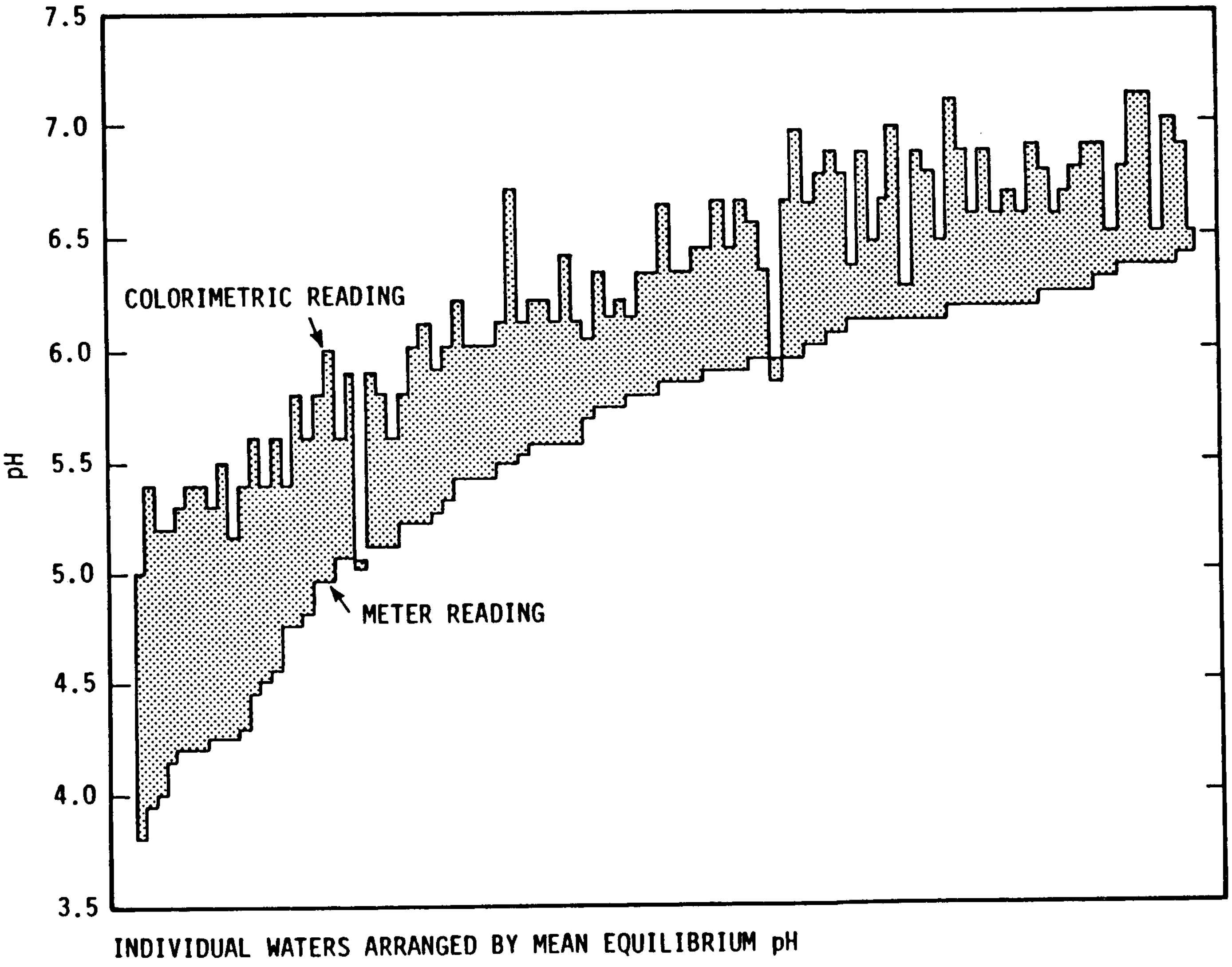


Figure 4-1. Comparison of pH values derived by glass electrode-meter and colorimetric (Helligel) methods for 138 Adirondack lakewaters sampled during August 1979 (Pfeiffer and Festa 1980a).

TABLE 4-1. PRECIPITATION MONITORING PROGRAMS COLLECTING SEPARATE WET SAMPLES[a]

Network	Number of stations	Period of data	Period of sample collection	Reference
National Atmospheric Deposition Program (NADP)	~80	1978-	Weekly	Henderson et al. (1981)
World Meteorological Organization[b] (EPA/NOAA/WMO)	~130 (12 U.S.)	1976-	Monthly	Henderson et al. (1981)
University of California	8	1978-1979	Event	McColl (1980)
California Institute of Technology	9	1978-1979	Event	Morgan & Liljestrand (1980)
Multi-State Atmospheric Power Production Pollution Study (MAP3S)	9	1976-	Event	MacCracken (1979)
Canadian Network for Sampling Precipitation (CANSAP)	56	1977-	Monthly	Henderson et al. (1981)
University of Florida	4	1978-1979	Event (1)/ biweekly (3)	Henderson et al. (1981)
Sulfate Regional Experiment (SURE)[c]	9	1978-1980	Event	Perhac (1978)
Organization for Economic Cooperation and Development (OECD)	70	1974-1977		Ottar (1977)
UNEP/WMO[d]	79	1978-1980	24h	U.N. (1980)

[a] Based on data from Bekowies and Murphy (1981) and Henderson et al. (1981).

[b] Now part of NADP system.

[c] No longer operates.

[d] Superceded OECD system.

Multi-State Atmospheric Power Production Pollution Study (MAP3S)--

The main objective of the MAP3S program is to develop models to predict the fate of energy-related emissions. The program operates nine sites in the eastern United States, with sampling on an event basis. The program began in the fall of 1976.

Canadian Network for Sampling Precipitation (CANSAP)--

The CANSAP program has 56 monitoring stations throughout Canada. Samples have been taken on a monthly basis since May 1977.

University of Florida--

The University of Florida established a statewide precipitation sampling network to study sulfate deposition. Wet precipitation was collected at four sites from May 1978 to April 1979. Samples from one site were collected on an event basis; samples from the others were collected biweekly (Brezonik, Edgerton, and Hendry 1980). Bulk samples were collected at additional sites throughout the State.

Sulfate Regional Experiment (SURE)--

The main objective of the SURE program is to establish a relationship between SO_2 emissions and ambient atmospheric concentrations. SURE, sponsored by the Electric Power Research Institute (EPRI) has collected ambient air quality data continuously at nine sites in the northeastern United States since 1977. In addition, 45 more stations were operated for 30 days at six different times. From the summer of 1978, until 1980 precipitation samples were taken on an event basis; this system no longer operates (Perhac 1978; EPRI 1978).

Organization for Economic Cooperation and Development (OECD)--

The OECD monitoring program was begun in 1972 as a cooperative effort to examine long-range transport. It involved a survey of SO_2 emissions in Europe, followed by modeling of dispersion patterns to provide estimates of SO_2 and sulfate concentrations. Results were compared with observations from about 70 ground stations and from aircraft. The program included ambient air and precipitation sampling. This program was superseded in 1977 by the United Nations Environment Program (UNEP) in cooperation with the World Meteorological Organization (WMO).

Planned new precipitation monitoring systems include the following:

- U.S. EPA Region X (Alaska, Idaho, Oregon, and Washington) - Contract with University of Washington for 7 to 9 sites.
- State of Wisconsin - Seven to nine sites.
- U.S. EPA Region IV (Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee) - Two sites in each state in the region; a few sites are already operational.

In summary, the number of monitoring systems now in place, new planned sites, greater awareness of the importance of using proper samplers, and quality assurance techniques for sampling and analysis should ensure that future precipitation and ambient monitoring studies will have a sound basis from which to draw conclusions.

PRECIPITATION AND AMBIENT MONITORING DATA

Precipitation data indicate the degree of acidity at specific sites, whereas ambient air data indicate concentrations of precursor pollutants. Analysis of these data can yield information on the occurrence of acid rain and its composition. Through statistical analyses, isopleth plotting, extrapolation, and other procedures, investigators can develop information concerning the formation and transport of precursors, which will indicate their sources. Analysis over a substantial time period can also indicate trends.

Unfortunately, more quality data are needed for full understanding of the problem. Many different approaches to the study of acidic precipitation have been used in the past. Direct measurements of acidity of precipitation, studies of atmospheric sulfates, plume monitoring, trajectory analyses, etc. have been used to develop clues to help in the investigation of acid rain. The primary purpose of some of these studies was to develop a better understanding of general atmospheric phenomena whereas others specifically addressed acid rain. Although large amounts of information have been generated, many conclusions are poorly supported and controversial. Mohnen (1981) discusses the difficulty in drawing firm conclusions from this growing mass of data and points to the past use of methods now considered obsolete as part of the problem. He further suggests that the more sophisticated methods now used are demonstrating that the problem is more complicated than some of the work in the late 1970's indicated. That interpretation of past work is difficult is further illustrated by the following quote by another researcher:

> "We, along with an increasing army of researchers, have been measuring aerosols and other pollutants in plumes, on roadways, in cities, in the country, and, in fact, almost everywhere that airplanes can fly and surface vehicles can travel. As the data have accumulated, we, along with everyone else, have become increasingly concerned with what it all means, not just in a qualitative sense, but in a quantitative sense that will permit our patient sponsors to develop better air pollution control measures" (Whitby 1980).

No attempt is made here to discuss the many implications of past work when the researchers directly involved take the position that quantitative conclusion on important issues, such as the relative importance of contributing sources, cannot be drawn from past work. Instead, the efforts have been directed toward presenting background that will give the reader an understanding of the state of the art and a perspective on the character of past activities.

Precipitation Studies

The uncertainties inherent in the present data base for acid rain can be illustrated by considering the limits of our knowledge about when acid rain first began to occur in the United States and whether it is worsening or spreading. Those who believe that there was less acidity in past years rely on indirect evidence from precipitation chemistry, e.g., data from studies made in the 1930's that indicate relatively large amounts of carbonate, which would not occur in the presence of strong acids, were present in rain samples (Likens and Bormann 1974). Other indirect evidence and a few direct pH measurements have led many to conclude that acid rain became a problem in the Northeastern United States in the early 1950's. Whether it is worsening is not known. Data from the longest continuous monitoring program (begun in 1963) indicate no increase in acidity at an experiment site in New Hampshire (Likens, Bormann, and Eaton 1980). Unfortunately, comparable data are not available for other sites. This lack of data was noted in a recent study (Pack 1980) in which data from two new networks were analyzed. This study concluded that the United States for the first time in two decades "has the capability to examine the chemistry of precipitation from individual storms as they pass across the country." It further concluded, however, that the data are preliminary and tell nothing about trends.

Others suggest, however, that, based on shorter-term studies and small amounts of historical data, acidity of precipitation is increasing in certain parts of the country. Lewis and Grant (1980) reported a significant downward trend in pH at a rural site in Colorado over a 3-year period. Other investigators reported increasing acidity in northern Florida on the basis of monitoring data from the 1977 to 1979 period and data collected by others in 1955 and 1956 (Brezonik, Edgerton, and Hendry 1980). Still another researcher (McColl 1980) had monitored sites in northern California during 1978 and 1979. He reports pH values lower than those indicated by historical data from the 1950's and 1960's; however, these data sets cannot directly be compared because the historical data is scattered and incomplete.

In northeastern United States, where acidic precipitation is considered to be the most serious environmental threat, little evidence suggests any change in acidity. Only one trend appears to have emerged, i.e., the contribution of nitrates relative to that of sulfates appears to be increasing (Likens, Bormann, and Eaton 1980).

Whether acid rain is spreading is less controversial. Data presented recently (Pack 1980) suggest that the eastern U.S. area of low pH is greater in size than earlier work had indicated. Other studies of precipitation pH and chemical content have produced a variety of results; e.g., one study concludes from the high nitrate concentrations in precipitation in California that the automobile is an important source of precursor compounds in that area (McColl 1980). Another study of 16 summer showers (Dawson 1978) showed that in the arid Southwest the pH typically decreases during the course of showers, apparently as a result of preferential washout of alkaline materials. Still others (Davies 1979; Kennedy, Zellweger, and Avanzino 1979) cite data to explain differences in the rainfall pH in city and rural sites. Data from another study of the acidity of precipitation events in

Ithaca, New York, were analyzed by means of a trajectory analysis method (Miller, Galloway, and Likens 1978); one conclusion drawn from the study was that "acidic precipitation (pH <5.6) came predominantly from the southwest sector where the largest antropogenic sources of acid-forming gases exist."

Other studies have shown that sources in the immediate vicinity of the precipitation event can influence its acidity. Henderson et al. (1980) concluded that the highest amounts of hydrogen ion deposition in the Adirondack Mountains on a per-event basis were associated with summer wind trajectories from the New York and New Jersey area, rather than from the Ohio Valley. Larger amounts of ammonia in summer in wind trajectories from the Ohio Valley were thought to be neutralizing the pH of the rain.

Ambient Air Studies

Studies have been conducted to define the relative contribution of different types of combustion sources to the occurrence of sulfates and nitrates in the ambient air, particularly in the Northeast. One approach that has been used involves tracking of air masses while measuring the pH of associated precipitation and/or the concentrations of SO_2 and sulfate. Other studies have examined trends in the observed ambient concentrations of SO_2 and sulfate over the years and attempted to relate them qualitatively to fuel use patterns and the relative role of different sources of precursor compounds. Most have focused on the role of large coal-burning power plants in the Midwest versus the role of sources located within the impacted area.

In the period from 1976 to 1980 the researchers of several studies drew conclusions believed by many to implicate the emissions from large coal-burning plants in the Midwest in the occurrence of acid rain in the Northeast. One investigator (Lioy et al. 1980) observed that "periods of high sulfate ($>15\ \mu g/m^3$) in New York City were associated with air parcels that had passed over major source areas in the Midwest while the periods of low sulfate ($<5\ \mu g/m^3$) lacked significant temporal and/or spatial interaction with those areas." The study further concluded that "the results reaffirm the necessity for regional control of the chemical precursors to sulfate." Another investigation (Galvin et al. 1978) led to the conclusion that "trajectory analysis provides evidence that high sulfate concentrations in New York State are products of sulfur dioxide emissions to the south and southwest of New York State. The highest concentrations occur in air that first stagnates in the area surrounding the Ohio River Valley..." A study of historical data for ambient concentrations of SO_2 and sulfates (Altshuller 1976) was reported to show that more than 75 percent of the sulfate measured at nonurban eastern sites can be accounted for by transport of pollutants into the region. The author did go on to suggest, however, the relative contribution of all source types need further study, and he did not specifically implicate a particular source type.

Some believe these and similar studies demonstrate the need for more effective control of large coal-burning plants in the Midwest. This belief led the States of New York and Pennsylvania to file petitions with the U.S. Environmental Protection Agency to determine whether emissions from specific coal-burning plants prevented New York and Pennsylvania from meeting and maintaining air quality requirements. Testimony at the resulting hearing included a critical review of studies of the type discussed above (Mohnen 1981). One conclusion was "the evidence at present does not provide a reliable basis for quantitative conclusions about the cause of sulfate levels in the Northeast or for the establishment of source-receptor relationships. In fact, to the extent that any conclusions can be drawn from the available data, the more recent and more sophisticated analyses indicate that the magnitude of SO_2 emissions from sources in the Midwest is not an important determinant of ambient sulfate levels in the Northeast."

Examples of the studies that support Mohnen's position include analyses of data from a station on Allegheny Mountain in Pennsylvania (Pierson et al. 1980), from which it was concluded, after emissions moving in from the Ohio River Valley were tracked, that there was no constant relationship between SO_2 and sulfate levels and no definable relationship between either pollutant and upwind power plant emissions. It was shown, however, that high sulfate levels occurred when stagnated air masses moved in from the Midwest. A later report by Lioy et al. (1981) reached the same conclusion regarding the lack of correlation between SO_2 and sulfate concentrations and upwind emissions of SO_2, and further concluded "sulfate concentrations will be influenced by both local and upwind processes."

In summary, many studies of precipitation and ambient air, their composition, and its movement have been conducted to further our understanding of the acid rain phenomenon. Nevertheless, although valuable information has been and is being collected, we are still far from understanding many of the fundamentals of this problem.

PART 2

RELATIVE CONTRIBUTIONS OF MANMADE SOURCES

Quantifying the contribution of specific pollution sources to acid rain in a given region would require understanding of

(1) The type and amount of pollutant that comes from each contributing source.

(2) All factors involved in transport and transformation of pollutants.

(3) All factors influencing the mechanisms whereby pollutants do or do not become incorporated in precipitation.

Fortunately, some of these factors are being clarified by studies focused on the industrial parts of the world where the most acidic rains occur regularly. It is known that in these areas manmade sources produce the greatest quantities of SO_x and NO_x precursor compounds. Also, it is known that combustion of fuels is the most important source of these pollutants. Considerable information is available on the character of emissions from the major fuel-burning sources.

Unfortunately, there are (as discussed earlier) many gaps in the information on the transport, transformation, and fate of these pollutants. Despite the gaps in information, a number of meaningful attempts have been made to characterize the role of different kinds of fuel-burning sources in acidification of rains. Computer simulation modeling using ambient and precipitation sampling data is being used to analyze the possible role of major sources. The adequacy of the long-range transport (LRT) models that have been developed to assess the impact of the very large combustion sources in the production of acid rain is a key issue in making judgments regarding the relative importance of the various manmade sources of precursor pollutants. Also apparent is the need for an understanding of the amount of each type of fuel that is burned in ways that can contribute to acidification of precipitation where such acidification is occurring. The three sections of Part 2 discuss the state of the art of LRT modeling, an analysis of fuel-use patterns in selected industrialized areas of the world, and a series of six case studies in which an attempt has been made to accumulate whatever circumstantial evidence is available to link pollution from combustion with the occurrence of acidic precipitation.

SECTION 5

MATHEMATICAL MODELING

Computer simulation modeling is considered the most feasible means for development of proof of cause and effect relationships between specific combustion sources in the occurrence of acid rain. Further, many investigators of acid rain phenomena believe that computer modeling will provide the basis for decisions regarding the control of acid rain. The economic ramifications of these decisions may be great. In this context, the following discussion attempts to briefly review the current state of the art of modeling and the status of long-range transport modeling in analysis of acid rain.

ATMOSPHERIC TRANSPORT MODELS

As a basis for decisions pertaining to the impacts of stationary, mobile, and natural sources on the environment, policymakers are in need of tools that relate the quantity of pollutants emitted from these sources to the ambient pollutant concentrations. As indicated earlier, a broad range of spatial and temporal factors can affect the dispersion and transport of atmospheric pollutants. Because the relationships between transport and dispersion processes are complex, computer simulation models have been developed to deal with these factors, their interrelationships, and their effects on ambient pollutant concentrations. The tool initially developed was the short-range or local source mathematical dispersion model.

Short-Range Mathematical Dispersion Models

Mathematical dispersion models expressing the relationship between pollutant emissions and ground-level concentrations of the pollutant have been under development since the early 1940's. The basic dispersion modeling theory was developed for isolated emission sources located in flat or very gently rolling terrain. These early models were generally developed to express the source/receptor relationship of non-reacting gases over distances of a few kilometers. As modeling theory has progressed over the years, the fundamental theory has undergone various adaptations to provide for modeling multiple sources, as well as sources located in complex terrain. The distance of applicability has been extended to 10 to 20 kilometers.

Most dispersion models used to study source/receptor relationships over distances up to 20 kilometers assume steady-state conditions. Such models generally do not provide for chemical and physical transformations and assume nonreactive pollutants. The model assumes that the pollutants are dispersed from a point or area source and that pollutants are distributed along the center-line of the plume in all directions. The amount of dispersion is dependent on the distance from the source and the atmospheric stability. Under ideal conditions, the accuracy of short-range dispersion models is generally within a factor of 2 of measured values.

Long-Range Transport Models

Long-range transport (LRT) models are based upon far more complex assumptions than that for local source models. The assumption of steady-state conditions is no longer applicable. An LRT model must account for the dynamic nature of the atmosphere and must be capable of accepting new meteorological data as the plume from a source is transported over hundreds and even thousands of kilometers. At the same time, an LRT model must be capable of simulating the chemical and physical changes in pollutants that occur in the atmosphere over a given time period (e.g., days) of residence time. To this end, the model must consider not only the rates of chemical transformation, but also the rates at which pollutants are returned to the earth's surface by wet and dry deposition.

The quantity of input data and complexity of computations associated with the application of an LRT model to a single source tax the ability of even very large computers. When the modeling is expanded to include the impacts of hundreds of sources, the magnitude of computations increases dramatically. In order to simplify computations, atmospheric scientists have made many assumptions to limit the variability in the input parameters. The assumptions simplify the handling of pollutant dispersion, contributions to and subtractions from the dispersed plume, wind direction, reaction rates, and many other items. The overall effect of these assumptions is largely unknown. Resource limitations have precluded considering all factors and collecting refined spatial and temporal inputs of meteorological parameters. Thus, rather than using the most rigorous of models, i.e., numerical integration grid models, many investigators consider simpler approaches to long-range transport, including modified Gaussian techniques, trajectory methods, statistical approximations, puff or particle models, or empirical assumptions.

It is worth noting that LRT regional modeling is not, as might be supposed, an extension of short-range modeling to progressively greater distances. In fact, there is a definite lack of dispersion models to deal with mid-range applications (Henderson et al. 1981). Because regulatory use of short-range models stops at 50 km, it is fairly safe to assume that a short-range model can be used to this distance, although the results would certainly be questionable for distances greater than 20 km. Long-range models include no provisions for deposition at any distances but those extremely remote from the emission point. It is obvious, however, that the fate of air pollutants is determined not only at nearby and distant points, but also at intermediate distances of 50 to 100 km. Better understanding of intermediate-range phenomena would certainly enhance the capability for dealing with long-range problems.

COMPARISON OF TYPICAL LRT MODELS

The "Ideal" LRT Model

Development of LRT models is still in the developmental stages. A number of the current LRT models do not include inputs for such important variables as primary sulfate and catalyst emissions, and do not have the flexibility to vary the rates of conversion/deposition for SO_2 and NO_x depending on the geographic area. The incorporation of characteristics discussed in the preceding section would yield an "ideal" LRT model; anything short of this reduces the ability of the model to determine relative contributions of local and remote sources and seriously impairs its accuracy as a reliable basis for developing control strategies.

Following are some additional factors that should be included in an "ideal" LRT model.

- Input of SO_2, $SO_4^=$, and NO_x emissions from mobile and stationary sources
- Input of all source parameters governing effluent release, including temporal variations
- Consideration of variable plume heights
- Description of appropriate wind fields at several levels, with an adequate data base to assume representative local and distant phenomena
- Consideration of turbulence and diffusion at spatial and temporal scales of the plumes
- Consideration of the transformation of SO_2 and NO_x and other related pollutants including higher-order processes and exchange mechanisms, e.g., concentration, temperature, sunlight, humidity, and the presence of other chemical species over variable spatial and temporal scales
- Inclusion of dry deposition processes and related factors, e.g., surface type; particle size, shape, and density; and agglomeration processes
- Consideration of wet deposition processes including event-specific processes for short-term modeling and areawide variations and averages for long-term estimates. Inclusion of in-cloud and extra-cloud physical mechanisms
- Estimation of pH on a local basis that considers differences in location, altitude, rainfall, etc.

The trajectory of all pollutants may be plotted by use of dispersion formulas, but calculations for wet and dry deposition and chemical changes should be done separately. The trajectory of pollutants should account for both vertical and horizontal movements. Both upper-air and ground-level measurements should be used. The wind data should be gathered from a large number of sites distributed uniformly over the geographic area of interest.

If models are to be calibrated with actual pH measurements, the model must ultimately convert the values for deposited pollutants into a value of pH in the rainwater. This conversion requires knowledge of local factors at the measurement site. For example, if the rainfall is heavier or more frequent on one side of a mountain than the other and the ambient concentration of pollutants is the same, the measured pH values will be different. Localized air movements caused by large terrain features may also affect dry deposition of pollutants. The ideal model would account for these localized effects at the monitoring sites and would be capable of predicting the pH of rain as it is collected at a meteorological station. These localized effects can be minimized by a judicious choice of receptors. Proper location of receptor sites has been a problem in recent acid rain monitoring studies and has limited the usefulness of the resulting data. Finally, to properly predict pH values, the ideal model must also account for all major pollutants, whether acidic or basic.

Although none of the LRT models meet the requirements of the ideal model, current models do attempt to include a manageable and understandable number of important processes within the constraints of current data bases. Following is an overview of several current LRT models; three are considered in detail.

Summary of Differences in Current Regional Transport Models

Several nationally funded programs, as well as proprietary research activities, are underway to develop and refine models to assess acid deposition. One prominent program among these studies is the Multistate Power Production Pollution Study/Regional Acidity of Industrial Emissions (MAP3S/RAINE) (MacCracken 1979), cofunded by the Department of Energy (DOE) and the Environmental Protection Agency (EPA).

Currently, the models available for study of long-range transport emphasize the fate of sulfur oxide pollutants in acid deposition. NO_x, chlorides, and other possible contributing pollutants are neglected. Some of these regional models are listed in Table 5-1. Several of these models, including the Argonne Advanced Statistical Trajectory Regional Air Pollution model (ASTRAP), the Source-Transport-Receptor Analysis Model (STRAM), the National Oceanic and Atmospheric Administration-Air Resources Laboratory (NOAA-ARL) model, and the Pacific Northwest Laboratories' (PNL) model, are being considered by the MAP3S/RAINE program.

The primary differences in regional models are the methods used to estimate transport, dispersion, transformation, and deposition. ASTRAP, for example, separates long-term horizontal and vertical effects and allows diurnal and seasonal variations of deposition velocities, transformation rates, emission rates, and stability profiles. STRAM is a variable-trajectory, reactive plume-segment model. It generates gridded wind data

TABLE 5-1. CHARACTERISTICS OF SOME TYPICAL LONG-RANGE TRANSPORT MODELS

Model	Type[a]	Chemistry[b]	Dry deposition	Wet deposition
ASTRAP	Statistical trajectory	Linear	Linear	Linear
BNL	Trajectory (K-theory in vertical)	Linear or pseudo-linear	Linear	Linear
CSU	Trajectory	Linear	Linear	Linear
SRI-ENAMAP	Trajectory	Linear	Linear	Linear
PNL	Trajectory	Linear	Linear	Linear or pseudolinear
OECD	Trajectory	Linear	Linear	Linear
STRAM	Trajectory	Nonlinear and modular	Linear or pseudo-linear	Linear
SAI	Grid	Linear and nonlinear	Linear	Linear
SURE	Grid	Linear and nonlinear	Linear	Linear
MESOPUFF	Trajectory	Linear	Linear	Linear
MESOGRID	Grid	Linear	Linear	Linear
NOAA-ARL	Trajectory	Linear	Linear	Linear
CAPITA	Statistical trajectory	Linear	Linear	Linear

[a] Statistical trajectory = trajectory randomized around averaged wind data.
Trajectory = wind defines pollutant path.
Grid = pollutant path defined by preselected boxes.

[b] Linear = function of time only.
Nonlinear = function of time as well as other independent variables such as temperature or pressure.

from typical National Weather Service (NWS) stations and isolates each transformation and deposition calculation to allow modifications as needed. The NOAA-ARL Model calculates individual puff trajectories using transport winds averaged every 6 hours in a vertical layer (Heffter 1980). A meteorological data base is included with the program. Diffusion and deposition calculations are included in each 6-hour trajectory. Finally, the PNL Model simulates plume transport by trajectories on a grid and includes derived gridded wind and precipitation fields as well as variations in stability, mixing heights, emissions, transformations, and depositions.

The balance of this discussion focuses on three LRT models that include important physical and chemical processes and that have been utilized in most long-range transport evaluations. These are (1) the SRI-ENAMAP model (Bhumralker et al. 1979), (2) the Argonne ASTRAP model (Shannon 1979), and (3) the CAPITA Monte Carlo model (Husar, Patterson, and Husar 1980). Each of these models was designed to emphasize the importance of different aspects of long-range transport. The model parameters are summarized in Table 5-2.

Both the ASTRAP and Monte Carlo models treat vertical and horizontal transport. The ASTRAP model assumes release of emissions in one of eleven vertical layers. The ENAMAP model assumes universal vertical mixing.

Meteorological data input to the models also varies. The ENAMAP model uses both surface and upper air data as well as hourly precipitation data. Neither the ASTRAP nor Monte Carlo models uses precipitation data. The ASTRAP model uses mean wind speed below 1800 meters in the summer and below 1000 meters in the winter. Data are collected from balloon measurements. The Monte Carlo model uses modified midday surface wind data.

Dry deposition of SO_2 is estimated to be approximately the same in the ENAMAP and Monte Carlo models, whereas the ASTRAP model estimates lower deposition rates and varies the rates as a function of season and time of day. Dry deposition of sulfate is estimated at 0.3 percent per hour by the Monte Carlo model, and at more than twice this rate by the ENAMAP model. The ASTRAP model also varies the deposition rate between 0.3 and 2.2 percent per hour, depending on the time of day and season.

The ENAMAP and ASTRAP models estimate wet deposition of SO_2 and $SO_4^=$ as a function of rainfall; the Monte Carlo model estimates wet deposition of SO_2 at 0.175 percent per hour and $SO_4^=$ at 1.2 percent per hour. The ENAMAP model predicts wet deposition of SO_2 to be 4 times that of $SO_4^=$, whereas the Monte Carlo model estimates it at about 1/7 of the $SO_4^=$ rate. The ASTRAP model assumes equal deposition.

Estimates of the conversion from SO_2 to $SO_4^=$ are approximately the same in all three models; however, the ASTRAP model varies the rates by time of day and season. All models consider SO_2 emissions; the ENAMAP model also considers $SO_4^=$ emissions, and the Monte Carlo Model can accept NO_x emissions.

TABLE 5-2. COMPARISON OF LRT MODELS[a]

	ENAMAP	ASTRAP	Monte Carlo
Pollutant dispersion	Treats both vertical and horizontal dispersion	Treats both vertical and horizontal dispersion	Assumes universal vertical mixing
Meteorological data	Surface, upper air and precipitation data	Mean wind speed below 1,800 m summer 1,000 m winter, no	Modified mid-day surface wind data, no precipitation data
Dry deposition SO_2	3.7%/h	Function of time of day and season, varies from 0.1 to 0.8 cm/s (≅0.3 to 2.2%/h)	3.325%/h
Dry deposition $SO_4^=$	0.7%/h	Function of time of day and season, approximately the same as for SO_2	0.3%/h
Wet deposition SO_2	(28)(precipitation rate, mm/h)	Function of the square root of precipitation amount	0.175%/h
Wet deposition $SO_4^=$	(7)(precipitation rate, mm/h)	Function of the square root of the precipitation amount	1.2%/h
Conversion $SO_2 \rightarrow SO_4$	1%/h	Function of time of day and season varies from 0.1%/h to 3.0%/h	1.3%/h
NO_x contribution	Not considered	Not considered	Treated similar to SO_x but with different transportation rates
Sources considered	Emissions from NEDS and SURE are input into 80x80 km grids	Emissions can include point and area sources, released at appropriate height; emissions are varied by time of day and season	Emissions are combined into equal quanta and released as puffs
Pollutant emissions considered	Includes SO_2 and SO_4	Only SO_2	Includes SO_2 and NO_x
Conversion $SO_4^= \rightarrow$ pH	Does not predict pH	Does not predict pH	Is adaptable to predict H^+ but not pH
Terrain	Terrain not considered	Terrain not considered	Terrain not considered

[a] Based on data from Husar, Patterson, and Husar (1980); Bhumralker et al. (1979); and Shannon (1979).

The ENAMAP model places all emissions in 80 km x 80 km grids, the ASTRAP model treats both area and point sources, and the Monte Carlo model combines emissions into equal quantities released as puffs. None of the models directly predicts pH values, but the Monte Carlo model may be adapted to predict hydrogen ion concentrations. None of the models considers terrain effects. The characteristics and major assumptions incorporated into each of these three models are presented in more detail in Appendix F.

THE ACCURACY OF LRT MODELS

The accuracy of any LRT model for this application is dependent upon two factors: (1) the degree to which the model can simulate the chemistry and physics of the atmosphere and (2) the accuracy of the input data for pollutant emissions and meteorological factors. Unfortunately there is no reliable method for testing the accuracy of models. As a result, they are generally evaluated by use of historical data on emissions, meteorology, and air quality to obtain what has been termed "inferred accuracy". This approach is of questionable value in that models can give the right answer for the wrong reason. Also, they can be "tuned" to give the desired results, especially where there is little hard data as input for important parameters, as is the situation with LRT models. Given this state of affairs, estimates of LRT model accuracy often must be based on subjective assessment of the quality of available data.

No attempt is made here to duplicate the recent comprehensive reviews of modeling or to second-guess the judgments of experts who have considered the capabilities of presently available LRT models. It is worth noting, however, that most of such in-depth reviews discuss the available models without taking a clear position on their accuracy or usefulness. One reviewing group suggested that present models were considered adequate for use in planning a strategy for reduction of acidity of rain in the northeastern United States (U.S. Department of Commerce 1981). Others who have recently reviewed the state of the art have taken a contrary position. Some have directly challenged this proposition. Mohnen (1981) has stated that "such models might be useful for the purpose of research and regional planning. For regulatory purposes, however, no LRT model currently available is sufficiently reliable, because none can establish with the requisite degree of confidence a source-receptor relationship between SO_2 emissions in one area and sulfate concentrations or deposition in a distant location" (Mohnen 1981). All reviewers agree that there is great need for better data as input for LRT models in acid rain assessment.*

Thus, while LRT models apparently are believed to be useful research tools, whether their accuracy is adequate for their use as a basis for decision-making is highly controversial. Some of the limitations were mentioned earlier and are further delineated in the following pages. Obtaining reliable results from LRT modeling depends on (1) enough understanding of atmospheric chemistry and physics to allow good mathematical

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* (Sigma Research, Inc. 1979; Hosker 1980; Turner 1979; Henderson et al. 1981; U.S. Department of Commerce 1981).

simulations, (2) availability of good meteorological data to describe transport mechanisms, and (3) a good definition of pollutant emissions that contribute to acid rain. Some comment on the status of the data base follows.

Atmospheric Chemistry and Physics

Models for acid rain must estimate a number of physical and chemical transformations that occur between the emission of reactive pollutants and the measurement of precipitation acidity. The only dispersion models that have attempted to model reactive pollutants are those for ozone. Some of the major transformations that affect the reliability of an LRT model for acid rain are:

- Conversion rate of SO_2 to $SO_4^=$
- Conversion rate of NO and NO_2 to NO_3^-
- Dry deposition rate of SO_2, $SO_4^=$, and NO_3^-
- Estimation of buffer compounds in the ambient air.
- Estimates of catalytic material in ambient air that would increase normal transformation rates.

Conversion rates for the oxidation of SO_2, NO, and NO_2 have been shown to be dependent on concentration, temperature, sunlight, and the presence of various catalysts. Dry deposition of the precursors is dependent on surface type (vegetation, water, soil), rate of transport to the surface, presence of moisture, and terrain. Wet deposition of the precursors is dependent on volume of rainfall, size of the droplets, pollutant concentrations, and presence of catalysts. Most models now vary the deposition on the basis of precipitation rate but not the other variables. It should be noted that estimates of dry deposition may be very misleading because there is no accepted measurement method.

Another commonly cited limitation of LRT models is that they deal only with sulfur compounds and do not address nitrogen compounds or chlorides.

The Emissions Inventory

The major pollutants thus far indentified as contributing to acid rain include SO_2, $SO_4^=$, NO, NO_2, NO_3^-, and Cl^-. Therefore, the starting point for acid rain modeling should be accurate emission inventories for these pollutants. Acid rain modeling to date has often been based on outdated NEDS SO_2 inventory data (1973 for example), which include no emission estimates for $SO_4^=$, NO, NO_2, NO_3^-, or Cl^-. Sometimes the SO_2 emissions of only the largest electric utilities are considered. These emission estimates generally are not verified or updated. Furthermore, some of the earlier inventories were taken before any SO_2 control measures were implemented under State Implementation Plans, at a time when the NEDS had only recently begun. Such an inventory can give only poor predictions for 1981. Moreover, the use of a single class of emitters, such as the largest electric utilities, with subsequent model adjustment for a good fit, will almost invariably identify these sources as the principal cause of the problem.

Very few of the LRT models consider emission height (stack, plume) except as specified by uniform release heights. The release height of the pollutant affects its impact hundreds of kilometers downwind and thus should be carefully considered.

The emission inventory requirements contained in Section 127(b)(4) of the Clean Air Act for nonattainment plans state that emission inventories must be "comprehensive, accurate, current inventory of acutal emissions from all sources...". If acid rain modeling is to be used to establish requirements for control of major contributing sources, then the emission inventory used in the model should satisfy these criteria also.

In addition to limits imposed by the incomplete and undefined accuracy of the annual emission estimates, the data bases available for LRT models do not account for daily and seasonal variations in emissions.

Meteorology

Current LRT models use various methods of representing the transport of pollutants over long distances. The most detailed approach involves numerical solution of theoretical equations governing atmospheric processes over time and space. Even with advanced computers, however, the practical application of such models is constrained by limitations on resources and time.

Alternative techniques are suggested to simplify the numerical simulation. One simplification suggests that over long averaging periods (a month or greater) the wind field may be approximated as uniform. Another simplification in some current models involves ignoring the variations in transport at different levels in the lower atmosphere, i.e., pollutants are assumed to be transported in mixed layers of constant height.

Some concern has been expressed that the effects of terrain are not adequately addressed in LRT modeling. Potential effects generally not considered are the variation of atmospheric stability over such features as mountains and bodies of water, the channeling of wind flow, and increased frequency of rain due to orographic lifting.

Improvements in characterization of the transport of pollutants will require detailed knowledge of wind fields over large regions throughout the vertical layers of interest for time scales commensurate with the atmospheric processes. Refining the data base to appropriate space and time scales to determine atmospheric influences will require similar precision with regard to emission and removal effects. Most models use the currently available meteorological observations, which yield unreliable data on transport winds. Sufficiently detailed observations, however, are highly resource-intensive and are beyond the scope of most funding programs except over very limited spatial and temporal scales.

Considerable work is now underway to collect the data needed to remove many of the limitations. Most workers believe that LRT model capability will greatly improve in the years ahead. It would appear, however, that use of the present LRT models in decision-making should be approached with great care until better data are available.

SECTION 6

FUEL TREND ANALYSIS

Because the occurrence of acid rain is closely linked with pollutants from fuel combustion, the analysis of fuel-use data appears to be a logical approach to assessing the possible causes. The premise is that focusing on all major fuel uses and precursor emissions that could contribute to acid rain in a given location might show a potentially significant relationship between fuel use and the occurrence of acid rain. The location and emissions from the very large plants, which have been given the most attention, are generally well documented; hence, the emphasis here is placed on development of data for combustion sources within or near areas where acid rain is occurring. Further, prior to the undertaking of this project experience had indicated high concentrations of oil burning in the Northeastern United States where acid rain is considered to be most pervasive. Consequently, emphasis is also placed on full documentation of the burning of oil products.

Given the state of the art for modeling the limited combustion source emission data expected to be available, no attempt is made to demonstrate a cause and effect relationship between acid rain and a given type of combustion. Instead, effort was focused on examination of patterns of fuel consumption and historical fuel consumption trends for all types of fuel in selected areas of the world, to determine whether some association exists between fuel use changes and concurrent changes in acidity of precipitation in heavily industrialized areas of the world.

GENERAL PATTERNS OF FUEL-USE TRENDS

Fuel burning trends in the United States are in many ways similar to those of other industrialized areas and thus may broadly typify the worldwide trends in such areas. Past and prevailing trends are shown in Figure 6-1, which gives historical data on U.S. fuel consumption from 1850, when we were mostly using wood to satisfy our energy needs. Between 1880 and 1890, coal became our most important fuel, and by 1910 U.S. coal production reached a level typical of that prevailing over the past 70 years. By that time small amounts of oil and natural gas were being used, and the use of wood as a major fuel was beginning a decline to insignificance. Coal remained the dominant fuel through the years of World War II, but consumption of oil and natural gas was growing at a rapid rate. By 1950, consumption of oil was about equal to that of coal. Since 1950 U.S. coal consumption has been variable, declining somewhat when oil and natural gas were cheap and plentiful and increasing somewhat in recent years with

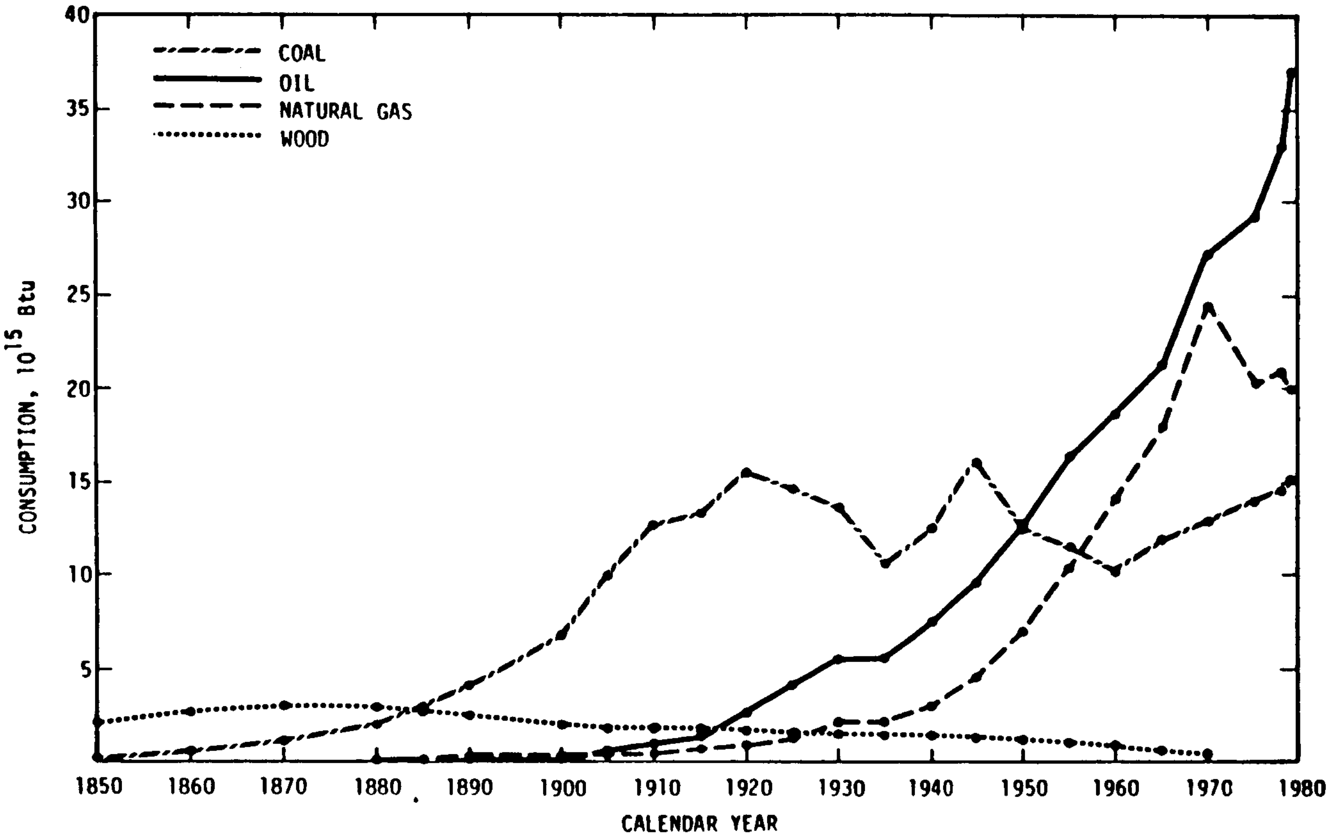


Figure 6-1. U.S. historical energy consumption by fuel type (U.S. DOE 1979; U.S. Department of Commerce 1975).

efforts to reduce dependence on foreign oil. Despite the efforts to reduce its use, petroleum consumption in the United States and other parts of the world has continued to grow. In 1979, U.S. consumption of petroleum products was 37.0 x 10^{15} Btu, while coal consumption was only 15.1 x 10^{15} Btu (U.S. DOE 1979), an amount about equal to previous highs in the mid-1920's and mid-1940's.

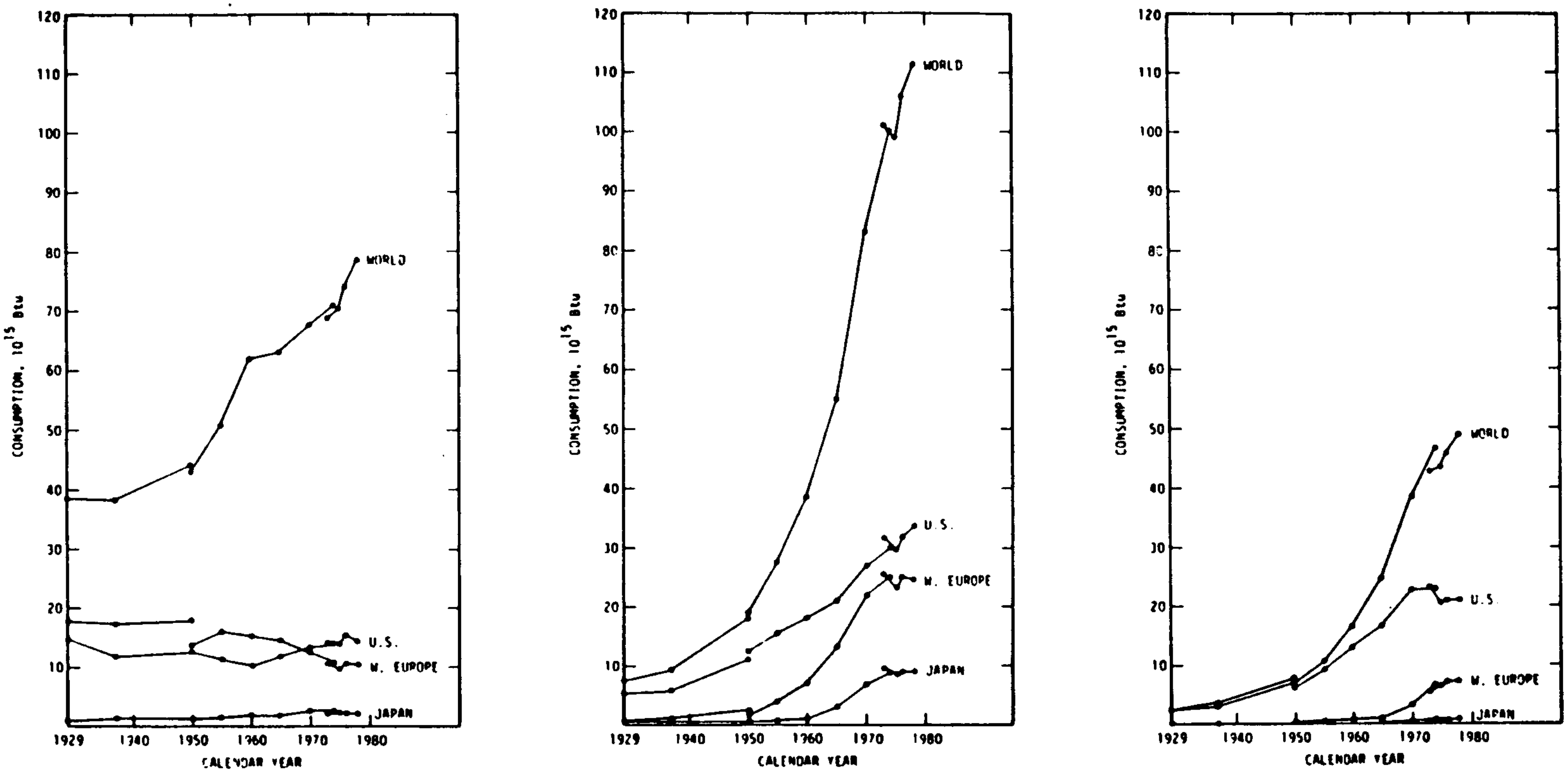
The usage patterns in Western Europe and Japan have been similar to those of the United States. Figure 6-2 shows the usage of solid, liquid, and gaseous fuels (primarily coal, petroleum products, and natural gas) in all three areas during the period 1929 to 1978. These data show pronounced shifts from solid fuels to liquid and gaseous fuels.

It is of interest to note that while the use of coal and other solid fuels in these highly industrialized areas has been steady or declining over the past 50 years, consumption worldwide has almost doubled. Increases in the past 30 years are especially large. Between 1950 and 1975, worldwide coal consumption increased from 1500 to 2500 x 10^6 metric tons per year. Most of the increase has occurred in the Communist countries. For example, the USSR and Communist countries in Europe increased their use of coal by 400 x 10^6 metric tons per year during the period. The USSR alone increased usage by 300 x 10^6 metric tons per year. The greatest increase in usage by any country was in China, where the annual coal consumption rate rose from 40 to 450 x 10^6 metric tons (United Nations 1976, 1979).

Figure 6-3 presents a further breakdown of types of liquid fuels used in the United States, Western Europe, and Japan in the years 1929 to 1978. The data show that much of the growth in the use of petroleum-derived fuels in the last 50 years is attributable to the increased use of fuel oils and is closely tied to industrial expansion. Japan currently uses about half as much fuel oil as the United States. This level of fuel oil use in Japan is especially striking when it is considered that Japan has less than 5 percent of the land area of the contiguous 48 United States.

Collectively the data on fuel consumption indicate that in the heavily industralized areas of the world, rebuilding and expansion after World War II were fueled mostly with liquid petroleum products and natural gas. The major increases in liquid fuel usage were in (1) gasoline motor fuels; (2) residual fuels burned in commercial, industrial, and utility boilers; (3) distillate fuels for residential and commercial space heat; and (4) diesel motor fuels. These uses account, in varying proportions, for 90 percent or more of all the liquid fuel consumption in the three industrial areas investigated. It is important to this analysis that significant amounts of acid rain precursor emissions are associated with all of these fuels.

Coincidentally, with the rapid post-war growth in the use of petroleum-derived fuels, acid rain was perceived as being a problem. It was noticed first in Scandinavia and later in other parts of Western Europe, the northeastern United States, and Japan. Although acid rain is now being reported in other parts of the world, the occurrences have been best

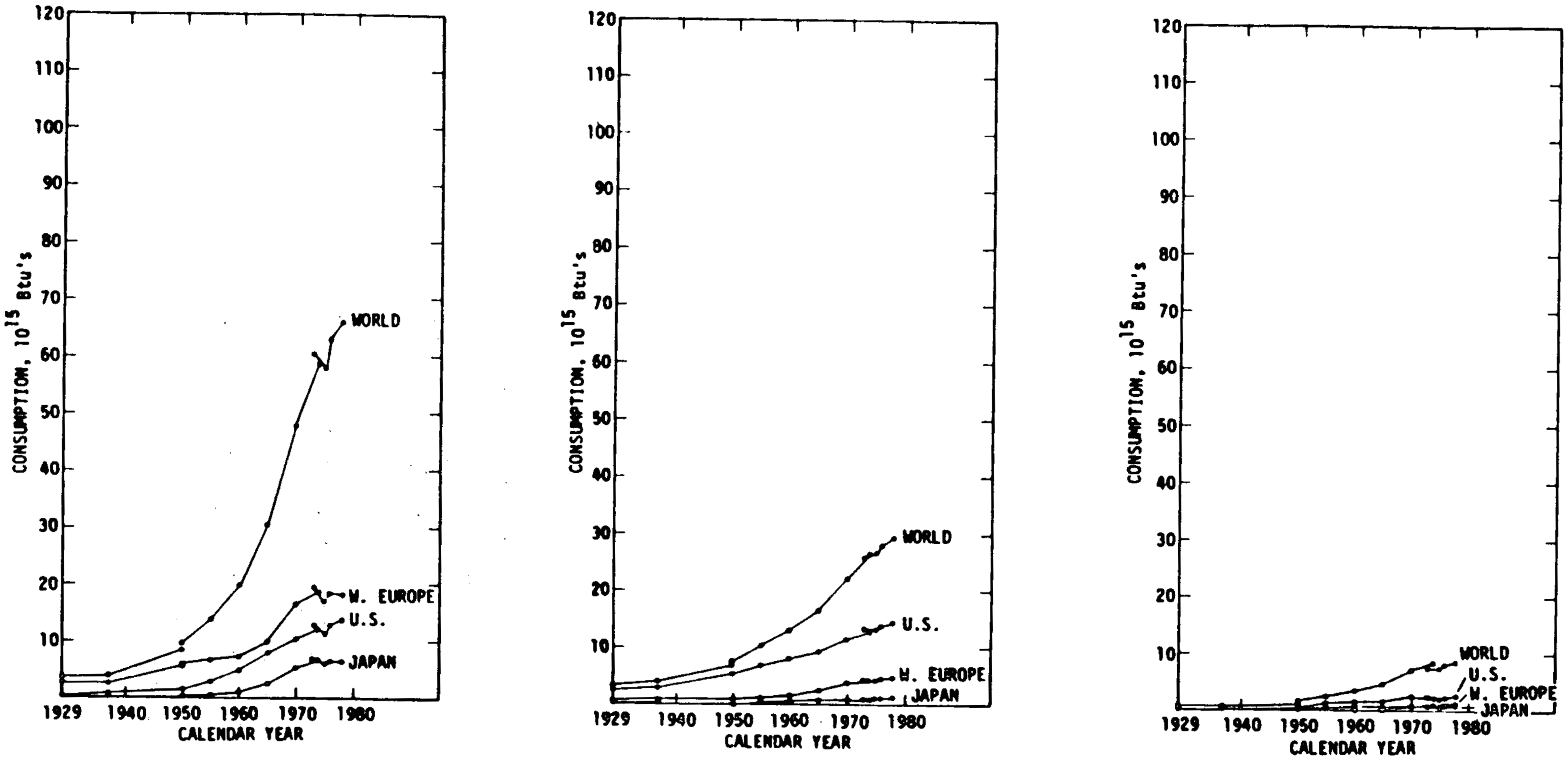


A. Solid fuels
(primarily coal)

B. Liquid fuels
(fuel oil, gasoline,
kerosene and jet fuels)

C. Natural gas

Figure 6-2. Apparent consumption of solid, liquid, and gaseous fuels in the United States, Western Europe, and Japan (United Nations 1952, 1976, 1979).



A. Fuel oils

B. Gasoline

C. Kerosene and jet fuels

Figure 6-3. Apparent consumption of fuel oils, gasoline, kerosene, and jet fuels in the United States, Western Europe, and Japan (United Nations 1952, 1976, 1979).

documented in these industrial regions. The next step, therefore, is a more detailed analysis of fuel usage and acid rain precursor emissions in these areas.

PATTERNS OF FUEL USE AND PRECURSOR EMISSIONS IN INDUSTRIALIZED AREAS

An analysis of fuel use and emission factors shows that a large portion of the total U.S. emissions of acid rain precursors comes from sources burning petroleum fuels. Table 6-1 presents data on usage of each major fuel type in the United States for all major end uses, together with emission factors for SO_x and NO_x generated in those applications. These data show that although emission factors for coal-burning are the largest, other applications, especially those involving residual oil, are potentially important where large amounts of fuel are burned in relatively small areas. Residual oil produces 4 to 5 times as much total SO_2 and NO_x as distillate oil and 2 to 3 times as much as gasoline.

Application of the emission factors in Table 6-1 to the fuel consumption data yields estimates of SO_x and NO_x emissions from the important source categories. These data are shown in Table 6-2.

Although these emission data again show the relative importance of coal on a national basis, they also show that oil burning contributes significantly, generating about one-third of the total national manmade emissions of SO_x and NO_x. This substantial fraction emanates from a large number of sources concentrated in a few areas.

The concentration of precursor emissions in localized areas may figure importantly in the occurrence of acid rain in those areas. Power plant oil, for example, is burned in small areas of the United States where the use of other types of fossil fuels such as gasoline and natural gas is also high and can contribute to acidity of rain through precursor emissions. Further, the mobile sources burning fuel oil, gasoline, and diesel fuel discharge precursors at relatively low levels, where they are likely to impact nearby. Finally, boilers using fuel oil discharge acid rain precursors along with primary acid sulfates and fine particulate matter believed to be capable of catalytic action. Such materials may contribute strongly to the formation of additional acidic materials from SO_2 and NO_x precursors in the plume or exhaust and in the ambient air.

Unlike the overall fuel-use patterns, the breakdown of liquid fuel consumption in other selected industrial areas worldwide is variable. Historical data on U.S. petroleum consumption are presented in Table 6-3, which shows the distribution by type (46 percent gasoline, 32 percent distillate oil, 22 percent residual oil in 1979); the data also show the increases in all types of petroleum product consumption that have occurred in the past 30 years. These usage patterns are not typical of those for Western Europe, where all fuel oil consumption exceeds gasoline consumption by a factor of 4 to 1, or for Japan, where fuel oil consumption exceeds that of gasoline by a factor of 7 to 1. (These data and the growth in liquid-fuel use in the three areas are shown in Figure 6-3). Most of the fuel oil

TABLE 6-1. RANKED CONSUMPTION OF FOSSIL FUELS IN THE UNITED STATES IN 1978 AND EMISSION FACTORS BY SECTOR[a]

	Fuel consumption, 10^{15} Btu	Emission factors, lb/10^6 Btu		
		SO_x	NO_x	$SO_x + NO_x$
1. Gasoline in motor vehicles	13.2	0.04	0.72	0.72
2. Coal in utility boilers	10.2	3.22[b]	0.85	4.07[b]
3. Natural gas in industrial furnaces	8.5		0.17	0.17
4. Natural gas in residential/commercial furnaces	7.6		0.10	0.10
5. Coal in nonutility boilers	7.2	2.92[c]	0.58	3.50[c]
6. Natural gas in utility furnaces	3.3		0.70	0.70
7. Distillate oil in commercial and residential furnaces and boilers for space heating	3.2	0.26[d]	0.14	0.40[d]
8. Residual oil in electric utility boilers	3.1	1.12[e]	0.52	1.64[e]
9. Diesel fuel in motor vehicles	2.5	0.23	2.38[f]	2.61
10. Residual oil in industrial boilers	1.5	1.60[g]	0.40	2.00[g]
11. Distillate oil in industrial boilers	1.2	0.26[d]	0.16	0.42[d]
12. Residual oil in commercial boilers	1.0	1.60[g]	0.40	2.00[g]
13. Distillate oil in utility boilers	0.4	0.29[h]	0.74	1.03[h]

[a] (U.S. DOE 1980b;U.S. EPA 1981).
[b] 1.81% S value determined for utility coal. See Appendix E.
[c] 2% S value assumed for industrial/commercial coal (Devitt, Spaite, and Gibbs 1979).
[d] 0.25% S value assumed for industrial/commercial distillate fuel. See Appendix E.
[e] 1.06% S average value assumed for utility residual fuel. See Appendix E.
[f] Based on diesel NO_x emission factor of 28.9 g/min. See Appendix E.
[g] 1.51% S value assumed for industrial/commercial residual oil (Devitt, Spaite, and Gibbs 1979).
[h] 0.28% S average value assumed for utility distillate fuel. See Appendix E.

TABLE 6-2. MAJOR U.S. SOURCES OF ACID RAIN PRECURSORS AND 1978 EMISSIONS (10^6 tons)

Source	Estimated uncontrolled emissions SO_x and NO_x	
Coal combustion		
Utility boilers	24.9	
Nonutility	6.2	
Total coal		31.1
Petroleum combustion		
Gasoline	5.0	
Diesel fuel	3.3	
Residual oil		
Utility	2.7	
Commercial/industrial	2.5	
Transportation (ships)	1.0	
Distillate oil		
Residential/commercial	0.6	
Industrial	0.3	
Total petroleum		15.4
Natural gas combustion		
Utility	1.1	
Industrial	0.7	
Residential/commercial	0.4	
Total natural gas		2.2
Total, all major sources		48.7

TABLE 6-3. U.S. CONSUMPTION[a] OF REFINED PETROLEUM PRODUCTS[b] (10^{15} Btu)

Year	Distillate fuels	Residual fuel oil	Motor gasoline
1949	2.49	3.12	4.77
1950	2.96	3.49	5.19
1951	3.32	3.56	5.70
1952	3.54	3.49	5.90
1953	3.67	3.53	6.24
1954	3.98	3.28	6.38
1955	4.34	3.51	6.92
1956	4.62	3.53	7.09
1957	4.60	3.44	7.23
1958	4.96	3.33	7.43
1959	5.04	3.53	7.70
1960	5.27	3.51	7.81
1961	5.44	3.44	7.95
1962	5.81	3.44	8.21
1963	5.96	3.40	8.46
1964	6.00	3.49	8.44
1965	6.30	3.69	8.80
1966	6.57	3.95	9.22
1967	6.97	4.11	9.51
1968	7.57	4.20	10.09
1969	7.80	4.54	10.60
1970	7.89	5.05	11.08
1971	8.21	5.28	11.52
1972	8.78	5.81	12.23
1973	9.16	6.47	12.79
1974	8.64	6.06	12.54
1975	8.40	5.65	12.79
1976	9.00	6.43	13.38
1977	9.59	7.04	13.77
1978	9.80	6.93	14.21
1979	9.55	6.40	13.48

[a] Computed from a daily to an annual basis at consumption rate of 365 days/yr. Converted from 10^6 barrels to 10^{15} Btu by the following factors:

Jet fuel (1952-1964) - 5.335
(1965-1979) - 5.513
Kerosene - 5.670
Distillate oil - 5.825 x 10^6 Btu/bbl
Residual oil - 6.287
Motor gasoline (1949-1951) - 5.226
(1952-1963) - 5.183
(1964-1979) - 5.253

[b] U.S. DOE (1979).

consumption in Japan is residual oil. Data on consumption of residual oil versus distillate oil in Western Europe are not presently available, but residual oil is believed to be the most important. Therefore, since residual oil is the heaviest producer of SO_x and NO_x, the overall production of these precursors per unit of liquid fuel consumption is likely to be even higher in Japan and Western Europe than it is in the United States. The final portion of this analysis further evaluates the potential relationships of fuel use and acid rain occurrence in all three areas.

ANALYSIS BY LOCALE

The analysis thus far has considered broad patterns of fuel use in three major industrial areas and the precursor emissions associated with these usage patterns. The following subsections deal in more detail with each of these areas. Additional analysis by locale, incorporating numerous other factors as well as fuel use patterns, is presented in Appendixes A through C. In addition, an analysis of acid rain occurrence in the Hawaiian Islands and Japan is presented in Appendix D.

Fuel Use and Acid Rain in the United States

In the United States, coal-burning power plants are often linked with the occurrence of acid rain. They produce over 60 percent of the SO_x emissions and are the second largest source of NO_x emissions. The tons of coal burned by utilities has increased by about 2-1/2 times in the past 20 years. Further, as shown in Figure 6-4, many large plants are located in the Ohio River Valley, where prevailing winds would tend to carry pollutants discharged from tall stacks into the Northeast, where acid rain is most prevalent.

There is evidence, however, to suggest that coal-burning utilities may not play the dominant role that has been assumed by many. For example, sulfate levels in the Northeast have risen only 5 to 10 percent over the past 20 years, even with increased amounts of coal burning in the Midwest (Altshuller 1980).

The point has been made that acid rain is occurring in the three States that are highest, by a considerable margin, in consumption of residual oil: California, Florida, and New York (Spaite et al. 1980). The concentrations of large residual oil burning by utilities in these three areas (about one-half of the total U.S. residual consumption) are illustrated in Figure 6-5. Although the acidity of rain in New York and surrounding states may be partly associated with remote coal burning, conditions in California and Florida are such that any significant impact from coal burning seems unlikely.

Northeastern United States--

Further analyses of fuel consumption patterns in the northeastern United States provides additional evidence implicating petroleum consumption in the acidification of rain. Data on consumption by end-use sectors (Tables 6-4 to 6-6) show that the eight northeastern states* that

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* New York, New Jersey, New Hampshire, Pennsylvania, Massachusetts, Connecticut, Rhode Island, and Vermont.

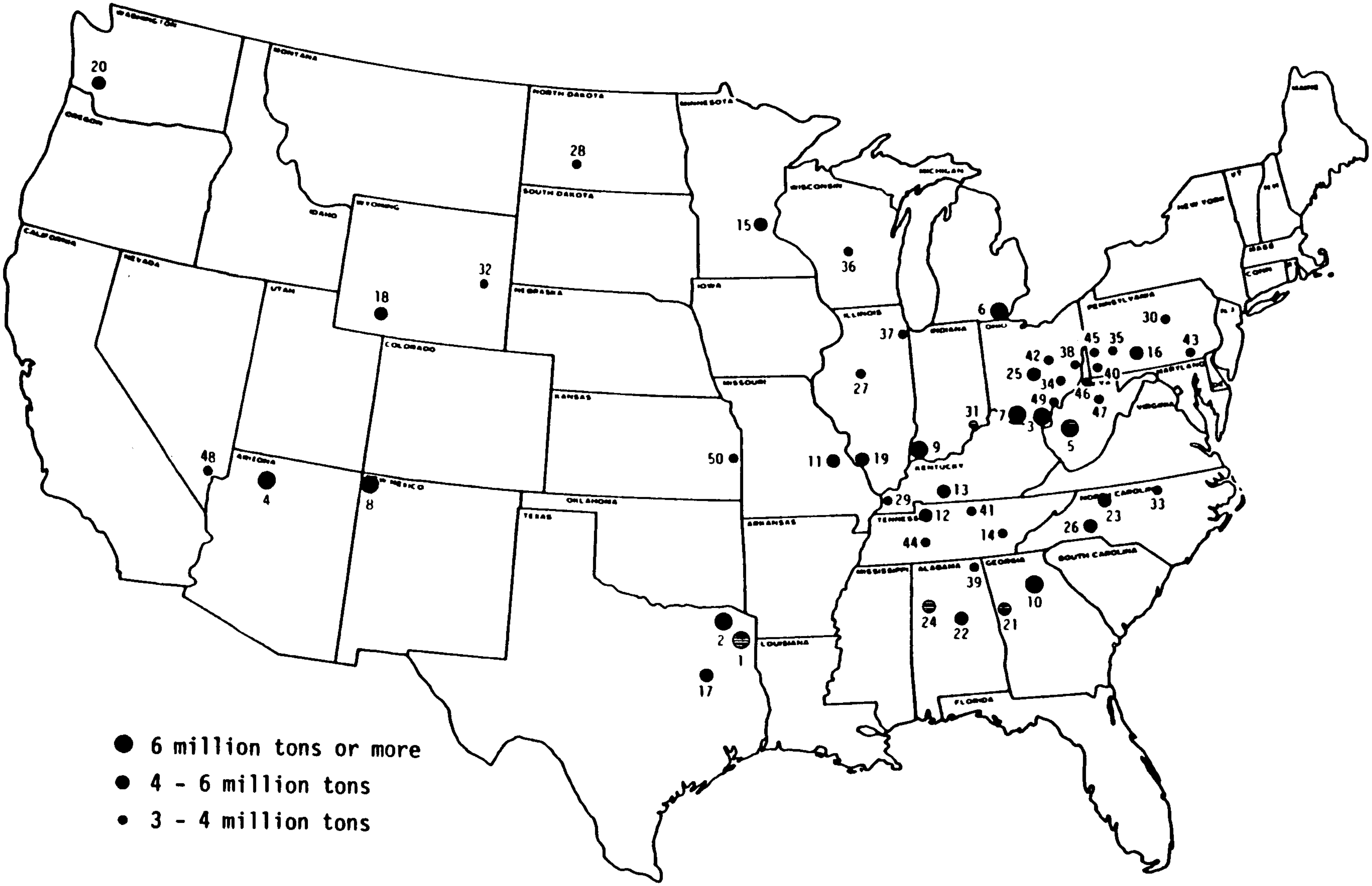
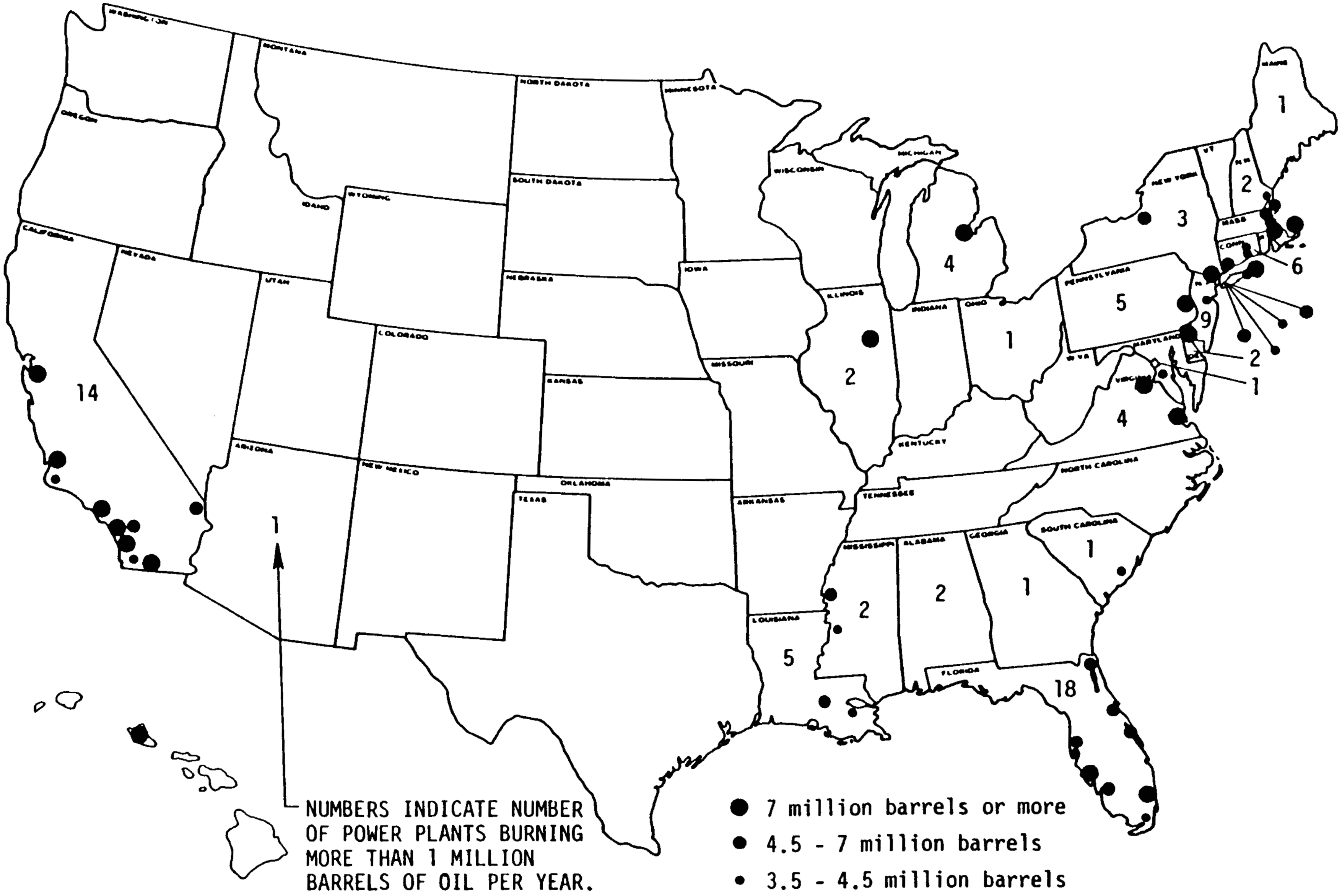


Figure 6-4. The top fifty U.S. coal-fired utility power plants, based on coal deliveries (U.S. DOE 1980a).



NUMBERS INDICATE NUMBER OF POWER PLANTS BURNING MORE THAN 1 MILLION BARRELS OF OIL PER YEAR.

● 7 million barrels or more

● 4.5 - 7 million barrels

• 3.5 - 4.5 million barrels

Figure 6-5. The top fifty oil-fired utility power plants in the United States based on oil deliveries (U.S. DOE 1980a).

TABLE 6-4. 1978 CONSUMPTION OF RESIDUAL OIL IN STATIONARY SOURCES BY SECTOR[a]
[10^{12} Btu (percent of U.S. total)]

Eight northeastern states	Commercial	Industrial	Utility	Total
Connecticut	34	64	127	225
Massachusetts	109	34	305	448
New Hampshire	7	8	20	35
New Jersey	75	91	167	333
New York	337	62	520	919 (16)
Pennsylvania	60	129	162	351
Rhode Island	11	6	8	25
Vermont	4	3	0	7
Subtotal, eight states	637	397	1309	2343 (40)
California	17	63	486	566 (10)
Florida	14	75	458	547 (9)
U.S. Total	1034	1454	3352	5840 (100)

[a] U.S. DOE 1980b.

TABLE 6-5. 1978 CONSUMPTION OF DISTILLATE OIL IN STATIONARY SOURCES BY SECTOR[a]
[10^{12} Btu (percent of U.S. total)]

	United States	Eight states	California	Florida
Residential[b]	2238	1119	6	22
Commercial	1117	445	15	0
Industrial	1154	146	75	32
Utility	423	51	9	24
Total	4932 (100)	1761 (36)	105 (2)	78 (4)

[a] U.S. DOE 1980b.

[b] Includes kerosene.

TABLE 6-6. 1978 CONSUMPTION OF GASOLINE AND NATURAL GAS[a]
[10^{12} Btu (percent of U.S. total)]

	Gasoline	Natural gas
Eight northeastern states	2402 (17)	1,760 (9)
California	1462 (10)	1,594 (8)
Florida	595 (4)	327 (<2)
United States, total	14211 (100)	19,999 (100)

[a] U.S. DOE 1980b.

approximate the area of maximum severity for acid precipitation (shown in Figure 6-4) consume 17 percent of all motor gasoline and 36 to 40 percent of all fuel oil burned in the United States. In addition to the utility boilers many industrial boilers in the area are fueled by residual oil. In addition, thousands of residential and commercial boilers are fired by distillate oil or kerosene. Although emissions of SO_2 from these latter two categories are less than those from residual oil-fired boilers, these oil-fired commercial and residential boilers are important sources of SO_x, NO_x, and especially primary sulfates because of their sheer numbers (Homolya and Lambert 1981). This concentration of fuel usage may be a key factor in occurrences of acid rain. These eight states account for a disproportionately large share of the total U.S. petroleum consumption (~21 percent), and an even larger share of fuel oil consumption, yet they constitute only 4-1/2 percent of the land area of the contiguous 48 states. Further because many oil-burning facilities are older plants and typically have shorter stacks, their emissions do not travel as far as those from tall stacks and can be deposited within a relatively short range of their point of emission (i.e., within ~50-100 km). Boldt et al. (1980), provided one example of this phenomenon.

Historical utility fuel trends in the eight states further indicate the recent rapid growth of oil burning in that relatively small area. The data for major fuel consumption by utilities in this region are shown in Table 6-7 for the years 1960 through 1978. These data show significant growth in utility burning of residual oil, while coal burning essentially remained steady (17%). Figure 6-6 shows the approximate location of coal- and oil-fired power plants in the eight-state area. About 60 percent (700 x 10^{12} Btu) of the coal burning by utilities took place in 17 plants in western Pennsylvania and New York (see Figure 6-6). This would appear to indicate that in the central part of the acid-rain-impacted Northeast coal burning has decreased substantially in the past 20 years, whereas oil burning has increased by more than 400 percent. The result of this change is that utility consumption of oil is now over 3 times that of coal.

Another important local source of precursor pollutants in the Northeast may be the large mobile source sector, with its associated emissions of NO_x and sulfuric acid (formed in catalytic converters). Surface wind patterns suggest that high levels of transportation-related NO_x are directed toward the Adirondacks from the congested traffic corridors between Philadelphia, New York City, and Albany during the summer months (Henderson et al. 1980). Some portion of these NO_x emissions is absorbed directly by the local environment and some additional amount is probably converted to acid form (HNO_3) either during transport or during precipitation events. Since both mobile and stationary sources emit NO_x, and since nitric acid represents an increasing share of the rainfall acidity in the Northeast (currently 30 percent), the role of all sources of NO_x emissions reaching the Northeast need thorough evaluation.

California--

California is a large consumer of petroleum fuels and is second only to New York in residual oil consumption, mostly by utilities. It leads the Nation in gasoline consumption. Coal supplies only about 1 percent of the

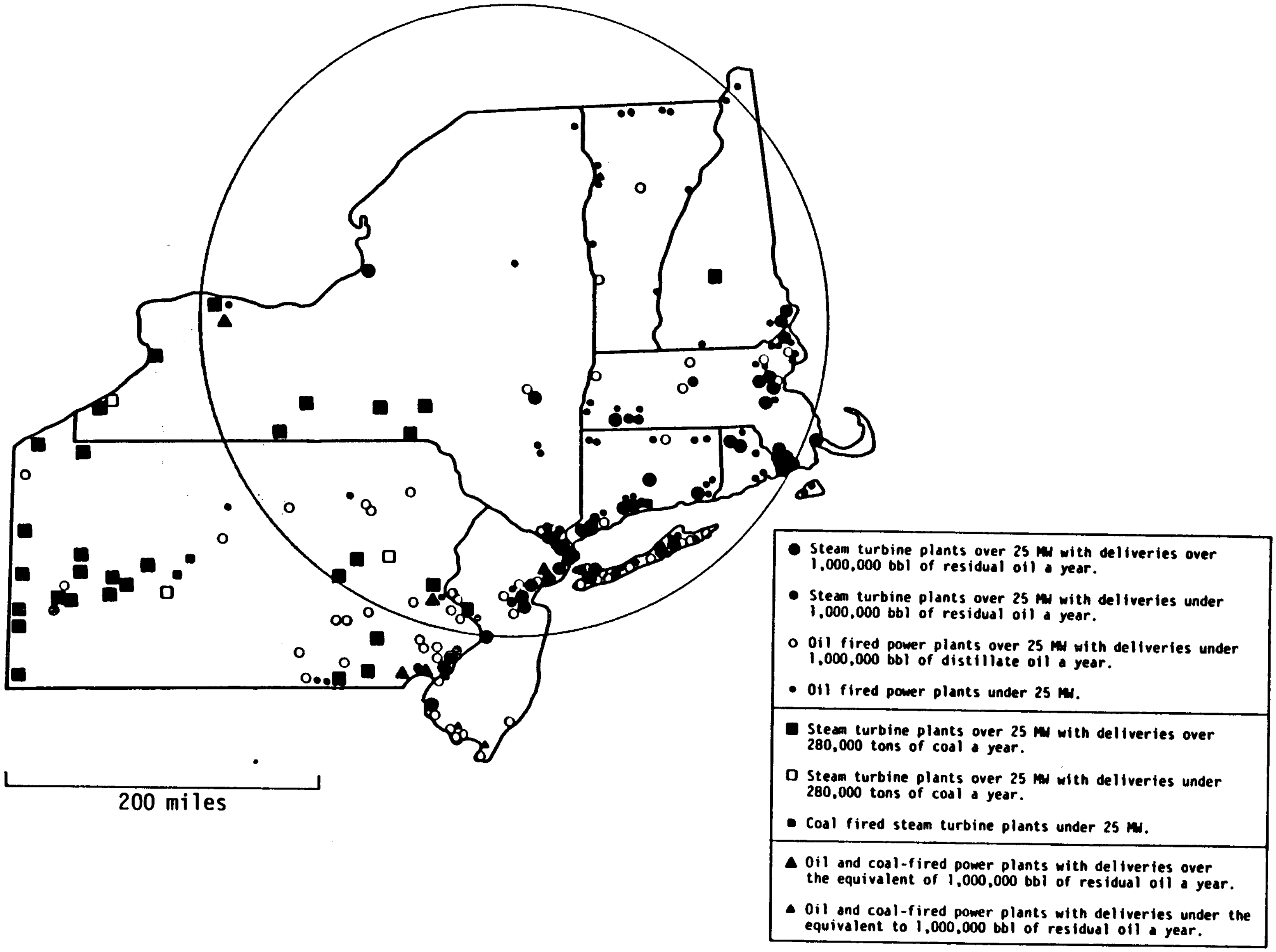


Figure 6-6. Utility power plants firing coal and/or oil in the Northeast (Gilliam 1980; U.S. DOE 1979).

TABLE 6-7. CONSUMPTION OF ENERGY BY THE ELECTRIC UTILITIES IN EIGHT NORTHEASTERN STATES[a] (10^{12}Btu)

Year	Total coal[b]	Natural gas (dry)	Petroleum	
			Distillate and jet fuel	Residual fuel
1960	1021	106	4	254
1961	1053	99	5	254
1962	1081	112	5	268
1963	1030	131	4	291
1964	1265	128	4	304
1965	1350	115	4	371
1966	1356	110	3	483
1967	1300	124	3	612
1968	1306	149	15	708
1969	1210	175	23	955
1970	1152	175	66	1173
1971	1114	166	105	1261
1972	1052	117	180	1385
1973	1164	106	147	1375
1974	1106	74	148	1248
1975	1112	27	76	1166
1976	1125	20	74	1202
1977	1117	16	78	1283
1978	1095	4	65	1309

[a] U.S. DOE (1980b).

[b] Bituminous and anthracite coals, and lignite.

total energy used (U.S. DOE 1980b). This usage of both residual oil and gasoline is concentrated aroung the metropolitan/industrial areas of Los Angeles, San Francisco, and San Diego, where acid rain is most notable. Significant amounts of natural gas are also burned in furnaces throughout the State. Figure 6-7 shows data from precipitation studies conducted in California during the winter rainy period from November 1978 to March 1979. The data show that acid rain is occurring throughout the state, with the mean pH of precipitation ranging from 4.4 at San Jose to 5.4 at Big Bear Lake.

Nitrates are the predominant anion in rainfall in the northern part of the state and in the remote and less-industrialized mountain areas in the south (Morgan and Liljestrand 1980; McColl 1980). Sulfates, on the other hand, are predominant in the Long Beach-Los Angeles-Westwood area, where utilities and refineries are concentrated (Morgan and Liljestrand 1980). The variable ratio of sulfuric acid and nitric acid derivatives in California precipitation may be indicative of the predominant type of source contributing to acid rain in a given area. A relatively high proportion of sulfate to nitrate is thought to indicate the contributions of stationary sources such as power plants, smelters, and heavy industry, whereas a relatively high proportion of nitrate is more suggestive of mobile sources.

Florida--

Florida, the Nation's third largest consumer of residual oil, burns 3 times as much residual oil as coal and uses large amounts of motor gasoline. Florida experiences acid rain, especially in the northern two-thirds of the State, where most of the oil-consuming sources (utilities) are located (Spaite et al. 1980).

Figure 6-8 shows that the annual pH level of rainfall in the northern two-thirds of the State now averages 4.7 or less, and there is some evidence of a trend toward increasing acidity (Brezonik, Edgerton, and Hendry 1980). Although the sulfate contribution to the acidity is, on average, 2.5 times that of nitrate, its relative proportion of the total is declining with an increase in the contribution of nitrates. This trend and other aspects of acid rain in Florida are discussed further in Appendix C. Data presented in Appendix C suggests that oil and gasoline consumption are largely responsible for the occurrence of acid rain in Florida. Edgerton and Brezonik (1981) confirms what fuel use patterns suggest indirectly, in that they indicate that atmospheric deposition patterns are primarily influenced by in-state emissions of SO_x and NO_x.

Fuel Use and Acid Rain in The Netherlands

The results of studies in The Netherlands offer interesting perspective on that already presented for all of Western Europe. Fuel consumption patterns of The Netherlands (shown in Figure 6-7) generally followed those in the rest of Western Europe from the end of World War II until about 1968. Coal, the primary fuel in 1946, declined over the years, and growing needs for energy were being met by importing cheap high-sulfur oil. Sulfur oxide emissions rose from 200,000 tons/yr from coal burning in 1946 to 900,000 to 1,000,000 tons/yr from all sources in 1967; during that period the use of coal continued to shrink so that by 1970 it comprised only 10 percent of the

LOCATION	MEAN pH
NORTHERN CALIFORNIA	
BERKELEY	4.66
MENLO PARK	5.30
DAVIS	5.20
SAN JOSE	4.42
HOPLAND	5.10
NAPA	4.84
CHALLENGE	4.88
TAHOE CITY	5.17
KEARNEY	4.96
Average	4.99
SOUTHERN CALIFORNIA	
WESTWOOD	4.53
LONG BEACH	4.54
LOS ANGELES	4.49
PASADENA	4.41
AZUSA	4.66
MT. WILSON	4.99
WRIGHTWOOD	4.90
RIVERSIDE	4.97
BIG BEAR LAKE	5.42
Average	4.76

Figure 6-7. Mean pH of rainfall at various locations in California, 1978-79 (Morgan and Liljestrand 1980; McColl 1980).

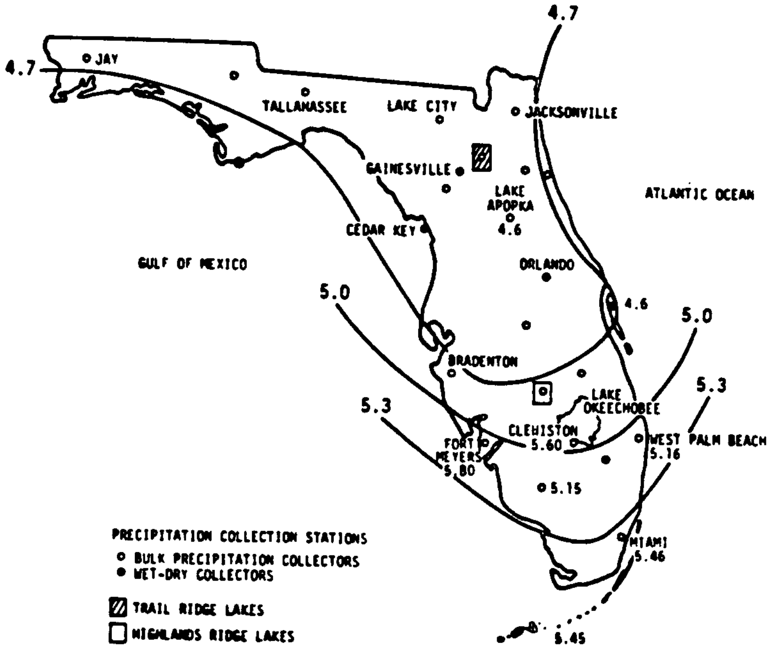


Figure 6-8. pH isopleths of Florida rainfall from May 1978 - April 1979 (Brezonik, Edgerton, and Hendry 1980).

total fuel use (Vermeulen 1980). During this same period rainfall in The Netherlands became progressively more acidic and that in other parts of Europe is shown in Figure 6-9. In the 1967-1968 period the average annual pH values were less than 4.0. At that time rain in The Netherlands was said to be more acidic (on an annual basis) than that in any other part of the world.

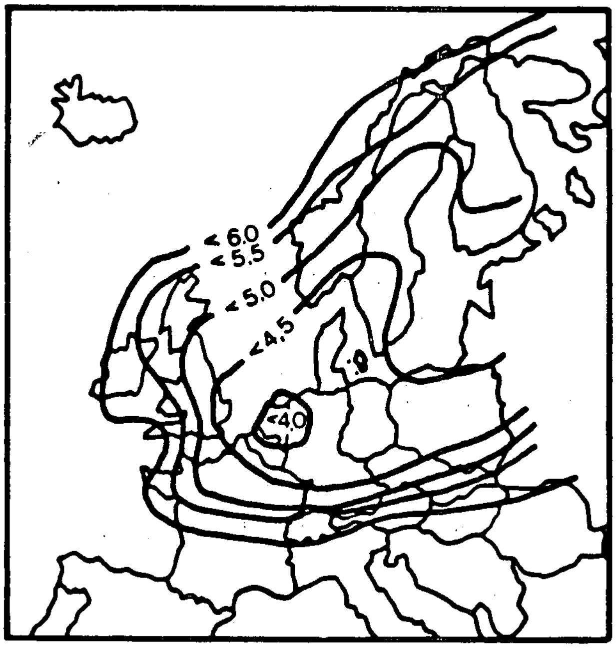


Figure 6-9. Acidification pattern in Europe in 1966, with the center over The Netherlands (Vermeulen 1980).

At that point the Government took actions to limit SO_2 emissions, enacting in 1968 the Dutch Clean Air Act. This act created pressure that, combined with discovery of extensive natural gas supplies, led to an increasing use of gas for industrial expansion. In 1967 gas accounted for 18 percent of The Netherlands total fuel consumption. This increased to 50 percent in 1972, and 60 percent in 1976. By 1975, power stations were burning 85 percent gas. Not only was the growth in oil consumption checked, but some decline in usage took place. The fuel oils that were burned were much lower in sulfur content, especially those burned in power plants. These fuel switches were accompanied by sharp reductions in total SO_x emissions in The Netherlands and sharp reductions in the acidity of rainfall.

It was concluded that the high acidity of rainfall was attributable to SO_x emissions from burning of fossil fuels (Vermeulen 1980). The data for national emissions of SO_x and the acid content of rain for corresponding years are shown in Figure 6-10. These data show acidity measurements at the monitoring station at DeBilt, which is part of the network of the International Meteorological Organization (IMO) established in the early 1950's. Although there are other IMO monitoring stations in The Netherlands, DeBilt, being centrally located, is most representative of the total yearly interior SO_2 emissions (Vermuelen 1980). The data in Figure 6-10 appear to substantiate the importance of the rate of SO_x emissions with respect to the occurrence of acid precipitation in The Netherlands. In addition, they suggest, taken along with other data, that the growth of the problem was associated with increases in consumption of high-sulfur fuel oil. The reduction in acidity after the 1968 period was accompanied by several potentially important changes: (1) the sulfur levels in fuel oils burned were lower, (2) oil consumption was reduced somewhat overall, and was greatly reduced in electric utilities, and (3) the decline in coal consumption continued. It is not clear as to which of these changes contributed most to the apparent decrease in rainfall acidity after 1968.

Fuel Use and Acid Rain in Japan

The heavy dependence of Japan on fuel oil is shown in Table 6-8. In 1978 over 50 percent of the total energy from fossil fuels was supplied by fuel oils. About 40 percent is attributable to the burning of residual oil alone. Coal comprised only about 20 percent of the total, and most of this was used for steelmaking, which, because of the nature of the processing would not contribute greatly to atmospheric sulfate concentrations or to acid rain. Similarly, sulfur emissions from smelting of sulfide-containing metal ores (the only other major source) are mostly recovered as sulfuric acid. Thus, in Japan the sulfur in fuel oil is the major source of sulfur compounds in the atmosphere.

Data on precipitation in Japan suggest that serious acid rain has occurred (Chemical Abstracts 1981). Studies of the pH of rainfall in Japan have shown that values of 3 to 4 occurred in the 1973 to 1977 period. It has also been reported that on three occasions between June 1973 and July 1975, acid mists caused widespread skin and eye irritation. Thus, it appears that Japan has experienced acid rains as severe as any that have been reported worldwide.

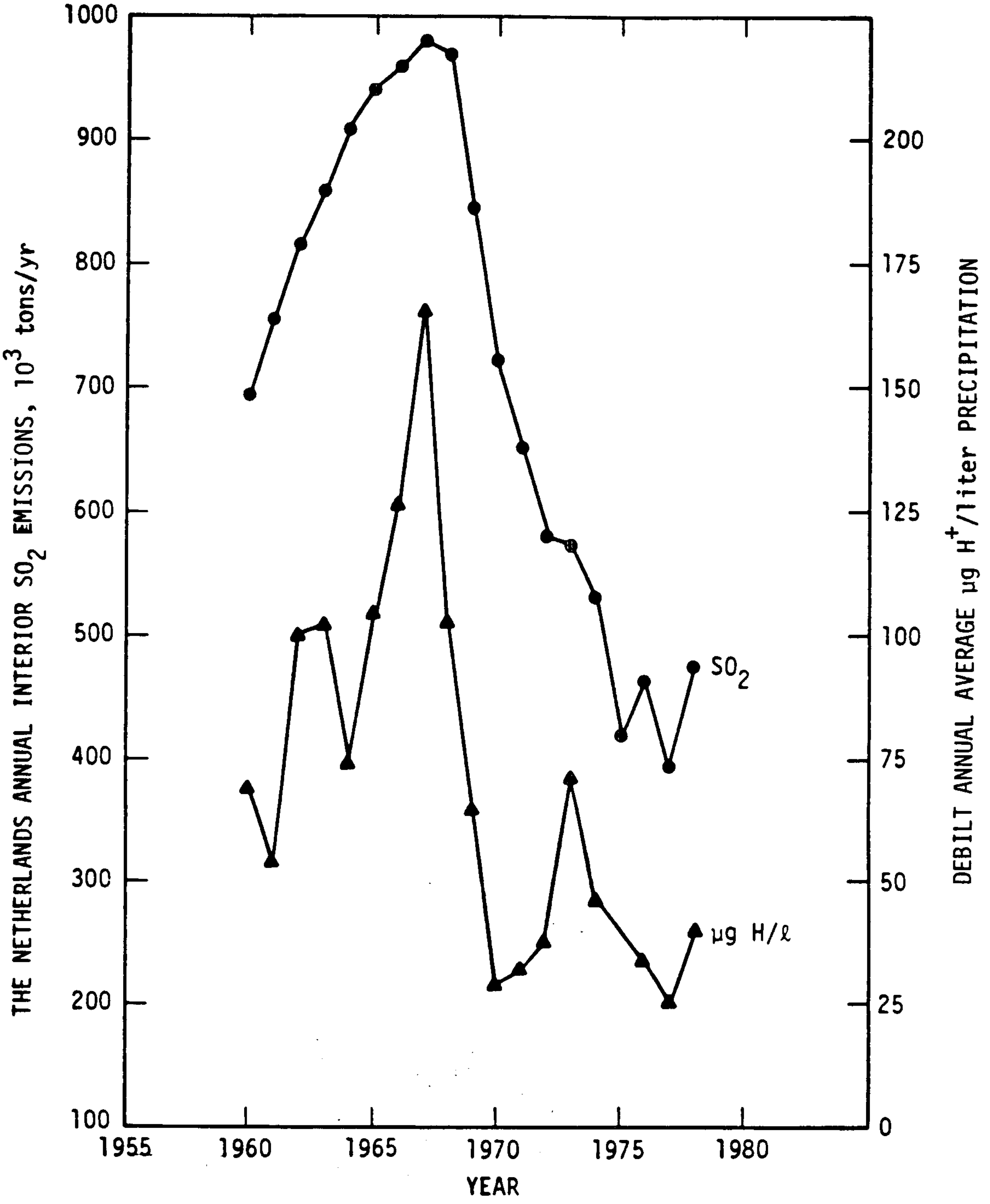


Figure 6-10. Annual average SO_2 interior emission and acid content of precipitation in The Netherlands, 1960-1978 (Vermeulen 1980).

TABLE 6-8. ENERGY CONSUMPTION IN JAPAN[a] (10^{15} Btu)

Year	Solid fuels	Liquid fuels[b]	Natural gas	Gasoline	Fuel oil
1950	1.1	0.06	0.003	0.02	0.04
1951	1.3	0.12	0.003	0.03	0.09
1952	1.3	0.18	0.003	0.05	0.13
1953	1.4	0.30	0.004	0.06	0.23
1954	1.3	0.33	0.005	0.07	0.24
1955	1.3	0.37	0.007	0.08	0.27
1956	1.4	0.45	0.009	0.10	0.31
1957	1.5	0.59	0.012	0.13	0.41
1958	1.4	0.61	0.018	0.14	0.42
1959	1.5	0.74	0.023	0.15	0.52
1960	1.8	1.00	0.031	0.19	0.76
1961	1.8	1.40	0.039	0.23	1.00
1962	2.0	1.60	0.051	0.26	1.20
1963	1.8	2.00	0.070	0.30	1.50
1964	1.8	2.40	0.077	0.33	1.80
1965	1.8	2.80	0.073	0.36	2.10
1966	1.9	3.20	0.076	0.40	2.40
1967	2.1	4.00	0.080	0.47	3.00
1968	2.2	4.70	0.086	0.53	3.50
1969	2.2	5.60	0.095	0.61	4.20
1970	2.5	6.70	0.150	0.69	5.10
1971	2.2	7.50	0.150	0.76	5.70
1972	2.1	8.00	0.150	0.82	5.90
1973	2.3	9.20	0.220	0.92	6.80
1974	2.4	8.80	0.300	0.91	6.40
1975	2.3	8.40	0.330	0.96	5.90
1976	2.2	8.90	0.390	1.00	6.20
1977	2.2	9.10	0.490	1.00	6.40
1978	2.2	9.20	0.640	1.10	6.20

[a] United Nations (1976, 1979).

[b] Includes small amount of feedstock.

The degree to which residual oil predominates in overall oil burning is shown in Table 6-9, which shows consumption of all fuel oil and consumption of residual oil for the years 1968 to 1976. These data suggest that the acid rain that was occurring in Japan is most likely attributable to residual oil burning, with some possible contributions from consumption of motor fuels.

TABLE 6-9. OIL CONSUMPTION IN JAPAN[a]
(10^{15} Btu)

Year	All fuel oil	Residual	Utility Grade C residual oil
1968	3.5	3.15	0.76
1969	4.2	3.28	0.95
1970	5.1	4.20	1.16
1971	5.7	4.34	1.22
1972	5.9	4.69	1.31
1973	6.8	4.48	1.39
1974	6.4	4.81	1.31
1975	5.9	4.56	1.25
1976	6.2	4.79	1.35

[a] Ando (1978).

With the growth of fuel oil usage and associated sulfur pollution, Japan began to require desulfurization of oil, application of flue gas desulfurization systems, and other measures for environmental protection. While oil consumption continued to increase, the average sulfur content of fuel oil decreased from 2.3 percent in 1968 to 1.4 percent in 1976. As a result, the amount of sulfur available for emission from oil burning has remained about constant. Reductions of 50 percent in atmospheric concentrations of SO_x have been reported for this period. Corresponding reductions were also reported for atmospheric concentrations of both sulfates and vanadium. These data, which are believed to indicate a connection between residual oil burning and concentrations of atmospheric sulfates, are discussed further in the section that follows and in Appendix D.

RESULTS OF THE ANALYSIS

In the industrial areas investigated in this report, where acid rain is occurring, petroleum-derived fuels are more widely used than coal. The majority of the precursor SO_x and NO_x produced within some of these areas comes from burning of petroleum fuels. Further, the growth of oil use in these areas generally coincides with the perception of acid rain as a problem, i.e., early 1950's.

Residual oil burning is suspect for several reasons. It appears to be the primary cause of severe acid rain in Japan, where residual oil burning is the most significant source of the precursor compounds. Further, the pollution control measures for residual-oil-fired boilers in Japan have been linked to reductions of ambient sulfate concentrations. Similarly, in The Netherlands, where acidity of rain has been reduced by changing fuel consumption patterns, one of the most important changes has been reduction of emissions from residual-oil-fired boilers. If residual oil burning does, as it appears, contribute strongly to the formation of acid rain, it could be an important factor in the acidification of rain in the northeastern United States.

Residual oil burning has increased sharply in the Northeast and other parts of the United States in the past 20 years, especially the amounts being burned in power plants. These power plants are, for the most part, poorly controlled with respect to particulate collection. Although the sulfur content of the oil burned has been reduced, fine particulates with potential for functioning as catalysts for formation of sulfate are being discharged. Also, these boilers appear to be especially productive of primary sulfates, which can participate directly in acidification of rain (see Appendix A). Further investigation should be focused on the role of residual oil burning in formation of acid rain.

Although the combustion of residual oil may be more important in production of acid rain than other forms of oil burning (per unit of fuel burned), the distillate fuels burned for home and commercial space heat may also contribute to acid rain in the Northeast, where very large amounts of distillate oil are burned in a relatively small land area. The combustors of these distillate fuels are generally small and are often poorly controlled so that they are likely to be especially productive of primary sulfates. Also, they discharge the sulfate at relatively low levels, where their impact will be felt locally.

Motor vehicles burning diesel fuel and gasoline also emit NO_x in amounts that are significant for each unit of fuel burned. At some locations in or near the areas most severely impacted by acid rain, motor vehicles produce precursor compounds in larger quantities than any other local source. Better definition of the role of motor vehicles in acid rain is needed.

In summary, it has been shown that there is heavy consumption of petroleum fuels with demonstrable potential for large-scale production of SO_2, NO_x, and primary sulfates in a number of industrialized areas in the world where acid rain is occurring. This suggests the need for further evaluation of the contribution of petroleum fuel burning to acid rain.

SECTION 7

THE IMPACT OF LOCAL SOURCES

The previous section described a number of industrialized areas in the world where changes in acidity of precipitation are concurrent with changes in patterns of fuel burning. However, this is only suggestive of an association between the two and at present, data are not available to prove a cause and effect relationship. There is, however, additional evidence to suggest that local sources (fuel burning and other) do affect the acidity of precipitation in their vicinity.

Some of the evidence to suggest an important role for local sources in acidification have already been discussed. Reductions of emissions from local oil burning in The Netherlands for example, led to an apparent reduction in acidification of local precipitation.

In Japan, when control of oil-burning plants was being implemented, reductions were made in atmospheric concentrations of both SO_2 and sulfates. It was further observed in the 1970 to 1974 period when this activity was taking place that comparable reductions in ambient concentrations of vanadium were observed in 10 major Japanese cities. These data, which are capable of many interpretations, are shown in Table 7-1. These results are inconsistent with experience in the U.S. where reductions of SO_2 emissions have produced only modest reductions in ambient sulfate levels downwind and no apparent relationship between sulfate levels and vanadium concentrations has been observed. The relationship observed in Japan, taken with what is known about fuel burning in that country, strongly suggests that vanadium concentrations in the atmosphere and ambient sulfate levels are relatable to oil burning. As indicated earlier, work in Florida has also produced indications that acid rain is attributable to local emissions. Rain is most acidic in the northern part of the State, where most power plants (mostly burning oil) are located. It has been suggested by one worker that emissions from neighboring states to the north may influence the acidity of rain in upper Florida (Tanaka et al. 1980) but a recent study attributed local atmospheric deposition patterns to in-state emissions of SO_x and NO_x (Edgerton and Brezonik 1981).

Other data are available to document the contribution of individual point sources of pollution to acidification of precipitation. Smelters, coal- and oil-fired utility boilers, oil-fired commercial boilers, etc. have been shown to impact on the precipitation in their vicinity. The following paragraphs highlight a number of local source effects.

TABLE 7-1. AMBIENT CONCENTRATIONS OF SULFUR DIOXIDE (SO_2), SULFATE ($SO_4^=$) AND VANADIUM (V) IN MAJOR CITIES IN JAPAN ($\mu g/Nm^3$) [a]

City	1970			1972			1974		
	SO_2	$SO_4^=$	V	SO_2	$SO_4^=$	V	SO_2	$SO_4^=$	V
Sapporo	-	11.2	0.03	-	8.3	0.03	-	7.0	0.02
Ichihara	-	14.7	0.06	-	15.5	0.07	-	11.8	0.03
Tokyo	-	17.3	0.07	-	16.1	0.08	-	12.0	0.05
Kawasaki	-	56.0	0.27	-	24.0	0.14	-	16.8	0.05
Nagoya	-	22.0	0.09	-	25.0	0.12	-	16.7	0.06
Osaka	-	31.6	0.15	-	27.0	0.13	-	14.6	0.05
Amagasaki	-	30.3	0.10	-	18.8	0.11	-	12.6	0.05
Matsue	-	8.7	0.01	-	10.3	0.02	-	7.3	0.02
Ube	-	27.5	0.05	-	20.9	0.07	-	13.4	0.05
Kitakyushu	-	29.0	0.10	-	17.1	0.07	-	12.5	0.05
Average	113	24.8	0.09	-	18.3	0.08	63	12.5	0.04

[a] Ando (1978).

Coal- and Oil-Fired Power Plants

Chalk Point is a 710-MW, oil-fired power plant in Maryland having two stacks 400 ft (122 m) high. Figure 7-1 shows the pattern of acid deposition in the immediate vicinity of the power plant during a series of summer convective storms (Chandler et al. 1980). The study clearly shows that rainfall in the immediate vicinity of the plant is most acid and that acidity drops off with distance. Also, winds and rainfall rates have a definite effect on the pattern of hydrogen ion deposition.

Vermeulen recently summarized the results of several other power plant studies in relation to local acid rain (Vermeulen 1980):

> Högström did in 1974 a study of the wet deposition of sulfur from a coal-fired power plant plume (130 ft stack) in Uppsala, Sweden. He found that 40 to 70 percent of the emitted SO_2 amount was deposited within 60 km of the stack. This was a very detailed study. The SO_2 washed out by precipitation consisted of 98 percent of sulfate and only 2 percent of SO_2. In the plume, this relation was just the opposite....Hales and others collected, during a study of the (coal-burning) Keystone generating station in Pennsylvania, highly acidic rain water samples within 4 miles of the 800 ft high stack. Just as Högström did, Hales found an increase in sulfate, but a very small amount of SO_2 in the rain water....During an investigation in South Maryland, in the direct surrounding of a 710-MW power plant, Landsberg found pH values between 3.0 and 5.7. The samples were clearly influenced by the emitted and washed out SO_2. Another investigation of Landsberg carried out with 13 rain samplers in the surroundins of a power plant confirmed his earlier results. In a study by Granat and Rhode, in which they made use of 78 rain samplers situated about a power plant, they found a significant influence of the emitted SO_2 on the proton concentration and the concentration of sulfate. Hutcheson and Hall had the same experience during their study in a similar situation (at a coal-fired power plant).
>
> Recently, Högström and others studied the wet fallout of sulfate and the SO_2 to sulfate transformation rate at an oil-fired, 1000-MW power plant in Sweden. This project comprised a number of wet fallout tests with not less than 100 sampling locations up to 60 km from the source. In their experiments, they made use of an inert tracer, SF_6. They found that about 70 percent of the emitted amount was deposited within 80 to 120 km from the source. This confirmed the earlier results from 1974. In the dispersion experiments, they found that on a day with close to 100 percent relative humidity, 70 percent of the sulfur from the power plant occurred as sulfate at a distance of 30 km from the source. On a much drier day, the corresponding figure was only 10 percent at 30 km.

Boldt et al. 1980 summarized the testing of the Niagra-Mohawk steam plant at Albany. This residual oil-fired plant was tested from mid-September to mid-October, 1978 as a primary sulfate emission source.

Initial examination of ambient sulfate levels in the Albany area indicated that they were consistently higher over a 13-year period than those in either Schenectady or Troy. The authors felt this reflected the influence of local emissions rather than long-range transport influences, which would not produce the consistently higher geometric means observed in Albany.

During the field test program it was found that while the Albany plant plume passed over or between test sites much of the time, on three days when the winds were blowing directly toward the monitoring station for at least 12 hours, the average increase in downwind sulfate over upwind sulfate was 34 to 60 percent of the downwind concentration. These observations along with pH isopleths constructed from the field test work led the authors to conclude that high local sulfate levels were attributable to local sulfate emissions.

Some power plants have also been shown to contribute to more alkaline pH values in the vicinity of the plants. One example is an isolated petroleum coke-fired power plant in the Ashabasia oil sands area of western Canada. Barrie (1980) found that snowpack within 5-25 km of the plant was more alkaline than snowpack 100 km away or greater in any direction. This was attributable to the soluble oxides of calcium and magnesium in the flyash. Deposition gradients near the source (5-25 km) were much greater for metals (10:1) than for sulfate and nitrate (3:1). Although Barrie indicated that a large fraction of the particulate-related substances were deposited within 25 km of the plant, he estimated that less than 2 percent of the volatile oxides of sulfur and nitrogen were deposited within 25 km.

Martin (1979) reported that in southwestern England (Swansea-Cardiff-Bristol areas), combustion of low-chloride coals is suggested as a major source of alkalinity for several nearby urban areas that experience more alkaline precipitation than in other urban and rural sections of the country. However, since all of these low-chloride coal power plants are located near large industrial areas, it is difficult to distinguish the relative contribution of alkalinity of the power plants from that of other alkaline sources from the industrial areas.

Smelter Studies--

The potential roles of local point sources in contamination of precipitation in their immediate vicinity has been demonstrated by a number of projects that have studied the fate of metal and sulfur compounds emitted from ore roasting operations producing nonferrous metals. The most studied nonferrous smelter is the Coppercliff smelter in Sudbury. Exploitation of ore deposits in the Sudbury area began about 1885 with operations that involved primitive methods resulting in release of massive amounts of pollution at ground level. The processing methods have changed over the years and now involve more sophisticated technology. However, the present operation is still unique in a number of respects. It is the largest single point source of SO_x emissions in the world, annually emitting over 1 million tons per year, or 20 percent of Canada's and 1 to 3 percent of the world's total anthropogenic emissions.

Pollutants are now discharged through the world's tallest stack (380 m) (Freedman and Hutchinson 1980b). Some studies that have specifically addressed the question of the extent to which the modern day operations impact locally (Freedman and Hutchinson 1980b) (Scheider, Jeffries and Dillon 1980) (Hutchinson and Whitby 1977) are discussed below. The Scheider, Jeffries and Dillion (1981) study compared the bulk deposition of metals (nickel and copper), free hydrogen ion, and sulfate at eight collectors near Sudbury and at eight collectors 225 km southwest of Sudbury. Comparisons included samples taken while the smelter was operating with those taken during a period of about 10 months when the smelter was shut down in the 1978-1979 period. Bulk depositions of total copper and nickel were "significantly lower (3 to 76 fold decrease)" up to 50 km from the smelter when it was not operating. Deposition of sulfur also "decreased significantly (5 to 50% decrease)" at stations within 12 km of the smelter during the shutdown. There was no significant decreases in deposition of sulfate, free hydrogen ion or total copper at the remote set of collectors. It was concluded that the smelter is a significant contributor to local deposition of sulfate, copper and nickel but that free hydrogen ion and sulfate in precipitation at the remote stations "are governed by long-range transport of pollutants originating from many sources".

Two additional studies of the Sudbury smelter (Hutchinson and Whitby 1977) (Freedman and Hutchinson 1980a) provide data for acidity of precipitation at various distances from the smelter before the short (152 m) stack was replaced by a 380 m stack in 1972. Data selected from these studies are shown in Figure 7-2. All data are for the summer growing season, the only period common to both reports. The symbols represent comparable month of the year reporting periods. These data indicate that the impact of the smelter discharge in lowering precipitation pH within about 5 km is minimized with the tall stack but low pH periods still occur. Also it indicates that the pH of samples collected remote to the stack (>50 km) have been lowered by the increased stack height.

A third smelter study (Larson et al. 1975) involved detailed analyses of a single rain occurrence in the Puget Sound region. One main objective was to determine the areal and chemical extent of rain modification by a large nonferrous smelter located in the area. The results indicated that arsenic was a good tracer of the influence of the smelter plume on rain chemistry. Also a definite correlation was obtained between hydrogen ion, sulfate ion and arsenic concentration increases downwind of the smelter. The influence of the smelter upon rain chemistry was reported to be detectable out to 40 km. Data for pH values observed during the storm are shown in Figure 7-3.

Area Sources

New York City Study--

Homolya and Lambert (1981), conducted a test program on 20 small boilers in commercial facilities or residences. These types of boilers have burned a hydrodesulfurized residual fuel oil averaging 0.3 percent sulfur and containing vanadium and nickel as the principal metals present since about 1965. Primary sulfate emissions from these sources averaged 13.4

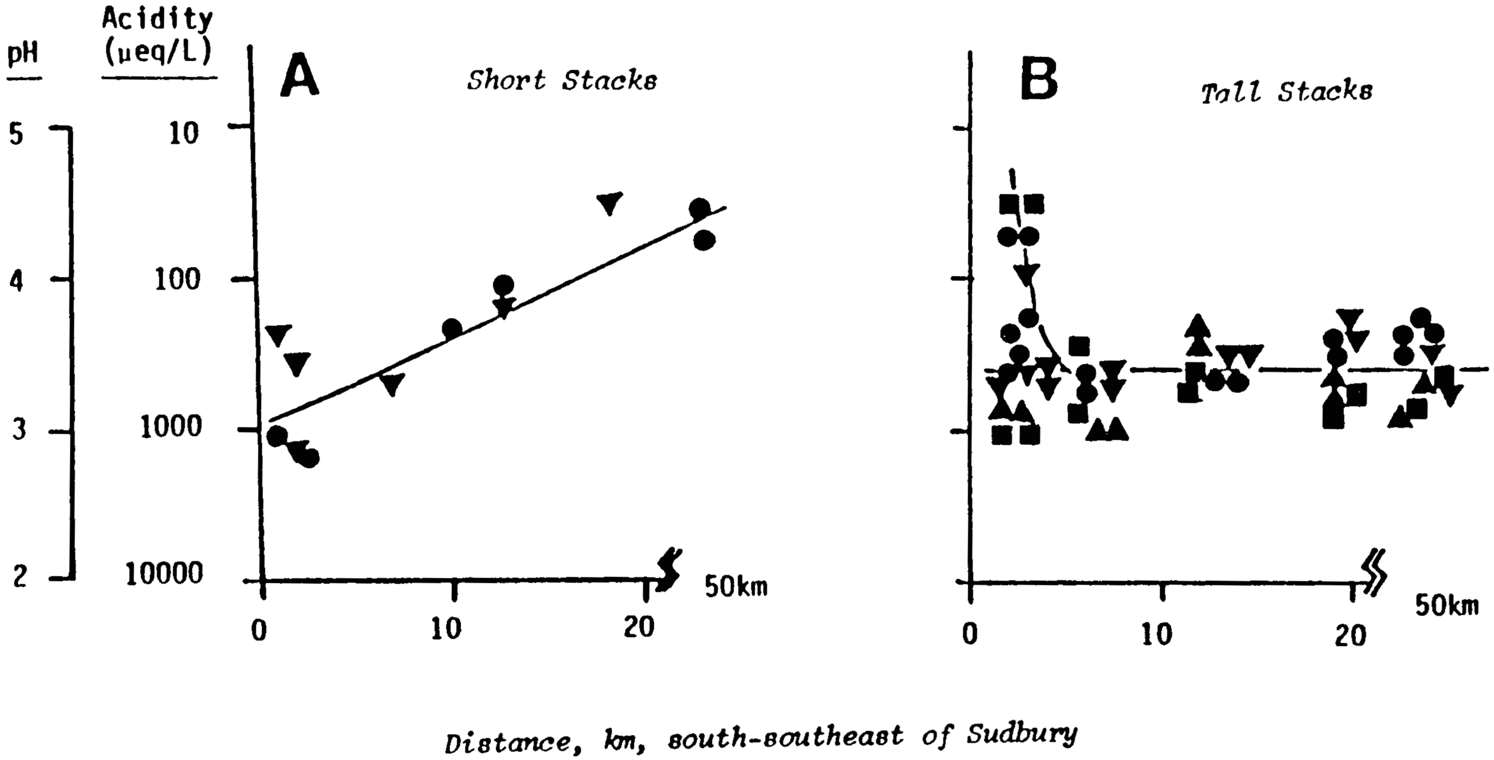


Figure 7-2. Precipitation acidity patterns around Sudbury, Ontario. Monthly averages during summer growing seasons. Different symbols represent different monthly reporting periods. Distances represent a south-southeast transect from Sudbury. (A). Pre-1972 period, short stacks from Hutchinson and Whitby, (1977). (B). Post-1972 period, tall stacks from Freedman and Hutchinson, (1980a).

Source: Resource Technologies Group, Inc., Morgantown, W. Va.

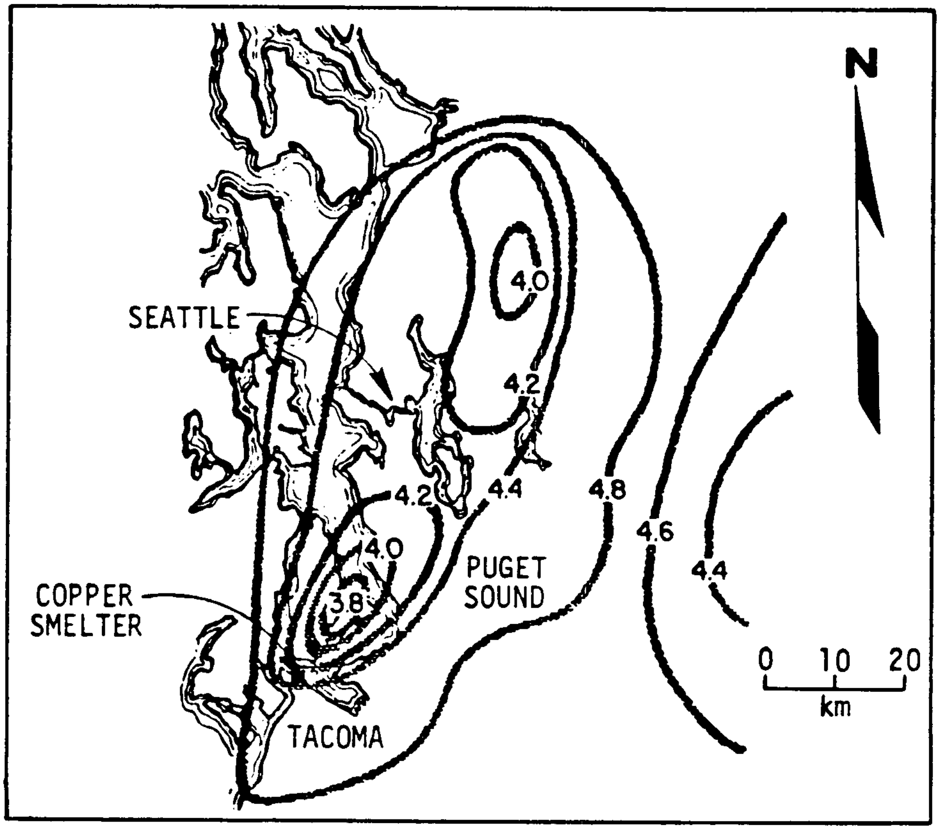


Figure 7-3. pH isopleths of a single 1973 storm in the Puget Sound region. (Larson et al. 1975). Monitoring network included 43 sampling sites. Sulfate and arsenic isopleths showed profiles similar to pH 3.8-4.2 Tacoma isopleths.

percent of the SO_x emissions. This is much higher than the reported emission factors of 1.2 percent for both oil and coal (U.S. EPA 1981).

The authors projected that 36.8 and 51.2 percent of the SO_x and sulfate emissions respectively, in the New York and Long Island areas are attributable to the commercial and institutional sectors. Adding in the industrial sector pushes the sulfate contribution to 57 percent. They indicate that such sources may account for episodic winter sulfate levels measured in metropolitan areas. They also cite a supporting reference (Altschuller 1980), which indicates that an analysis of monitoring data from 1965-1978 at northeast sites shows that most of the excess urban sulfate above regional background was accounted for by local scale primary sulfate emissions.

Local Sources in Michigan--

Richardson and Merva (1976) reported local source effects from both point and area sources on acidity measurements in Michigan. The point sources were paper mills and primary sources in the northern part of the State and were said to decrease pH measures 0.4 units compared to monitoring sites unaffected by point sources.

Area sources in Saginaw Bay, an area source urban plume, were reported to decrease weighted mean pH values to 4.90 from 5.27 in central Michigan stations to the west of Saginaw Bay. A monitoring site at Vassar, Michigan, which is 25 to 40 km from the Saginaw Bay urban plume showed the highest acidity, with a weighted mean average pH of 4.2

In summary it seems well established that large point sources can have a demonstratable impact on the composition of rain at varying distances from the point of emission, and there is evidence to suggest that area sources such as oil-burning boilers and automobiles can also impact on acidity of local precipitation. The evidence to support arguments that local sources are important to the character of local precipitation, like that to support claims that long-range transport from large remote sources is an important factor, are circumstantial. Until further work is done, the relative importance of different types of sources will be in doubt.

PART 3

IMPLICATIONS OF THE FINDINGS

Current analyses show that the acidification of precipitation results, at least in part, from burning of fuels in heavily industrialized areas of the world. It is unclear whether significant damage is occurring and whether acidification is spreading or worsening. Most importantly, it is not clear what kinds of fuel burning contribute most to the acidification. At the same time, there is great pressure to take some action that will protect the environment from possible adverse consequences of acidification. Thus we are in a position where we must decide what actions should be taken to prevent environmental damage from a largely undefined problem. This portion of the report examines the study findings for implications relevant to this problem.

THE ROLE OF COAL BURNING

Coal burning has been identified by some as a dominant contributor to acidification of rain, especially in the United States. Large coal-burning installations do in fact produce awesome amounts of precursor compounds, which are generally discharged through very tall stacks and thus are available for long-range transport to areas where acid rain is occurring. Long-range transport modeling has been used in attempts to make a connection between coal-burning plants and areas of high acidification. The conclusion that coal-burning plants are the primary source of acid rain may not be accurate, however, because the relative contribution of precursor sources, especially petroleum-based combustion sources, is uncertain.

Any acid rain control strategy based on control of large coal-burning plants would have great economic impact. An installation cost of $11 billion (1980 dollars) has been estimated for SO_x controls on the 50 largest coal-burning facilities in the area generally upwind of the northeastern areas of the United States, where precipitation is most acid. This would in effect provide for 90 percent control of the SO_x emitted from these installations; but we do not know what would be the actual impact on acidification, 70 percent of which is attributable to SO_x. Hence, we need better definition of the impact of large, remote, coal-burning plants on the Northeast.

THE ROLE OF OIL BURNING IN BOILERS AND FURNACES

Fuel consumption patterns in industrial areas suggest that oil burning (particularly residual oil burning) may be making an important contribution to acid rain directly and indirectly. Pollutants discharged by oil burning include SO_x, especially high levels of primary sulfate, and materials that may catalyze SO_2 to sulfate in the atmosphere. Experience in The Netherlands indicates that oil burning can cause acid rain in the region where it is burned. The Dutch work also indicates that limiting the burning of oil in power generation and reducing the sulfur content of that which is burned can reduce acidification. Experience in Japan suggests that oil burning can be the dominant cause of acidification of precipitation and indicates that control of emissions from residual oil burning can reduce ambient concentrations of SO_x precursors and sulfates. It seems likely that this should reduce acidification of precipitation as well, but this has not been established. In development of any control strategy for the United States, the role of oil burning should be carefully considered and the experience in Japan and The Netherlands should be studied.

Attention should be given to the Japanese experience with control techniques related to residual oil burning, which is apparently a major contributor in various parts of the world. We need to know the degree to which these controls have reduced the acid rain problem in Japan and their cost-effectiveness. Potential control measures for reducing acid rain precursor emissions from oil-fired boilers include low-excess-air burners, use of low-sulfur or desulfurized oil, catalyst removal through demetallization, use of boiler additives, and use of electrostatic precipitators for particulate control.

THE ROLE OF THE MOTOR VEHICLE

The role of the motor vehicle in acid rain has received very little attention, despite evidence suggesting that it may be important. Both gasoline- and diesel-powered vehicles emit significant amounts of NO_x precursors. Further, the photochemical reactions of the type associated with automotive emissions are also associated with high conversion of SO_2 to sulfate. Another clue to the impact of vehicular emissions is that the area highest in hydrogen ion deposition in the United States (by most recent estimates) coincides with an area of very high traffic density. Moreover, this area is not centered where it might be if the deposition resulted from upwind dumping of acid rain on the western slopes of the mountains in the East. Studies of acid rain in California have indicated that motor vehicles can be a primary cause of acid rain within some regions. Collectively, this information strongly suggests that the role of the motor vehicle needs careful consideration in a strategy to combat acid rain in the United States.

EXPANDING THE DATA BASE

Any attempt to define the role of major emission sources and develop a strategy for control of acid rain in the United States will require development of an improved data base and better understanding of a number of critical areas. Those that seem most important at this stage are discussed below.

Mitigation Measures

Feasible measures for mitigating the effects of acid rain on vulnerable receptors should be examined. One possibility is the liming of or addition of limestone to affected lakes in the Northeast. The cost of a liming program for the Adirondack lakes is estimated at $14.9 million for one treatment (1979 dollars) (Horn 1980). Liming would be required roughly every 3 years. Additional monitoring and administration would cost $1 to 3 million per year. The total cost is a small fraction of the cost of implementing SO_2 control strategies, and earlier liming projects indicate that this technique is effective in protecting fishing resources. Studies should be done on the possible side effects of a massive liming program. If results are favorable, this technique could be used until better resolution of the relative source contribution is achieved.

Effects of Acid Rain

The actual effects of acid rain are unclear. Various receptor areas are affected differently, and many effects studies are inconclusive. Thus, additional work is needed to (1) determine the spatial and temporal extent of acidification on northeastern lakes and stream headwaters, and (2) better define effects of acid rain on human health, drinking water supplies, fish populations, vegetation, soils, and materials. Closely related is the need for data on socioeconomic impacts such as tourist trade and sport fishing. Solid information on all of these effects is needed for a realistic evaluation of the cost-effectiveness of proposed control measures. Efforts should be made to affix dollar values, at least order-of-magnitude, to actual and potential losses that may be resulting from acid rain, e.g., costs involved in treatment of water supplies and losses attributable to decline in tourism and recreational resources on the lake regions.

As in many aspects of the acid rain problem, the economic impacts are difficult to evaluate because they cannot be clearly separated from the impacts of other forms of air pollution.

Natural versus Manmade Sources of Acid Rain

Some technical and analytical effort should be expended to improve the highly variable and incomplete efforts to estimate global emissions of sulfur and nitrogen compounds from natural sources. In industrialized areas, manmade emissions appear to overwhelm those occurring in nature. Some findings indicate however, that natural sources may be important nonetheless. Controversy concerning the relative importance of natural emissions should be resolved. The resolution might also clarify uncertainties about the often-used pH value of 5.6 as the standard for natural rainfall. (It appears that natural rainfall can range from pH 4 to 8.)

Offshore-onshore sampling comparisons in marine areas experiencing acid rain may provide helpful information. An improved global map of comparable pH and hydrogen ion concentrations should be developed with data from ongoing monitoring systems throughout the world.

Monitoring and Data Analysis

Efforts should continue toward improving the quality of precipitation and ambient air data. Particularly important is the development of new techniques for measuring all of the forms of dry deposition (gravitational, impaction and diffusion) for which there is presently no accepted measurement technique.

Dews, frosts, and fogs occur in finely divided form with large surface areas and have the potential to be very acidic. Little is known about the impact of these phenomena and additional study is warranted. Any new monitoring programs should be coordinated with the techniques to be later applied in data analysis.

Future analysis of precipitation and ambient air data should be well planned and consistent if clues are to provided to a number of questions such as those regarding trends in occurrence and spread of acid rain, relative source contributions, urban versus rural concentrations and the significance of metal catalysts and carbon as oxidation enhancers in formation of acid rain precursors.

Long-Range-Transport Modeling

Results obtained in present LRT modeling should be approached with great caution if used as a basis for making control policy decisions. The reason is that many of the inputs required to link sources and receptors are poorly understood and variable. The main areas that require improvement are the parameters of atmospheric chemistry and physics that affect formation of acid rain precursors, and emissions and meteorological data, including effects of terrain. The LRT models also should be flexible enough to accept a large number of variables and then change them appropriately with movement of an air mass over different geographical areas. The nitrogen compounds should be incorporated into LRT modeling, which now accommodates only SO_x.

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Throughout this study we have necessarily pointed to areas of uncertainty and to weaknesses in the data base. We attribute this to the fact that it is only in the past 5 years or so that the acid rain problem has undergone in-depth analysis. It is hoped that identifying the needs that are perceived to be the most important will be useful in developing possible solutions.

REFERENCES

Adams, W. R., Jr. 1980. Acid Rain: A Growing Threat to Our New England Environment. U.S. EPA, Region I, Environment News, pp. 6-7.

Altshuller, A. P. 1976. Regional Transport and Transformation of Sulfur Dioxide to Sulfate in the U.S. JAPCA, 26(4):318-324.

Altshuller, A. P. 1980. Seasonal and Episodic Trends in Sulfate Concentrations (1963-1978) in the Eastern United States. Environmental Science and Technology, 14(11):1337-1348.

Ando, J. 1978. SO_2 Abatement for Stationary Sources in Japan. EPA-600/7-78-210.

Arnold, D. E. 1980. Probable Effects of Acid Precipitation on Pennsylvania Waters. Presented at National Symposium on Acid Rain, Pittsburgh, Pennsylvania, September 23 and 24.

Barnes, R. A. 1979. The Long Range Transport of Air Pollution; A Review of European Experience. JAPCA, 29(12):1219-1235.

Barrie, L. A. 1980. The Fate of Particulate Emissions from an Isolated Power Plant in the Oil Sands Area of Western Canada. In: Aerosols: Anthropogenic and Natural Sources and Transport. Annals of the New York Academy of Sciences, 338:434-451.

Bekowies, P. J., and L. T. Murphy. 1981. European and Japanese Research Related to Trends in Acid Rain. Prepared for U.S. Dept. of Energy under Contract No. DE-AP21-81MC17130 by Resource Technologies Group, Inc., Morgantown, West Virginia.

Bhumralker, C. M., et al. 1979. Regional Patterns and Transfrontier Exchanges of Airborne Sulfur Pollution in Europe. Prepared for Umweltbundisamt by SRI International.

Boldt, K. R., et al. 1980. Impact of a Primary Sulfate Emission Source on Air Quality. EPA-600/2-80-109-20.

Bolin, B. and R. J. Charlson. 1976. The role of the tropospheric sulphur cycle in ~~the~~ short-wave radiative climate of the Earth. Ambio, 5:47-54.

Brezonik, P. L., E. S. Edgerton, and C. D. Hendry. 1980. Acid Precipitation and Sulfate Deposition in Florida. Science, 208:1027-1029.

Burn, R. C., and R. W. F. Hardy. 1975. Nitrogen Fixation in Bacteria and Higher Plants. Springer-Verlag, New York.

Chameides, W. L., et al. 1977. NO_x Production in Lightning. Journal of Atmospheric Science, 34:143-149.

Chang, S. G. 1980. The Importance of Soot Particles and Nitrons Acid in Oxidizing SO_2 in Atmospheric Aqueous Droplets. University of California, Lawrence Berkeley Laboratory. Report No. LBL-1130.

Chang, S. G., and T. Novakov. 1981. Chemical and Catalytic Properties of Elemental Carbon. In: Particulate Carbon: Atmospheric Life Cycle. Siegla, B. C. and G. W. Smith, editors. Plenum Press, New York.

Chandler, M. W., et al. 1980. Summary Report of the NCAQ Atmospheric Dispersion Modeling Panel, Volume 1. Prepared for National Commission on Air Quality by Dames and Moore, 5-AQ-7379.

Chemical Abstracts. 1981. Computer Search in Chemical Abstracts on Acid Rain in Japan.

Cheng, R. T., M. Corn, and J. O. Frohliger. 1971. Contribution to the Reaction Kinetics of Water Soluble Aerosols and SO_2 in Air at PPM Concentrations. Atmospheric Environment, 5:987-1008.

Cogbill, C. V. 1980. Historical Geography of Deposition. Presented at National Symposium on Acid Rain, Pittsburgh, Pennsylvania, September 23 and 24.

Cogbill, C. V., and G. E. Likens. 1974. Acid Precipitation in the Northeastern United States. Water Resources Research, 10(6):1133-1137.

Combustion. 1980. Acid Precipitation Monitoring. Combustion, 51(4):16 October.

Cooper, H. B. H., Jr., J. M. Demo, and J. A. Lopez. 1976. Chemical Composition of Acid Precipitation in Central Texas. In: Proceedings of the First International Symposium of Acid Precipitation and the Forest Ecosystem. USDA Forest Service. General Technical Report NE-23.

Crisman, T. L., and P. L. Brezonik. 1980. Acid Rain: Threat to Sensitive Aquatic Ecosystems. Presented at 73rd Annual Meeting of APCA, Montreal, June 22-27.

Cullis, C. F., and M. M. Hirschler. 1980. Atmospheric Sulfur: Natural and Man-Made Sources. Atmospheric Environment, 14:1263-1278.

Current Science. 1973. Acid Rain in the U.S. 59(14):1-5 and, Scientific American, 1974, 230(6):125-127.

Davey, T. R. A. 1978. Anthropogenic balance for Australia, 1976. Australian Mineral Industries Council Environmental Workshop, Hobart, October.

Davies, T. D. 1979. Dissolved Sulphur Dioxide and Sulfate in Urban and Rural Precipitation (Norfolk, U.K.). Atmospheric Environment, 13:1275-1285.

Davis, M. J. 1980. Acid Precipitation. U.S. EPA, External Review Draft, June.

Dawson, G. A. 1978. Ionic Composition of Rain During Sixteen Convective Showers. Atmospheric Environment 12:1991-1999.

Delwiche, C. C. 1970. The Nitrogen Cycle. Scientific American, 223(3): 137-146.

Devitt, T., P. Spaite, and L. Gibbs. 1979. Population and Characteristics of Industrial/Commercial Boilers in the U.S. EPA-600/7-79-178a.

Drake, R. L., and S. M. Barrager. 1979. Mathematical Models for Atmospheric Pollutants. Electric Power Research Institute, Palo Alto, California. EA-1131.

Edgerton, E. S., and P. L. Brezonik. 1981. A Mass-Balance Atmospheric Sulfur Model for Florida. Presented at the Division of Environmental Chemistry, American Chemical Society, Atlanta, Georgia, March.

Electric Power Research Institute. 1978. SURE Takes to the Air. EPRI Journal, 3(10):14-17.

Electric Power Research Institute. 1980. Ecological Effects of Acid Deposition. EPRI Journal 5:42-43, July/August.

Eliassen, A., and J. Saltbones. 1978. The OECD Study of Long Range Transport of Air Pollutants: Long Range Transport Modeling. Atmospheric Environment, 12:479-487.

Environment Canada. 1980. National Inventory of Natural Sources and Emissions of Sulphur Compounds. Report EPS 3-AP-79-2.

Environmental Data and Information Service. 1977. Global Monitoring of the Environment for Selected Atmospheric Constituents 1977. Joint Publication of the World Meteorological Organization, the U.S. EPA, and the U.S. Department of Commerce/National Oceanic and Atmospheric Administration. Ashville, North Carolina.

Envirosphere Company. 1980. Review and Assessment of EPA Policies Regarding Atmospheric Sulfate Levels in the Urban Northeastern United States. Envirosphere Company, Division of Ebasco Services, Inc.

Eriksson, E. 1963. The Yearly Circulation of Sulphur in Nature. Journal of Geophysical Research, 68:4001-4008.

Feth, J. H., et al. 1964. Chemical Composition of Snow in the Northern Sierra Nevada and Other Areas. U.S.G.S. Water Supply Paper 1535-J.

Freedman, B., and T. C. Hutchinson. 1980a. Pollutant Inputs from the Atmosphere and Accumulations in Soils and Vegetation Near a Nickel-Copper Smelter at Sudbury, Ontario, Canada. Canadian Journal of Botany, 58:108-132.

Freedman, B., and T. C. Hutchinson. 1980b. Smelter Pollution Near Sudbury, Ontario, Canada, and Effects on Forest Litter Decomposition. NATO Conference Series I: Ecology, Vol. 4.

Friend, J. P. 1973. The Global Sulphur Cycle. In: Chemistry of the Lower Atmosphere (Edited by S. I. Rasool), Chapter 4, pp. 177-201. Plenum Press, New York.

Frohliger, J. O. 1980. The Misconceptions (Myths) About Acid Rain. Presented at National Symposium on Aicd Rain, Pittsburgh, Pennsylvania. September 23 and 24.

Galloway, J., and E. Cowling. 1978. The Effects of Precipitation on Aquatic and Terrestrial Ecosystems: A Proposed Precipitation Chemistry Network. JAPCA, 28(3):229-235.

Galloway, J., and D. Whelpdale. 1980. An Atmospheric Sulfur Budget for Eastern North America. Atmospheric Environment, 14:409-417.

Galloway, J. N., and G. E. Likens. 1976. Calibration of Collection Procedures for the Determination of Precipitation Chemistry. Water, Air, and Soil Pollution, 6:241-258.

Galloway, J. N., and G. E. Likens. 1978. The Collection of Precipitation for Chemical Analysis. Tellus, 30:71-82.

Galloway, J. N., G. E. Likens, and E. C. Edgerton. 1976. Acid Precipitation in the Northeastern United States: pH and Acidity. Science, 194:722-724.

Galloway, J. N., et al. 1978. A National Program for Assessing the Problem of Atmospheric Deposition (Acid Rain). National Atmospheric Deposition Program, Report to Council on Environmental-Quality NC-141.

Galvin, P. J., et al. 1978. Transport of Sulfate to New York State. Environmental Science and Technology, 12(5):580-584.

Garland, J. A. 1977. The Dry Deposition of Sulphur Dioxide to Land and Water Surfaces. Proc. R. Soc., A354:245-268.

GCA Corporation. 1981. Acid Rain Information Book. Final Report. Prepared for U.S. Dept. of Energy under contract No. DE-AC02-79EV10273-1, Task Order No. 5, November.

Gilliam, L. R. 1980. Inventory of Power Plants in the United States - December 1979. U.S. Dept. of Energy, DOE/EIA-0095(79).

Glass, N. R., G. E. Likens, and L. S. Dochinger. 1978. The Ecological Effects of Atmospheric Deposition. In: Energy/Environment III. EPA-600/9-78-022. pp. 113-119.

Granat, L. 1976. A Global Atmospheric Sulphur Budget. SCOPE Report No. 7. Ecology Bulletin (Stockholm) 22:102-122.

Hallberg, R. O. 1976. A Global Sulphur Cycle Based on a Pre-industrial Steady-State of the Pedosphere. Scope Report No. 7. Ecology Bulletin (Stockholm) 22:93-101.

Harr, T. E., and P. E. Coffey. 1975. Acid Precipitation in New York State. N.Y. State Dept. Environmental Conservation. Technical Paper No. 43.

Henderson, R. E., et al. 1981. An Overview of the Atmospheric Processes and Modeling Aspects of Acid Rain. Final report prepared for U.S. Dept. of Energy under Contract No. 80ET13800-T014 by the MITRE Corporation, McLean, Virginia.

Henderson, R. E., et al. 1980. Atmospheric Processes of Acid Rain. Mitre Corporation, McLean Virginia. Briefing for U.S. Department of Energy personnel, Pittsburgh Energy Technology Center, November 16.

Heffter, J. 1980. Air Resources Laboratories, Atmospheric Transport and Dispersion Model (ARL-ATAD). National Oceanic and Atmospheric Administration. Technical Memorandum ERL-ARL-81.

Hendry, C. D., and P. L. Brezonik. 1980. Chemistry of Precipitation at Gainesville, Florida. Environmental Science and Technology, 14(7):843-849.

Hitchcock, D. R. 1976. Atmospheric Sulfates from Biological Sources. JAPCA, 26(3):210-215.

Homolya, J. B., and S. Lambert. 1981. Characterization of Sulfate Emissions from Non-utility Boilers Firing Low-S Residual Oils in New York City. JAPCA, 31(2):139-143.

Horn, E., et al. 1980. Response, LRTAP: Acid Precipitation. JAPCA, 30(5):462-464.

Hornbeck, J. W., G. E. Likens, and J. S. Eaton. 1977. Seasonal Patterns in Acidity of Precipitation and Their Implications for Forest Stream Ecosystem. Water, Air and Soil Pollution, 7:355-365.

Hosker, R. P., Jr. 1980. Practical Application of Air Pollutant Deposition Models--Current Status, Data Requirements, and Research Needs. Draft. To Appear In: Proceedings of International Conference on Air Pollutants and Their Effects on the Terrestrial Ecosystem. John Wiley and Sons, New York.

Husar, R. B., D. E. Patterson, and J. D. Husar. 1980. Budget of Man-Made Sulfur, Nitrogen, and Hydrogen Over the Eastern U.S. and S.E. Canada Airshed. Year 1 Report (Draft). Prepared for U.S. EPA by Center for Air

Pollution Impact and Trend Analysis, Washington University, St. Louis, Missouri.

Hutchinson, T. C. and L. M. Whitby. 1977. The Effects of Acid Rainfall and Heavy Metal Particulates on a Boreal Forest Ecosystem Near the Sudbury Smelting Region of Canada. Water, Air and Soil Pollution, 7:421-438.

Jacobson, J. S., L. O. Heller, and P. Van Leuken. 1976. Acid Precipitation at a Site Within the Northeastern Conurbation. In: Proceedings of the First International Symposium of Acid Precipitation and the Forest Ecosystem. USDA Forest Service. General Technical Report NE-23.

Junge, C. E. 1958. The Distribution of Ammonia and Nitrate in Rain Water Over the United States. Transactions, American Geophysical Union 39(2): 241-248.

Junge, C. E. 1963. Atmospheric Chemistry and Radioactivity. Academic Press, New York.

Junge, C. E. and P. E. Gustafson. 1956. The Concentration of Chloride, Sodium, Potassium, Calcium, and Sulfate in Rainwater over the United States, Journal of Meteorology, 15(5):417-425.

Kellogg, W. D., et al. 1972. The Sulfur Cycle. Science, 175:587-596.

Kennedy, V. C., G. W. Zellweger, and R. J. Avanzino. 1979. Variation of Rain Chemistry During Storms at Two Sites in Northern California. Water Resources Research, 15(3):687-702.

Klein, W. H. 1957. Principle Tracks and Mean Frequences of Cyclones and Anticyclones in the Northern Hemisphere. U.S. Weather Bureau. Research Paper No. 40.

Korshover, J. 1971. Climatology of Stagnating Anticyclones East of the Rocky Mountains, 1936-1970. National Oceanic and Atmospheric Administration Technical Memorandum ERL ARL-34.

LaBastille, A. 1979. The Deadly Toll of Acid Rain: All of Nature is Suffering. Science Digest, 86:61-66.

Larson, T. V. 1980. Secondary Aerosols: Production Mechanisms of Sulfate Compounds in the Atmosphere. In Aerosols: Anthropogenic and Natural, Sources and Transport, Annals of New York Academy of Sciences, 338:26-38.

Larson, T., et al. 1975. The Influence of a Sulfur Dioxide Point Source on the Rain Chemistry of a Single Storm in the Puget Sound Region. Water, Air and Soil Pollution, 4:319-328.

Leslie, A. C. D. 1978. Aerosol Characterization for Sulfur Oxide Health Effects Assessment. Atmospheric Environment, 12:729-733.

Lewis, W. M., Jr., and M. C. Grant. 1980. Acid Precipitation in the Western United States. Science, 207:176-177.

Li, T. Y., and H. E. Landsberg. 1975. Rainwater pH Close to a Major Power Plant. Atmospheric Environment, 9:81-88.

Likens, G. E. 1972. The Chemistry of Precipitation in the Central Finger Lakes Region. Cornell University Water Resources and Marine Science Center, Ithaca, New York, Technical Report 50.

Likens, G. E. 1976. Acid Precipitation. Chemical and Engineering News, 54(48):29-31.

Likens, G. E., and F. H. Bormann. 1974. Acid Rain: A Serious Regional Environmental Problem. Science, 184:1176-1179.

Likens, G. E., F. H. Bormann, and J. S. Eaton. 1980. Variations in Precipitation and Streamwater Chemistry at the Hubbard Brook Experimental Forest During 1964 to 1977. In: Effects of Acid Precipitation on Terrestrial Ecosystems. Nato Conference Series I: Ecology, Vol. 4. Plenum Press, New York.

Liljestrand, H. 1976. Acid Rain and Atmospheric Acid Transport in Southern California. Master's Thesis, California Institute of Technology, Pasadena, California.

Liljestrand, H. M., and J. J. Morgan. 1978. Chemical Composition of Acid Precipitation in Pasadena, California. Environmental Science and Technology, 12(11):1271-1273.

Liljestrand, H. M. and J. J. Morgan. 1979. Error Analysis Applied to Indirect Methods for Precipitation Acidity. Tellus, 31:421-431.

Lioy, P. J. et al. 1980. The Distribution and Transport of Sulfate "Species" in the New York Metropolitan Area During the 1977 Summer Aerosol Study. Atmospheric Environment, 14:1391-1407.

Lioy, P. J., et al. 1981. The Occurrence of Ozone and Sulfate in the Northeastern U.S. Under Summertime Conditions. Presented at 74th Annual Meeting of the Air Pollution Control Association, Philadelphia, Pennsylvania, June 21-26.

Liu, S. C., et al. 1977. Sources and Sinks of Atmospheric N_2O and the Possible Ozone Reduction Due to Industrial Fixed Nitrogen Fertilizers. Tellus, 29:251-263.

Lodge, J. P., Jr., et al. 1968. Chemistry of United States Precipitation, Final Report on the National Precipitation Sampling Network. National Center for Atmospheric Research, Boulder, Colorado.

Lynch, M. C. 1980. Old Ice Indicates Acid Was Present in Rain Long Ago. Wall Street Journal (issue date unknown).

Martin. A. 1979. Survey of the Acidity of Rainfall Over Large Areas of Great Britain. Science of the Total Environment, 10:119-130.

MacCracken, M. C. 1979. The Multistate Atmospheric Power Production Study - MAP3S. Chapter 12. Prepared by Lawrence Livermore Laboratory, University of California, Livermore, California for U.S. Dept. of Energy. DOE/EV-0040.

McColl, J. G. 1980. A Survey of Acid Precipitation in Northern California. Prepared for University of California and California Air Resources Board under Project Nol CA-B-SPN-3664-H and Contract No. A7-149-30.

McColl, J. G. and D. S. Bush. 1978. Precipitation and Throughfall Chemistry in the San Francisco Bay Area. Journal of Environmental Quality, 7(3):352-357.

Miller, J. M. 1979. The Acidity of Hawaiian Precipitation as Evidence of Long-Range Transport of Pollutants. Presented at the Conference on Long-Range Transport of Pollutants, Sofia, Bulgaria.

Miller, J. M. 1980. NOAA's Present and Future Role in the Acid Rain Research. Presented at The National Symposium on Acid Rain, Pittsburgh, Pennsylvania, September 23-24.

Miller, J. M., J. N. Galloway, and G. E. Likens. 1978. Origin of Air Masses Producing Acid Precipitation at Ithaca, New York. Geophysical Research Letters, 5(9):757-760.

Mohnen, V. A. 1981. Testimony Before the U.S. Environmental Protection Agency in the Matter of Petitions of the State of New York and Commonwealth of Pennsylvania under Section 126 of the Clean Air Act for Interstate Pollution Abatement, June 19.

Morgan, J. J., and H. M. Liljestrand. 1980. Measurement and Interpretation of Acid Rainfall in the Los Angeles Basin. California Institute of Technology.

Nader, J. S. Primary Sulfate Emissions from Stationary Industrial Sources. 1980. In: Atmospheric Sulfur Deposition, Environmental Impact and Health Effects. Ann Arbor Science Publisher, Inc., Ann Arbor, Michigan.

National Academy of Science. 1975. Air Quality and Stationary Source Emission Control. Senate Committee Report.

Nisbet, I. 1975. Sulfates and Acidity in Precipitation: Their Relationship to Emissions and Regional Transport of Sulfur Oxides. In: Commission on Natural Resources, National Academy of Sciences, National Academy of Engineering, National Research Council, Air Quality and Stationary Source Emission Control, prepared for the Committee on Public Works, U.S. Senate.

Ottar, B. 1977. International Agreement Needed to Reduce Long-Range Transport of Air Pollutants in Europe. Ambio, 6(5):262-266.

Pack, D. H. 1980. Precipitation Chemistry Patterns: A Two-Network Data Set. Science, 208:1143-1146.

Patrick, R., V. P. Birnette, and S. G. Halterman. 1981. Acid Lakes from Natural and Anthropogenic Sources. Science, 211:446-448.

Penkett, S. A., et al. 1979. A Study of SO_2 Oxidation in Stored Rainwater Samples. Atmospheric Environment, 13:139-147.

Perhac, R. M. 1978. Sulfate Regional Experiment in Northeastern United States: The 'SURE' Program. Atmospheric Environment, 12:641-647.

Pfeiffer, M. H., and P. J. Festa. 1980a. Acidity Status of Lakes in the Adirondack Region of New York in Relation to Fish Resource. Presented at Nevelle Country Club.

Pfeiffer, M. H., and P. J. Festa. 1980b. Acidity Status of Lakes in the Adirondack Region of New York in Relation to Fish Resources. New York State Department of Environmental Conservation.

Pierson, W. R., et al. 1980. Ambient Sulfate Measurements on Allegheny Mountain and the Question of Atmospherc Sulfate in the Northeastern United States. In: Aerosols: Anthropogenic and Natural, Sources and Transport, Annals of New York Academy of Sciences, 338:145-173.

Richardson, C. J., and G. E. Merva. 1976. The Chemical Composition of Atmospheric Precipitation from Selected Stations in Michigan. Water, Air and Soil Pollution, 6:385-393.

Robinson, E., and R. C. Robbins. 1968. Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants. Stanford Research Institute. Menlo Park, California. PR-6755.

Robinson, E., and R. C. Robbins. 1975. Gaseous Atmospheric Pollution from Urban and Natural Sources. In: The Changing Global Environment, D. Reidel Publishing Co., Boston. pp. 111-123.

Scheider, W. A., D. S. Jeffries, and P. J. Dillon. 1981. Bulk Deposition in the Sudbury and Muskoka-Haliburton Areas of Ontario During the Shutdown of Inco, Ltd. in Sudbury. Atmospheric Environment, 15:945-956.

Schofield, C. 1976. Acid Precipitation: Effects on Fish. Ambio, 5:228-230.

Schroeder, M. J., and C. C. Buck. 1970. Fire Weather. U.S. Department of Agriculture, Agricultural Handbook No. 360.

Science News. 1980. The Lead Factor in Acid Rainwater. Science News 117:410.

Semonin, R. G. 1976. The Variability of pH in Convective Storms. Water, Air, and Soil Pollution 6:395-406.

Shannon, J. D. 1979. The Advanced Statistical Trajectory Regional Model (ASTRAP). Argonne National Laboratory. Report No. ANL/RER-79-1.

Shannon, J. D. 1981. A Model of Regional Long-Term Average Sulfur Atmospheric Pollution, Surface Removal, and Net Horizontal Flux. Atmospheric Environment, 15:689-701.

Sigma Research, Inc. 1979. Proceedings: Advisory Woskshop to Identify Research Needs on the Formation of Acid Precipitation. EPRI EA-1074, WS-78-98, Workshop Report.

Sharpe, W. E., E. S. Young, and D. R. Hershey. 1980. Lead and Cadmium in Union County Cistern Water Supplies. Rural Development, 4(4).

Soderlund, R., and B. H. Svensson. 1976. The Global Nitrogen Cycle. In: Nitrogen, Phosphorus, and Sulfur - Global Cycles. Ecology Bulletin. (Stockholm), 22:23-73.

Spaite, P. W., et al. 1980. Acid Rain: The Impact of Local Sources. Prepared for U.S. Department of Energy by PEDCo Environmental, Inc. under Contract No. DE-APZ1-81MC 17131.

Tanaka, S., et al. 1980. Sulfur and Associated Elements and Acidity in Continental and Marine Rain from North Florida. Journal of Geophysical Research, 85(C8):4519-4526.

Tonnessen, K., and J. Harte. 1981. The Potential for Acid Precipitation Damage to Aquatic Ecosystems of the Sierra Nevada, California (USA). Energy and Environment Division, Lawrence Berkeley Laboratory, Berkeley, California. Presented at Symposium on Acid Rain, San Francisco, California, January 14-15.

Topal, L. E., et al. 1981. Quality Assurance Handbook for Precipitation Chemistry Measurement Systems. Draft report prepared for U.S. EPA under Contract No. 68-02-3262.

Turner, D. B. 1979. Atmospheric Dispersion Modeling, A Critical Review. JAPCA, 29(5):502-519.

United Nations. 1952. World Energy Supplies in Selected Years, 1929-1950. Statistical Papers Series J, No. 1.

United Nations. 1976. World Energy Supplies 1950-1974. Department of Economic and Social Affairs. Statistical Papers, Series J, No. 19.

United Nations. 1979. World Energy Supplies 1973-1980. Department of International Economic and Social Affairs. Statistical Papers, Series J, No. 22.

United Nations Economic and Social Council, Economic Commission for Europe. 1980. Strategies and Policies for the Abatement of Air Pollution Caused by Sulphur Compounds. Report ENV/IEB/R.2, September 1.

U.S. Department of Commerce. 1975. Historical Statistics of the U.S. Colonial Times to 1970. Bureau of Census.

U.S. Department of Commerce. 1979. Climatic Atlas of the United States. National Oceanic and Atmospheric Administration.

U.S. Department of Commerce. 1981. United States-Canada Memorandum of Intent on Transboundary Air Pollution. National Oceanic and Atmospheric Administration. Atmospheric Modeling, Interim Report.

U.S. Department of Energy. 1979. Energy Information Administration. Annual Report to Congress 1979, Volume Two: Data.

U.S. Department of Energy. 1980a. Cost and Quality of Fuels for Electric Utility Plants - 1979. DOE/EIA-019(79).

U.S. Department of Energy. 1980b. State Energy Data Report. Statistical Tables and Technical Documentation 1960-1978. DOE/EIA-0214(78).

U.S. Environmental Protection Agency. 1978a. National Air Pollutant Emission Estimates, 1940-1976. EPA-450/1-78-003. July.

U.S. Environmental Protection Agency. 1978b. National Air Quality, Monitoring and Emissions Trends Report, 1977. EPA-450/2-78/052.

U.S. Environmental Protection Agency. 1979. Research Summary - Acid Rain. EPA-600/8-79-028. October.

U.S. Environmental Protection Agency. 1980. 1977 National Emissions Report: National Emissions Data System of the Aeromatic and Emissions Reporting System. EPA-450/4-80-005.

U.S. Environmental Protection Agency. 1981. Compilation of Air Pollutant Emission Factors, 2nd Edition. Publication No. AP-42.

Vermeulen, A. J. 1980. The Acidic Precipitation Phenomenon. A Study of this Phenomenon and of a Relationship Between the Acid Content of Precipitation and the Emission of Sulfur Dioxide and Nitrogen Oxides in the Netherlands. In: Polluted Rain. Proceedings of Twelfth Rochester International Conference on Environmental Toxicity, May 21-23, 1979. Plenum Press Publishers, New York.

Washington Post. 1981. Acid Rain Seen Threatening 'A Disaster' in the Sierra Nevadas. The Washington Post, February 16. p. A22.

Whelpdale, D. M. 1978. Large-Scale Atmospheric Studies in Canada. Atmospheric Environment, 12:661-670.

Whitby, K. T. 1980. Aerosol Formation in Urban Plumes. In: Aerosols: Anthropogenic and Natural, Sources and Transport, Annals of New York Academy of Sciences, 338:258-275.

Whitehead, H. C. and J. H. Feth. 1964. Chemical Composition of Rain, Dry Fallout and Bulk Precipitation at Menlo Park, California 1957-1959. Journal of Geophysical Research 69(16):3319-3333.

Wolff, G. T., et al. 1978. Acid Precipitation in the New York Metropolitan Area: It's Relationship to Meteorological Factors. Environmental Science and Technology, 13(2):209-212.

Wood, T. 1975. Acid Precipitation. Sulfur in the Environment, Missouri Botanical Garden, St. Louis. p. 189.

APPENDIX A

CASE STUDY ANALYSIS OF SOURCES OF ACID RAIN IN THE NORTHEASTERN UNITED STATES

INTRODUCTION

The Northeastern United States was selected for case study analysis because the acidity of the rain falling there is greater than in other parts of the country, and also because the sources responsible for the acid rain have been the subject of considerable controversy.

The area represented in this case study is the eight-state region of the northeastern United States extending 200 miles in all directions, the Adirondack Mountains. As shown in Figure A-1, it includes all or portions of the States of New York, New Jersey, New Hampshire, Rhode Island, Connecticut, Vermont, Pennsylvania, and Massachusetts. Winds to the Adirondack area are primarily out of the southwest and northwest, although during the summer months they are often from the south, moving from New York City northward through Albany toward the Adirondacks (U.S. Department of Commerce 1979). Average temperatures range from about 20° to 40°F in January to about 60° to 85°F in July. Unlike Florida and California, normal precipitation shows little month-to-month variation in the Northeast, except that it is somewhat heavier in the warmer months. Rain or snow occurs 10 days per month or 1 out of every 3 days in the Northeast.

OCCURRENCE OF ACID RAIN

The Northeast is the first area in the United States where acid precipitation was found, and current measurements show some of the lowest precipitation pH values in the Nation. Although data are limited, there are indications that rainfall was not always acid in the Northeast but became so sometime between the 1920's and the 1950's. Precipitation in Geneva, New York, between 1919 and 1928 was analyzed and found to contain carbonic acid; for this reason, it is believed to have had a pH value ranging from 5.46 to 6.36 (Sigma Research, Inc. 1979; Likens 1972). Other parts of eastern North America such as Virginia and Tennessee had rainfall with calculated pH levels ranging from 5 to 7 in the 1920's (Cogbill 1980).

The earliest measured pH values are from Mt. Washington, New Hampshire, where the pH of cloudwater was measured at 4.5 in 1937 to 1940, and Washington, D.C., where the pH of raindrops was measured at 4.2 in 1940 (Cogbill 1980). By the 1950's, the pH of rainfall in New York and other northeastern states was calculated to be about 4.5, indicating a possible 10-fold

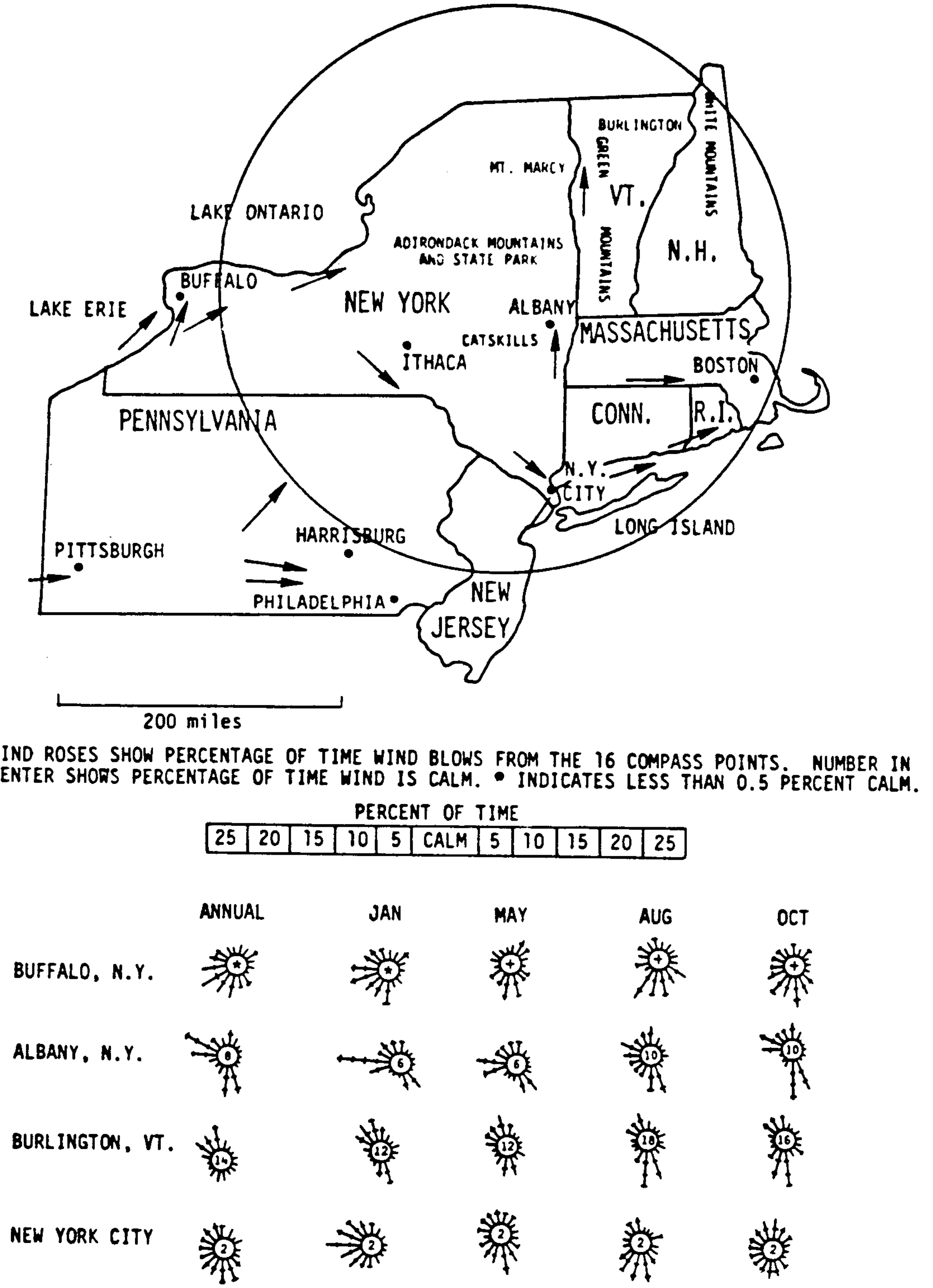

Figure A-1. Northeastern case study area. Circle describes area having 200-mile radius with center at foothills of Adirondacks. Arrows show annual prevailing wind directions. Wind roses show seasonal changes in surface winds from cities in New York and Vermont (U.S. Department of Commerce 1979).

increase in acidity over that which was thought to have existed previously (Cogbill and Likens 1974). Confidence in these data sets is limited, however, because sampling sites in the different time periods were not the same, because sample collection methods varied, and because the pH values were measured by outdated techniques or were calculated.

Nevertheless, it seems that an increase in acidity occurred at some time during the 30-year period from the 1920's to the 1950's. Likens and Bormann (1974) have suggested that the change occurred closer to 1950 as a consequence of a reduction in alkaline fly-ash emissions from coal-fired boilers in combination with an increase in SO_x and NO_x emissions.

Evidence of continued increases in rainfall acidity since the 1950's has been developed by Cogbill and Likens (Cogbill and Likens 1974; Likens 1976). Using the earliest available precipitation monitoring data for New York and other northeastern states, they performed calculations designed to reconstruct the original pH values of the samples. From these calculated pH values, they developed isopleth maps showing the pH of rainfall in the Northeast in 1955-56. Next, they compared these results with data from a 1965-66 monitoring study in which the pH values of rainfall samples were also back-calculated, and with 1972-73 monitoring data based on measured pH values. The pH isopleths for the Northeast from the three periods are often displayed side by side, as shown in Figure A-2, and have been used to support claims of increasing and more widespread acid rain.

The comparison of these isopleths for purposes of demonstrating trends has been criticized for several reasons. First, the sampling methods used in these studies were significantly different. Because the 1955-56 samples included both wet and dry precipitation, the calculations by Cogbill and Likens are likely to show less acidity than would be expected if only wet precipitation had been collected, as in 1965-66 and 1972-73. In other words, it is likely that the actual pH of the rainfall in the 50's was more acid than the isopleths indicate.

Second, it is now known that the early samples were stored inappropriately, so that changes in sample chemistry could have been large enough to shift the pH by as much as 0.5 unit.

Third, because pH levels have been found to vary with location, some critics believe that a valid trend comparison can be made only among identical monitoring sites. For the three periods compared by Cogbill and Likens, the monitoring sites were often different. When one compares values from only the 10 sites that were common to the 1955-56 and 1965-66 studies, no trend can be seen; four of the ten samples were higher in pH value, two were lower, and four remained the same (GCA 1981). Similarly, when isopleths of the 1965-66 study are compared with isopleths from the 1972-73 study, acid rain appears to be spreading; yet in this case, only eight monitoring sites were common to both studies. Of these, the samples from three were higher in pH value, two were lower, and three remained the same, indicating no net change or trend (GCA 1981). Comparison of values from sites common to the 1955-56 and 1972-73 studies gives the same result (GCA 1981).

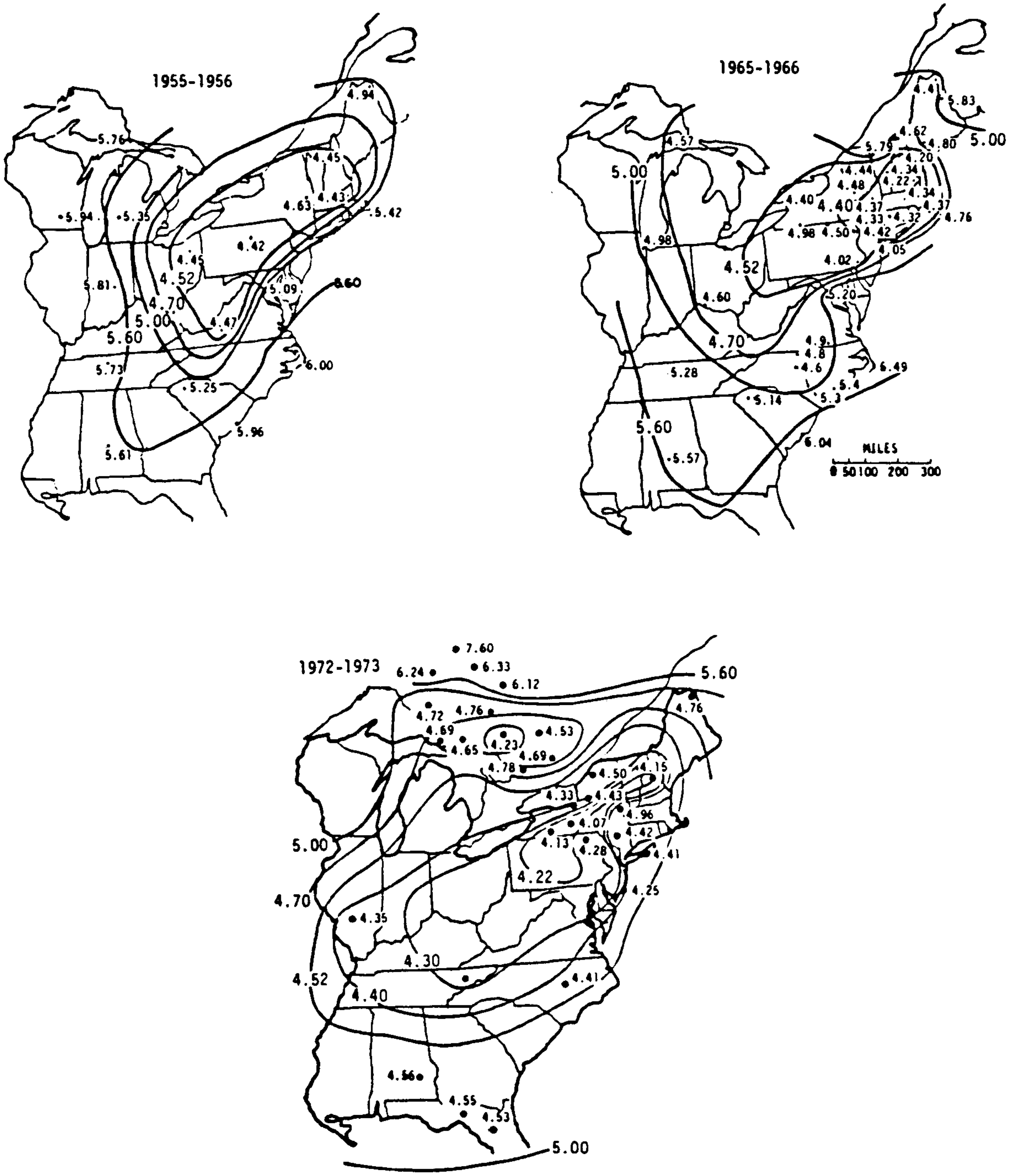

Figure A-2. Isopleths of the weighted annual average pH of precipitation in the eastern United States in 1955-56, 1965-66, and 1972-73 (Cogbill and Likens 1974; Likens 1976).

Even with these limitations on earlier isopleth data, one can still conclude with reasonable probability that acid rain has increased in intensity and occurrence in the Northeast since the 1920's. But this conclusion then leads to the question of why the expansion or spread of acid rain appears to be moving southwestward from New York and Pennsylvania toward Florida and Illinois instead of farther toward the East, a movement that would be consistent with the direction of prevailing winds.

If the observed southwestward expansion of acid deposition is real, one can ask to what extent it is due to long-range transport of pollutants from increased coal consumption in the Midwest or is related to local changes in fuel consumption patterns within the affected areas. Historical fuel consumption patterns for the northeastern states, for example, suggest that the increases in oil consumption beginning in the 1940's and continuing to the 1970's may account for some of the increasing acidity of rainfall in those states. The Southeast has also required increasing fuel supplies in the past 20 years because of the growth and expansion of urban and industrial activities; this in turn has led to an increase in emissions of SO_x and NO_x. Thus, there is reason to believe that the spread of acid rain parallels the spread of urban and industrial development. Fuel use trends in the Northeast are addressed in detail later in this Appendix. The Southeast is not examined as a region but is addressed through a detailed study of Florida in Appendix C.

The supposition of a trend toward increasing acidity, especially since the 1960's, has also been disputed on the grounds that many northeastern monitoring sites surveyed from 1964 to 1970 have shown no significant trend over the time period, even though they receive acid precipitation. Time series of measurements at nine USGS sites in New York and Pennsylvania show no trend over the entire 1965-1973 sampling period, as seen in Figure A-3. The 1964-1977 data from Hubbard Brook, New Hampshire, (Figure A-4) also show no strong evidence of a trend toward increasing acidity. Five years of monitoring in Washington, D.C., by NOAA (Figure A-5) show an opposite trend--a slow but steady increase in pH (Miller 1980).

One investigator has stated that when the data from the few midwestern monitoring sites included in the 1965-66 isopleths are interpreted on the basis of a measurement uncertainty of 0.5 pH unit, no evidence of westward expansion of acidity can be established (GCA 1981). It also has been pointed out that the apparent increase of acidity in the Southeast, shown by published isopleth maps (see Figure A-2), may well have resulted from the use of an incomplete data base (GCA 1981). Cogbill and Likens noted regarding their study that the decrease in pH levels in New York and New England evident in the 1965-66 data was caused primarily by greater resolution provided by additional monitoring sites (Cogbill and Likens 1974).

Chemical analysis of precipitation in the Northeast has shown that sulfates are the dominant anion; the sulfates are therefore thought to be largely responsible for the acidity. Approximately 60 to 70 percent of precipitation acidity is attributed to sulfate, 30 percent to nitrate, and the remainder to chloride. During the last decade, however, the proportions

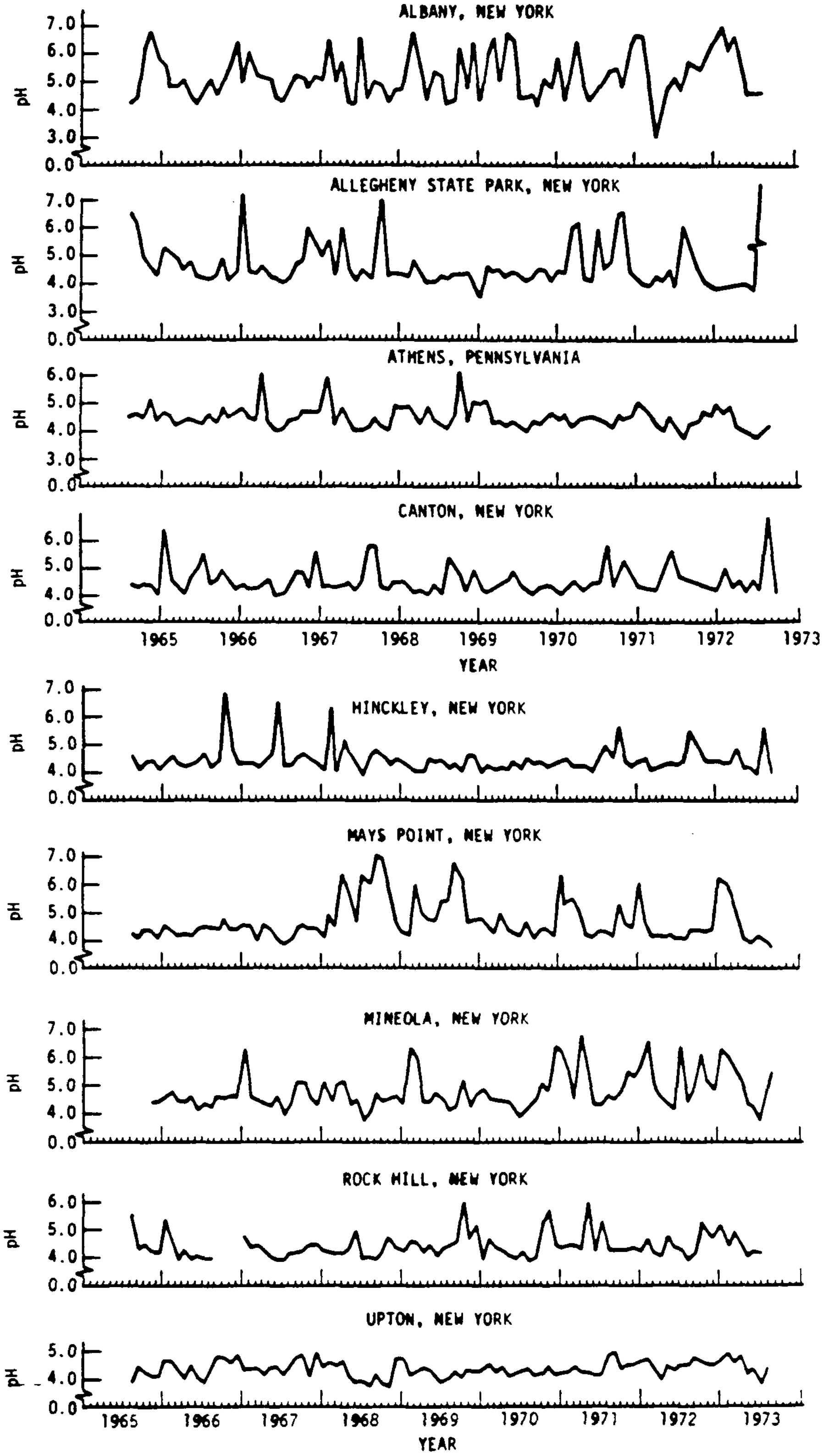

Figure A-3. History of acidic precipitation at various sites in New York and Pennsylvania (Harr and Coffey 1975).

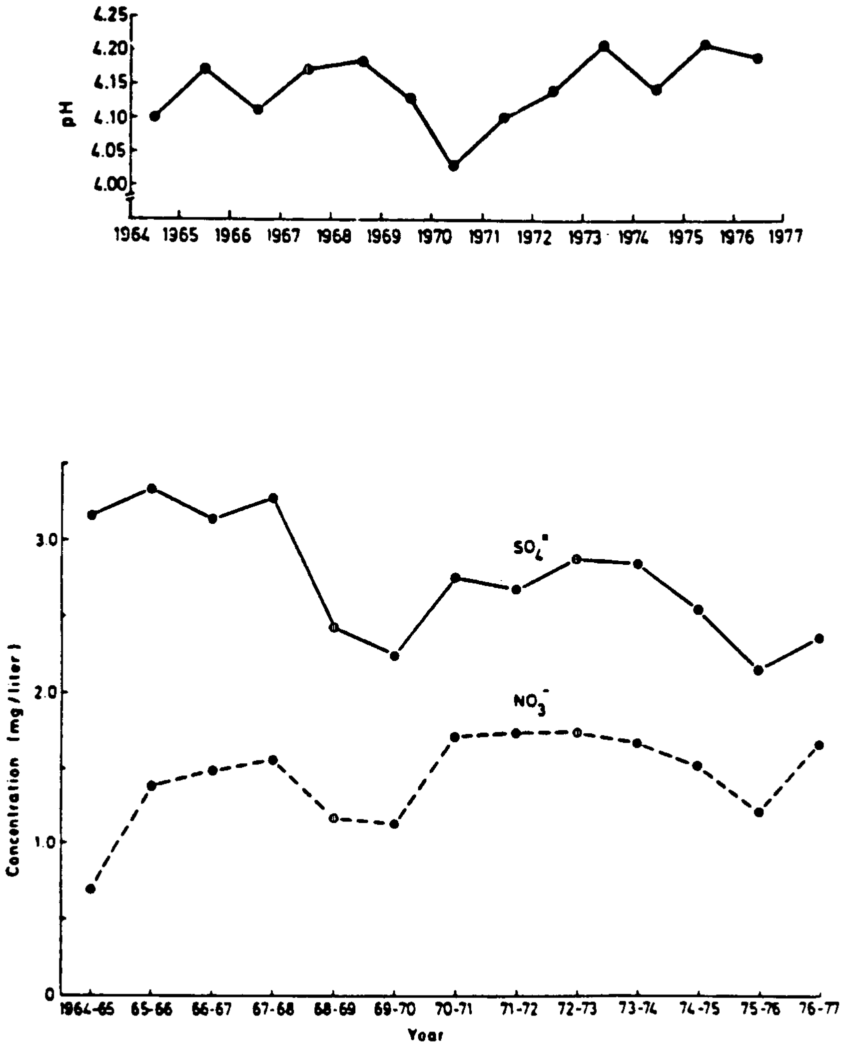

Figure A-4. Annual weighted pH and concentrations of sulfate and nitrate in precipitation at the Hubbard Brook Experimental Forest from 1964 to 1977 (Likens, Bormann and Eaton 1980).

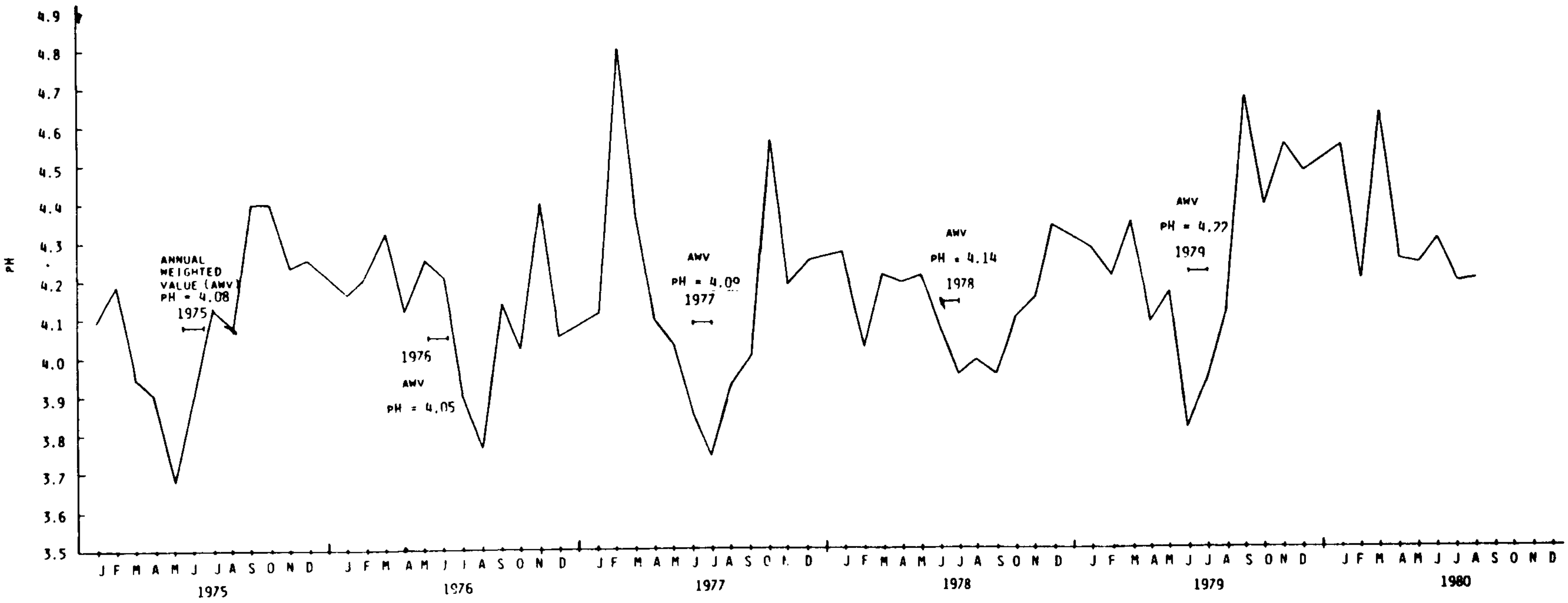

Figure A-5. Acidity of rainfall in Washington, D.C. from 1975 to 1980 (Miller 1980).

attributable to nitrate and chloride contributions have been increasing while the proportion attributable to sulfate has been decreasing (Glass, Likens, and Dochinger 1978; Likens 1976). Even though sulfuric acid is thought to be the dominant supplier of hydrogen ions, the observed increases in total acidity may be related not to total sulfur input, but rather to the type of sulfur input (i.e., primary acidic sulfates, metal catalysts, carbon, etc.) or to increases in nitrogen input.

A year-long monitoring program was conducted at Yonkers, New York, in 1974, covering 58 precipitation events. Results show that the events were highly acidic and that sulfate, nitrate, and to some extent chloride concentrations contributed to this acidity (Jacobsen, Heller, and Van Leuken 1976). The maximum pH recorded during the study was 4.9, the minimum was 3.4, and the mean was 4.1. In general, sulfate ions comprised the largest portion of the acidity, but in some instances the nitrate portions were larger. A closer look at the data revealed that the lower pH value of the event, the greater was the influence of nitrate in the sample.

Rainfall acidity appears to peak during the summer months in the Northeast, as shown in Figure A-6. This seasonal peak is attributed primarily to higher temperatures, which increase the oxidation rate and therefore increases the formation of sulfates and nitrates. Although the frequency of rainfall and variations in emission levels can also be seasonal factors, they are probably of lesser importance in the Northeast.

Rainfall in northeastern rural areas does not appear to be any more or less acid than rainfall in the cities. For example, a study of 200 wet precipitation samples collected from February to September 1975 at two rural locations (in the Adirondack Mountains of New York and the White Mountains of New Hampshire) and at the semi-urban community of Ithaca, New York, showed the same range of pH values (pH 3.5 to 4.5) (Galloway, Likens, and Edgerton 1976).

In another urban-rural study, 72 precipitation events occurring between 1975 and 1977 were monitored within the New York metropolitan area (Wolff et al. 1978). Samples were collected at eight locations--one rural, three urban, and four suburban. The mean pH of all events was 4.28, the lowest values occurring during July through September and the maximum values from October through December. The lowest pH values occurred in precipitation from showers and thunderstorms associated with cold fronts and air masses from the west and southwest. Urban-rural differences were not apparent. The weighted average pH value based on 183 observations at the suburban sites was 4.33; at the three urban sites, the weighted average pH was 4.36 based on 116 observations, and at the one rural site the average was 4.25 based on 25 observations.

Preliminary findings from the Sulfate Regional Experiment (SURE) in the Northeast have shown that the pH levels can vary drastically from one storm to the next. Measurements from precipitation events only a few days apart have varied by as much as 2.0 or 2.5 pH units (Combustion 1980). If it is assumed that within the period of a few days emissions from all sources remain steady, then the pH variance must be due to other factors. Temperature, wind direction and speed, levels of other pollutants (ozone, ammonia,

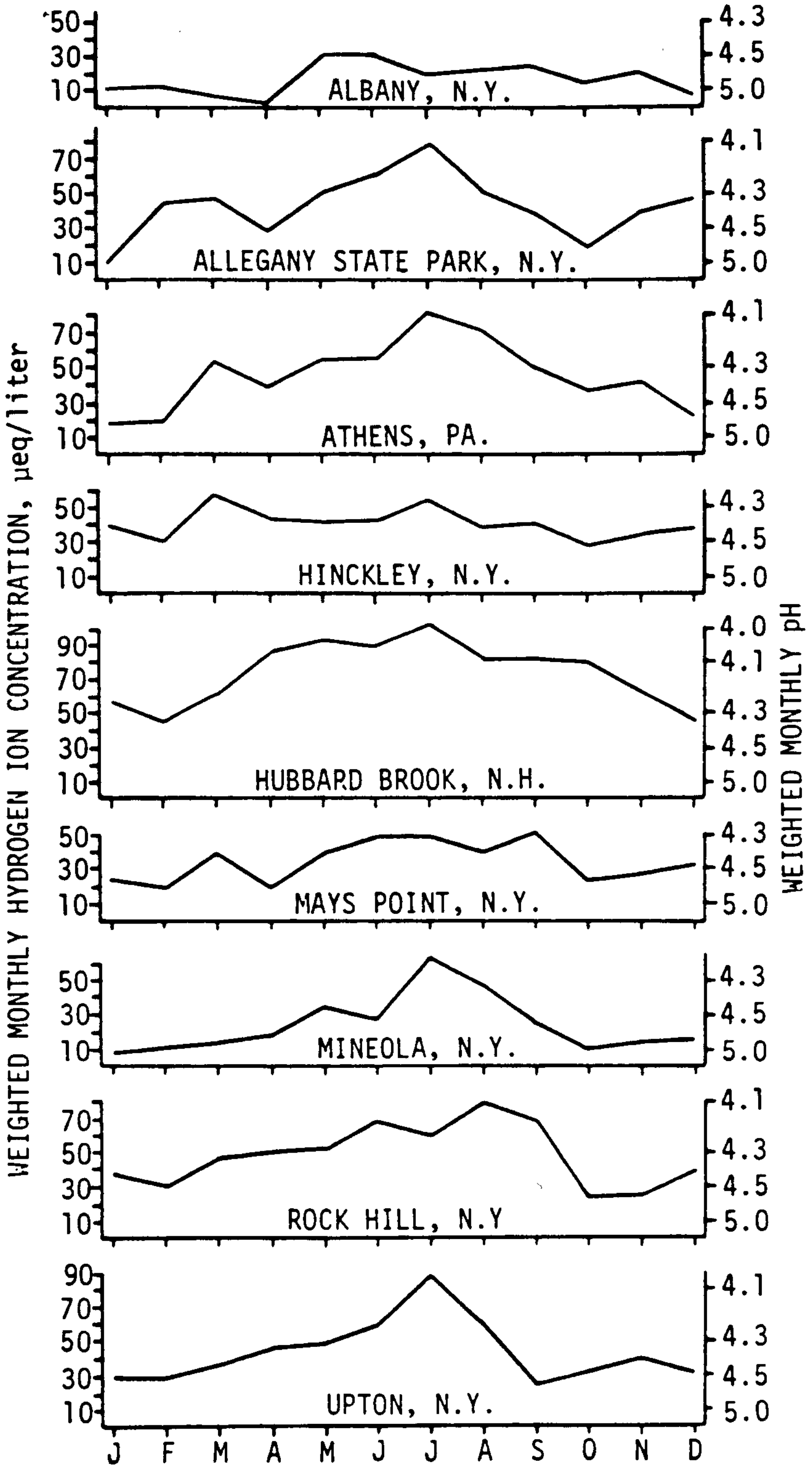

Figure A-6. Weighted hydrogen ion concentration and pH of precipitation curves showing seasonal peak in rainfall acidity during summer months in the northeastern United States. The curves are based on 8 or more years of data for each location (Hornbeck, Likens, and Eaton 1977).

metals, soil dust), sunlight intensity, mixing layer depth, precipitation in upwind areas, and other factors all combine to influence the pH measured at any given location.

SOURCES OF ACID RAIN IN THE NORTHEAST

Many have attributed the acidity in the Northeast to discharges from remote coal-burning power plants that emit large amounts of SO_x and NO_x from tall stacks. Most of these sources are located 500 miles or more from the Adirondacks; many are in the Ohio River Valley. They are plants of 500-MW capacity or larger, and use stacks up to 1000 or more feet tall to disperse the effluent gases over large areas. It is believed that such discharges are transported over hundreds of miles and that during this transport SO_x and NO_x are transformed to sulfate and nitrate ions, which precipitate as acid rain at distant receptors such as the Northeast sector.

Although the long-range transport theory undoubtedly accounts for some part of the acidity falling on the Northeast, other evidence indicates that sources located within the affected area should be given greater attention as potential significant contributors to the acid rain problem. These sources are examined in this section.

Natural Sources

The magnitude of natural source emissions of sulfur in the Northeast area is uncertain, though it is probably small compared with those from anthropogenic sources. Estimates based on figures of Galloway and Whelpdale (1980) indicate that natural sources in the eight-state area emit something on the order of 7×10^9 grams of sulfur per year (i.e., 7000 metric tons of sulfur).* This is less than 1 percent of the amount emitted by anthropogenic combustion sources in the area.

At some locations, biological sources may be more important than these figures indicate (Envirosphere 1980). Hitchcock believes that as much as 50 percent of the sulfate-sulfur found in the air near polluted bodies of water may arise from natural sources (Hitchcock 1976). Although much of the natural sulfur is emitted in reduced form such as hydrogen sulfide (H_2S) or carbonyl sulfide (COS), it is probably oxidized to SO_2 and sulfate in the atmosphere. Examples of such areas in the Northeast where natural sources could be particularly important are Buffalo on Lake Erie, Niagara Falls and Rochester on Lake Ontario, and New York City near Long Island Sound. Although the evidence to this effect is now limited, it deserves further investigation as part of the total effort to correctly identify and rank contributory sources of acid rain precursors in the Northeast and elsewhere.

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* Calculations are based on work of Galloway and Whelpdale (1980) in which natural sulfur emissions in eastern United States were estimated at 0.04 Tg of sulfur per year for an area of 2.1×10^{12} m^2. This results in an average natural emission factor of 0.019 g/yr per m^2. The eight-state case study area discussed in this report has an area of 136,138 $mi^2 \times 10^9$ m^2. Applying the emission factor to this area results in an estimate of 6.7×10^9 g/yr of sulfur from natural sources.

The amount of NO_x contributed by natural sources in the Northeast is not known. The ratio to manmade emissions may range from 1:1 to 15:1 (GCA 1981). Significant amounts may be produced by lightning (U.S. EPA 1978a). Terrestrial decomposition of nitrates also results in the release of reduced nitrogen in the form of ammonia (NH_3) gas, which can then be oxidized again to NO_x in the atmosphere. This natural process may be particularly important in the Northeast because of the extensive vegetative cover. As with natural sources of SO_x, the contributory role of natural NO_x in the Northeast and elsewhere should be investigated to allow the identification and ranking of all source types in the production of acid rain.

Manmade Sources

Emissions of SO_2 and NO_x from all manmade sources in the eight-state northeastern study area are shown in Table A-1. Pennsylvania and New York are the largest emitters of both SO_2 and NO_x. The table shows that fuel combustion accounts for 89 percent of all SO_2 and 97 percent of all anthropogenic NO_x emissions in the study area.

Emissions of SO_2 and NO_x from the Ohio Valley states exceed those of the northeastern states by factors of 2 and 1.5, respectively. The SO_2 and NO_x emitted in the Northeast each constitute about 14 percent of the total United States emissions of SO_2 and NO_x, as estimated by NEDS. The northeast SO_2 emissions equal the total SO_2 emission budget for eastern Canada (Galloway and Whepdale 1980).

An analysis of SO_2, NO_x, and sulfate emissions from combustion sources was conducted for this study. The combustion emission inventory data for the Northeast study area are summarized in Tables A-2 and A-3. (Complete details are given in Appendix E.) Table A-2 shows that in the Northeast study area, combustion emissions of SO_2 arise primarily from utility fuel consumption, although industrial and commercial fuel use are also important. NO_x emissions, on the other hand, arise primarily from transportation and motor fuel consumption, followed by utility and industrial combustion processes.

Although coal burning is believed to be an important contributing factor, the burning of oil products within the Northeast and other study areas is also believed to have special significance with respect to acid rain. This significance is derived from four important facts about oil burning emissions:

1. Compared with coal firing, the firing of oil--especially residual oil--produces significantly higher quantities of primary sulfates per unit of sulfur in the fuel (Homolya and Lambert 1981; Nader 1980). Primary sulfates participate directly in wet (acid rain) and dry acid deposition processes. Since they are already acidic, they need not undergo further chemical oxidation in the atmosphere.

2. Significantly higher quantities of metal catalysts such as manganese, vanadium, nickel, and graphitic carbon are contained in fuel for and emitted from oil-fired boilers than

TABLE A-1. ESTIMATED 1977 SULFUR AND NITROGEN OXIDE EMISSIONS[a]

SO_2, tons

State	Grand total all sources	Combustions sources only: Stationary fuel combustion only	Transportation only	Total fuel combustion
Connecticut	85,947	78,472	6,800	85,272
Massachusetts	302,802	288,835	10,925	299,760
New Hampshire	120,329	117,459	1,610	119,069
New York	1,021,724	935,977	34,720	970,697
New Jersey	311,726	216,167	26,339	242,506
Pennsylvania	2,495,317	2,101,216	36,457	2,137,673
Rhode Island	20,380	18,529	1,494	20,023
Vermont	11,180	9,595	1,445	11,040
8-state total	4,369,405	3,766,250[b]	119,790	3,886,040[c]
Ohio Valley[d]	9,713,943	9,250,692	105,656	9,356,348
U.S. total	31,477,757	24,928,945	856,434	25,785,379
Eastern Canada[e]	4,600,000			

NO_x, tons

State	Grand total all sources	Combustions sources only: Stationary fuel combustion only	Transportation only	Total fuel combustion
Connecticut	189,306	79,059	109,191	188,250
Massachusetts	323,654	148,548	170,131	318,679
New Hampshire	78,524	44,078	32,560	76,638
New Jersey	453,621	167,613	261,276	428,889
New York	906,342	452,716	435,524	888,240
Pennsylvania	1,023,061	550,060	424,942	975,002
Rhode Island	40,205	11,692	28,060	39,752
Vermont	26,524	4,167	21,891	26,058
8-state total	3,041,237	1,457,933	1,483,575	2,941,508[f]
Ohio Valley	4,477,960	2,909,918	1,411,787	3,321,705
U.S. total	21,736,603	11,023,056	9,415,763	20,438,849
Eastern Canada				

[a] **1977 National Emissions Report (EPA 1980).**

[b] **SO_x from stationary fuel combustion is 86 percent of eight-state total.**

[c] **SO_x from all combustion sources is 89 percent of eight-state total.**

[d] **Ohio Valley states include Ohio, Kentucky, Indiana, Illinois, and West Virginia.**

[e] **Source: Galloway and Whepdale (1980).**

[f] **NO_x from fuel combustion is 97 percent of eight-state total.**

TABLE A-2. ANTHROPOGENIC EMISSIONS OF SO_2 FROM COMBUSTION SOURCES IN THE NORTHEAST IN 1978[a] (10^3 tons)

State	Utility	Industrial	Commercial	Residential	Transportation	Total
Connecticut	25.65	43.14	23.55	5.22	5.89	103.45
Massachusetts	254.23	24.69	78.37	9.08	11.41	377.78
New Hampshire	50.24	5.36	5.24	1.62	1.80	64.26
New Jersey	115.27	67.58	56.67	8.57	17.14	265.23
New York	514.09	232.08	238.50	32.16	33.15	1,049.98
Pennsylvania	1,510.15	1,083.42	95.38	67.18	28.69	2,784.82
Rhode Island	3.92	3.97	8.20	3.62	1.44	21.15
Vermont	0.29	1.95	3.32	1.95	1.18	8.69
8-state total	2,473.84	1,462.19	509.23	129.40	100.70	4,675.36
U.S. total	18,363.26	6,755.84	1,094.38	372.37	685.34	27,271.19

[a] Based on PEDCo calculation of emissions from all combustion sources. See Appendix E for discussion of methods used to develop these estimates.

TABLE A-3. ANTHROPOGENIC EMISSIONS OF NO_x FROM COMBUSTION SOURCES IN THE NORTHEAST IN 1978[a] (10^3 tons)

State	Utility	Industrial	Commercial	Residential	Transportation	Total
Connecticut	33.37	15.54	8.67	8.27	80.76	146.61
Massachusetts	80.71	11.00	31.92	15.93	140.94	280.51
New Hampshire	12.17	2.16	2.61	2.43	24.08	43.45
New Jersey	66.00	25.34	25.67	16.61	222.05	355.67
New York	197.83	64.48	83.26	47.76	357.53	750.86
Pennsylvania	377.15	241.09	27.81	29.52	365.56	1,041.13
Rhode Island	2.14	1.85	3.44	2.54	21.14	31.11
Vermont	0.08	1.06	1.67	1.21	16.58	20.60
8-state total	769.45	362.52	185.05	124.27	1,228.65	2,669.94
U.S. total	6,113.91	2,143.22	457.92	443.46	8,176.27	17,334.78

[a] Based on PEDCo calculation of emissions from all combustion sources. See Appendix E for discussion of methods used to develop these estimates.

from coal-fired. The presence of these catalysts is probably responsible for the higher primary sulfate emissions from oil burning. In addition, once released to the atmosphere, Chang and Novakoff (1981) predict that carbon catalysis of some of these 8 catalysts can lead to further sulfate formation from sulfur oxides in the plume or ambient air.

3. Unlike coal-fired boilers, oil-fired units in the United States are largely uncontrolled. Flue gas desulfurization and particulate collection are not practiced. Also, emissions from older oil-fired boilers are generally released closer to the ground (from shorter stacks) than those from coal-fired units, and therefore have more local impact on air and rainwater quality. They are also less likely to be transported over long distances before being deposited. Coal-fired emissions released at higher elevations from newer plants undergo larger dilution volumes and therefore probably constitute a small portion of the SO_2 and sulfate measured at distant sites. In areas where large volumes of oil are consumed, such as New York City and vicinity, associated emissions would be expected to constitute the larger portion of local ambient SO_2 and sulfate concentrations (Homolya and Lambert 1981).

Fuel consumption patterns for the Northeast (Figure A-7) show that the use of coal has clearly declined, whereas the use of petroleum fuels of all types, especially residual oil and gasoline, has continued to grow since at least 1960. This pattern of decreasing coal and increasing petroleum usage began in the 1940's and has been continuing. Today, more than 60 percent of the Northeast's energy needs are met by petroleum products. New York State is first among the 50 states in terms of residual oil consumption, followed by California and Florida.

Energy (as Btu's) is consumed in near equal proportions by all sectors (utility, residential, commercial, industrial, and transportation) in the Northeast case study area (U.S. DOE 1980b). No one sector is an outstanding energy consumer. Fuel consumption patterns, however, do differ importantly among the sectors, and these differences result in different emission patterns that could have substantial influence on acid deposition in the area.

Utilities in the Northeast today are fueled primarily by oil (38 percent), followed by nuclear and hydroelectric power (32 percent), then by coal (30 percent). See Table A-4.

Figure A-8 shows the distribution of oil- and coal-consuming utilities within the eight-state study area. There are 178 utilities burning oil in the area, and many of these are small (less than 25 megawatts). Thirty-five utilities burn coal, and seven burn both coal and oil in near equal amounts.

Figure A-9 illustrates the change in utility fuel use patterns that has taken place since 1960. Based on the data presented in Table A-4, Figure A-9 shows that Northeast utility coal consumption peaked in the mid 1960's

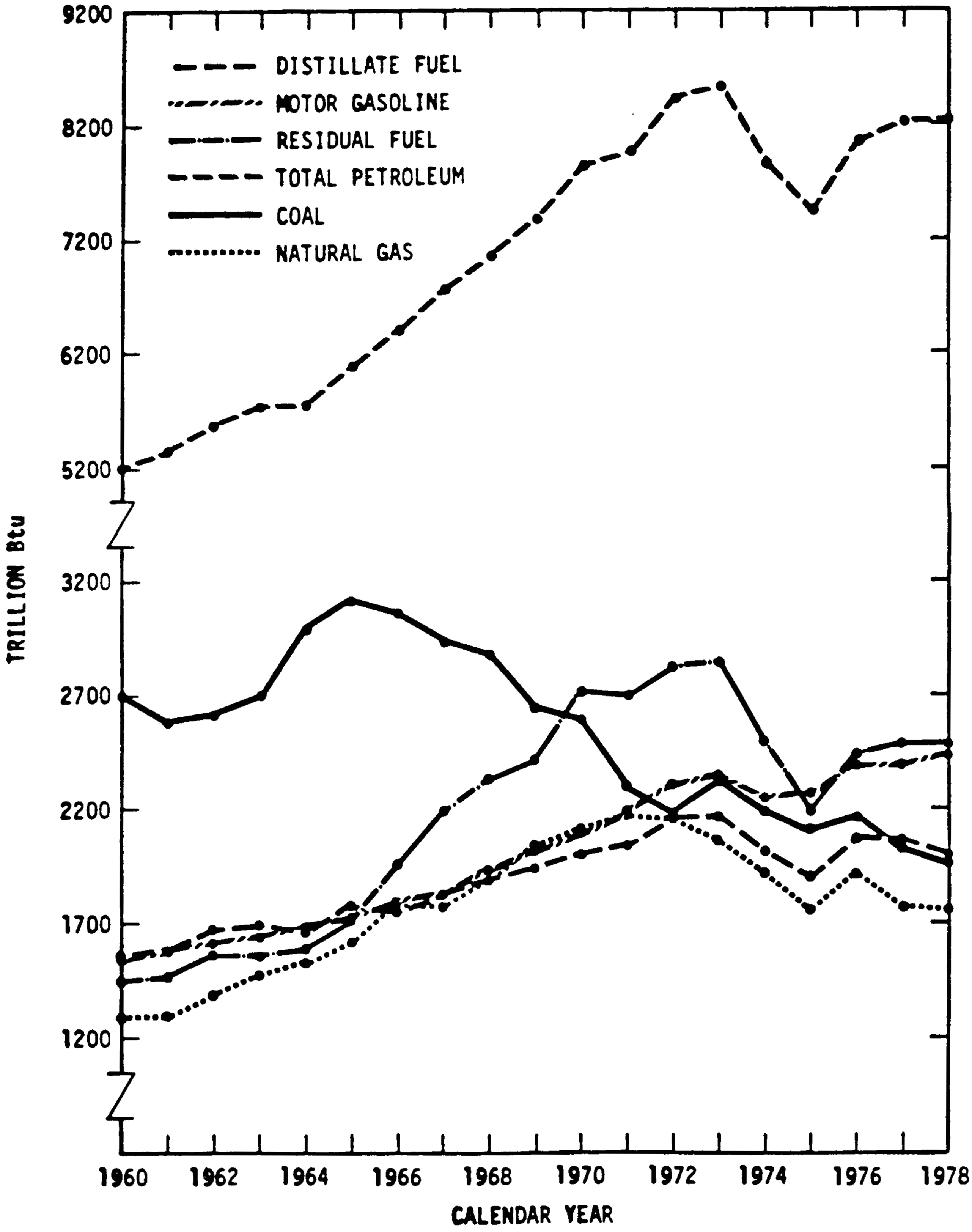

Figure A-7. Northeastern U.S. fossil fuel consumption by type (U.S. DOE 1980b).

TABLE A-4. CONSUMPTION OF FOSSIL FUEL ENERGY BY THE ELECTRIC UTILITIES IN THE NORTHEAST EIGHT-STATE REGION[a]

(10^{12} Btu)

			Petroleum			
Year	Total coal[b]	Natural gas (dry)	Distillate and jet fuel	Residual fuel	Other sources[c]	Total energy consumed
1960	1021.089	105.749	4.009	253.636	223.6	1608.0
1961	1053.496	99.406	4.660	253.679		
1962	1081.179	111.541	4.529	267.985		
1963	1129.554	130.711	4.311	291.218		
1964	1264.771	128.128	3.743	304.391		
1965	1350.14	115.343	4.002	370.745		
1966	1356.323	109.887	3.105	483.222		
1967	1299.697	124.421	2.506	611.563		
1968	1306.379	148.917	15.210	707.623		
1969	1210.671	174.525	22.880	955.007		
1970	1151.583	174.776	66.112	1172.621		
1971	1113.522	166.029	104.511	1260.789		
1972	1052.061	117.362	180.059	1384.629		
1973	1163.617	105.814	146.544	1375.082		
1974	1106.347	74.067	148.143	1248.465		
1975	1111.66	26.626	75.725	1165.535		
1976	1125.485	19.875	73.695	1201.854		
1977	1116.678	15.523	78.150	1282.793		
1978	1094.897	4.164	64.511	1309.142	1169.9	3642.6

[a] U.S. DOE (1980b).

[b] Bituminous, anthracite, coals, and lignite.

[c] Includes hydroelectric power and nuclear fuel. Most of the increase is due to growth of nuclear fuel.

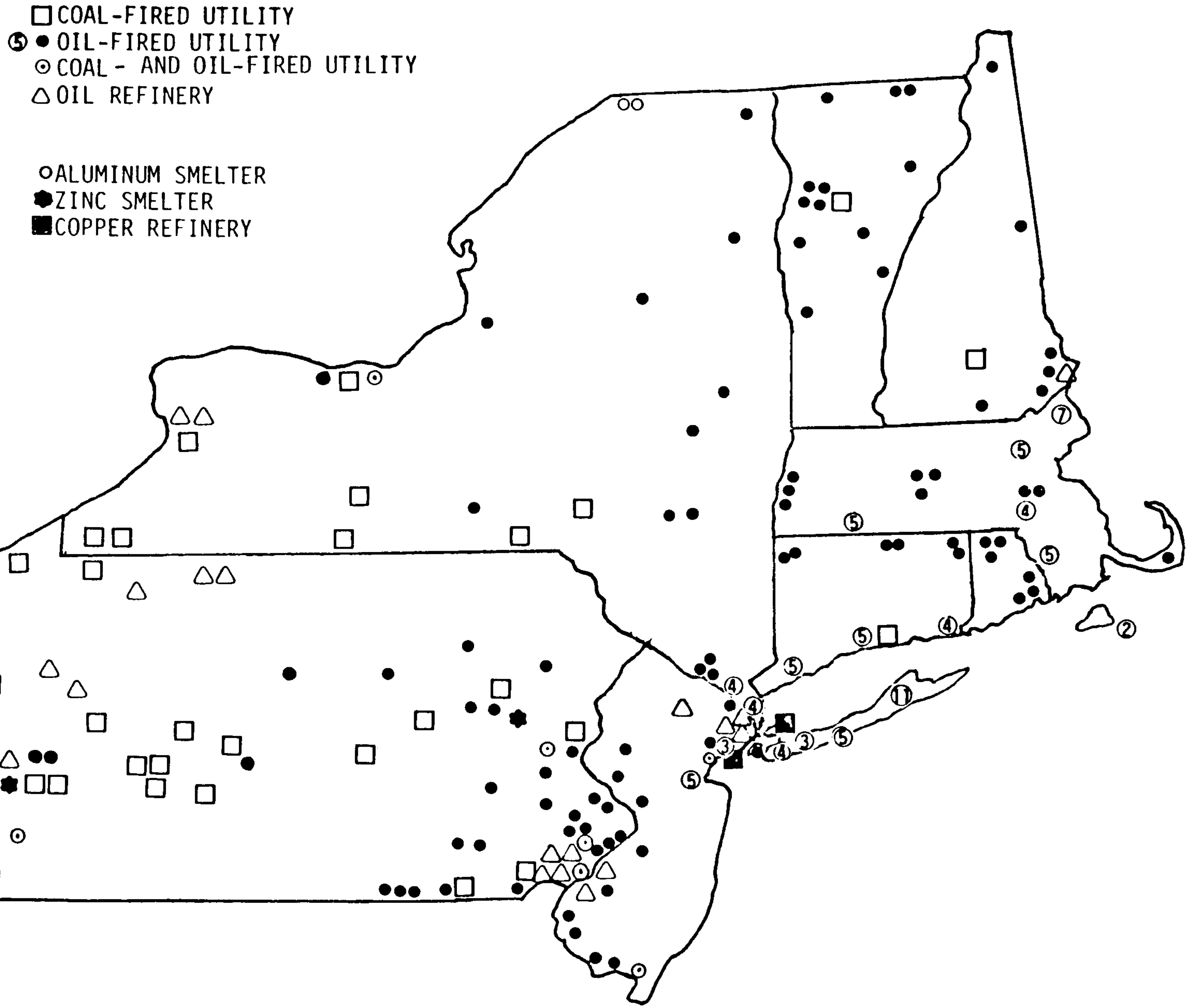

Figure A-8. Coal and oil-fired sources in the Northeast.

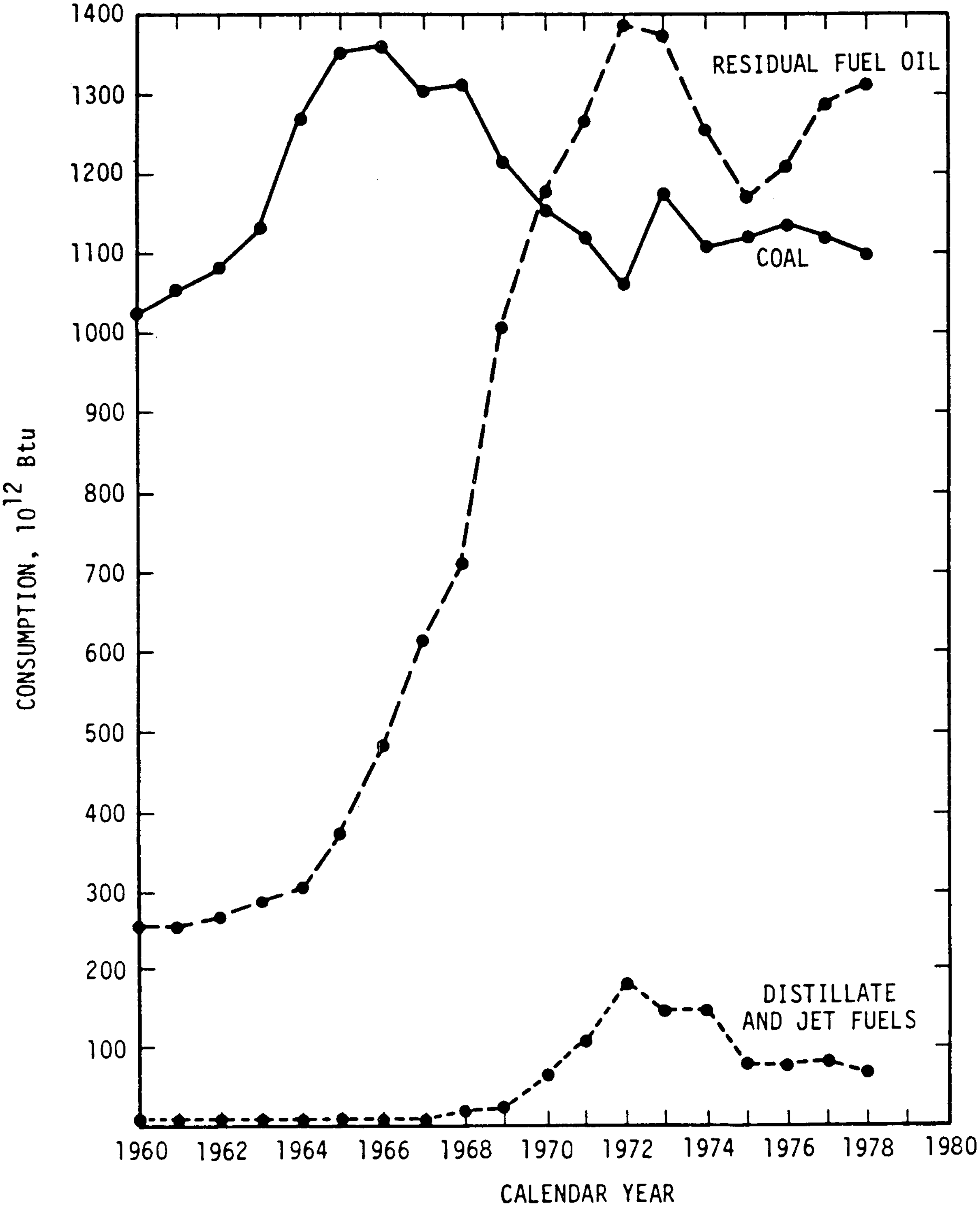

Figure A-9. Fuel consumption patterns in the northeastern U.S. utility sector (U.S. DOE 1980b).

and was subsequently displaced by residual oil as the dominant fuel in the early 1970's. In 1960, Pennsylvania utilities consumed the most coal (441×10^{12} Btu), followed by New York (327×10^{12} Btu), New Jersey (95×10^{12} Btu), Connecticut (74×10^{12} Btu), and Massachusetts (65×10^{12} Btu) utilities. Utilities in Vermont, Rhode Island, and New Hampshire used relatively little coal (total 19×10^{12} Btu). Between 1960 and 1978, New York utilities halved their use of coal and dramatically increased their residual oil consumption by a factor of 9, from 66×10^{12} Btu in 1960 to 546×10^{12} Btu in 1978. This switch to oil has made New York the largest consumer of residual oil in the nation. New Jersey utilities also halved their use of coal and doubled their consumption of residual oil during this 18-year period. Vermont, Rhode Island, Connecticut, and Massachusetts utilities completely eliminated their use of coal and replaced it with residual oil. In contrast, while all the other states were busy cutting coal consumption, Pennsylvania doubled its use to 866×10^{12} Btu, thereby increasing its share of Northeast utility coal consumption from 43 percent in 1960 to 79 percent in 1978.

Today 40 percent of all the residual oil burned in the United States is burned in the Northeast study area, and of that amount, 56 percent is used by the utilities. The remainder is consumed by the commercial and industrial sectors. See Table A-5.

Table A-6 gives data on the sulfur oxide emissions from oil-burning sources in the Northeast and United States. The data show that SO_2 emissions from oil burning in the Northeast are one-third the total SO_2 emitted nationally from oil firing. Oil burning is also responsible for one-third of the SO_2 emitted in the Northeast from all combustion sources (compare with Table A-2).

Figure A-10 shows that significant amounts of primary sulfates are emitted by coal- and oil-burning sources in New York and Pennsylvania. Most of these emissions in eastern Pennsylvania and throughout the rest of the case study area are attributed to oil burning. The high values in Ohio, Indiana, and western Pennsylvania reflect the higher coal consumption rates in these areas. Comparison of Figure A-10 with Figure A-11 shows that the amount of primary sulfate emissions associated with the utility and industrial sectors varies among the states. It should be noted that the emission factors for sulfates from utility and industrial oil-fired boilers are at least 5 times higher than those given in the emissions handbook (U.S. EPA 1981). Additional testing is required to substantiate emission factors from oil-fired boilers in the industrial source category. Field studies on coal-fired boilers without SO_2 controls, by contrast, have substantiated that the emissions of sulfates are in the 1 to 2 percent range of the sulfur in the fuel, as presented in U.S. EPA (1981) (Nader 1980).

The Northeast industrial sector uses both coal and oil to supply most of its energy needs. Industrial sources located within 200 to 300 miles of the Adirondack Mountains and within the Northeast case study area may be important contributors to the acid rain problem there. Of special interest are the following: the two aluminum smelters at Massina, New York, which lie only 100 km or so to the southwest of the Adirondacks. These plants

TABLE A-5. 1978 CONSUMPTION OF RESIDUAL AND DISTILLATE OILS IN STATIONARY SOURCES[a]
(10^{12} Btu)

	United States	Northeast[b]	Percentage of U.S. total
Residual oil			
Commercial	1034	637	61.6
Industrial	1454	397	27.3
Utility	3352	1309	39.1
Total	5840	2343	40.1
Distillate oil			
Residential	2238	1119	50.0
Commercial	1117	445	39.8
Industrial	1154	146	12.7
Utility	423	51	12.1
Total	4932	1761	35.7

[a] U.S. DOE (1980b).

[b] The Northeast includes the states of New York, New Jersey, New Hampshire, Vermont, Connecticut, Rhode Island, Pennsylvania, and Massachusetts.

TABLE A-6. 1978 SULFUR OXIDE EMISSIONS FROM OIL-FIRING IN STATIONARY SOURCES[a]
(10^3 tons)

	United States	Eight states	Percentage of U.S. total
Residual oil	3700.85	1397.48	37.8
Distillate oil	467.60	90.54	19.4
Total	4168.45	1488.02	35.7

[a] Based on PEDCo calculation of emissions from all oil-fired sources including small commercial and residential sources not included in NEDS data.

emit SO_2, hydrogen sulfide, acid fluorides, and aluminum particulates. Emission levels are a direct function of how well the processes at these plants are controlled. If not well monitored for anode effects, emissions may be quite high and could be contributing directly to the acidification of lakes in the Adirondacks. Sulfur emissions from these plants may amount to 2000 to 3000 metric tons/yr as SO_2.* Particulate aluminum emissions from these sources may also be partly responsible for the increased aluminum content noted in some Adirondack lakewaters.

- Several large oil refineries are operating to the southeast of the Adirondacks in New Jersey and eastern Pennsylvania, and to the west in Buffalo, New York and western Pennsylvania. These sources are some 200 to 250 miles (350 to 400 km) from the Adirondacks, a distance that is considered intermediate in terms of source, receptors, and pollutant transport. Consumption of fuel oil to operate these plants results in emissions of primary sulfate, SOx, and metal (i.e., vanadium) particulates. During the summer, surface winds from the area are directed toward the Adirondacks and may carry metals, sulfur, and other pollutants that contribute to acid rain. Two copper refineries and a zinc smelter are also located in the case study area, and they may emit particulate metals that become catalytically active in the acid rain process.

- Large steel mills are located within 400 to 500 km (250 to 300 mi) of the Adirondacks in Buffalo, New York, and Hamilton, Ontario. Farther away (about 400 mi) are the steel mills of Pittsburgh and western Pennsylvania.

- The Sudbury nickel and copper smelter is located in Ontario, some 600 to 650 km (370 to 400 mi) from the Adirondacks. It is intermediately located with respect to the Northeast, and it is the largest single source of SO_2 in the world. Winds from the Sudbury area are often directed toward the Adirondacks (Freedman and Hutchinson 1980b). Sulfur dioxide may be oxidized to sulfate in the plume by trace amounts of nickel or copper and deposited over hundreds of miles to the east and southeast of the smelter, including the Adirondacks.

Another potentially important source of precursor pollutants impacting the study area is Canada. As much as 0.7×10^6 metric tons sulfur per year or 1.4×10^6 metric tons SO_2 per year are directed toward the United States

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* Calculation: (0.45)(wt. Al produced)(2% S) = wt. S
wt. S x 2 = wt. SO_2

For Aluminum Co. of America: (0.45)(209,000 metric tons)(0.02)(2)
= 3762 metric tons SO_2

For Reynolds Metal Co.: (0.45)(114,000 metric tons)(0.02)(2)
= 2052 metric tons SO_2

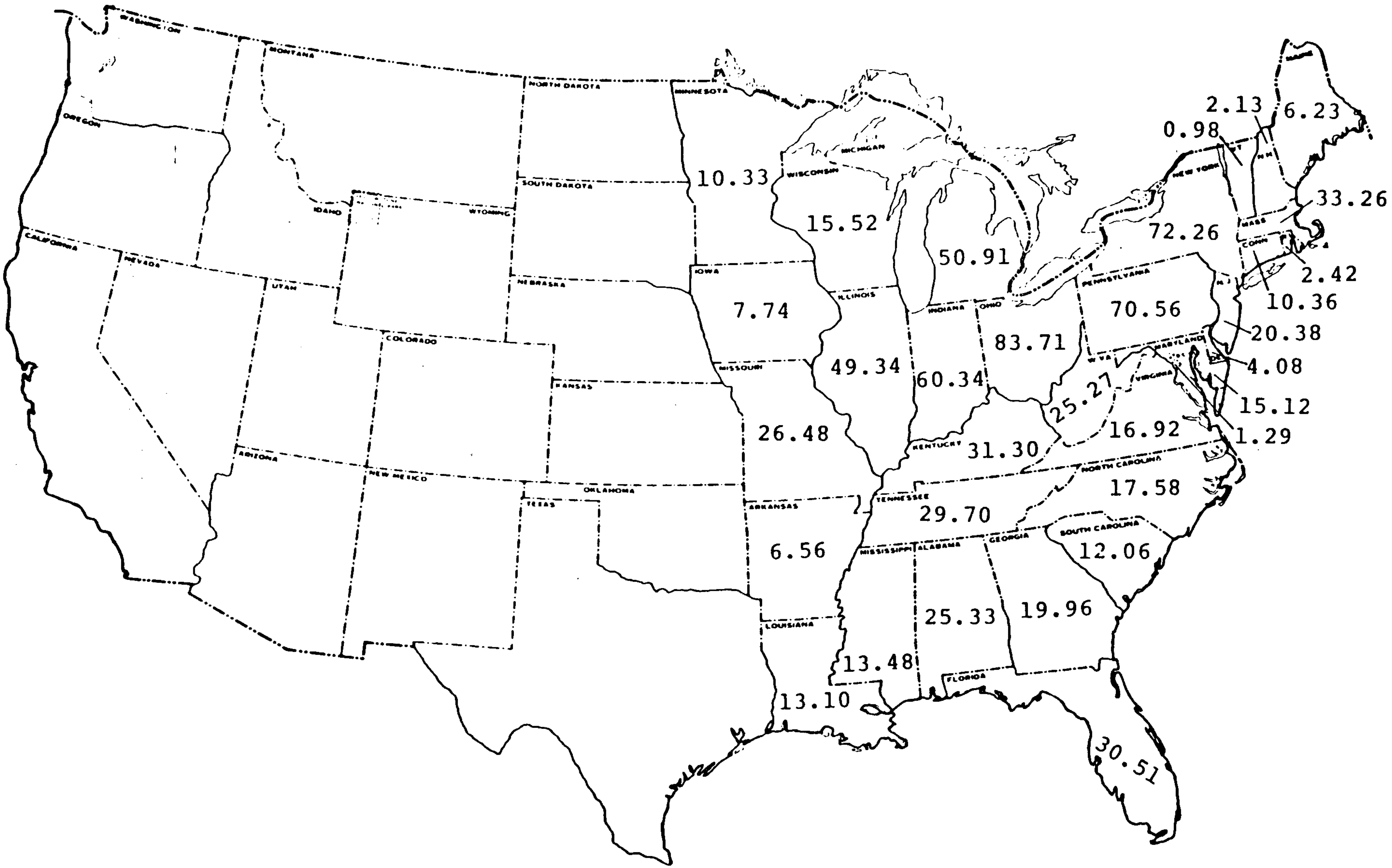

Figure A-10. Primary sulfate emissions from stationary coal and oil combustion in the eastern United States, 10^3 tons.

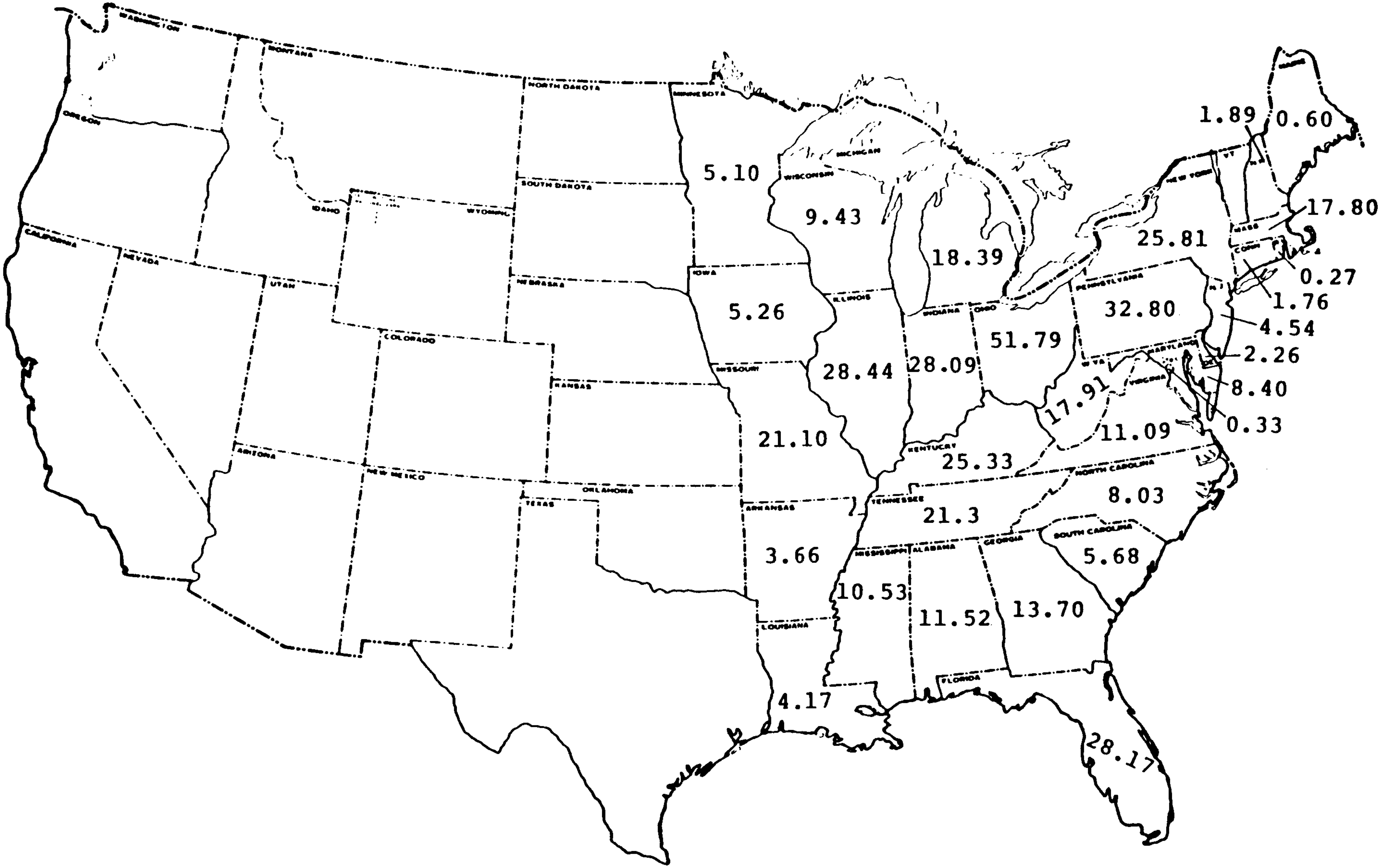

Figure A-11. Primary sulfate emissions from utility coal and oil combustion in the eastern United States, 10^3 tons.

from Canada, (Galloway and Whepdale 1980) and most of these emissions impact the northeastern United States, since they are principally derived from the Canadian provinces of Ontario and Quebec.

The commercial/residential sector is also a significant source of precursor pollutants in the Northeast. Control of excess air emissions from the small oil-fired boilers used in this sector is much less precise than with industrial- or utility-sized oil-fired boilers, and these smaller units thus produce proportionally higher primary sulfate emissions (Homolya and Lambert 1981).

Another important point is that the primary sulfate emissions for these small oil-fired units are apparently independent of the sulfur content of the fuel. A recent test program in New York City on 20 small commercial/residential boilers burning low-sulfur oil showed that primary sulfate emissions averaged 13.4 percent of the SO_2 emissions (Homolya and Lambert 1981). These boilers were selected to represent a cross-section of the approximately 35,000 similar boilers that operate in New York City. Although individual mass emissions from these small boilers are lower than emissions from the industrial and utility sources, they are significant because some 75,000 of these small oil-fired boilers operate in the major northeastern metropolitan areas (New York, Boston, Baltimore, Washington). In fact, it has been estimated that up to 50 percent of the sulfate burden in New York City is caused by these small boilers fired with low-sulfur oil. It should be noted also that significant amounts of vanadium (a catalyst for oxidation of SO_2 to sulfate) were detected in the emissions from the 20-boiler study.

Sulfate emissions from small oil-fired commercial/residential boilers may explain in part the so-called sulfate anomaly in New York City, where sulfate levels have remained high although SO_2 emissions have decreased.

APPENDIX B

CASE STUDY ANALYSIS OF SOURCES OF ACID RAIN IN CALIFORNIA

INTRODUCTION

California was selected for case study analysis because of its location, meteorology, and geography. Although acid rain is occurring in California, it probably is not caused by remote sources but more likely by local sources.

California is bounded by the Pacific Ocean on the west, by mountains and desert on the east, and by nonindustrial areas to the north and south. Winds to the state are typically from the west or northwest, as shown in Figure B-1. From November through February, surface winds along the coast in San Francisco and Los Angeles exhibit diurnal effects, blowing inland off the ocean and seaward off the land with near-equal frequency. During the remainder of the year, ocean breezes predominate. Unlike the Northeast and Florida, California receives 70 to 80 percent of its rainfall during the winter months, and the period from November through March is known as the rainy season (U.S. Department of Commerce 1979). The California climate is very mild, with normal average temperatures ranging from 40° to 60°F in January, 55° to 75°F in July along the coast, and 60° to 100°F in July at inland locations (U.S. Department of Commerce 1979).

OCCURRENCE OF ACID RAIN IN CALIFORNIA

It has been established that rainfall in many parts of California now has an average weighted pH value of 4.5 to 5.0. The lowest values tend to occur in the metropolitan and industrialized areas near Los Angeles and San Francisco.

Table B-1 shows a composite history of rainfall studies throughout California. Most of the studies conducted in the State prior to 1977 to 1978* cannot be compared statistically to determine with confidence whether a trend toward increasing acidity in precipitation is occurring or when it began. The reason is that studies from the 1950's and 60's were conducted for brief periods of time at different sites with different sample collection methods. In many cases, the pH level was not measured but was calculated later. Quality assurance measures designed to protect the quality

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* Liljestrand and Morgan (1979) and Whitehead and Feth (1964), provide good reviews of early rainfall studies in California.

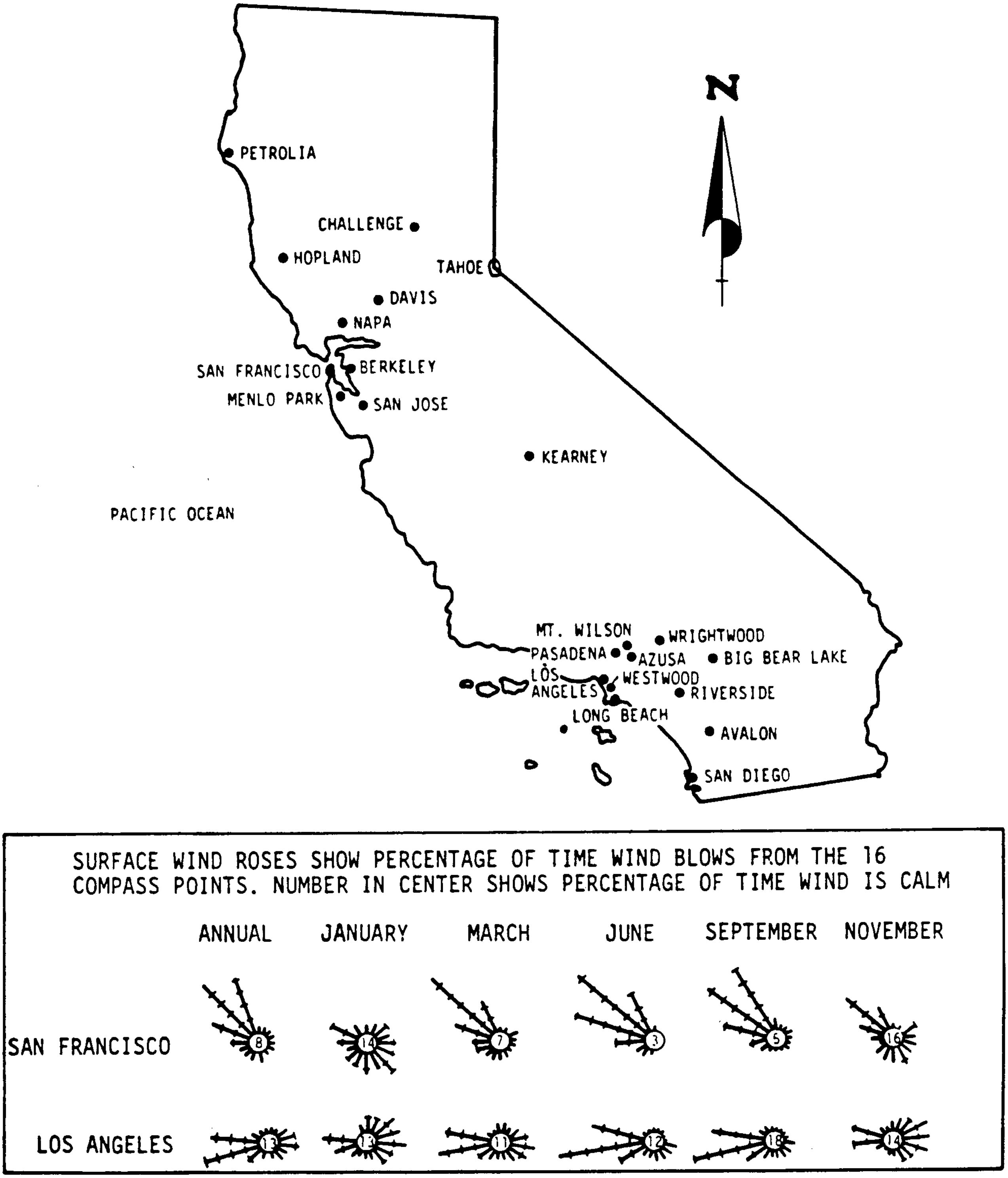

Figure B-1. Map of California showing locations where rainfall acidity has been measured. Arrows indicate annual prevailing wind directions. Wind roses show monthly surface wind characteristics for San Francisco and Los Angeles (U.S. Department of Commerce 1979).

TABLE B-1. HISTORY OF CALIFORNIA RAINFALL ACIDITY

Northern California	1955-1956	1957-1959	1960-1966	1964	1971-1973	1973	1974-1975	1976-1977	1978-1979	1978-1979
Berkeley							4.5-5.7			4.66
Menlo Park										5.3
Davis										5.20
San Jose										4.42
Hopland										5.10
Napa										4.84
Challenge										4.88
Tahoe City				5.8						5.17
Kearney										4.96
Sierras										
Bishop					6.10					
Fresno	7.05									
San Francisco						5.0				
Redding	5.84									
Santa Barbara (approx.)	6.88		7.18							
Southern California										
Avalon			4.03							
Westwood									4.53	
Long Beach									4.54	
Los Angeles		4.15-5.8				4.0-5.0			4.49	
Pasadena								4.06	4.41	
Azusa									4.66	
Mt. Wilson									4.99	
Wrightwood									4.90	
Riverside									4.97	
Big Bear Lake									5.42	
San Diego	5.01									
Menlo Park		5.6-5.9								
Santa Maria	5.4-7.3		4.1-7.6							
San Diego	4.0-7.4									
Catalina Island			3.7-6.8							
Comments	Calculated pH	Rain bulk pptn. pH = 6.4	Rain	Snow		School survey	Bulk pptn. (rain and dry dep.) in Berkeley Hills	Rain		
Source	Junge & Gustafson 1956; Liljes trand 1976, Liljestrand and Morgan, 1979	Whitehead & Feth, 1964 Liljestrand and Morgan, 1979	Lodge et al, 1968 Liljestrand and Morgan, 1979	Feth et al, 1964	Wood, 1975	Current Science, 1973	McColl & Bush, 1978	Liljestrand & Morgan, 1978	Morgan & Liljestrand, 1980	McColl, 1980

of the data were often lacking or not recorded. Data on individual measurements were not published; rather, authors reported average, median, or weighted mean pH values. For all of these reasons, comparison among the different data sets must be limited.

These scattered early data nevertheless do tell us that in the 1950's and 1960's the pH of rainfall in California generally was about 6 to 7 except near Los Angeles and San Diego, where the pH was probably around 5 or less. Quite interestingly, acid snow was also observed in the early 1960's in the Sierra Nevada Mountains near Tahoe (Liljestrand 1976). By the early-to-mid 1970's, rainfall with a pH of 4 to 5 was being observed frequently in both the Los Angeles and San Francisco areas (National Academy of Science 1975; Kennedy, Zelleveger, and Avanzino 1979).

It was not until the late 1970's that two independent and well-controlled studies of precipitation acidity in California were begun. Dr. John McColl (1980) of the University of California at Berkeley studied eight northern California sites near San Francisco, and Drs. Morgan and Liljestrand (1980) of the California Institute of Technology in Pasadena studied nine sites in southern California near Los Angeles. Both studies were conducted during the winter season, between autumn 1978 and spring 1979. The net results of this work are shown in Table B-2. The data indicate that rainfall throughout California is moderately acid, with mean pH values ranging from 4.4 to 5.4. Nitrates are more predominant in most areas except in the Los Angeles-Long Beach-Westwood-Pasadena area, where sulfates predominate.

Although a winter rainy-season peak in California acidity would seem likely, such a seasonal variation has not yet been fully established. Some 70 to 80 percent of the total rainfall events (>0.1 inch) and total rainfall amount (inches) occurs in the winter between November and March. The most thorough studies (i.e., those of McColl, and of Liljestrand and Morgan) were conducted only in winter and were not continued through the summer. Some earlier studies (Junge 1958; Lodge et al. 1968) were conducted for nearly full-year terms, but published results were not interpreted on a seasonal basis.

SOURCES OF ACID RAIN IN CALIFORNIA

Some fraction of the California rainfall acidity, especially along the coast, may be due to natural source contributions, such as sea sulfur and chloride from Pacific Ocean spray. The mechanism by which sea sulfur contributes to rainfall acidity is unclear. Such natural contributions are probably small relative to emissions from anthropogenic activities. An off-shore/on-shore paired comparison study would help to resolve this uncertainty.

Anthropogenic sources of SO_x and NO_x are largely associated with the combustion of fossil fuels, and the ratio of excess sulfate to nitrate in precipitation is indicative of the predominant type of source contributing

TABLE B-2. PRECIPITATION ACIDITY IN CALIFORNIA, 1978-1979

Location	Mean pH	Mean nitrate, μeq/ℓ	Excess sulfate,[c] μeq/ℓ	Ratio nitrate to sulfate	Comments
Northern California[a]					
Berkeley	4.66	13.7	10.2	1.3	Industrial and urban source area. Elevation 400 m
Menlo Park	5.3				Urban area
Davis	5.20	22.6	19.0	1.2	Urban and agricultural source area. Elevation 18 m
San Jose	4.42	16.4	10.0	1.6	Industrial and urban source area. Elevation 22 m
Hopland	5.10	11.1	6.2	1.8	Grazing and watershed area in Coast Range. Elevation 165 m
Napa	4.84	16.4	11.7	1.4	Woodland ridge in Coast Range. Elevation 280 m
Challenge	4.88	19.9	8.6	2.3	Conifer forest in lower Sierra foothills. Elevation 790 m
Tahoe City	5.17	6.7	13.3	0.5	Sierra forest, watershed, and recreation area. Elevation 2076 m
Kearney	4.96	43.4	13.8	3.1	San Joaquin Valley; agricultural. Elevation 100 m
Average	4.99	16.3	11.6		

(continued)

TABLE B-2 (continued)

Location	Mean pH	Mean nitrate, μeq/ℓ	Excess sulfate,[c] μeq/ℓ	Ratio nitrate to sulfate	Comments
Southern California[b]					
Westwood	4.53	27.0	39.0	0.7	Located about 8 mi N-NW of Los Angeles, near coast
Long Beach	4.54	19.2	46.5	0.4	Urban, industrial source area south of Los Angeles, on coast
Los Angeles	4.49	34.0	51.4	0.7	Urban, industrial source area
Pasadena[d]	4.41	31.4	35.6	0.9	Urban source area
Azusa	4.66	43.9	34.9	1.3	Suburban
Mt. Wilson	4.99	23.2	36.7	0.7	Remote area on western side (L.A. side) of San Garbiel Mountains
Wrightwood	4.90	10.6	6.7	1.6	On eastern side of San Gabriel Mountains
Riverside	4.97	32.6	30.4	1.1	Suburban
Big Bear Lake	5.42	17.0	6.0	2.8	Remote recreation area on eastern side of San Gabriel Mountains
Average	4.76	26.5	31.9		

[a] McColl (1980); McColl and Bush (1978).
[b] Morgan and Liljestrand (1980).

[c] Total sulfate minus sea-sulfate equals excess sulfate.

[d] Results of an earlier study conducted in Pasadena by Liljestrand and Morgan in 1976 and 1977 (Liljestrand and Morgan 1978) showed the reverse ratio. Nitrates were more predominant than sulfates in Pasadena rainfall (i.e., the equivalent was 1.32). This apparent contradiction in the Pasadena studies has not been explained.

to the acid rain. Thus, the relatively high proportion of sulfate in Los Angeles-Long Beach-Westwood rainfall is indicative of stationary sources in the area such as oil-burning power plants and refineries, whereas the relatively high proportion of nitrate in northern California rainfall suggests a strong influence by mobile sources.

Table B-3 shows the estimated contributions of SO_x and NO_x from the major combustion sectors in California. Utilities, industry, and transportation emit more than 94 percent of the SO_x in California, the utilities predominating slightly. More than 70 percent of the NO_x emissions come from transportation sources, and most of the remainder comes from utilities. The SO_x and NO_x emissions from transportation sources are concentrated in traffic areas of greatest density, primarily the largest metropolitan areas: Los Angeles, San Francisco, and San Diego.

Figure B-2 shows California's fuel use history since 1960. It shows that coal is not an important energy source in this State; coal supplies only 1 percent of California'a annual energy requirement, compared with a national figure of about 20 percent (U.S. DOE 1980b). Residual oil, on the other hand, supplies 14 to 15 percent of California's energy, compared with a national figure of 8 to 9 percent. In fact, California ranks second in consumption of residual oil, next to New York. It is the largest consumer of gasoline in the Nation.

The utility sector is responsible for the largest portion of SO_x emissions in the State (refer to Table B-3). Since the utilities use no coal, their SO_x emissions arise almost entirely from the burning of residual oil. Of the total residual oil burned in California (140,595,000 barrels or 884 x 10^9 Btu), 55 percent or 486 x 10^9 Btu is consumed within the utility sector (U.S. DOE 1980b). Figure B-3 shows the locations of California's oil-burning utilities. Most of these facilities are concentrated in the Los Angeles, San Francisco, and San Diego areas.

The only known use of coal in California to date has been by the industrial sector, but this use is very small compared with petroleum consumption. For the past 20 years, industry in this State has been consuming 6 to 7 times as much energy (Btu's) from total petroleum products as from coal (U.S. DOE 1980b). Among petroleum products used by the industrial sector, however, consumptions of residual oil (63 x 10^6 Btu) and distillate oil (75 x 10^9 Btu) are similar to that of coal (69 x 10^9 Btu).

Oil refineries are major sources of SO_x in the California industrial sector. There are 41 refineries in the State. They operate on a continuous basis, refine 2,506,370 barrels of crude oil per calendar day (capacity rate), and consume (burn) an estimated 55 million barrels* of oil per year for operation. This is half of the total petroleum consumption of the entire industrial sector in California (U.S. DOE 1980b). Figure B-3 shows

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* Refineries consume about 5 to 10 percent of their production. Assuming 7 percent consumption, petroleum fuel usage is calculated as follows:

$$(0.07)(2{,}500{,}000\ \frac{\text{barrels}}{\text{day}})(\frac{312\ \text{days}}{\text{year}}) = 55{,}000{,}000\ \frac{\text{barrels}}{\text{year}}$$

TABLE B-3. ESTIMATED 1978 EMISSIONS IN CALIFORNIA BY SECTOR[a]

Fuel user	SO_x emissions		NO_x emissions	
	1000 tons	% of total	1000 tons	% of total
Utilities	88.72	34.79	205.61	17.76
Industry	76.30	29.92	84.98	7.34
Commercial establishments	13.29	5.21	17.80	1.54
Transportation	75.05	29.43	820.06	70.84
Residences	1.67	0.65	29.11	2.52
Total	255.03	100.00	1157.56	100.00

[a] Appendix E gives a complete description of the derivation of these data. The total SO_x emissions (255,000 tons/yr) in the State of California are low compared with those in other states (Florida, 741,000 tons/yr SO_x; New York, 1,050,000 tons/yr SO_x; Pennsylvania, 2,785,000 tons/yr SO_x). California SO_x emissions are of the same magnitude as those in some cities (Cleveland Ohio, and Tampa Bay, Florida, each with about 300,000 tons/yr). California's annual NO_x emissions (1,158,000 tons/yr), on the other hand, are comparatively large. They are second only to those of Texas (1,595,000 tons/yr), and slightly larger than those of Ohio (1,075,000 tons/yr), Pennsylvania (1,041,000 tons/yr), and Illinois (885,000 tons/yr). All other states emit half as much NO_x as California or less.

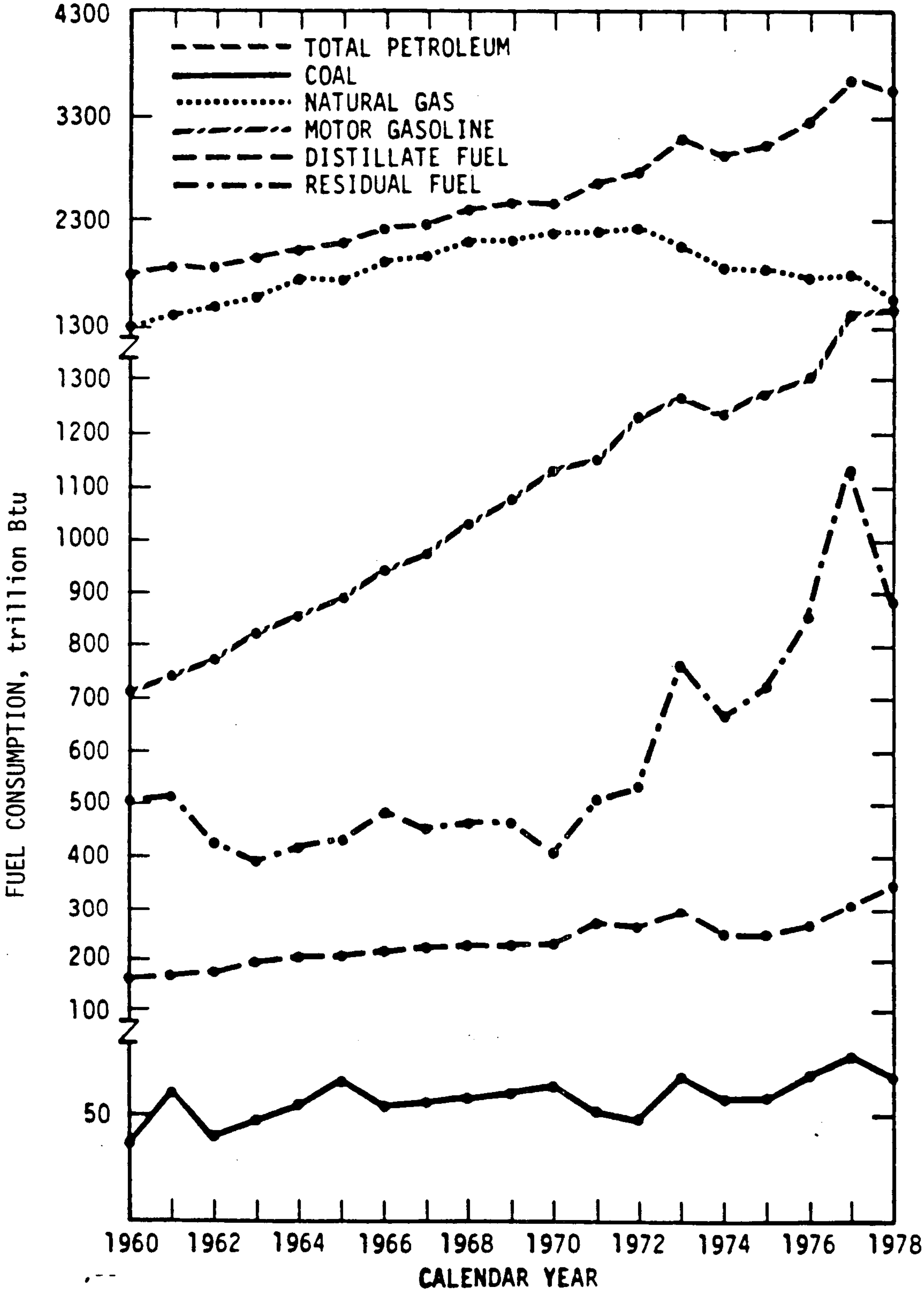

Figure B-2. California fossil fuel consumption, by type (U.S. DOE 1980b).

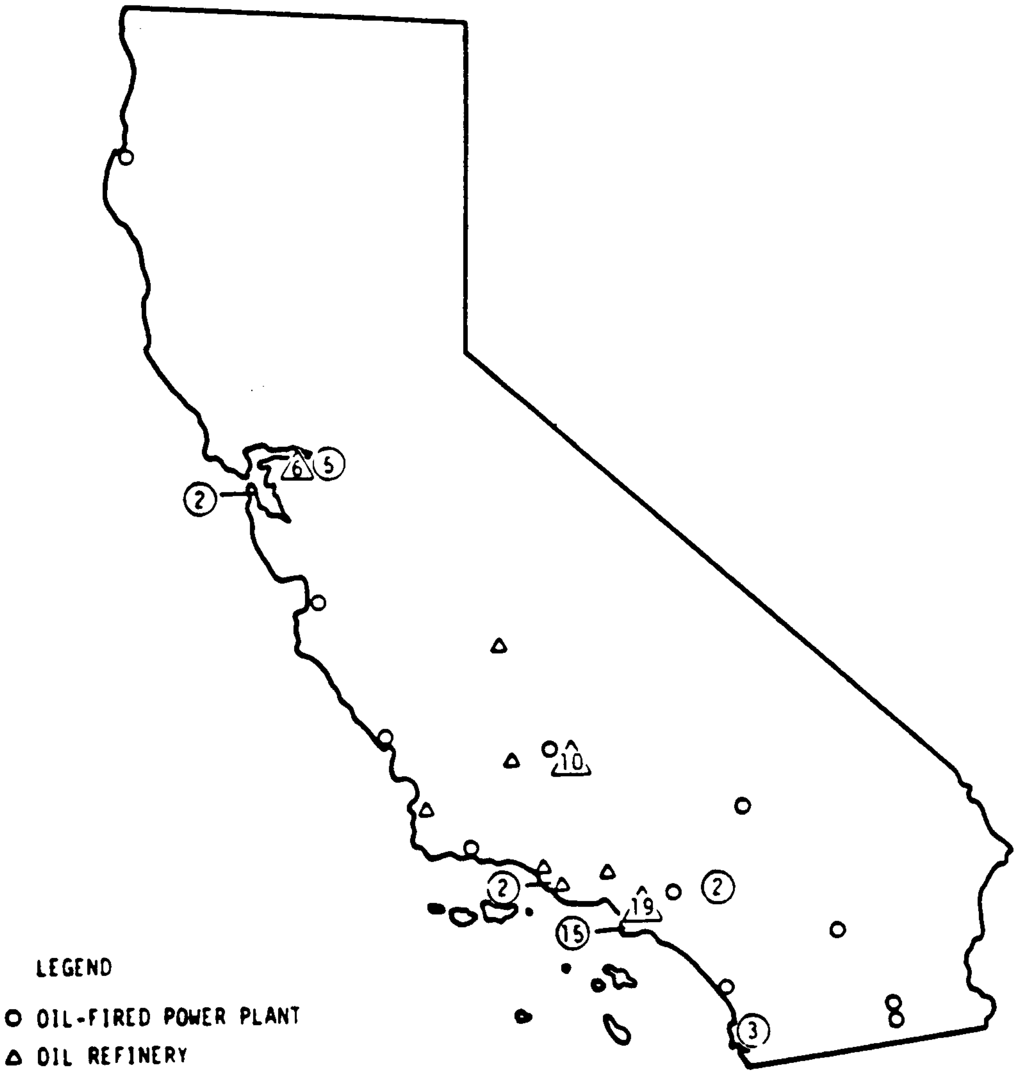

Figure B-3. Locations of California's oil-fired power plants and oil refineries.

that over half of California's refineries are located in the Los Angeles-Long Beach area. The rest are clustered in the Bakersfield and San Francisco areas. Emissions from these refineries vary with processes and control systems, but they include primary sulfates and catalytic material which would be expected to contribute to the sulfate acidity of local precipitation.

The third important SO_x-emitting sector in California is transportation. Transportation is not a significant source of SO_2 in the Nation as a whole. It is significant in California, however, because SO_x emissions from other source sectors (industrial and utility) are relatively small in comparison with other areas of the country. The SO_x from automotive emissions is emitted largely as primary sulfate (sulfuric acid) because of the use of catalytic converters (U.S. EPA 1981). Therefore, sulfate emissions from mobile sources would be expected to add directly to the acidity of rainfall in areas where auto emissions are most dense, i.e., in the San Francisco, Los Angeles, and San Diego areas.

The overwhelming emission factor in terms of rainfall acidity throughout most of California is the large NO_x emission, which arises mainly from transportation. It is not known how much of the automotive emission of NO_x is primary nitrate.

APPENDIX C

CASE STUDY ANALYSIS OF SOURCES OF ACID RAIN IN FLORIDA

INTRODUCTION

Florida was selected for case study analysis because acid rain is occurring there, and a large amount of petroleum products are also consumed.

Florida is a geographically isolated state, bounded on three sides by water. It is approximately 400 miles long from north to south, and about 100 miles wide across the lower peninsula from Miami to Ft. Meyers. The panhandle area is only 30 to 50 miles wide from north to south. Florida has a subtropical climate, with average temperatures ranging from 70° to 90°F in summer (June-September) and 45° to 75°F in winter (December-March). Rainfall is heavier and more frequent in the summer months. Wind patterns in the central and northern portion of the state show strong seasonal variations, whereas winds to the lower part of the peninsula and along the Atlantic coast are off the ocean at all times, as shown in Figure C-1.

OCCURRENCE OF ACID RAIN IN FLORIDA

Researchers at the University of Florida have been monitoring rainfall throughout the state since the fall of 1977 (Brezonik, Edgerton, and Hendry 1980). Their sampling network includes 24 sites positioned across the panhandle and down the peninsula to the lower keys. Figures C-2 and C-3 depict locations of sites from which samples were collected biweekly (or more frequently) and analyzed for pH, conductivity, major ions, and other chemical parameters.* Bulk precipitation samplers were used at 20 sites, and wet-dry collectors were used to obtain more detailed information at 4 sites. Rain was sampled on an event basis in Gainesville only. Information presented in Figures C-2 and C-3 indicates that rainfall acidity in Florida varies with geography and season. The isopleths in Figure C-2 show that annual average rainfall pH values below 4.7 occur over the northern three-quarters of the State. Sulfuric and nitric acids account for nearly all the acidity, the former being 2 to 2.5 times greater. Rainfall in southern Florida (below Lake Okeechobee) shows less seasonal variation and is less acidic, only slightly below the assumed value for geochemical neutrality on an annual basis. For the State as a whole, the pH value of rainfall in summer (May-October) generally averages 0.2 to 0.3 unit lower than in winter (November-April). Although not shown in the figures, total sulfate

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* For clarity, results are not shown for some sites located close to others.

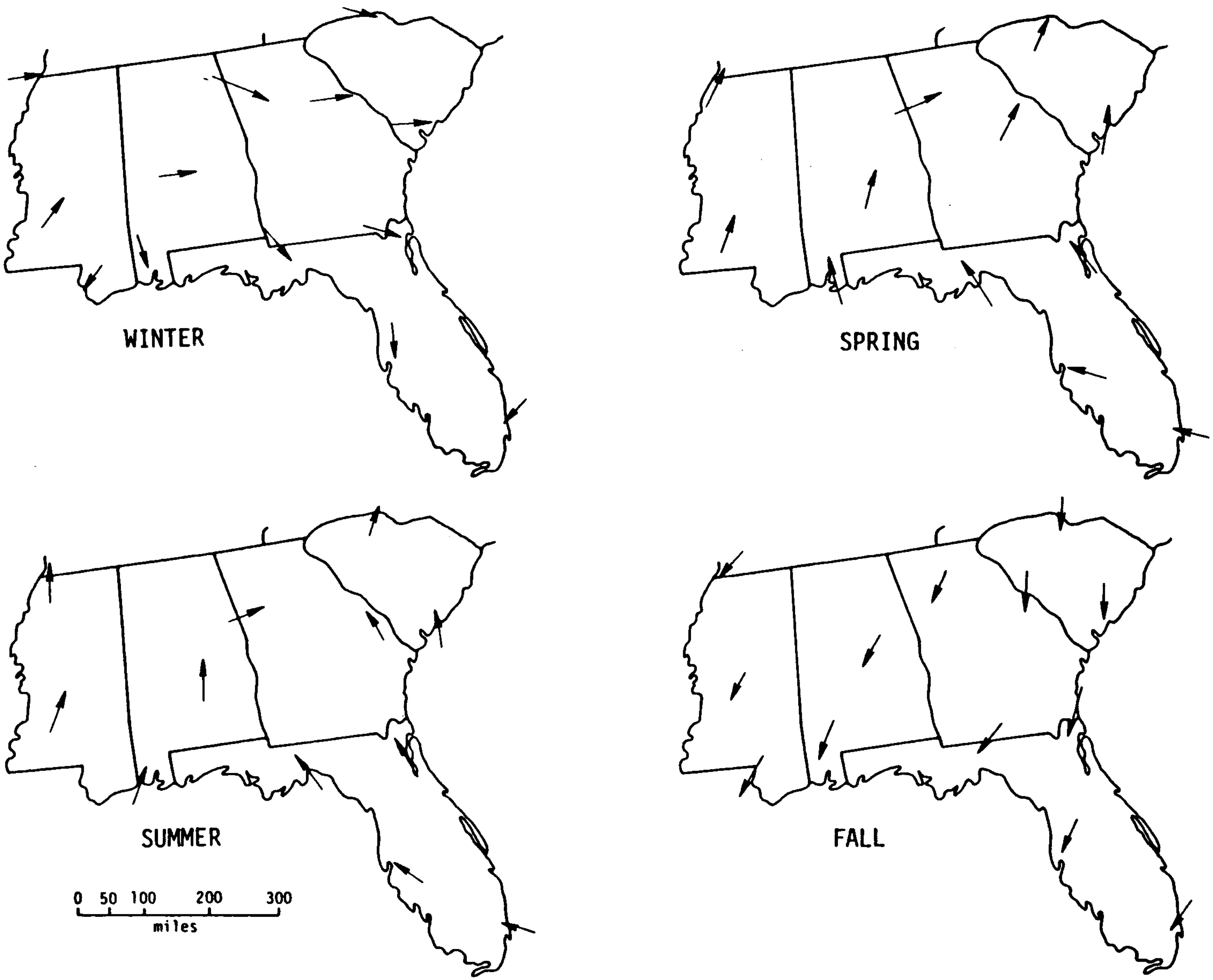

Figure C-1. Seasonal prevailing wind positions in Florida and neighboring states (U.S. Department of Commerce 1979).

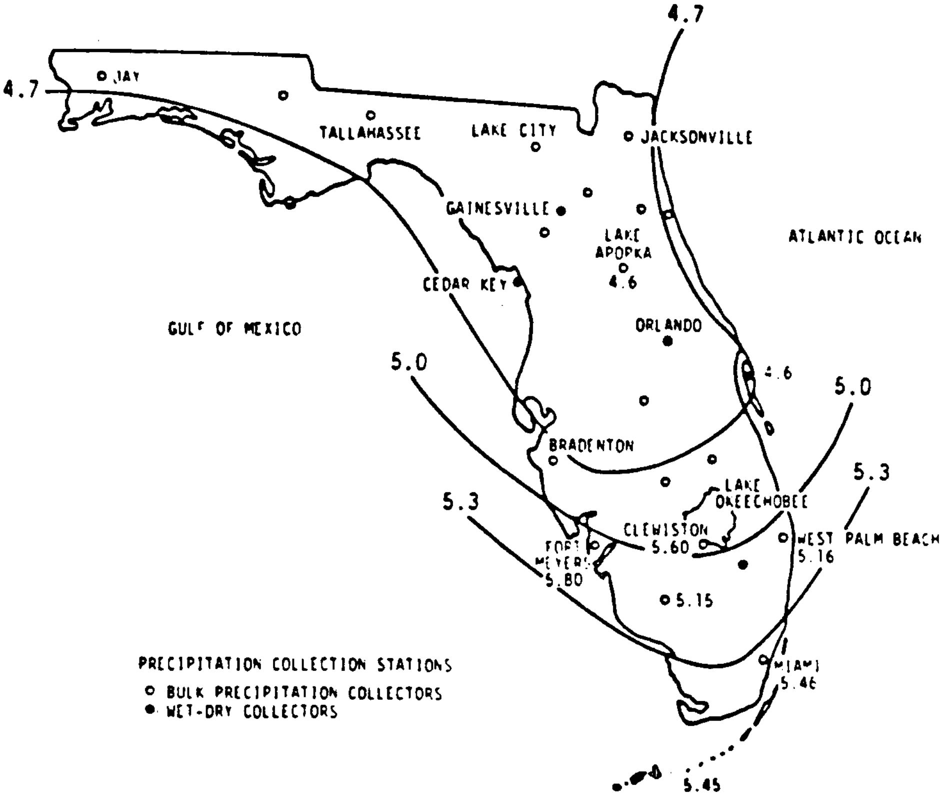

Figure C-2. pH isopleths of Florida rainfall from May 1978 - April 1979 (Brezonik, Edgerton, and Hendry 1980).

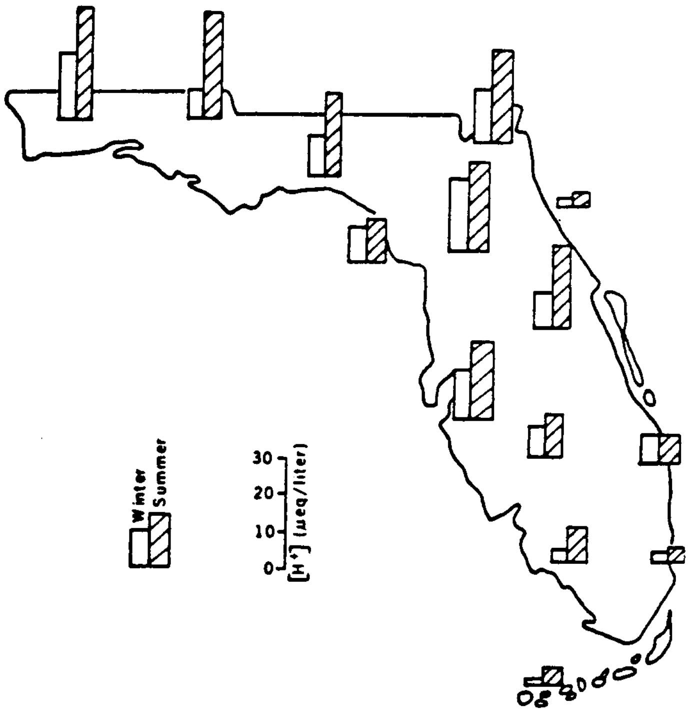

Figure C-3. Volume-weighted hydrogen ion concentrations in winter (November 1978 through April 1979) and summer (May 1978 through October 1978) rainfall (Brezonik, Edgerton, and Hendry 1980).

deposition was found to be higher in summer than in winter in the northern half of the State; in the southern half, total winter sulfate often exceeded summer sulfate. Deposition of excess sulfate (i.e., total minus sea-salt sulfate) seemed greater in the upper half of the state--for example at Tampa, Orlando, Jacksonville, Gainesville, Tallahassee, and two other monitoring sites near the northern border.

Brezonik, Edgerton, and Hendry (1980) compared their 1978-79 data with 1955-56 data for several localities in the State (Table C-1). The data clearly show that rainfall has become markedly more acidic in the past 25 years. Nitrate concentrations in 1978-79 are 4.5 times those in 1955-56; sulfate concentrations have increased less (1.6X or 160 percent). The largest increases in sulfate deposition have occurred in northern Florida. The authors postulate that if natural fluxes of sea sulfur, biogenic sulfur, ammonia nitrogen, and nitrogen oxides have remained constant over the 25 year period, then the differences observed represent a substantial increase in anthropogenic emissions.

Limited testing of wet-only and bulk precipitation samples (Brezonik, Edgerton, and Hendry 1980; Hendry and Brezonik 1980) has led to the finding that, at least in Gainesville, rainfall is the predominant deposition mechanism for sulfate, ammonium, nitrate, magnesium, and potassium, while dry fallout is of comparable importance for deposition of sodium, chloride, and calcium. Of the total sulfate and nitrate measured, 75 to 80 percent was associated with the wet-only collector. The volume-weighted mean pH value of wet-only precipitation was 4.53; lowest values occurred in late winter-early summer (February-June) and highest values in mid-summer to early winter (Figure C-4). The pH level of bulk precipitation was slightly higher, with no apparent seasonal pattern, an indication of less net (free) acidity and more neutralization. Acidity titrations and ionic balances indicate that rainfall acidity in Gainesville resulted mainly from sulfuric acid (69%) and nitric acid (23%).

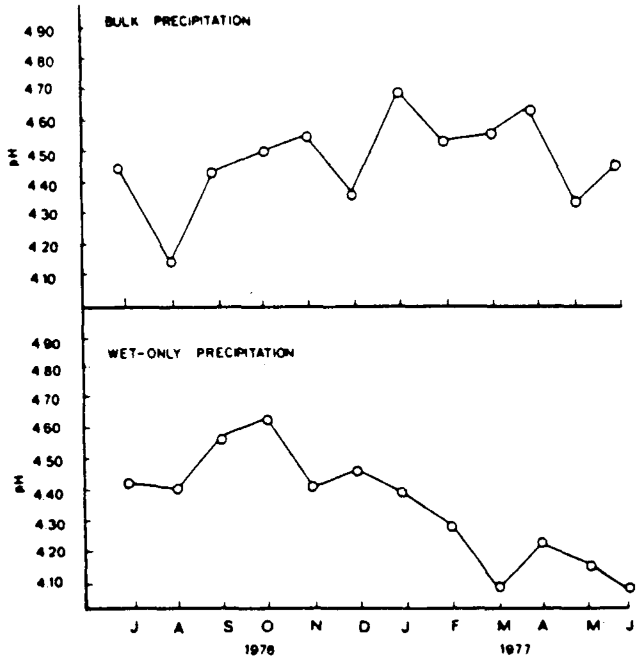

Figure C-4. Volume-weighted mean pH of bulk and wet-only precipitation at Gainesville, Florida, by month (Hendry and Brezonik 1980).

TABLE C-1. CHEMICAL PARAMETERS RELATED TO THE ACIDITY OF FLORIDA RAINFALL IN 1955-1956 AND 1978-1979[a]

	Weighted mean concentration, μeq/liter					
	H^+		Excess $SO_4^=$		NO_3^-	
Location	1955-56	1978-79[b]	1955-56	1978-79[b]	1955-56	1978-79[b]
Pensacola-Jay	<2.5[c]	24.0	16.0[d]	34.7	2.6	13.9
Tallahassee	<2.5	17.4	18.8	33.0	2.9	13.9
Jacksonville	<2.5	18.3	27.9	43.5	2.9	16.2
Tampa-Bradenton	<2.5	20.1	28.8	36.4	2.7	14.3
West Palm Beach-Stuart	<2.5	6.9	13.5	20.1	4.1	12.1
Mean	<2.5	17.3	21.0	33.5	3.1	14.1
1979/1956	>8.4		1.6		4.5	

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[a] Brezonik , Edgerton, and Hendry (1980).

[b] The data for 1979 are for bulk precipitation (rainfall collectors open at all times), whereas the 1956 data are for rainfall only (collectors open to the atmosphere during rain events). Adjacent wet-only (W) and bulk (B) collectors at Gainesville have yielded the following volume-weighted concentrations (in microequivalents per liter); excess $SO_4^=$, 35.1 (B) and 26.6 (W), B/W = 1.3; NO_3^-, 16.9 (B) and 13.6 (W), B/W = 1.24. Thus differences in collector type do not wholly explain the increases in concentrations.

[c] Proton concentrations calculated from the anion-cation balance.

[d] Total sulfate minus sea salt sulfate yields excess sulfate. This is the portion of total sulfate deposition that is usually attributed to anthropogenic activity.

Brezonik's published work does not include an analysis of wind trajectories associated with major storms monitored in his studies.

Researchers at Florida State University's Department of Oceanography in Tallahassee report that their sampling indicates that rains there are more acidic when associated with air masses from the north. They studied 14 precipitation events, all of which occurred in the 11-week period between November 7, 1978, and January 26, 1979 (Tanaka et al. 1980). Air originating from the more populated areas to the north produced rain with an average pH of 4.4 and a low of 3.7. Southern air moving in from the Gulf produced rainfall with an average pH of 5.3 and a low of 4.6. A strong correlation was observed between pH and the log of the sulfur concentration in northern rain, but not in southern rain. An earlier study (Leslie 1978) conducted by Florida State University substantiates this aspect concerning geographic trends in sulfur over the panhandle and northern parts of Florida in terms of source regions and air flow patterns. Evidence points strongly to the origin of fine-particle sulfur (especially particles of 0.5 to 1 μm) primarily outside Florida in areas to the north and west, moving eastward across the northern portion of the state, depending on prevailing winds, with dilution and wet or dry deposition occurring en route. The principal sulfur component in the fine particle mode is more likely to be ammonium sulfate than sulfuric acid; the latter is probably converted to ammonium sulfate during transport and aging. Particles of the size ranging 0.5 to 1 μm diameter are indicative of anthropogenic sources in contrast to larger sulfur particles, which are more typical of natural sources (e.g., sea spray).

The Florida State studies were not conducted during the summer months when prevailing winds are from the south, and when, according to Brezonik's data, acidity is at its peak. This does not necessarily mean that results of the two studies are conflicting, but only that year-round monitoring of rainfall acidity and meteorological conditions are necessary for understanding of the relationship between probable sources and acid rain occurrence.

SOURCES OF ACID RAIN IN FLORIDA

Since Florida is bounded almost entirely by salt water, some fraction of the rainfall acidity being experienced there is probably attributable to natural marine sources. Although the relative amount of acid from natural sources is not known, it is probably small compared with that from anthropogenic sources within the state. An offshore/onshore paired comparison study of single rainstorm events would help to clarify this point.

Anthropogenic sources of SO_x and NO_x are largely those associated with the combustion of fossil fuels. Table C-2 shows the estimated contributions of SO_x and NO_x from major combustion sectors in Florida and its neighbor states to the north. The table shows that, for the three-state area as a whole and for each state individually, utilities are the largest emitters of SO_x; NO_x emissions come in nearly equal proportions from the utility and transportation sectors.

TABLE C-2. 1978 SO$_x$ AND NO$_x$ EMISSIONS BY SECTOR[a]
(10^3 tons)

	Utility	Industrial	Commercial	Residential	Transportation	Total
			SO$_x$			
Florida	596.5	95.7	14.6	3.6	30.3	740.6
Alabama	570.0	393.8	20.0	3.9	13.8	1001.6
Georgia	612.1	57.8	14.3	1.1	20.0	705.3
			NO$_x$			
Florida	232.6	29.2	5.0	4.6	327.7	599.0
Alabama	153.6	82.0	5.6	4.8	175.3	421.3
Georgia	172.2	23.6	6.7	6.5	224.2	433.2

[a] A complete description of the derivation of these figures may be found in Appendix D.

Florida depends more heavily on petroleum products for its energy needs than does the Nation as a whole. Nearly 80 percent of Florida's 1978 energy requirements (in Btu's) was met by consumption of petroleum products, whereas the national figure is 53 percent (U.S. DOE 1980b). Coal consumption supplied only about 9 percent of Florida's energy needs; the national figure was nearly 20 percent. Most of the petroleum consumed in Florida is in the form of residual oil and motor gasoline. In fact, Florida ranks third in consumption of residual oil in the United States today; only New York and California consume more. It is eighth in gasoline consumption.

Figure C-5 shows that Florida's utilities rely heavily on petroleum for energy production. This is also unlike the national picture for utilities, which shows a primary dependence on coal (compare with Figure C-6). In 1978, Florida utilities consumed 85 percent of all the residual oil burned in the State (U.S. DOE 1980b). The rest was consumed in residential and commercial furnaces. Florida has 56 utility plants of which 52 burn oil; only 4 burn coal. Figure C-7 shows that most of Florida's utilities are located within the upper two-thirds of the State, within the same general area that receives acid rain (compare with Figure C-2). The dependence of Florida utilities on oil as a fuel source for electricity production has grown nearly 6-fold in the past 20 years from 12,753 barrels in 1960 to 72,856 barrels in 1978. This oil generates 45 to 55 percent of Florida's electricity; the remainder is derived in near-equal proportions from nuclear energy, natural gas, and coal. By comparison, only about 25 percent of the energy produced by all U.S. utilities is provided by burning oil.

It has been pointed out that several of the Nation's largest oil-fired utilities are located in Florida. Since oil is used so extensively throughout the State, substantial quantities of primary sulfates, metal catalysts

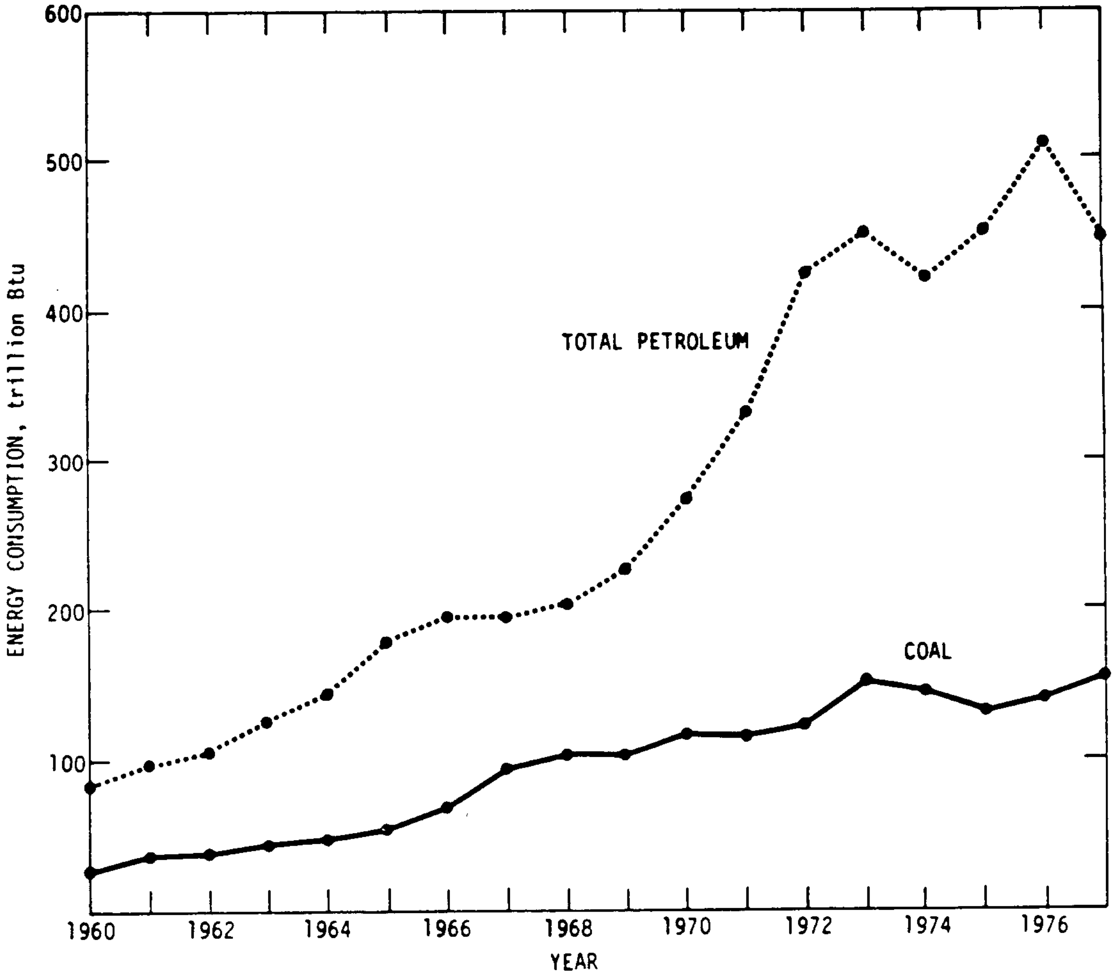

Figure C-5. Energy consumption by Florida electric utilities by type (U.S. DOE 1980b).

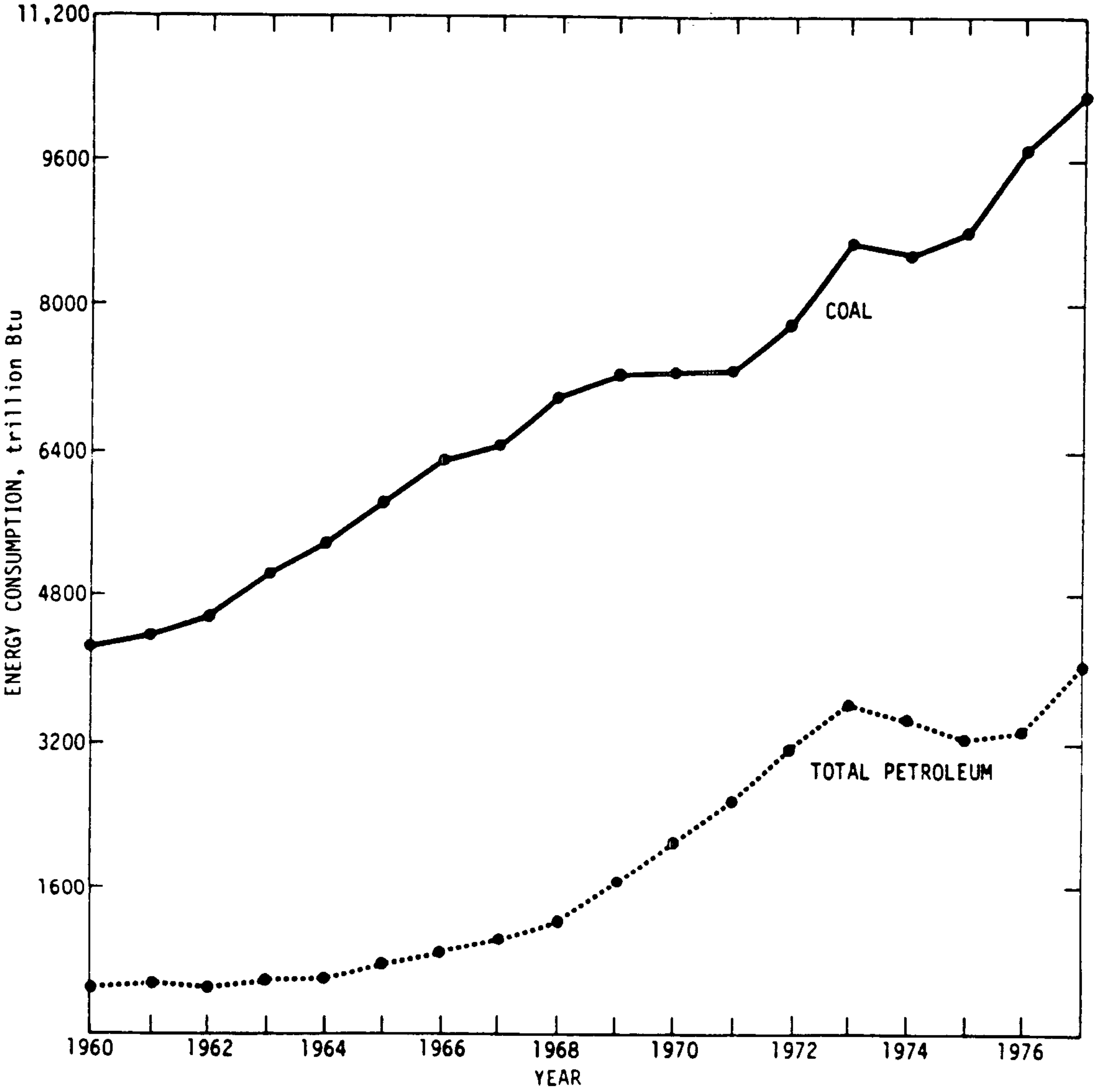

Figure C-6. National energy consumption by electric utilities by type (U.S. DOE 1980b).

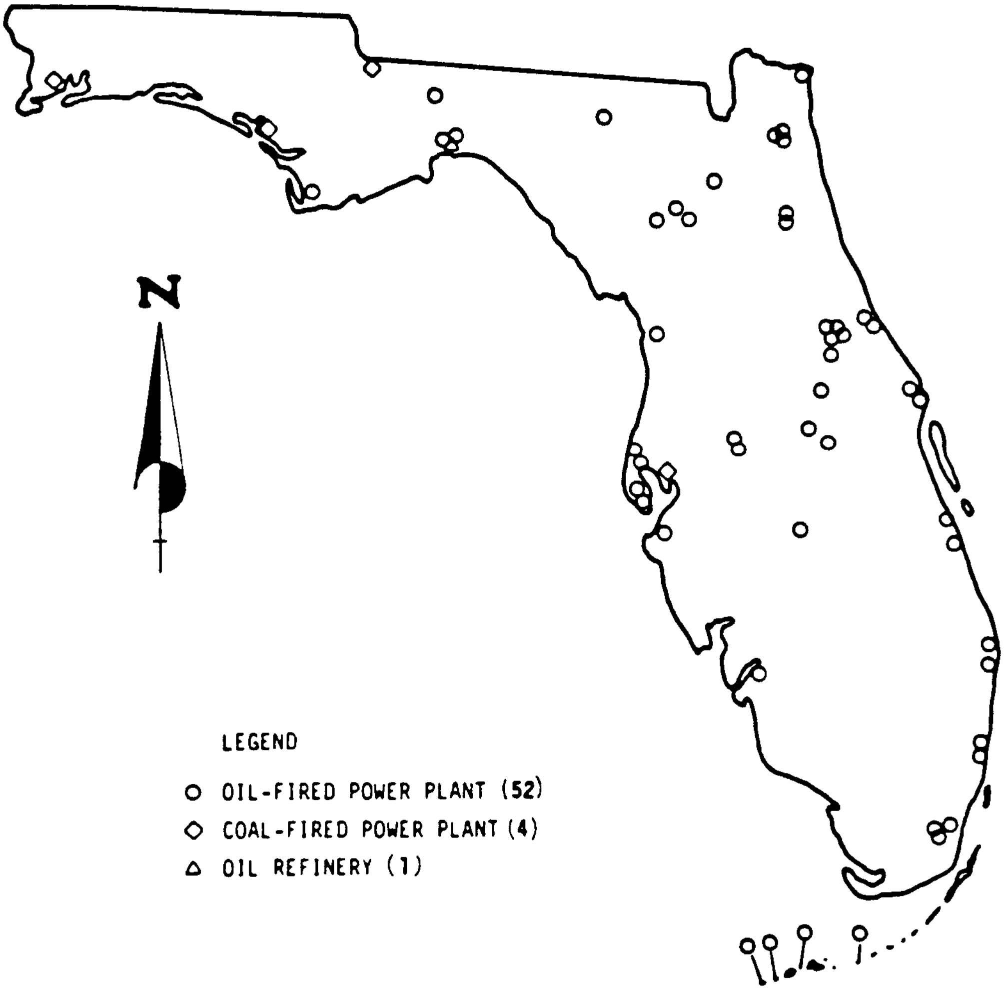

Figure C-7. Locations of electric utilities and oil refinery in Florida.

and carbon must be emitted. Emission estimates indicate that over 30,000 tons of primary sulfates are emitted annually in Florida, largely as a result of oil burning. Older oil-burning utilities typically do not have tall stacks and emit pollutants directly to the lower atmospheric mixing layer, where they can react with other pollutants before being deposited. Also, because of the relatively low stack heights, a large part of these SO_x and NO_x emissions probably is deposited within 50 to 100 miles of the sources. Thus, Florida utility emissions of SO_2, sulfate, and NO_x as well as NO_x from transportation sources appear to be influencing the acidity of local precipitation. This appears to be especially true within the peninsular portion of the State during the warmer months, when the heaviest concentrations of acid rain occur and fewer frontal systems move into the State from the north.

Acid rain in the northern part of the State is also likely to be influenced by utility emissions, though not necessarily from Florida utilities alone. As discussed earlier, prevailing winds may carry acid rain precursors into Florida from neighboring States of Georgia and Alabama during the months from September to February. About 70 percent of the SO_x emitted in Georgia and Alabama originate from utilities that burn oil and coal. Since most of the oil-burning utilities are located in the southern portions of these neighbor States, their emissions may be contributing more heavily to precipitation acidity in northern Florida during the winter months when much of Florida experiences northerly winds. At times, these seasonal effects may be felt as far south as Tampa, since northern cold fronts sometimes penetrate the State to that extent. Edgerton and Brezonik (1981), however, have performed an atmospheric mass balance for sulfur, and indicated that atmospheric deposition patterns are chiefly a result of in-state emissions, taking season, spatial and type of sulfur source into account.

APPENDIX D

ANALYSIS OF SOURCES OF ACID RAIN IN HAWAII AND JAPAN

HAWAII

Five years of monitoring by NOAA have shown that Hawaii receives acid rain with pH values ranging from 4 to 5 (Miller 1979, 1980). Figure D-1 shows the locations of the NOAA precipitation sampling sites. The Mauna Loa Observatory is located at the foot of the Mauna Loa Volcano about 3400 m above sea level. The other sampling sites are nearby at Kulani (2500 m above sea level), Hilo, and Kumukahi (both near sea level). The acidity patterns of rainfall at these sites are depicted in Figure D-2.

Local emissions from natural sources or from utility and industrial sources may be responsible for the acid rain in Hawaii. The U.S. EPA estimates that 65,000 tons of SO_x and 60,000 tons of NO_x are emitted locally in the islands from petroleum combustion sources (U.S. EPA 1980). These sources are essentially all petroleum-fired since coal and natural gas are not used. Hawaii's anthropogenic emissions of SO_x and NO_x pollutants are comparable to those of the State of New Hampshire.

Natural sources of sulfur may also be affecting the pH of the rain. Unfortunately, the influence of sea sulfur is not known, and figures on the emissions of natural sulfur and chloride (HCl) from the Mauna Loa volcano were not available at this writing.

Hawaii is almost totally dependent on petroleum for its energy needs, as shown in Table D-1. One third of Hawaii's energy usage (80×10^{12} Btu) is in the form of residual oil and three-fourths of that amount, or 60×10^{12} Btu, is consumed by the island utilities; the remainder of the residual oil is consumed in the industrial and transportation (ships) sectors (U.S. DOE 1980b). Another third of the energy consumed in Hawaii is attributed to jet-fuel consumption. This is an inflated figure, however, because it represents refueling of jet aircraft on the island rather than actual consumption. The remainder of Hawaii's energy needs are met by motor gasoline (16 percent), distillate oil (7 percent), and other miscellaneous petroleum products (12 percent) such as asphalt, LPG, and lubricants.

Residual-oil-burning accounts for most of the total anthropogenic SO_x emissions in Hawaii. Combustion of the other predominant petroleum products such as distillate, jet fuel, and motor gasoline results in much lower SO_x emissions. If 10 to 12 percent of the SO_x emitted from residual-oil-burning boilers is in the form of sulfate, and if the use of residual oil is assumed to account for 80 percent of the total SO_x emissions in Hawaii, then an

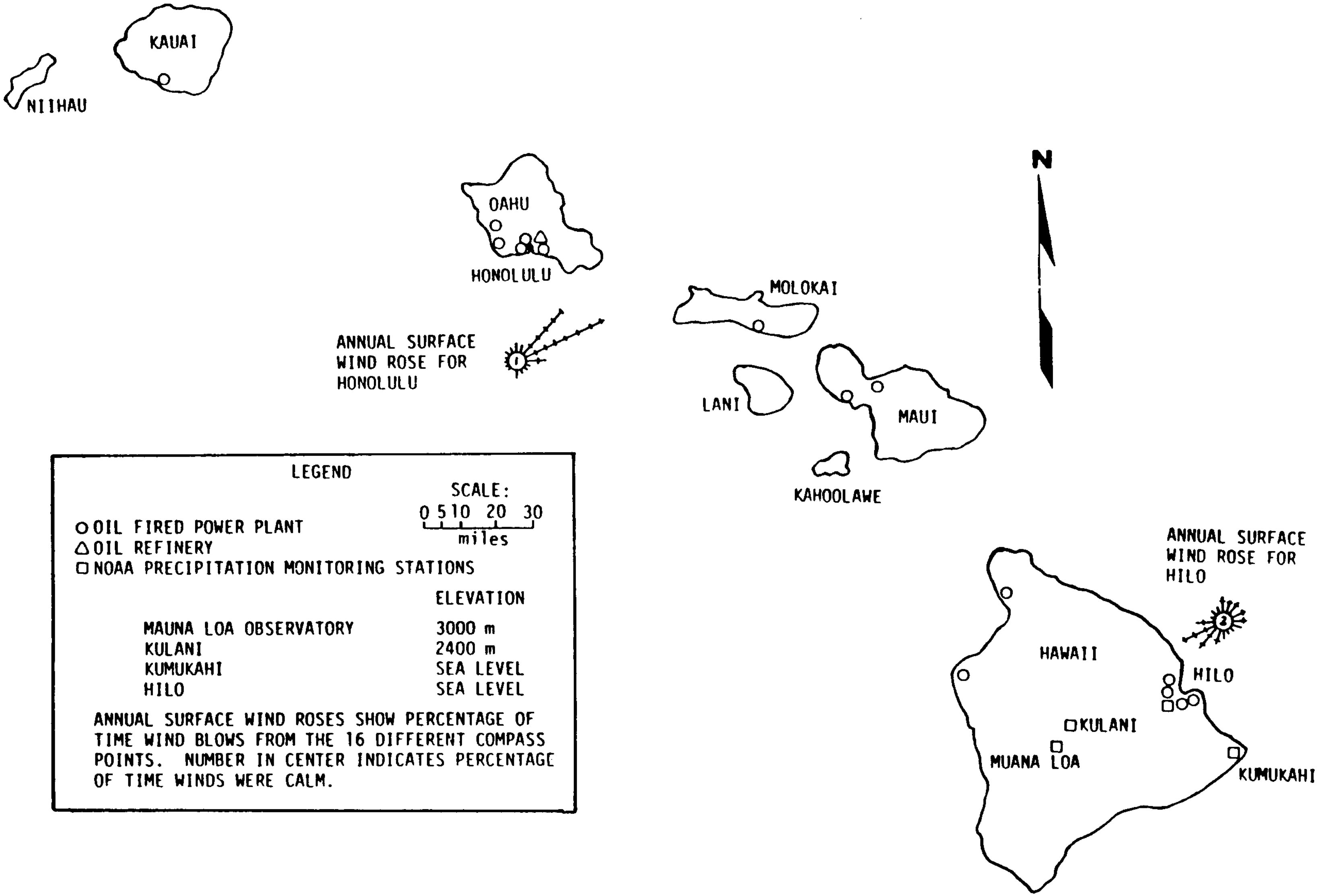

Figure D-1. Map of Hawaiian Islands showing locations of oil-fired power plants, oil refineries, and NOAA precipitation monitoring stations.

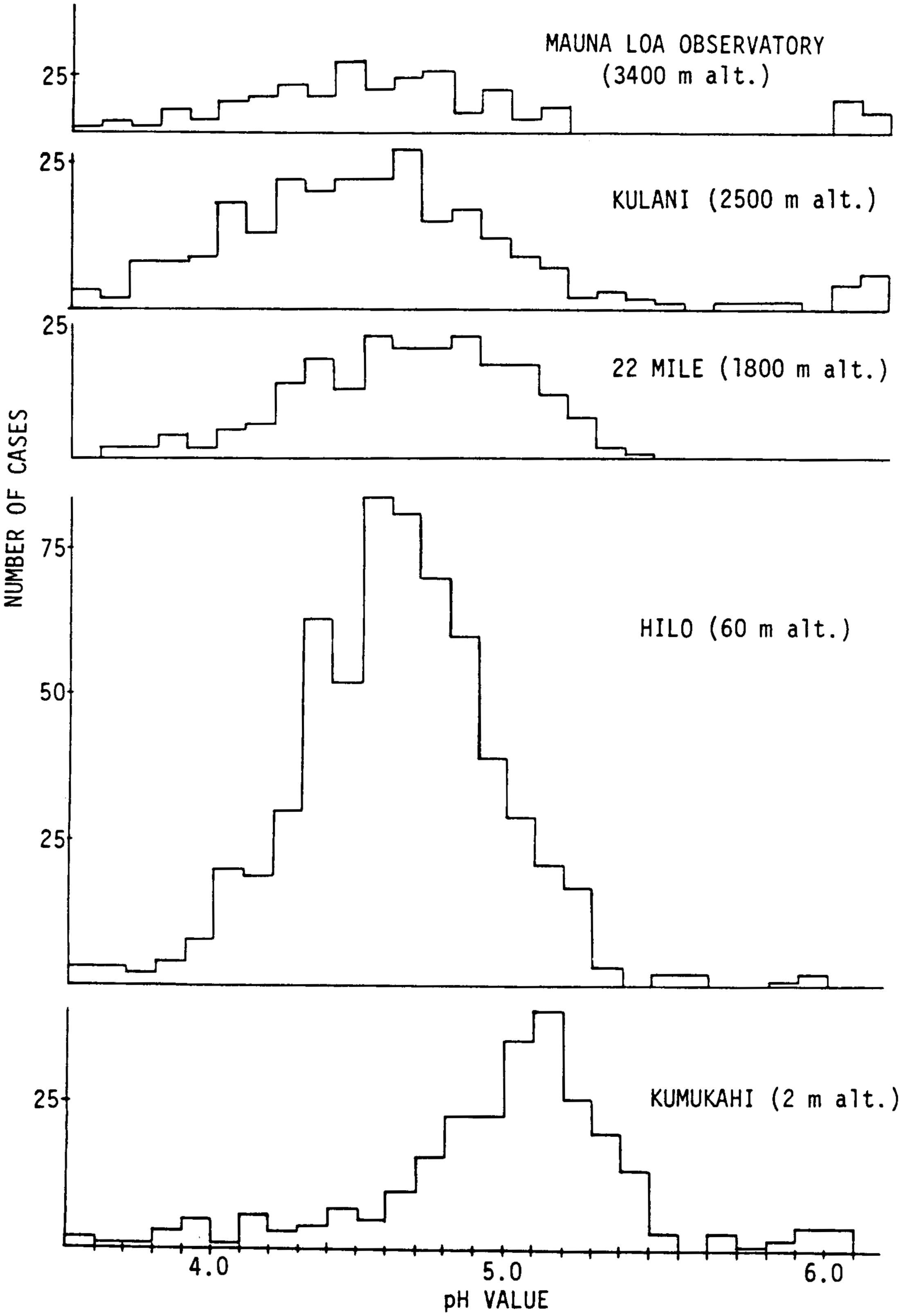

Figure D-2. Acidity of Hawaiian precipitation, June 1975 - June 1980 (Miller 1980).

TABLE D-1. ENERGY CONSUMPTION IN THE STATE OF HAWAII[a]
(Trillion Btu)

	Distillate oil	Jet fuel	Motor gasoline	Residual oil	Total petroleum[b]	Total energy consumed[c]
1960	5.2	28.0	28.6	35.9	118.6	120.2
1962	9.6	30.9	24.1	42.0	125.1	125.1
1964	10.3	43.1	21.6	47.2	139.0	140.2
1966	7.8	57.0	22.6	49.7	154.6	156.1
1968	8.1	82.1	25.6	61.1	193.1	195.7
1970	9.9	83.3	29.9	63.9	209.1	211.4
1972	9.4	94.4	32.6	71.1	228.7	230.3
1974	11.1	86.6	34.4	70.5	224.7	229.0
1976	13.8	81.1	36.9	74.0	229.0	234.2
1978	18.9	85.1	40.1	80.4	247.4	253.4

[a] U.S. DOE (1980b).

[b] Includes other petroleum products such as LPG, asphalt, kerosene, road oil, and miscellaneous.

[c] Includes total petroleum, plus very small contributions from hydroelectric and wood and waste sources. Nuclear power, natural gas and coal are not used in Hawaii.

estimated 5200 to 6200 tons of primary acid sulfates is emitted directly to the Hawaiian atmosphere each year by utilities and industry. As shown in Figure D-1, several utilities are located on the island of Hawaii, where the NOAA acid precipitation monitoring sites are located. Winds blowing from the utilities toward the sampling sites would be expected to bring with them acid sulfates, SO_2 and other pollutants from the utility plume. As rainfall washes these primary sulfates from the air, the result would be acid rain. Miller has noted that winds from the northern hemisphere often bring additional acid rains to the Mauna Loa sampling site (Miller 1979). This may reflect emissions from the utilities on the island of Hawaii or from utilities on the other islands (i.e., within 200 miles of Mauna Loa). It may also reflect long-range transport of acid rain pollutants from the Asian or American continents, or possibly natural sources, but these explanations seem less likely.

JAPAN

Information on acid rain in Japan is limited but nevertheless clearly links the rise of SO_x emissions with the occurrence of acid rain. Like The Netherlands, Japan is a small, densely populated country that has grown more and more dependent upon imported oil for meeting its energy needs. Today, Japan uses oil to provide more than 70 percent of its energy and SO_x emissions from residual-oil-fired boilers produce the greatest amount of acid rain precursors. Other local sources of SO_x are of much less importance; they include iron ore sintering operations, smelters, and coal-fired boilers.

Two factors have led to impressive reductions in emissions of SO_2, sulfate, and vanadium since the mid-1960's. They are the installation of FGD systems on over 1000 of Japan's oil-fired boilers and a switch to oils containing less sulfur (Ando 1978). This program to desulfurize both fuels and flue gases began in 1966. Since then, the average sulfur content of heavy oils used in Japan has fallen nearly 40 percent, from 2.3 percent to 1.4 percent, and ambient levels of SO_2, sulfate and vanadium have been cut in half (see Table D-2) (Ando 1978). Studies of the pH of rainfall in Japan between 1974 and 1977 have shown that values of 3 and 4 are not uncommon. Table D-3 shows a sample of values reported in Chemical Abstracts and by the World Monitoring Organization. Acid fogs and mists with pH values of 3 have also occurred.

Figure D-3 (Chemical Abstracts 1981) shows that Japan's demands for sulfur-containing fuels are expected to continue to rise through 1990. Coal is expected to displace oil to some extent and therefore to become a more important fuel than it has been. If SO_x emissions rise again as a result of increasing fuel consumption, acid rain may become an even greater concern in Japan.

TABLE D-2. AMBIENT CONCENTRATIONS OF SULFUR DIOXIDE (SO_2), SULFATE ($SO_4^{=}$) AND VANADIUM (V) IN MAJOR CITIES IN JAPAN (μg/Nm3) [a]

City	1970			1972			1974		
	SO_2	$SO_4^{=}$	V	SO_2	$SO_4^{=}$	V	SO_2	$SO_4^{=}$	V
Sapporo	-	11.2	0.03	-	8.3	0.03	-	7.0	0.02
Ichihara	-	14.7	0.06	-	15.5	0.07	-	11.8	0.03
Tokyo	-	17.3	0.07	-	16.1	0.08	-	12.0	0.05
Kawasaki	-	56.0	0.27	-	24.0	0.14	-	16.8	0.05
Nagoya	-	22.0	0.09	-	25.0	0.12	-	16.7	0.06
Osaka	-	31.6	0.15	-	27.0	0.13	-	14.6	0.05
Amagasaki	-	30.3	0.10	-	18.8	0.11	-	12.6	0.05
Matsue	-	8.7	0.01	-	10.3	0.02	-	7.3	0.02
Ube	-	27.5	0.05	-	20.9	0.07	-	13.4	0.05
Kitakyushu	-	29.0	0.10	-	17.1	0.07	-	12.5	0.05
Average	113	24.8	0.09	-	18.3	0.08	63	12.5	0.04

[a] Ando (1978).

TABLE D-3. ACID RAIN IN JAPAN

Location	Average pH	pH range	Dates	Reference[a]
Kanagawa		2.9-7.9	1976	CA91:78319j
	3.88-4.65		1977	CA90:126623g
Gunma[b]	4.8	3.2-6.5	1977	CA90:156732j
Yokohama[c]	3.02-3.68		1977	CA93:172775t
Kawasaki[c]	3.58-4.92		1977	CA93:172775t
Hidatsufo[c]	3.6-4		1977	CA93:172775t
Sendai	4.95	4-5	1975-77	CA93:119440d
		3.76-7.16	1975-76	CA93:119443d
Industrial area	4.2	3.2 minimum	1977	CA88:140984r
Kanto	<4		1974	CA88:75744g
Ryori	5.6		1976	WMO[d]
	5.2		1977	WMO[d]

[a] CA denoted Chemical Abstracts numbers.

[b] Sulfate values in rainwater increased from 0.34 ppm in 1946-47 to 10 to 100 times that amount in 1977.

[c] Uncertain whether values are a range of averages or a range of individual values.

[d] Environmental Data and Information Service (1977).

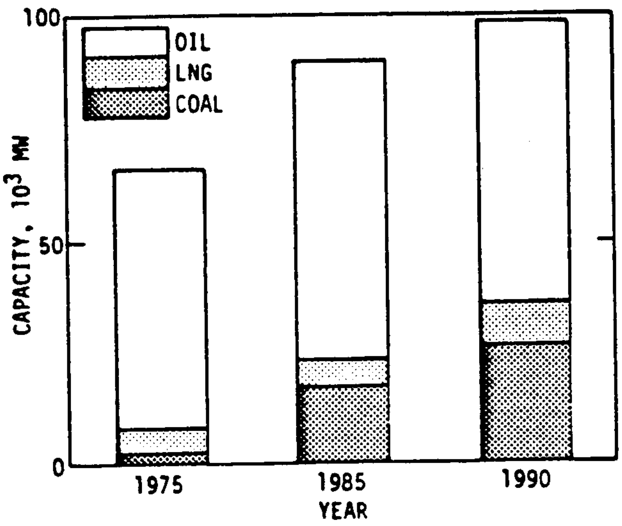

Figure D-3. Fuel mix required for Japan's desired increase in electrical generation capacity (Ando 1978).

APPENDIX E

METHOD OF ESTIMATING UNCONTROLLED SO_x AND NO_x EMISSIONS FROM FUEL CONSUMPTION IN THE UNITED STATES

This Appendix explains the methods used in estimating 1978 SO_x and NO_x emissions based on fuel consumption by sector and by state for the contiguous United States. They exclude SO_x and NO_x emissions from natural sources and from noncombustion sources such as primary metal smelting. The estimates encompass the major fossil fuels such as coal, residual and distillate oil, kerosene, gasoline, natural gas, LPG and jet fuels, but exclude minor fuels such as wood, lubricants, asphalt, and other miscellaneous petroleum products.

METHOD AND ASSUMPTIONS

The Department of Energy's "State Energy Data Report," provides statistics on energy consumption in different sectors for every state by type of fuel. The five energy consumption sectors are electric utilities, industrial, commercial, residential, and transportation. At times the latter four are grouped collectively into the nonutility sector. All fuel consumption data are for 1978.

Utility Sector

Coal, residual and distillate oil, and natural gas provide over 99 percent of the fossil fuel heat input to electric utilities. Emissions of SO_x from these fuels are due to the sulfur content of the fuels, whereas NO_x emissions are due primarily to the method of fuel combustion, in addition to the nitrogen content of the fuel. The sulfur contents of coal and oil were calculated for each state from data contained in the National Coal Association's "Steam Electric Plant Factors 1979." Weighted average sulfur levels were determined from the data for individual power plants within each state. The sulfur content of distillate oil was obtained from the Department of Energy's "Cost and Quality of Fuels for Electric Utility Plants - 1978," which presents statistics on fuel oil used in utility combustion turbines and internal combustion units. It was assumed that this fuel oil was representative of all distillate oil fired by electric utilities. PEDCo assumed the sulfur content of natural gas to be negligible. Emission factors from EPA's "Compilation of Air Pollutant Emission Factors," AP-42, and the "NEDS Source Classification Codes and Emission Factor Listing," were used in conjunction with sulfur content and consumption data to estimate the uncontrolled SO_x emissions from electric utilities in 1978. The SO_x emission factors are 38S pounds of SO_x per ton of coal fired, 159S pounds of SO_x

per 1000 gallons of residual oil fired, and 144S pounds of SO_x per 1000 gallons of distillate oil fired, where S equals the sulfur content of the fuel. These factors remain the same for each sector.

NO_x emissions were determined in a similar manner. All coal was assumed to have been fired in dry-bottom, pulverized-coal-fired units with an emission factor of 18 pounds of NO_x per ton of coal fired. For boilers firing residual oil, AP-42 lists two NO_x emission factors, one for tangential firing and another for normal firing. An average of these two values, 78 pounds of NO_x emitted per 1000 gallons of residual oil fired, was used in these estimates. The value of 105 pounds of NO_x per 1000 gallons of No. 2 distillate oil is the NEDS emission factor. As with residual oil, AP-42 gives two NO_x emission factors for natural gas fired in tangential and nontangential boilers and an average value, 500 pounds of NO_x per million cubic feet of natural gas fired, was used in these estimates.

Industrial Sector

For the industrial sector, the estimates include emissions from firing liquefied petroleum gas (LPG) in addition to the four fossil fuels discussed above because LPG represents about 10 percent of the total heat input from petroleum in this sector. The sulfur contents of natural gas and LPG were assumed to be negligible. Sulfur contents for coal and residual oil were obtained from "The Population and Characteristics of Industrial/Commercial Boilers," PEDCo Environmental, Inc., May 1979. A value of 0.25 percent sulfur was assumed for distillate oil in each state unless the value obtained for the utility sector was lower, in which case, the utility value was used.

A value of 15 pounds NO_x emitted per ton of coal fired was selected to estimate NO_x emissions due to coal firing. Emission factors for residual and distillate oils are 60 and 22 pounds of NO_x per 1000 gallons of oil, respectively. AP-42 presents ranges for NO_x emission factors for natural gas fired in boilers and LPG fired in industrial process furnaces. The average values used to estimate NO_x emissions were 175 pounds of NO_x per million cubic feet of natural gas and 11.7 pounds of NO_x per 1000 gallons of LPG.

Commercial Sector

For the commercial sector, emissions from four fuels were considered: coal, natural gas, residual oil, and distillate oil. Sulfur contents of each fuel were determined in the same manner as described for the industrial sector.

A value of 6 pounds of NO_x emitted per ton of coal fired was applied. The NO_x emission factor for residual-oil-firing is the same as in the industrial sector, 60 pounds of NO_x per 1000 gallons of oil. It was assumed that distillate oil in the commercial sector is fired in boilers and space heaters, and an average emission factor of 20 pounds of NO_x per 1000 gallons was used to estimate emissions from the firing of distillate oil. The AP-42 emission factor for natural gas NO_x emissions from commercial units is 120 pounds of NO_x per million cubic feet.

Residential Sector

The SO_x and NO_x emissions from residential burning of coal, natural gas, distillate oil, kerosene, and LPG were estimated. No residual oil is consumed in this sector. The sulfur contents of each fuel were determined as described for the industrial sector. It was assumed that the sulfur content and SO_x emission factors for kerosene were the same as those of distillate oil.

The NO_x emission factor for coal firing was calculated to be 4.5 pounds of NO_x per ton of coal. This value is the average of factors for underfeed stokers and handfired units. For natural gas the selected emission factor of 100 pounds of NO_x per million cubic feet is an average of the AP-42 value for domestic heating units and the NEDS value for institutional boilers. AP-42 lists a factor of 18 pounds of NO_x per 1000 gallons of distillate oil for domestic units, and this emission factor was also assumed to apply to kerosene. An average value of 7.5 pounds of NO_x per 1000 gallons of LPG was assumed to apply.

Transportation Sector

Motor gasoline, distillate fuel, and jet fuel supply almost 91 percent of the total heat input to the transportation sector. Emissions from consumption of these three fuels were estimated on the following basis:

1. The "dominant" fuels used in the sector were assumed to be gasoline, diesel fuel, and jet fuel.

2. Since AP-42 was inconclusive as to the factor to be used for overall NO_x emissions in 1978, the factors in EPA's Mobile Source Emissions Factors Manuals (EPA-400/9-78-005 and 006) were used for gasoline and diesel vehicles.

3. Although a variety of factors influence NO_x emissions, a scenario depicting overall driving conditions and general sector model mixes of vehicle types was developed. It was found that the NO_x emissions (in g/mi) were dependent only on the running condition assumed (i.e., cold, hot, warm). Generally a factor of 3.6 g/mi depicted emissions from all vehicles under normal conditions.

4. Since a gasoline-only scenario had an overall emission factor of 3.1 g NO_x/mi, a weighted average determination from the percent of total miles by vehicle type was performed to identify the diesel-only contribution. This calculation is:

   $$0.969\ (3.1) + 0.031\ (x) = 3.6\ \text{g}\ NO_x/\text{mi}$$

   (gas percent) (factor) + diesel percent(x) = overall factor

   The resulting diesel NO_x factor is 28.9 g/mi.

5. Next, the 1978 vehicle mpg figures for all vehicles were determined by contacting the Motor Vehicle Manufacturers Association in Detroit at (313)872-4311. Results are listed below.

1978 VEHICLE MPG*

	Diesel fuel	Motor gasoline
Passenger cars		14.06
Motorcycles		50.0
Commercial buses	5.02	
School buses	7.35	
All buses		5.95
Single unit trucks	10.10	
Truck combinations	5.39	
All trucks		8.64
All motor vehicles		12.38

*Source: MVMA Motor Vehicle Facts and Figures, 1978.

Using the EPA's distribution of model vehicle types, the following mpg figures were calculated:

$$\text{Gasoline} = 0.803\ (14.06) + 0.045\ (7.35) + 0.116\ (10.1) + 0.005\ (50) = 13.2 \text{ mpg}$$

$$\text{Diesel}^* = \left(\frac{5.02 + 5.39}{2}\right) = 5.2 \text{ mpg}$$

(*This average was used because no information was readily available on the distribution of percent miles for buses and heavy duty trucks.)

6. Combination of the mpg and emission factors yields a lb NO_x/1000 gal factor:

Gasoline: 13 mpg x 3.1 g/mi = 40.3 g NO_x/gal
x 0.00220462 lb/g x 1000 gal
= 90 lb/1000 gal .

Diesel: 5.2 mpg x 28.9 g/mi = 150.4 g NO_x/gal
x 0.00220464 lb/g x 1000 gal
= 300 lb/1000 gal

7. AP-42 factors for jet fuel are:

SO_x = 13.0 lb/1000 gal (AP-42, p. C-7)

NO_x = 14.6 lb/1000 gal (AP-42, p. C-7)$^{\text{(turbojet)}}$

8. AP-42 figures for gasoline and diesel SO_x are:

Gasoline = 0.18 g/mi (AP-42, p. D.2-11)
Diesel = 2.8 g/mi (AP-42, p. D.5-4)

9. To put these values into consistent units, the following conversion was applied:

0.18 x 0.00220462 x 1000 x 13 = 5.2 lb SO_x/1000 gal
2.8 x 0.00220462 x 1000 x 5.205 = 32.1 lb SO_x/1000 gal

RESULTS

Tables E-1 and E-2 summarize PEDCo's estimates of uncontrolled 1978 emissions of SO_x and NO_x, respectively, in 48 states and the District of Columbia by sector. It appears that the utility sector is responsible for 67 percent (18,363.26 x 10^3 tons) of the total SO_x emissions. The transportation sector is the largest emitter of NO_x, with an estimated 8,176.27 x 10^3 tons of NO_x or 47.2 percent of the total in 1978. Figures E-1 and E-2 display the results geographically, showing SO_x and NO_x emissions from the utility and nonutility sectors. A further breakdown of emissions in each sector by state is presented in Tables E-3 through E-7 for SO_x and Tables E-8 through E-12 for NO_x.

TABLE E-1. 1978 SO_x EMISSIONS FROM FOSSIL FUEL CONSUMPTION
(10^3 tons)

State	Utility	Industrial	Commercial	Residential	Transportation	Nonutility subtotal	Total
Alabama	570.04	393.81	19.98	3.93	13.83	431.55	1,001.59
Arizona	61.30	10.81	0.74	0.38	9.90	21.83	83.13
Arkansas	57.41	26.54	3.48	0.55	8.58	39.15	96.56
California	88.72	76.30	13.29	1.67	75.05	166.31	255.03
Colorado	77.94	22.66	11.04	1.00	9.86	44.56	122.50
Connecticut	25.65	43.14	23.55	5.22	5.89	77.80	103.45
Delaware	52.11	13.92	4.85	1.23	1.71	21.71	73.82
District of Columbia	4.67	1.51	5.22	0.90	1.13	8.76	13.43
Florida	596.46	95.74	14.60	3.58	30.26	144.18	740.64
Georgia	612.05	57.81	14.43	1.06	19.98	93.28	705.33
Idaho	0.00	7.11	4.71	2.61	3.55	17.98	17.98
Illinois	1,343.30	318.31	68.97	27.97	35.43	450.68	1,793.98
Indiana	1,395.86	931.20	49.10	14.96	16.54	1,011.80	2,407.66
Iowa	261.05	54.25	10.18	6.49	9.55	80.47	341.52
Kansas	249.41	24.22	3.31	1.02	8.88	37.43	286.84
Kentucky	1,265.28	174.52	26.55	13.58	12.07	226.72	1,492.00
Louisiana	59.64	77.35	8.34	0.68	16.78	103.15	162.79
Maine	8.60	27.38	13.66	6.03	3.47	50.54	59.14
Maryland	216.79	114.81	16.61	6.28	9.71	147.41	364.20
Massachusetts	254.23	24.69	78.37	9.08	11.41	123.55	377.78
Michigan	811.03	317.39	34.08	19.29	21.84	392.60	1,203.63
Minnesota	238.92	59.51	15.03	11.44	11.93	97.91	336.83

(continued)

TABLE E-1 (continued)

State	Utility	Industrial	Commercial	Residential	Transportation	Nonutility subtotal	Total
Mississippi	198.98	22.51	5.89	0.90	8.33	37.63	236.61
Missouri	1,046.16	120.28	21.53	8.72	16.74	167.27	1,213.43
Montana	44.24	11.50	4.36	1.12	4.45	21.43	65.67
Nebraska	36.62	11.78	2.77	1.59	7.49	23.63	60.25
Nevada	46.24	1.50	0.32	0.41	4.51	6.74	52.98
New Hampshire	50.24	5.36	5.24	1.62	1.80	14.02	64.26
New Jersey	115.27	67.58	56.67	8.57	17.14	149.96	265.23
New Mexico	102.14	6.52	0.90	0.35	6.85	14.62	116.76
New York	514.09	232.08	238.50	32.16	33.15	535.89	1,049.98
North Carolina	393.18	102.79	17.48	9.87	16.22	146.36	539.54
North Dakota	98.13	10.14	5.00	1.83	3.24	20.21	118.34
Ohio	2,566.13	1,140.86	73.84	43.39	28.62	1,286.71	3,852.84
Oklahoma	16.01	11.87	2.19	0.17	10.44	24.67	40.68
Oregon	0.02	13.08	6.61	1.64	10.22	31.55	31.57
Pennsylvania	1,510.15	1,083.42	95.38	67.18	28.69	1,274.67	2,784.82
Rhode Island	3.92	3.97	8.20	3.62	1.44	17.23	21.15
South Carolina	195.66	84.06	3.16	3.11	8.76	99.09	294.75
South Dakota	41.97	3.76	0.51	0.77	2.59	7.63	49.60
Tennessee	1,037.91	269.78	15.35	6.44	17.15	308.72	1,346.63
Texas	307.95	128.14	23.47	3.07	60.37	215.05	523.00
Utah	32.42	39.82	7.07	1.43	5.18	53.50	85.92
Vermont	0.29	1.95	3.32	1.95	1.18	8.40	8.69
Virginia	217.03	67.56	8.80	7.70	17.62	101.68	318.71

(continued)

TABLE E-1 (continued)

State	Utility	Industrial	Commercial	Residential	Transportation	Nonutility subtotal	Total
Washington	80.45	31.26	10.55	3.09	14.26	59.16	139.61
West Virginia	891.77	280.05	11.37	5.05	5.08	301.55	1,193.32
Wisconsin	466.31	105.35	17.63	16.84	12.05	151.87	618.18
Wyoming	99.52	25.89	8.18	0.83	4.42	39.32	138.84
Total	18,363.26	6,755.84	1,094.38	372.37	685.34	8,907.93	27,271.19

TABLE E-2. 1978 NO$_x$ EMISSIONS FROM FOSSIL FUEL CONSUMPTION (10^3 tons)

State	Utility	Industrial	Commercial	Residential	Transportation	Nonutility subtotal	Total
Alabama	153.64	82.03	5.55	4.78	175.27	267.63	421.27
Arizona	83.40	10.75	2.18	1.87	106.71	121.51	204.91
Arkansas	33.92	20.02	3.21	3.90	105.75	132.88	166.80
California	205.61	84.98	17.80	29.11	820.06	951.95	1,157.56
Colorado	89.28	20.26	7.72	6.02	109.15	143.15	232.43
Connecticut	33.37	15.54	8.67	8.27	80.76	113.24	146.61
Delaware	21.74	4.78	1.87	1.06	18.88	26.59	48.33
District of Columbia	8.15	0.75	2.48	1.12	15.50	19.85	28.00
Florida	232.55	29.16	4.96	4.63	327.70	366.45	599.00
Georgia	172.22	23.62	6.65	6.52	244.23	261.02	433.24
Idaho	0.01	6.84	1.97	1.74	42.76	53.31	53.32
Illinois	324.81	95.71	29.36	36.46	398.66	560.19	885.00
Indiana	269.47	158.38	15.53	16.32	216.40	406.63	676.10
Iowa	80.18	22.82	4.73	7.74	124.40	159.69	239.87
Kansas	104.01	22.45	4.89	6.71	111.28	145.33	249.34
Kentucky	221.10	29.57	5.74	6.84	152.10	194.25	415.35
Louisiana	134.77	165.81	6.46	5.09	196.29	373.65	508.42
Maine	3.04	8.58	5.28	3.25	39.75	56.86	59.90
Maryland	77.35	33.40	7.32	6.89	127.66	175.27	252.62
Massachusetts	80.71	11.00	31.92	15.93	140.95	199.80	280.51
Michigan	237.58	80.74	17.86	25.25	295.12	418.97	656.55

(continued)

TABLE E-2 (continued)

State	Utility	Industrial	Commercial	Residential	Transportation	Nonutility subtotal	Total
Minnesota	112.90	29.47	9.19	11.71	148.53	198.90	311.80
Mississippi	58.92	13.42	3.37	3.26	105.07	125.12	184.04
Missouri	196.62	23.44	9.76	12.60	203.01	248.81	445.43
Montana	29.01	6.96	2.44	2.08	53.11	64.59	93.60
Nebraska	26.51	10.82	3.46	4.05	87.71	106.04	132.55
Nevada	46.27	2.13	1.33	0.87	38.52	42.85	89.12
New Hampshire	12.17	2.16	2.61	2.43	24.08	31.28	43.45
New Jersey	66.00	25.34	25.67	16.61	222.05	289.67	355.67
New Mexico	88.73	9.87	1.98	1.87	76.82	90.54	179.27
New York	197.83	64.48	83.26	47.73	357.53	553.00	750.83
North Carolina	174.91	30.51	5.13	6.89	212.13	254.66	429.57
North Dakota	78.93	7.23	2.01	1.64	35.18	46.06	124.99
Ohio	461.83	189.66	20.11	30.04	373.23	613.04	1,074.87
Oklahoma	106.48	31.22	4.09	6.07	128.62	170.00	276.48
Oregon	0.08	10.32	3.09	2.00	124.16	139.57	139.65
Pennsylvania	377.15	241.09	27.81	29.52	365.56	663.98	1,041.13
Rhode Island	2.14	1.85	3.44	2.54	21.14	28.97	31.11
South Carolina	70.33	26.20	2.12	3.40	112.45	144.17	214.50
South Dakota	25.70	2.75	0.99	1.77	30.57	36.08	61.78
Tennessee	205.95	48.06	4.34	4.05	210.93	267.38	473.33
Texas	609.93	243.70	19.13	19.43	703.13	985.39	1,595.32
Utah	30.53	28.64	2.91	2.95	61.64	96.14	126.67
Vermont	0.08	1.06	1.67	1.21	16.58	20.52	20.60

(continued)

TABLE E-2 (continued)

State	Utility	Industrial	Commercial	Residential	Transportation	Nonutility subtotal	Total
Virginia	85.68	31.86	5.55	6.99	201.44	245.84	331.52
Washington	38.16	19.35	5.40	3.23	153.85	181.83	219.99
West Virginia	233.81	59.63	3.19	3.58	67.70	134.10	367.91
Wisconsin	110.04	33.82	8.65	14.52	160.75	217.74	327.78
Wyoming	100.31	20.99	3.07	1.26	51.40	76.72	177.03
Total	6,113.91	2,143.22	457.92	443.80	8,176.27	11,211.21	17,335.12

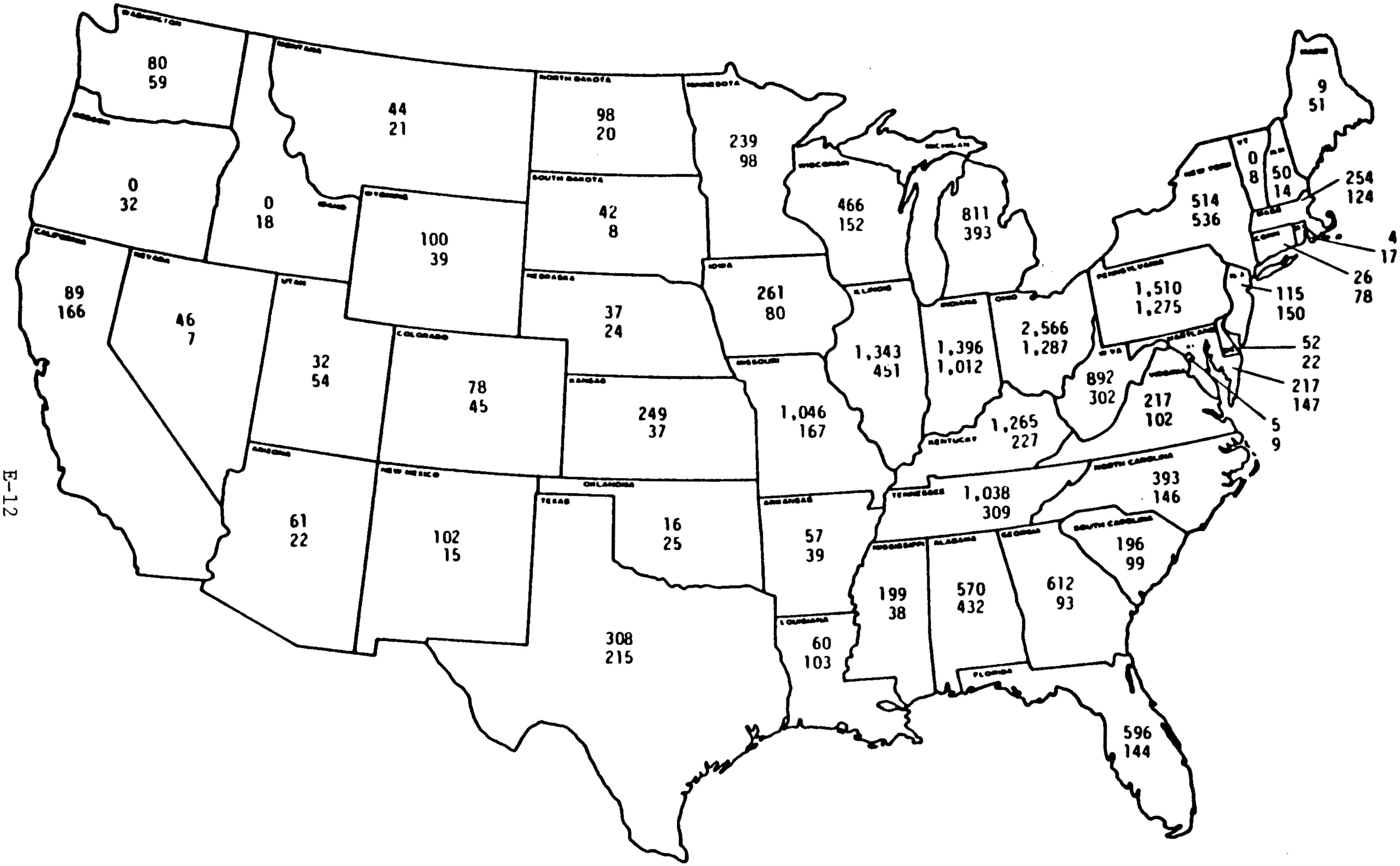

Figure E-1. 1978 utility and nonutility uncontrolled SO_x emissions.
(Top number indicates utility emissions and bottom number indicates nonutility emissions, in 10^3 tons.)

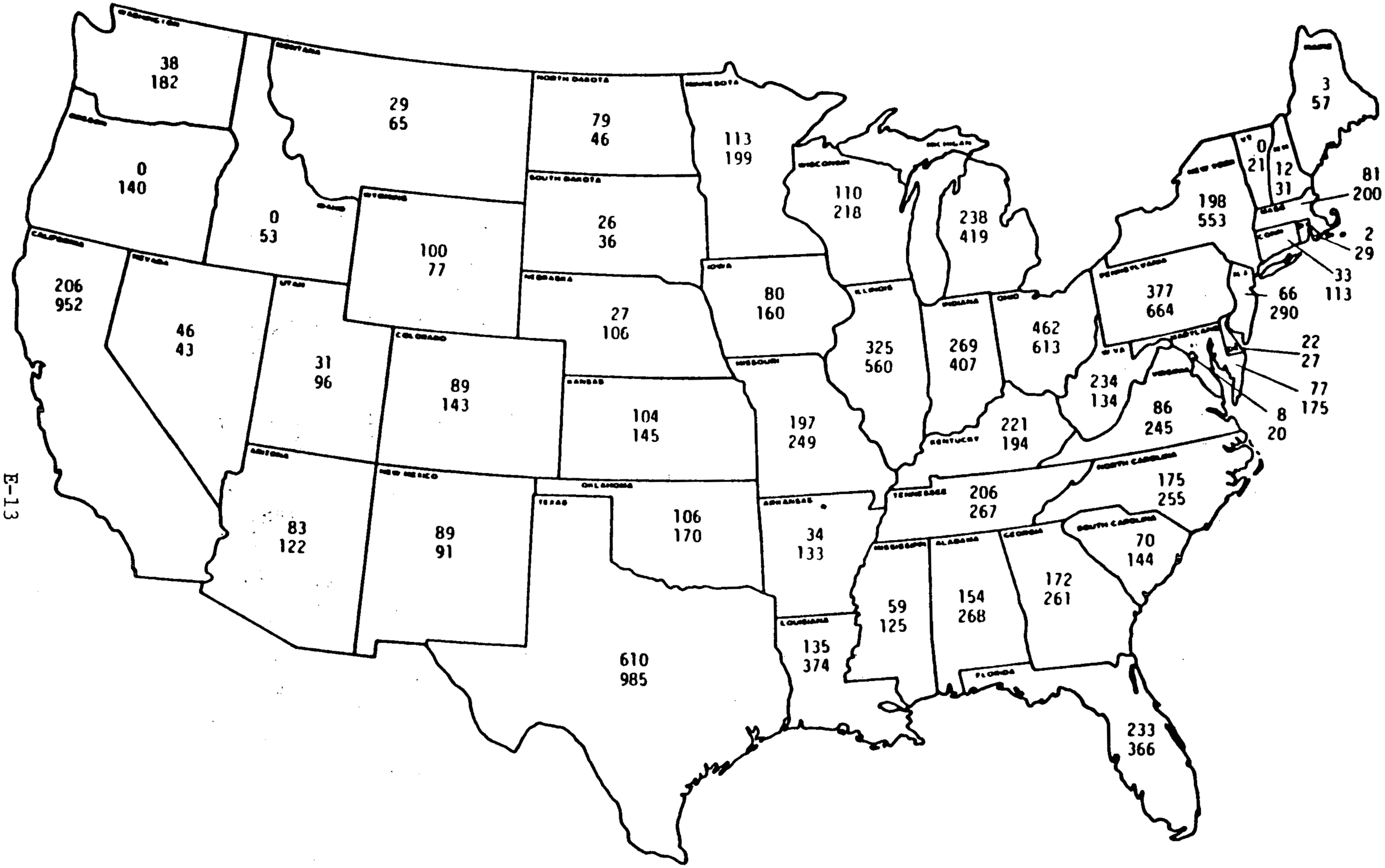

Figure E-2. 1978 utility and nonutility uncontrolled NO_x emissions. (Top number indicates utility emissions and bottom number indicates nonutility emissions, in 10^3 tons.)

TABLE E-3. 1978 UTILITY SO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Residual oil	Distillate oil	Oil subtotal	Coal	Total
Alabama		2.42	2.42	567.62	570.04
Arizona	7.18	0.87	8.05	53.25	61.30
Arkansas	49.33	0.78	50.11	7.30	57.41
California	87.78	0.94	88.72	0.00	88.72
Colorado	1.12	0.34	1.46	76.48	77.94
Connecticut	24.96	0.02	24.98	0.67	25.65
Delaware	23.51	0.81	24.32	27.79	52.11
District of Columbia	1.76	2.91	4.67	0.00	4.67
Florida	321.11	3.72	324.83	271.63	596.46
Georgia	27.12	2.05	29.17	582.88	612.05
Idaho	0.00	0.00	0.00	0.00	0.00
Illinois	25.53	6.03	31.56	1311.74	1343.30
Indiana	0.00	3.64	3.64	1392.22	1395.86
Iowa	0.00	0.84	0.84	260.21	261.05
Kansas	19.37	1.05	20.42	228.99	249.41
Kentucky	0.00	0.52	0.52	1264.76	1265.28
Louisiana	57.84	1.80	59.64	0.00	59.64
Maine	8.58	0.02	8.60	0.00	8.60
Maryland	80.33	1.17	81.50	135.29	216.79
Massachusetts	254.10	0.13	254.23	0.00	254.23
Michigan	40.97	2.26	43.23	767.80	811.03
Minnesota	5.75	0.64	6.39	232.53	238.92
Mississippi	127.85	3.21	131.06	67.92	198.98
Missouri	1.80	1.72	3.52	1042.64	1046.16
Montana	0.00	0.08	0.08	44.16	44.24
Nebraska	3.67	0.12	3.79	32.83	36.62
Nevada	6.29	0.01	6.30	39.94	46.24
New Hampshire	17.67	0.01	17.68	32.56	50.24
New Jersey	44.47	0.30	44.77	70.50	115.27
New Mexico	0.12	0.23	0.35	101.79	102.14
New York	309.28	1.20	310.48	203.61	514.09
North Carolina	2.12	1.22	3.34	389.84	393.18
North Dakota	0.00	0.09	0.09	98.04	98.13
Ohio	4.82	4.52	9.34	2556.79	2566.13
Oklahoma	0.00	0.24	0.24	15.77	16.01
Oregon	0.00	0.02	0.02	0.00	0.02
Pennsylvania	50.82	1.02	51.84	1458.31	1510.15
Rhode Island	3.92	0.00	3.92	0.00	3.92
South Carolina	34.32	0.91	35.23	160.43	195.66
South Dakota	0.19	0.12	0.31	41.66	41.97
Tennessee	0.00	10.91	10.91	1027.00	1037.91
Texas	5.96	1.42	7.38	300.57	307.95
Utah	0.07	0.05	0.12	32.30	32.42
Vermont	0.00	0.00	0.00	0.29	0.29
Virginia	132.68	2.33	135.01	82.02	217.03
Washington	0.00	0.02	0.02	80.43	80.45
West Virginia	0.04	1.34	1.38	890.39	891.77
Wisconsin	0.08	2.10	2.18	464.13	466.31
Wyoming	0.00	0.00	0.00	99.52	99.52
Totals	1782.51	66.15	1848.66	16,514.60	18,363.26

TABLE E-4. 1978 INDUSTRIAL SO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Residual oil	Distillate oil	Oil subtotal	Coal	Total
Alabama	39.42	3.57	42.99	350.82	393.81
Arizona	2.58	3.99	6.57	4.24	10.81
Arkansas	20.92	2.12	23.04	3.50	26.54
California	43.29	7.83	51.12	25.18	76.30
Colorado	7.82	1.76	9.58	13.08	22.66
Connecticut	42.56	0.51	43.07	0.07	43.14
Delaware	8.86	0.51	9.37	4.55	13.92
District of Columbia	0.17	0.06	0.23	1.28	1.51
Florida	77.30	4.22	81.52	14.22	95.74
Georgia	33.51	2.48	35.99	21.82	57.81
Idaho	2.08	1.46	3.54	3.57	7.11
Illinois	63.84	4.08	67.92	250.39	318.31
Indiana	63.61	3.57	67.18	864.02	931.20
Iowa	0.18	2.01	2.19	52.06	54.25
Kansas	15.34	2.62	17.96	6.26	24.22
Kentucky	9.29	3.46	12.75	161.77	174.52
Louisiana	67.86	7.54	75.40	1.95	77.35
Maine	26.57	0.20	26.77	0.61	27.38
Maryland	11.44	2.47	13.91	100.90	114.81
Massachusetts	22.92	0.44	23.36	1.33	24.69
Michigan	14.39	3.68	18.07	299.32	317.39
Minnesota	8.02	1.74	9.76	49.75	59.51
Mississippi	15.65	3.30	18.95	3.56	22.51
Missouri	6.09	2.27	8.36	111.92	120.28
Montana	7.79	1.20	8.99	2.51	11.50
Nebraska	0.58	1.42	2.00	9.78	11.78
Nevada	0.09	0.77	0.86	0.64	1.50
New Hampshire	5.19	0.08	5.27	0.09	5.36
New Jersey	61.21	0.81	62.02	5.56	67.58
New Mexico	4.13	1.46	5.59	0.93	6.52
New York	41.62	2.60	44.22	187.86	232.08
North Carolina	66.58	3.44	70.02	32.77	102.79
North Dakota	2.10	0.25	2.35	7.79	10.14
Ohio	31.54	8.36	39.90	1100.96	1140.86
Oklahoma	4.84	2.68	7.52	4.35	11.87
Oregon	8.65	2.25	10.90	2.18	13.08
Pennsylvania	86.17	2.94	89.11	994.31	1083.42
Rhode Island	3.81	0.09	3.90	0.07	3.97
South Carolina	47.65	1.24	48.89	35.17	84.06
South Dakota	0.42	0.54	0.96	2.80	3.76
Tennessee	9.95	3.61	13.56	256.22	269.78
Texas	91.51	12.18	103.69	24.45	128.14
Utah	14.86	1.74	16.60	23.22	39.82
Vermont	1.79	0.10	1.89	0.06	1.95
Virginia	27.59	3.17	30.76	36.80	67.56
Washington	23.10	2.90	26.00	5.26	31.26
West Virginia	8.36	1.49	9.85	270.20	280.05
Wisconsin	5.42	1.34	6.76	98.59	105.35
Wyoming	8.21	2.86	11.07	14.82	25.89
Totals	1166.87	125.41	1292.28	5463.56	6755.84

TABLE E-5. 1978 COMMERCIAL SO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Residual oil	Distillate oil	Oil subtotal	Coal	Total
Alabama	13.29	1.53	14.82	5.16	19.98
Arizona	0.00	0.74	0.74	0.00	0.74
Arkansas	2.69	0.76	3.45	0.03	3.48
California	11.65	1.61	13.26	0.03	13.29
Colorado	8.59	1.13	9.72	1.32	11.04
Connecticut	22.95	0.56	23.51	0.04	23.55
Delaware	3.81	0.96	4.77	0.08	4.85
District of Columbia	4.52	0.68	5.20	0.02	5.22
Florida	14.57	0.03	14.60	0.00	14.60
Georgia	13.20	0.79	13.99	0.44	14.43
Idaho	2.37	0.97	3.34	1.37	4.71
Illinois	35.86	7.80	43.66	25.31	68.97
Indiana	39.30	3.47	42.77	6.33	49.10
Iowa	3.06	1.08	4.14	6.04	10.18
Kansas	1.75	1.07	2.82	0.49	3.31
Kentucky	2.84	2.08	4.92	21.63	26.55
Louisiana	6.50	1.84	8.34	0.00	8.34
Maine	12.55	1.07	13.62	0.04	13.66
Maryland	12.97	3.12	16.09	0.52	16.61
Massachusetts	73.06	5.25	78.31	0.06	78.37
Michigan	17.55	7.41	24.96	9.12	34.08
Minnesota	7.90	3.75	11.65	3.38	15.03
Mississippi	3.06	2.68	5.74	0.15	5.89
Missouri	9.12	2.25	11.37	10.16	21.53
Montana	3.64	0.59	4.23	0.13	4.36
Nebraska	1.32	1.19	2.51	0.26	2.77
Nevada	0.17	0.13	0.30	0.02	0.32
New Hampshire	4.46	0.78	5.24	0.00	5.24
New Jersey	50.46	5.49	55.95	0.72	56.67
New Mexico	0.43	0.47	0.90	0.00	0.90
New York	225.61	4.62	230.23	8.27	238.50
North Carolina	12.36	1.90	14.26	3.22	17.48
North Dakota	2.82	0.16	2.98	2.02	5.00
Ohio	14.13	4.76	18.89	54.95	73.84
Oklahoma	0.34	1.82	2.16	0.03	2.19
Oregon	5.43	1.06	6.49	0.12	6.61
Pennsylvania	40.16	3.79	43.95	51.43	95.38
Rhode Island	7.56	0.64	8.20	0.00	8.20
South Carolina	2.26	0.21	2.47	0.69	3.16
South Dakota	0.31	0.16	0.47	0.04	0.51
Tennessee	6.10	1.59	7.69	7.66	15.35
Texas	15.67	7.80	23.47	0.00	23.47
Utah	4.45	0.88	5.33	1.74	7.07
Vermont	2.73	0.57	3.30	0.02	3.32
Virginia	4.51	2.16	6.67	2.13	8.80
Washington	7.46	1.97	9.43	1.12	10.55
West Virginia	4.38	0.01	4.39	6.98	11.37
Wisconsin	5.73	3.77	9.50	8.13	17.63
Wyoming	5.82	0.94	6.76	1.42	8.18
Totals	751.47	100.09	851.56	242.82	1094.38

TABLE E-6. 1978 RESIDENTIAL SO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Distillate oil	Kerosene	Oil subtotal	Coal	Total
Alabama	0.59	0.54	1.13	2.80	3.93
Arizona	0.20	0.18	0.38	0.00	0.38
Arkansas	0.07	0.47	0.54	0.01	0.55
California	0.60	1.06	1.66	0.01	1.67
Colorado	0.18	0.11	0.29	0.71	1.00
Connecticut	5.08	0.07	5.15	0.07	5.22
Delaware	1.00	0.11	1.11	0.12	1.23
District of Columbia	0.87	0.01	0.88	0.02	0.90
Florida	2.79	0.79	3.58	0.00	3.58
Georgia	0.76	0.06	0.82	0.24	1.06
Idaho	1.80	0.07	1.87	0.74	2.61
Illinois	12.73	0.97	13.70	14.27	27.97
Indiana	10.41	0.99	11.40	3.56	14.96
Iowa	3.08	0.11	3.19	3.30	6.49
Kansas	0.66	0.12	0.78	0.24	1.02
Kentucky	1.17	0.75	1.92	11.66	13.58
Louisiana	0.06	0.62	0.68	0.00	0.68
Maine	5.43	0.56	5.99	0.04	6.03
Maryland	5.55	0.40	5.95	0.33	6.28
Massachusetts	8.83	0.15	8.98	0.10	9.08
Michigan	13.17	0.69	13.86	5.43	19.29
Minnesota	9.19	0.40	9.59	1.85	11.44
Mississippi	0.08	0.77	0.85	0.05	0.90
Missouri	3.10	0.17	3.27	5.45	8.72
Montana	1.00	0.04	1.04	0.08	1.12
Nebraska	1.14	0.31	1.45	0.14	1.59
Nevada	0.38	0.02	0.40	0.01	0.41
New Hampshire	1.46	0.11	1.57	0.05	1.62
New Jersey	6.99	0.50	7.49	1.08	8.57
New Mexico	0.04	0.31	0.35	0.00	0.35
New York	22.55	1.23	23.78	8.38	32.16
North Carolina	4.66	3.48	8.14	1.73	9.87
North Dakota	0.73	0.01	0.74	1.09	1.83
Ohio	10.11	3.01	13.12	30.27	43.39
Oklahoma	0.04	0.12	0.16	0.01	0.17
Oregon	1.40	0.17	1.57	0.07	1.64
Pennsylvania	8.44	0.57	9.01	58.17	67.18
Rhode Island	3.56	0.06	3.62	0.00	3.62
South Carolina	2.14	0.60	2.74	0.37	3.11
South Dakota	0.67	0.08	0.75	0.02	0.77
Tennessee	0.59	1.72	2.31	4.13	6.44
Texas	0.16	2.91	3.07	0.00	3.07
Utah	0.28	0.03	0.31	1.12	1.43
Vermont	1.68	0.23	1.91	0.04	1.95
Virginia	5.29	1.25	6.54	1.16	7.70
Washington	2.23	0.25	2.48	0.61	3.09
West Virginia	1.01	0.13	1.14	3.91	5.05
Wisconsin	11.94	0.49	12.43	4.41	16.84
Wyoming	0.07	0.00	0.07	0.76	0.83
Totals	175.96	27.80	203.76	168.61	372.37

TABLE E-7. 1978 TRANSPORTATION SO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Jet fuel	Distillate oil	Gasoline	Total oil
Alabama	0.59	7.77	5.47	13.83
Arizona	2.14	4.28	3.48	9.90
Arkansas	0.64	4.62	3.32	8.58
California	17.67	27.46	29.92	75.05
Colorado	2.17	3.76	3.93	9.86
Connecticut	0.55	1.75	3.59	5.89
Delaware	0.46	0.46	0.79	1.71
District of Columbia	0.00	0.58	0.55	1.13
Florida	7.57	10.46	12.23	30.26
Georgia	3.98	8.12	7.88	19.98
Idaho	0.34	1.87	1.34	3.55
Illinois	6.85	14.76	13.82	35.43
Indiana	0.76	8.21	7.57	16.54
Iowa	0.31	5.11	4.13	9.55
Kansas	0.46	4.99	3.43	8.88
Kentucky	0.68	6.53	4.86	12.07
Louisiana	1.54	9.84	5.40	16.78
Maine	0.69	1.30	1.48	3.47
Maryland	0.95	3.55	5.21	9.71
Massachusetts	2.22	2.94	6.25	11.41
Michigan	1.95	7.32	12.57	21.84
Minnesota	1.33	5.18	5.42	11.93
Mississippi	0.44	4.56	3.33	8.33
Missouri	2.13	7.44	7.17	16.74
Montana	0.20	2.93	1.32	4.45
Nebraska	0.54	4.73	2.22	7.49
Nevada	1.82	1.43	1.26	4.51
New Hampshire	0.27	0.39	1.14	1.80
New Jersey	1.68	6.76	8.70	17.14
New Mexico	0.76	4.05	2.04	6.85
New York	10.05	7.62	15.48	33.15
North Carolina	1.26	6.86	8.10	16.22
North Dakota	0.53	1.75	0.96	3.24
Ohio	1.85	13.11	13.66	28.62
Oklahoma	1.29	4.44	4.71	10.44
Oregon	0.67	5.96	3.59	10.22
Pennsylvania	2.31	13.32	13.06	28.69
Rhode Island	0.07	0.38	0.99	1.44
South Carolina	0.87	3.56	4.33	8.76
South Dakota	0.37	1.17	1.05	2.59
Tennessee	1.21	9.44	6.50	17.15
Texas	7.79	30.69	21.89	60.37
Utah	0.52	2.80	1.86	5.18
Vermont	0.04	0.46	0.68	1.18
Virginia	3.31	7.11	7.20	17.62
Washington	3.12	6.05	5.09	14.26
West Virginia	0.08	2.69	2.31	5.08
Wisconsin	0.60	5.43	6.02	12.05
Wyoming	0.05	3.46	0.91	4.42
Totals	97.68	299.45	288.21	685.34

TABLE E-8. 1978 UTILITY NO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Residual oil	Distillate oil	Oil subtotal	Coal	Natural gas	Total
Alabama		2.52	2.52	149.37	1.75	153.64
Arizona	4.63	2.12	6.75	63.06	13.59	83.40
Arkansas	20.68	2.85	23.53	8.64	1.75	33.92
California	126.65	3.42	130.07		75.54	205.61
Colorado	0.59	0.82	1.41	80.51	7.36	89.28
Connecticut	33.10	0.13	33.23	0.14		33.37
Delaware	12.40	1.97	14.37	7.00	0.37	21.74
District of Columbia	1.08	7.07	8.15			8.15
Florida	119.34	9.04	128.38	64.66	39.51	232.55
Georgia	7.08	4.99	12.07	158.68	1.47	172.22
Idaho	0.00	0.00	0.00		0.01	0.01
Illinois	2.89	14.65	17.54	301.63	5.64	324.81
Indiana		8.86	8.86	259.82	0.79	269.47
Iowa		2.05	2.05	76.09	2.04	80.18
Kansas	5.79	2.56	8.35	66.14	29.52	104.01
Kentucky		0.54	0.54	220.26	0.30	221.10
Louisiana	35.91	6.56	42.47		92.30	134.77
Maine	2.90	0.14	3.04			3.04
Maryland	30.79	2.85	33.64	43.60	0.11	77.35
Massachusetts	79.40	0.92	80.32		0.39	80.71
Michigan	29.55	5.49	35.04	193.46	9.08	237.58
Minnesota	1.92	1.55	3.47	109.05	0.38	112.90
Mississippi	29.87	3.34	33.21	14.90	10.81	58.92
Missouri	1.34	4.18	5.52	184.28	6.82	196.62
Montana		0.12	0.12	28.66	0.23	29.01
Nebraska	1.70	0.30	2.00	21.30	3.21	26.51
Nevada	4.41	0.03	4.44	36.39	5.44	46.27
New Hampshire	5.10	0.06	5.16	7.01		12.17
New Jersey	43.63	2.18	45.81	20.00	0.19	66.00
New Mexico	0.12	0.83	0.95	71.96	15.82	88.73
New York	135.46	5.66	141.12	56.40	0.31	197.83
North Carolina	0.97	2.96	3.93	170.98	0.00	174.91
North Dakota		0.21	0.21	78.71	0.01	78.93
Ohio	3.15	10.99	14.14	446.90	0.79	461.83
Oklahoma		0.89	0.89	18.68	86.91	106.48
Oregon		0.08	0.08			0.08
Pennsylvania	42.26	7.40	49.66	327.38	0.11	377.15
Rhode Island	2.14		2.14			2.14
South Carolina	8.59	2.21	10.80	58.46	1.07	70.33
South Dakota	0.11	0.28	0.39	25.30	0.01	25.70
Tennessee		11.36	11.36	194.59		205.95
Texas	6.09	5.18	11.27	225.99	372.67	609.93
Utah	0.12	0.19	0.31	28.33	1.89	30.53
Vermont		0.01	0.01	0.06	0.01	0.08
Virginia	40.94	5.65	46.59	38.85	0.24	85.68
Washington		0.05	0.05	38.10	0.01	38.16
West Virginia	0.09	3.25	3.34	230.47	0.00	233.81
Wisconsin	0.12	5.10	5.22	102.74	2.08	110.04
Wyoming				100.31	0.00	100.31
Totals	840.91	153.61	994.52	4328.86	790.53	6113.91

TABLE E-9. 1978 INDUSTRIAL NO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Residual oil	Distillate oil	Liquified petroleum gas	Oil subtotal	Coal	Natural gas	Total
Alabama	7.63	2.18	0.39	10.20	60.21	11.62	82.03
Arizona	0.74	2.44	0.21	3.39	3.35	4.01	10.75
Arkansas	4.59	1.62	1.02	7.23	2.30	10.49	20.02
California	12.56	5.98	3.91	22.45	19.88	42.65	84.98
Colorado	2.17	1.08	0.55	3.80	10.33	6.13	20.26
Connecticut	12.75	0.78	0.55	14.08	0.02	1.44	15.54
Delaware	2.65	0.31	0.20	3.16	0.86	0.76	4.78
District of Columbia	0.05	0.04	0.00	0.09	0.63	0.03	0.75
Florida	14.96	2.58	0.74	18.28	1.94	8.94	29.16
Georgia	6.48	1.51	1.01	9.00	4.79	9.83	23.62
Idaho	0.59	0.89	0.23	1.71	2.82	2.31	6.84
Illinois	14.69	2.49	5.27	22.45	41.18	32.08	95.71
Indiana	14.64	2.18	2.74	19.56	121.81	17.01	158.38
Iowa	0.04	1.23	2.95	4.22	10.28	8.32	22.82
Kansas	3.53	1.60	1.31	6.44	0.77	15.24	22.45
Kentucky	2.42	2.11	0.66	5.19	19.35	5.03	29.57
Louisiana	13.13	5.76	1.09	19.98	1.28	144.55	165.81
Maine	7.96	0.31	0.11	8.38	0.13	0.07	8.58
Maryland	3.43	1.51	0.44	5.38	24.89	3.13	33.40
Massachusetts	6.87	0.67	0.66	8.20	0.52	2.28	11.00
Michigan	3.75	2.25	1.14	7.14	49.23	24.37	80.74
Minnesota	1.84	1.06	0.96	3.86	15.10	10.51	29.47
Mississippi	3.03	2.01	1.09	6.13	0.54	6.75	13.42
Missouri	1.40	1.39	1.18	3.97	13.39	6.08	23.44
Montana	2.16	0.73	0.07	2.96	1.42	2.58	6.96
Nebraska	0.14	0.87	0.94	1.95	4.29	4.58	10.82
Nevada	0.03	0.47	0.03	0.53	0.63	0.97	2.13
New Hampshire	1.55	0.12	0.36	2.03	0.02	0.11	2.16
New Jersey	18.33	1.23	0.84	20.40	1.16	3.78	25.34
New Mexico	1.15	1.11	0.35	2.61	0.62	6.64	9.87
New York	12.46	3.97	1.05	17.48	39.03	7.97	64.48
North Carolina	12.88	2.10	1.67	16.65	11.76	2.10	30.51
North Dakota	0.51	0.15	0.17	0.83	5.12	1.28	7.23
Ohio	9.45	5.11	1.51	16.07	144.86	28.73	189.66
Oklahoma	1.16	2.05	1.20	4.41	2.86	23.95	31.22
Oregon	2.51	1.72	0.18	4.41	1.73	4.18	10.32
Pennsylvania	25.81	4.49	1.83	32.13	186.90	22.06	241.09
Rhode Island	1.14	0.13	0.15	1.42	0.02	0.41	1.85
South Carolina	9.22	0.75	0.68	10.65	10.68	4.87	26.20
South Dakota	0.10	0.33	0.33	0.76	1.38	0.61	2.75
Tennessee	1.93	2.21	0.39	4.53	34.88	8.65	48.06
Texas	20.93	9.31	4.72	34.96	16.09	192.65	243.70
Utah	4.15	1.33	0.13	5.61	18.33	4.70	28.64
Vermont	0.54	0.15	0.20	0.89	0.02	0.15	1.06
Virginia	8.26	1.94	0.60	10.80	18.16	2.90	31.86
Washington	6.70	2.22	0.31	9.23	4.16	5.96	19.35
West Virginia	2.50	0.91	0.12	3.53	50.79	5.31	59.63
Wisconsin	1.25	0.82	1.36	3.43	16.92	13.47	33.82
Wyoming	2.28	1.75	0.22	4.25	11.70	5.04	20.99
Totals	289.04	89.95	47.82	426.81	989.13	727.28	2143.22

TABLE E-10. 1978 COMMERCIAL NO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Residual oil	Distillate oil	Oil subtotal	Coal	Natural gas	Total
Alabama	2.57	0.85	3.42	0.35	1.78	5.55
Arizona	0.00	0.41	0.41	0.00	1.77	2.18
Arkansas	0.59	0.53	1.12	0.01	2.08	3.21
California	3.38	1.12	4.50	0.01	13.29	17.80
Colorado	2.38	0.63	3.01	0.42	4.29	7.72
Connecticut	6.87	0.78	7.65	0.00	1.02	8.67
Delaware	1.14	0.54	1.68	0.01	0.18	1.87
District of Columbia	1.35	0.38	1.73	0.00	0.75	2.48
Florida	2.82	0.02	2.84	0.00	2.12	4.96
Georgia	2.55	0.44	2.99	0.04	3.62	6.65
Idaho	0.67	0.54	1.21	0.43	0.33	1.97
Illinois	8.25	4.33	12.58	1.67	15.11	29.36
Indiana	9.04	1.93	10.97	0.36	4.20	15.53
Iowa	0.70	0.60	1.30	0.48	2.95	4.73
Kansas	0.40	0.60	1.00	0.02	3.87	4.89
Kentucky	0.74	1.16	1.90	1.04	2.80	5.74
Louisiana	1.26	1.28	2.54	0.00	3.92	6.46
Maine	3.76	1.48	5.24	0.00	0.04	5.28
Maryland	3.89	1.74	5.63	0.05	1.64	7.32
Massachusetts	21.88	7.29	29.17	0.01	2.74	31.92
Michigan	4.57	4.11	8.68	0.60	8.58	17.86
Minnesota	1.82	2.09	3.91	0.41	4.87	9.19
Mississippi	0.59	1.49	2.08	0.01	1.28	3.37
Missouri	2.10	1.25	3.35	0.49	5.92	9.76
Montana	1.01	0.33	1.34	0.03	1.07	2.44
Nebraska	0.32	0.66	0.98	0.04	2.44	3.46
Nevada	0.05	0.07	0.12	0.01	1.20	1.33
New Hampshire	1.34	1.09	2.43	0.00	0.18	2.61
New Jersey	15.11	7.62	22.73	0.06	2.88	25.67
New Mexico	0.12	0.32	0.44	0.00	1.54	1.98
New York	67.57	6.42	73.99	0.69	8.58	83.26
North Carolina	2.39	1.06	3.45	0.46	1.22	5.13
North Dakota	0.68	0.09	0.77	0.53	0.71	2.01
Ohio	4.23	2.64	6.87	2.89	10.35	20.11
Oklahoma	0.08	1.26	1.34	0.01	2.74	4.09
Oregon	1.58	0.74	2.32	0.04	0.73	3.09
Pennsylvania	12.03	5.27	17.30	3.87	6.64	27.81
Rhode Island	2.26	0.89	3.15	0.00	0.29	3.44
South Carolina	0.44	0.12	0.56	0.08	1.48	2.12
South Dakota	0.08	0.09	0.17	0.01	0.81	0.99
Tennessee	1.18	0.89	2.07	0.41	1.86	4.34
Texas	3.58	5.41	8.99	0.00	10.14	19.13
Utah	1.24	0.61	1.85	0.55	0.51	2.91
Vermont	0.82	0.80	1.62	0.00	0.05	1.67
Virginia	1.35	1.20	2.55	0.42	2.58	5.55
Washington	2.16	1.37	3.53	0.35	1.52	5.40
West Virginia	1.31	0.01	1.32	0.52	1.35	3.19
Wisconsin	1.32	2.10	3.42	0.56	4.67	8.65
Wyoming	1.61	0.52	2.13	0.45	0.49	3.07
Totals	207.18	77.17	284.35	18.39	155.18	457.92

TABLE E-11. 1978 RESIDENTIAL NO_x EMISSIONS FOR EACH FUEL TYPE (10^3 tons)

State	Liquified Petroleum gas	Distillate oil	Kerosene	Oil subtotal	Coal	Natural gas	Total
Alabama	1.22	0.30	0.27	1.79	0.14	2.85	4.78
Arizona	0.17	0.10	0.09	0.36	0.00	1.51	1.87
Arkansas	1.17	0.04	0.29	1.50	0.00	2.40	3.90
California	1.21	0.37	0.66	2.24	0.00	26.87	29.11
Colorado	1.11	0.09	0.05	1.25	0.17	4.60	6.02
Connecticut	0.23	6.35	0.09	6.67	0.01	1.59	8.27
Delaware	0.11	0.50	0.06	0.67	0.01	0.38	1.06
District of Columbia	0.00	0.44	0.00	0.44	0.00	0.67	1.11
Florida	1.75	1.40	0.40	3.55	0.00	1.08	4.63
Georgia	1.27	0.38	0.03	1.68	0.02	4.82	6.52
Idaho	0.23	0.90	0.04	1.17	0.18	0.39	1.74
Illinois	2.88	6.36	0.49	9.73	0.70	26.03	36.46
Indiana	2.04	5.21	0.50	7.75	0.15	8.42	16.32
Iowa	1.92	1.54	0.05	3.51	0.19	4.04	7.74
Kansas	1.34	0.33	0.06	1.73	0.01	4.97	6.71
Kentucky	1.24	0.59	0.37	2.20	0.42	4.22	6.84
Louisiana	0.56	0.04	0.39	0.99	0.00	4.10	5.09
Maine	0.22	2.71	0.28	3.21	0.00	0.04	3.25
Maryland	0.39	2.78	0.20	3.37	0.02	3.50	6.89
Massachusetts	0.36	11.03	0.19	11.58	0.01	4.34	15.93
Michigan	1.65	6.58	0.34	8.57	0.27	16.41	25.25
Minnesota	1.40	4.60	0.20	6.20	0.17	5.34	11.71
Mississippi	1.32	0.04	0.38	1.74	0.00	1.52	3.26
Missouri	2.81	1.55	0.09	4.45	0.20	7.95	12.60
Montana	0.40	0.50	0.02	0.92	0.01	1.15	2.08
Nebraska	0.90	0.57	0.15	1.62	0.02	2.41	4.05
Nevada	0.08	0.19	0.01	0.28	0.00	0.59	0.87
New Hampshire	0.27	1.82	0.14	2.23	0.00	0.20	2.43
New Jersey	0.36	8.73	0.63	9.72	0.07	6.82	16.61
New Mexico	0.35	0.03	0.20	0.58	0.00	1.29	1.87
New York	0.97	28.19	1.53	30.69	0.52	16.55	47.76
North Carolina	0.88	2.33	1.74	4.95	0.19	1.75	6.89
North Dakota	0.43	0.36	0.01	0.80	0.22	0.62	1.64
Ohio	1.45	5.05	1.51	8.01	1.19	20.84	30.04
Oklahoma	1.78	0.02	0.07	1.87	0.00	4.20	6.07
Oregon	0.11	0.88	0.11	1.10	0.02	0.88	2.00
Pennsylvania	0.67	10.55	0.71	11.93	3.28	14.31	29.52
Rhode Island	0.05	1.78	0.03	1.86	0.00	0.68	2.54
South Carolina	0.59	1.07	0.30	1.96	0.03	1.41	3.40
South Dakota	0.66	0.33	0.04	1.03	0.00	0.74	1.77
Tennessee	0.74	0.29	0.86	1.89	0.17	1.99	4.05
Texas	3.77	0.10	1.82	5.69	0.00	13.74	19.43
Utah	0.15	0.17	0.02	0.34	0.22	2.39	2.95
Vermont	0.20	0.84	0.11	1.15	0.00	0.06	1.21
Virginia	0.47	2.65	0.63	3.75	0.17	2.71	6.63
Washington	0.17	1.39	0.16	1.72	0.14	1.37	3.23
West Virginia	0.12	0.51	0.06	0.69	0.22	2.67	3.58
Wisconsin	1.64	5.97	0.24	7.85	0.23	6.44	14.52
Wyoming	0.34	0.05	0.00	0.39	0.18	0.69	1.26
Totals	44.15	128.60	16.62	189.37	9.55	244.54	443.46

TABLE E-12. 1978 TRANSPORTATION NO_x EMISSIONS FOR EACH FUEL TYPE[a] (10^3 tons)

State	Jet fuel	Distillate oil	Gasoline	Total oil
Alabama	0.66	79.90	94.71	175.27
Arizona	2.41	44.01	60.29	106.71
Arkansas	0.72	47.50	57.53	105.75
California	19.85	282.29	517.92	820.06
Colorado	2.43	38.69	68.03	109.15
Connecticut	0.61	18.00	62.15	80.76
Delaware	0.51	4.68	13.69	18.88
District of Columbia	0.00	5.95	9.55	15.50
Florida	8.50	107.48	211.72	327.70
Georgia	4.47	83.44	136.32	224.23
Idaho	0.39	19.20	23.17	42.76
Illinois	7.70	151.72	239.24	398.66
Indiana	0.85	84.45	131.10	216.40
Iowa	0.35	52.56	71.49	124.40
Kansas	0.51	51.33	59.44	111.28
Kentucky	0.76	67.17	84.17	152.10
Louisiana	1.73	101.15	93.41	196.29
Maine	0.77	13.35	25.63	39.75
Maryland	1.07	36.47	90.12	127.66
Massachusetts	2.49	30.24	108.22	140.95
Michigan	2.19	75.29	217.64	295.12
Minnesota	1.49	53.24	93.80	148.53
Mississippi	0.50	46.93	57.64	105.07
Missouri	2.39	76.54	124.08	203.01
Montana	0.22	30.09	22.80	53.11
Nebraska	0.61	48.68	38.42	87.71
Nevada	2.04	14.68	21.80	38.52
New Hampshire	0.30	4.03	19.75	24.08
New Jersey	1.88	69.56	150.61	222.05
New Mexico	0.86	41.61	34.35	76.82
New York	11.28	78.37	267.88	357.53
North Carolina	1.42	70.55	140.16	212.13
North Dakota	0.59	18.00	16.59	35.18
Ohio	2.08	134.80	236.35	373.23
Oklahoma	1.44	45.60	81.58	128.62
Oregon	0.75	61.24	62.17	124.16
Pennsylvania	2.59	136.96	226.01	365.56
Rhode Island	0.07	3.96	17.11	21.14
South Carolina	0.98	36.57	74.90	112.45
South Dakota	0.42	12.02	18.13	30.57
Tennessee	1.36	97.07	112.50	210.93
Texas	8.75	315.50	378.88	703.13
Utah	0.58	28.77	32.29	61.64
Vermont	0.04	4.77	11.77	16.58
Virginia	3.72	73.10	124.62	201.44
Washington	3.50	62.19	88.16	153.85
West Virginia	0.08	27.66	39.96	67.70
Wisconsin	0.68	55.86	104.21	160.75
Wyoming	0.06	35.54	15.80	51.40
Totals	109.65	3078.76	4987.86	8176.27

[a] Coal and natural gas not used.

APPENDIX F

DESCRIPTIONS OF THREE LONG-RANGE TRANSPORT MODELS

INTRODUCTION

Section 5 presented an evaluation of the differences between several long-range transport models currently in use for acid rain modeling. This appendix provides additional information on some of the major assumptions used in these models. The models are:

- The SRI Eastern North American Air Pollution (ENAMAP) Model
- The Argonne Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model
- The CAPITA Monte Carlo Model

The SRI Eastern North American Air Pollution (ENAMAP) Model

The ENAMAP model is a modification of the European Regional Model of Air Pollution (EURMAP) model (Bhumralker, et al. 1979). The model is a trajectory type regional air-pollution model designed specifically for studying transboundary pollutant movements. The model is used for calculating monthly, seasonal, and annual averages for SO_2 and $SO_4^=$. The model also calculates SO_2 and $SO_4^=$ dry and wet deposition patterns as well as interregional exchanges for both SO_2 and $SO_4^=$. Characteristics of the model are summarized in Table E-1.

Discrete puffs of SO_2 and $SO_4^=$ are emitted every 12 hours from the center of 80 km x 80 km cells. The puffs are tracked in 3-hour time steps until they move out of the study area or until the pollutant concentrations drop to an insignificant level. The puffs are transported according to a transport wind field.

Diffusion on the regional scale is assumed to be not as significant as the transport and removal processes; therefore, very simple treatments of horizontal and vertical diffusion are used. Vertical diffusion is assumed to be uniform and instantaneous. Horizontal diffusion is treated by allowing the lateral extent of the puff to increase on the basis of Fickian diffusion. During transport the pollutant concentration is always uniform throughout each puff. At each step, concentrations are adjusted to account for wet and dry deposition of both SO_2 and $SO_4^=$. Wet deposition is related

TABLE F-1. CHARACTERISTICS OF THE SRI EASTERN NORTH AMERICAN MODEL AIR POLLUTION (ENAMAP) MODEL

Parameter	Method of treatment	Equation	Explanation of symbols	Comments
Pollutant dispersion	Diffusion assumptions: Fickian ($\sim t^{1/2}$) in horizontal; uniform mixing in vertical up to mixing height	a	a	Mixing height = 1.50 km in summer; 1.30 km spring to fall and 1.15 km winter
Meteorological input	Surface and upper air data are combined (WINFIL program) and then merged with hourly precipitation data (PRECIP program)	N/A	N/A	Weather data may be plotted using POPWEA program
Dry deposition, SO_2	Dry deposition amounts assigned to each receptor cell at each time step according to cell areas covered by puff		m = mass of SO_2 M = mass of $SO_4^=$	Dry deposition SO_2 = 3.7%/h
Dry deposition, $SO_4^=$	Dry deposition amounts assigned to each receptor cell at each time step according to cell areas covered by puff	$\frac{dm}{dt} = -km$ where $k = k_t + k_d + k_w$	t = time k = SO_2 decay rate/h k_t = $SO \rightarrow TSO_4$ transformation rate/h k_d = SO_2 dry deposition rate/h	Dry despositon $SO_4^=$ = 0.7 %/h
Wet deposition, SO_2	Wet deposition amounts assigned to each receptor cell at each time step according to cell areas covered by puff	$k_w = \lambda R$ and $\frac{dm}{dt}$ -KM where	k_w = SO_2 wet deposition rate/h λ = SO_2 washout coefficient/mm R = precipitation rate (mm/h)	Wet deposition SO_2 = 28 R %/h
Wet deposition, $SO_4^=$	Wet deposition amounts assigned to each receptor cell at each time step according to cell areas covered by puff	$K = K_c + K_w$ $K_w = \tau R$	K = $SO_4^=$ decay rate/h K_d = $SO_4^=$ dry deposition rate/h K_w = $SO_4^=$ wet deposition rate/h τ = $SO_4^=$ washout coefficient/mm	Wet deposition $SO_4^=$ = 7R %/h
Conversion $SO_2 \rightarrow SO_4^=$	SO_2 decreases and $SO_4^=$ increases are assigned to each receptor cell at each time step according to cell areas covered by puff			$SO_2 \rightarrow SO_4^=$ = 1%/h
NO_x contribution	Not considered	N/A	N/A	N/A
Sources considered	Emission data is gathered from the NEDS and SURE systems and divide into a grid system	N/A	N/A	NEDS data is appended to SURE data
Pollutant emissions considered	SO_2 and $SO_4^=$ are emitted. The model does not include NO_x emissions	N/A	N/A	Emission puffs are released every 12 hours from each emissions grid cell (80 x 80 km); seasonally adjusted
Conversion $SO_4^= \rightarrow pH$	Model does not predict pH	N/A	N/A	N/A
Terrain	Terrain is not considered	N/A	N/A	N/A

[a] The dispersion equations were not contained in the documentation reviewed by PEDCo.

N/A = Not applicable.

to the precipitation rate in that cell. The precipitation rate is obtained from hourly precipitation data. Transformation of SO_2 to $SO_4^=$ is also assumed to occur at the rate of 1 percent per hour. Pollutants are assigned to cells in proportion to the area of a puff that is contained in that cell.

Precipitation data available in the eastern United States area on an hourly basis for approximately 2000 stations are used as input. The mixing height varies from 1.50 km in the summer to 1.15 km in the winter.

Emission data are obtained from the Sulfate Regional Experiment (SURE) data base supplemented with data from the National Emissions Data System (NEDS). All emissions within an 80 km x 80 km cell are assumed to be diffused instantaneously at 12-hour intervals. Area source emissions calculated by county are assigned to the grid containing the center of the county.

Results of the model runs are compared with ambient concentrations measured in the SURE monitoring network and with air quality data contained in the Storage and Retrieval of Aerometric Data (SAROAD) system. Ambient measurements are averaged over monthly seasonal or annual periods and compared with model predicted values.

The Argonne ASTRAP Model

A key feature of the ASTRAP model is the assumption of statistical independence of long term horizontal and vertical dispersion. The model calculates horizontal dispersion from the statistics of the long term regional-scale distribution of two-dimensional trajectories of simulated tracers. Vertical dispersion is calculated separately through numerical integration of one-dimensional diffusion equations (Shannon 1981). The equations for horizontal and vertical dispersion are shown in Table F-2 as are the equations or methods of treatment for other parameters.

The model also includes diurnal and seasonal variations for dry deposition of sulfur. The deposition velocities in ASTRAP for summer are presented in Figure F-1. Deposition velocities for winter are presented in Figure F-2. These dry deposition velocity variations simulate experimental results indicating that the deposition velocity of $SO_4^=$ may be of the same order of magnitude as for SO_2, not an order of magnitude less as assumed in other models (Shannon 1981).

The rate of transformation of SO_2 to $SO_4^=$ simulates a proposed photochemical effect. The diurnal pattern used in ASTRAP are presented in Figure F-3. The emission rate variation used in ASTRAP to simulate the diurnal patterns of source emissions of factors such as daily patterns of electrical demand are presented in Figure F-4.

Wet deposition is treated as a function of the square root of the 6-hour precipitation amount, an empirical assumption. The contribution of NO_x emissions to acid rain is not considered. The output of the model is the ambient concentrations of SO_2 and $SO_4^=$, and the wet and dry deposition total sulfur. Conversion of the deposited sulfur to pH of rainwater is a separate step not specifically included in ASTRAP.

TABLE F-2. CHARACTERISTICS OF THE ARGONNE ADVANCED STATISTICAL TRAJECTORY REGIONAL AIR POLLUTION (ASTRAP) MODEL

Parameter	Method of treatment	Equation	Explanation of symbols	Comments
Pollutant dispersion	Horizontal - Lagrangian simulated tracers transported in the mean wind field	$H_{k,\ell}(x,y)=\frac{1}{2\pi\sigma_x\sigma_y}e^{-1/2}\left(\frac{x-\bar{x}}{\sigma_x}\right)^2 e^{-1/2\left(\frac{y-\bar{y}}{\sigma_y}\right)^2}$	$H_{k,\ell}$ = horizontal distribution X = concentration of SO_2 σ = ψ = concentration of $SO_4^=$	Dominated by variations in plume centerline rather than by diffusion about plume centerline
	Vertical - One-dimensional numerical integration (Gaussian)	$\frac{dX}{dt}=\frac{d(K\frac{dX}{dz})}{DZ}-TX$ and $\frac{d\psi}{dt}=\frac{d(K\frac{d\psi}{dz})}{dz}+1.5\,TX$	K = vertical eddy diffusivity (function of height, time of day) T = rate of transformation of $SO_2 \rightarrow SO_4^=$ z = vertical movement t = time	Equations solved for 11 layers:4,50 m; 3,100 m; 2,200 m; 1,400m, 1800 m. Absolute lid at 2,100 m.
Meteorological input	The mean wind below 1800 m (summer) and below 1000 m (winter) is calculated for each 6-hour period from rawinsonde data	N/A	N/A	N/A
Dry deposition, SO_2	SO_2 may be treated separately or with SO_4= as total sulfur	$DD\,(x,y)=\sum_{k=1}^{M}E_k\sum_{\ell=1}^{20}N_{k,\ell}H_{k,\ell}(x,y)D_\ell$	M = number of sources DD (x,y) = total dry deposition at location (x,y)	Function of time of day, season. Varies from 0.1 cm/s at night to 0.8 cm/s at noon (0.6 cm/s in winter)
Dry deposition, $SO_4^=$	$SO_4^=$ may be treated separately or with SO_2 as total sulfur		D_ℓ is normalized dry deposition during the ℓth plume age increment k = source number ℓ = plume age increment $N_{k,\ell}$ = number of tracers from source k at plume age increment ℓ E_k = average pollutant emissions (6 h)	Function of time of day, season. Varies from 0.1 cm/s at night to 0.8 cm/s at noon (0.6 cm/s in winter)

(continued)

TABLE F-2 (continued)

Parameter	Method of treatment	Equation	Explanation of symbols	Comments
Wet deposition, SO_2	SO_2 may be treated separately or with $SO_4^=$ as total sulfur	$WD(x,y) = \sum_{k=1}^{M} E_k \sum_{\ell=1}^{20} S_\ell N^*_{k,\ell} \frac{1}{2\pi\sigma^*_x \sigma^*_y} e^{-1/2(\frac{x-\bar{x}^*}{\sigma_x})^2} e^{-1/2(\frac{y-\bar{y}^*}{\sigma^*_y})^2}$	WD (x,y) total wet deposition at location (x,y) S_ℓ is normalized mass of total sulfur in a dry tracer of age ℓ *Wet deposited tracers	Ratio of mass of sulfur deposited to mass of sulfur originally airborne, a function of the square root of the precipitation amount
Wet deposition, $SO_4^=$	$SO_4^=$ may be treated separately or with SO_2 as total sulfur			
Conversion $SO_2 \rightarrow SO_4^=$	Photochemical reaction; almost no conversion at night. Values given hourly	See Figure E-1	N/A	Function of time of of day and season. Varies from 0.2 at night to 3.0 percent/h at noon in summer and from 0.1 percent/h to 1.5 in winter
NO_x contribution	Not treated by model	N/A	N/A	N/A
Sources considered	Can include point and area sources. Emissions are released in one of the eleven layers	See Figure E-2	N/A	Emission varied to simulate heating, cooling load (season and diurnal)
Pollutant emissions considered	Only SO_2 emissions are considered as total sulfur	N/A	N/A	All reactions after emissions may be separated by SO_2 and $SO_4^=$
Conversion $SO_4^= \rightarrow pH$	Conversion to pH made from predicted sulfur deposition, not done by model	N/A	N/A	Model does not predict pH directly
Terrain	Terrain not applicable	N/A	N/A	N/A

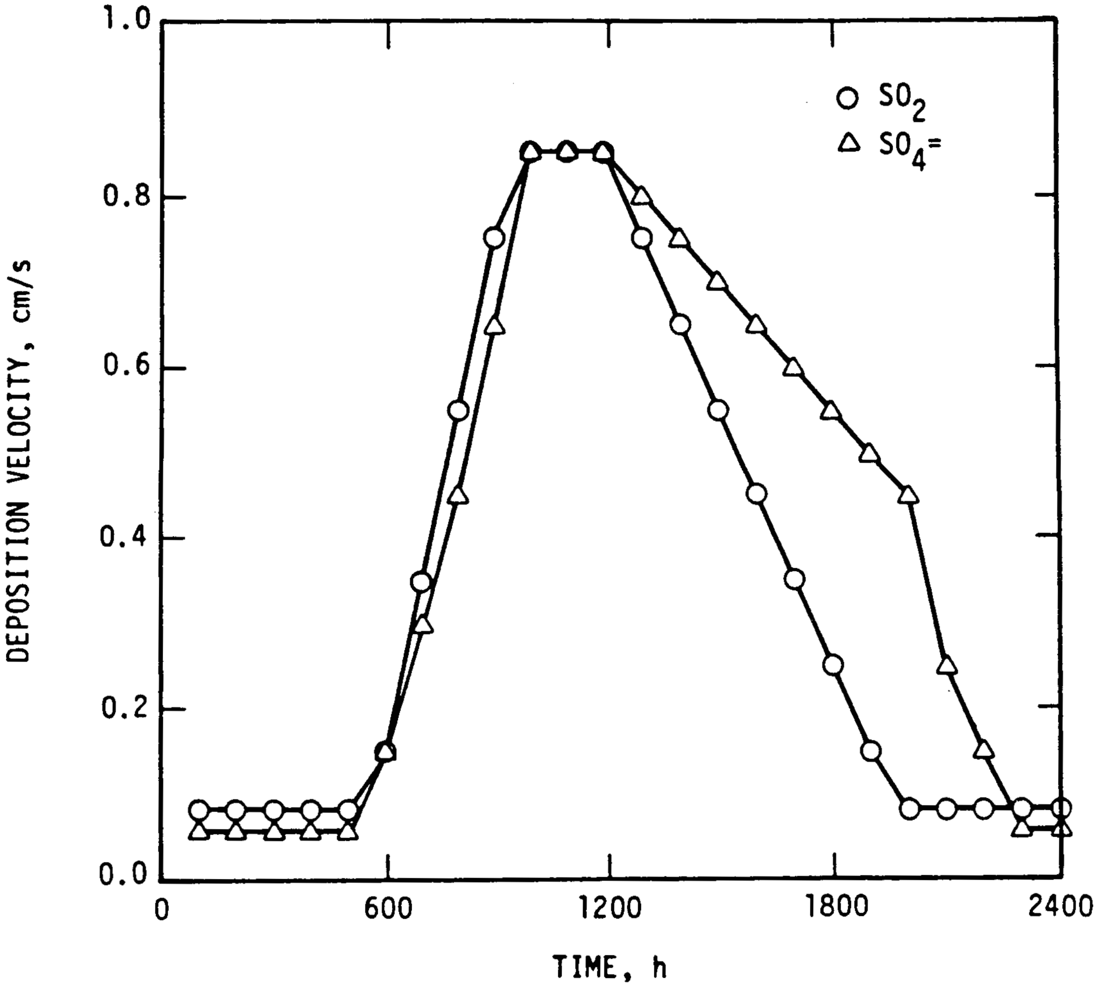

Figure F-1. Summer diurnal pattern of dry deposition velocities for SO_2 and $SO_4^=$ used in ASTRAP (Shannon 1981).

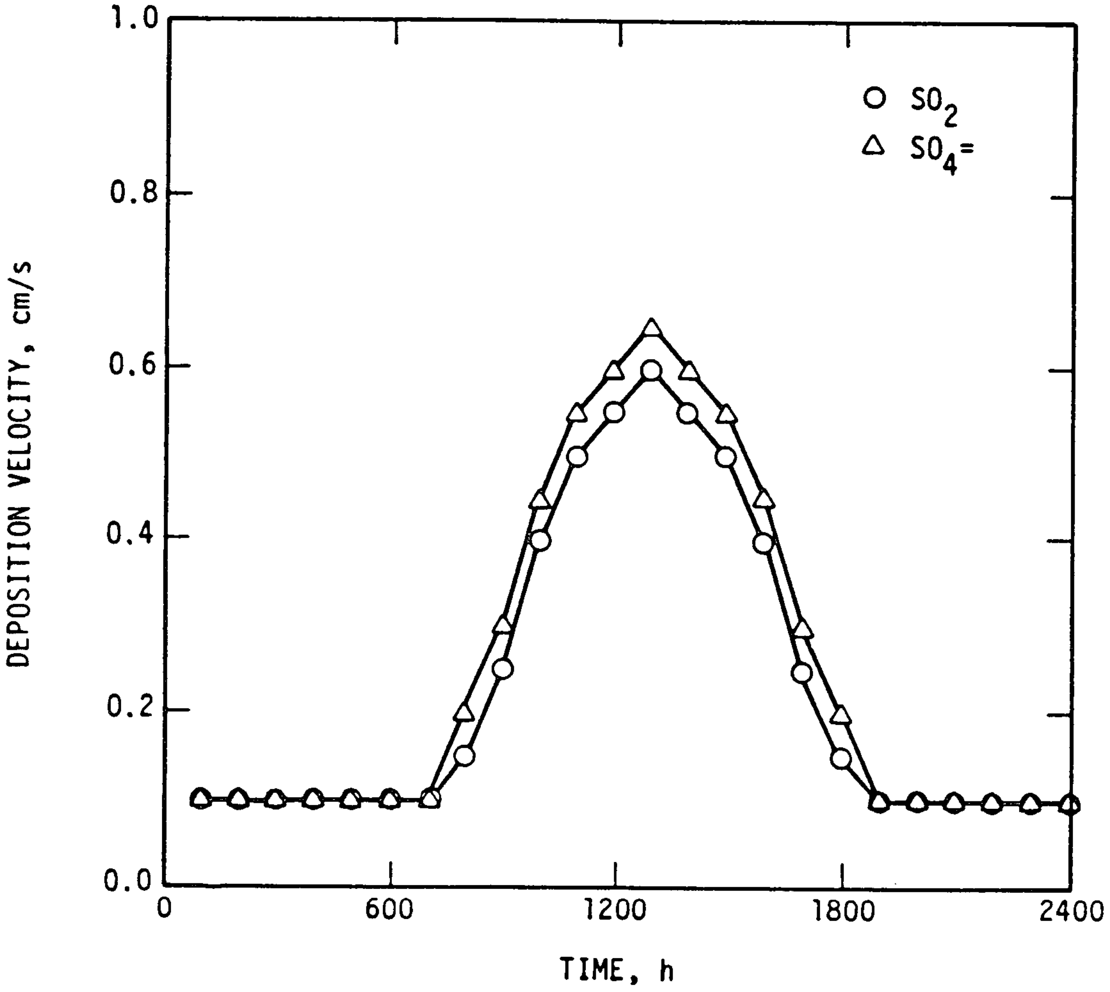

Figure F-2. Winter diurnal pattern of dry deposition velocities for SO_2 and SO_4= used in ASTRAP (Shannon 1981).

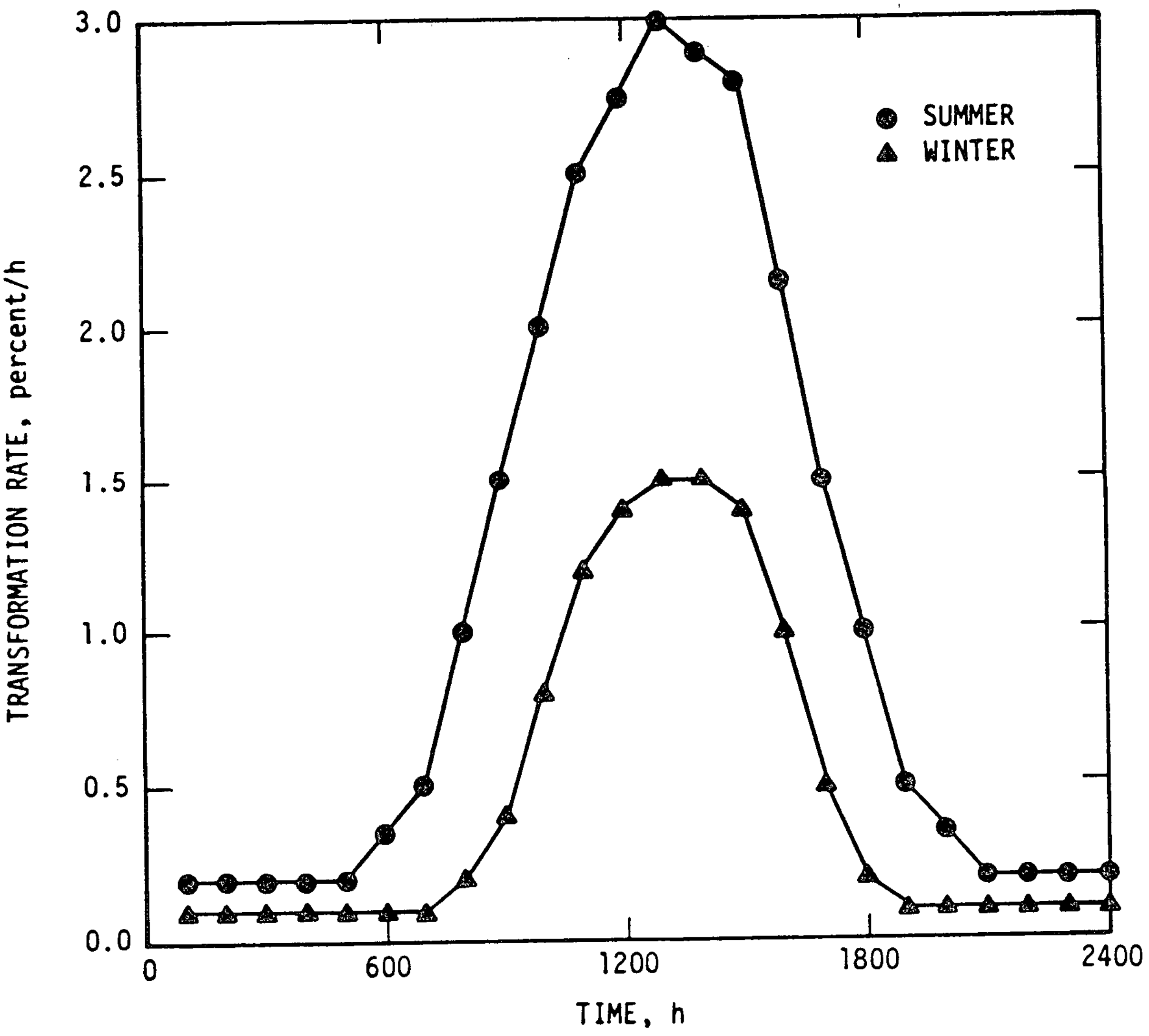

Figure F-3. Diurnal pattern of the rate of transformation of SO_2 to $SO_4^=$ (Shannon 1981).

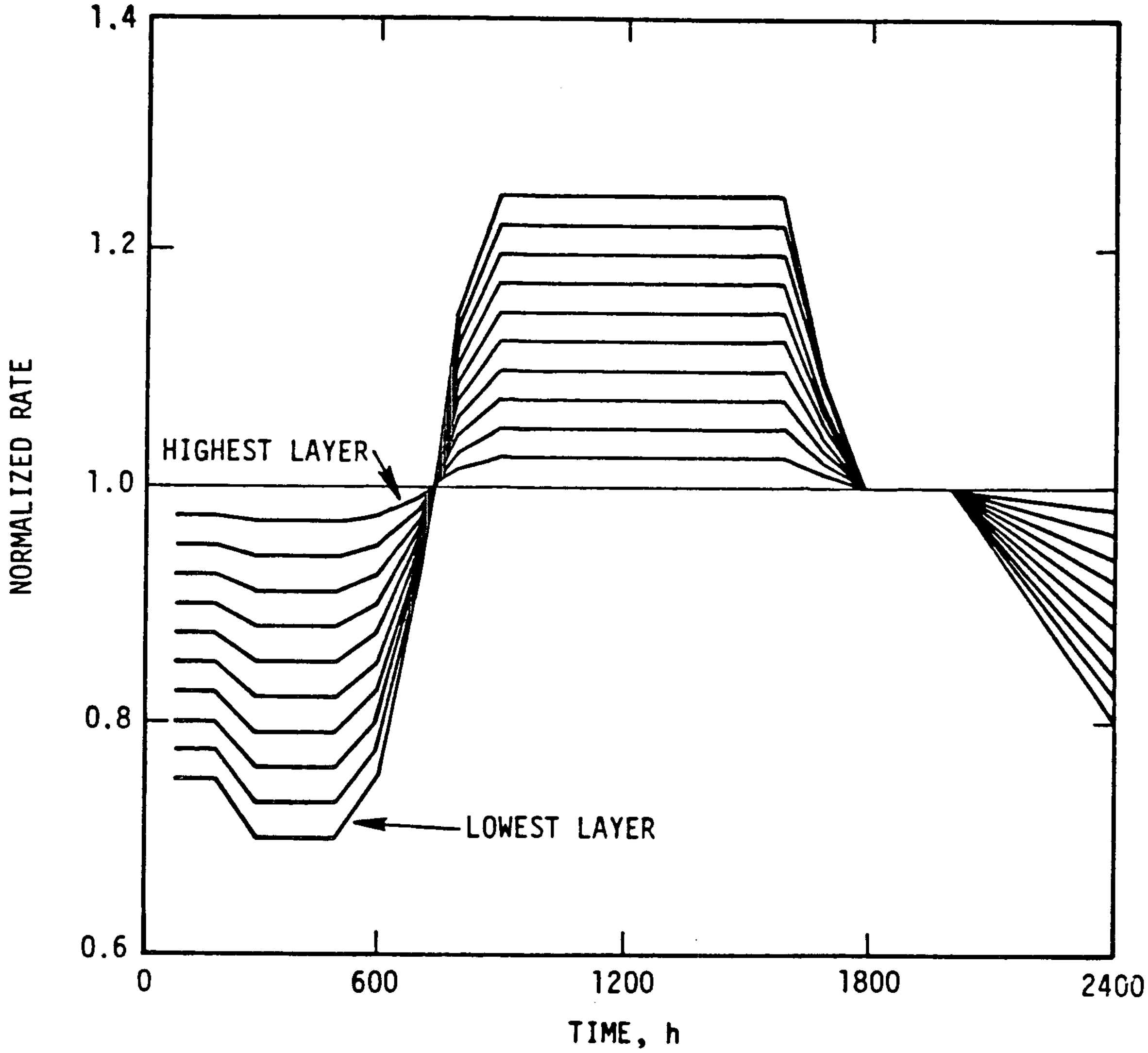

Figure F-4. Variation of emission rates as a function of time of day and layer (emission height) (Shannon 1981).

The CAPITA Monte Carlo Model

The inputs used by the CAPITA Monte Carlo simulation include scale height (HT), wind speed multiplier (WSM), transformation rate $SO_2 \rightarrow SO_4^{=}$ (KT), deposition rate SO_2 (KR) and deposition rate $SO_4^{=}$ (DP). Seasonal variations for the parameters as applied to the northeastern United States are shown in Figure F-5. Two of four meteorological variables remain constant: the diffusion coefficient ($10^5 m^2/s$) and the surface wind direction veer (10°). The multiplier applied to surface wind speed varies from 1.7 in the winter to 2.2 in the summer. Scale height of sulfate varies from 450 m to 1250 m. Of the kinetic parameters, the $SO_4^{=}$ deposition rate (1.5 percent per hour) remains constant, but the SO_2 deposition and transformation rates each vary sinusoidally with season. The SO_2 deposition varies from 1.1 to 3.5 percent per hour and the SO_2 to $SO_4^{=}$ transformation from 0.4 to 1.3 percent per hour. The characteristics of the CAPITA Monte Carlo model are shown in Table F-3.

Twice daily rawinsonde wind measurements are spatially interpolated to 1200 m in August and to 400 m in January and compared to interpolated midday surface winds. Daily spatial averages are obtained for the ratio rawinsonde/surface wind speeds and the difference rawinsonde-surface wind directions. During both the summer and winter months day-to-day values of the mean, median, and mode of the wind speed ratio are calculated and compared for consistency.

Seasonal variation in scale height is presumed to be proportional to climatic variations in maximum afternoon mixing height. The "optimal" rate constants are obtained from measured daily SURE region average $SO_4^{=}$ and previously assembled estimates of $SO_4^{=}$ deposition. Assuming that SO_2 transformation is proportional to total SO_2 decay, the rates are then chosen by iterative convergence to a "best fit" for each month. The results for the summer and winter are then used to generate a sinusoidal form for the parameters.

Model output is converted to daily average gridded concentration fields, consistent with SURE data and light extinction plots, by averaging the quantum $SO_4^{=}$ masses from the 3 hour model steps. The location of each quanta determines the associated grid point, and a final smoothing is applied to the daily 60 km x 60 km grid just as was done for measured fields. This initial field, in units of mass/area, is converted to concentration by assuming that the scale height is invariant in space and changes only slowly (seasonally) with time. A SURE region spatial average of the daily simulated concentration is computed as the mean of all grids lying within the squared boundary so that the spatial average measured and modeled concentrations are exactly comparable.

Simulated concentration fields arise from counting the number of $SO_4^{=}$ quanta which impact on the area. A complete time history of the position, origin, age, and chemical composition of each simulated emission is maintained.

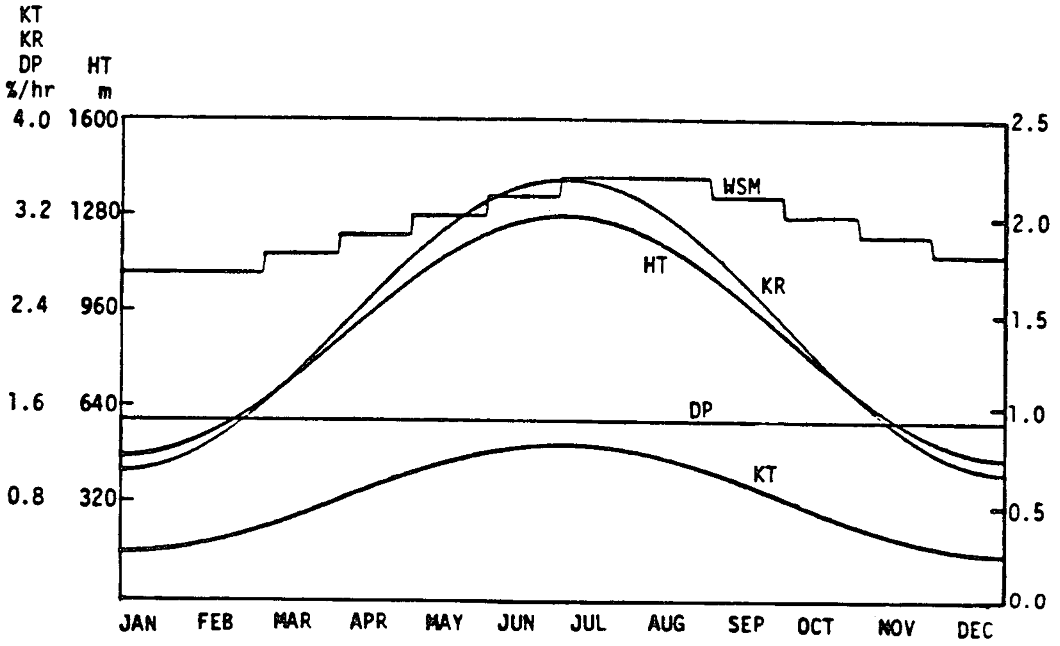

Figure F-5. Seasonal variation of CAPITA Monte Carlo model parameters (Husar, Patterson and Husar, 1980).

TABLE F-3. CHARACTERISTICS OF THE CAPITA MONTE CARLO MODEL

Parameter	Method of treatment	Equation	Explanation of symbols	Comments
Pollutant dispersion	Air parcel is moved by mean transport winds and dispersed by vertical wind shear and veer	a	a	Mixing height varies from 450 m to 1,250 m.
Meteorological input	Uses modified midday surface winds for horizontal transport	N/A	N/A	Four input parameters are varied by season.
Dry deposition, SO_2	Expressed as a percent deposited per hour	$D(t) = \frac{b}{a+b}(1-e^{-(a+b)t})$	D = SO_2 deposited t = time a = $SO_2 \rightarrow SO_4^=$ conversion b = SO_2 deposition rate W = $SO_4^=$ deposited P = SO_2 mass C = $SO_4^{2=}$ removal rate	$SO_2 \rightarrow SO_4^=$ conversion 1.3 percent/h SO_2 dry deposition = 3.325 percent/h
Dry deposition, $SO_4^=$	Expressed as a percent deposited per hour	$W(t) = P(c=0)-P$ where $P(t)=\frac{a}{a+b-c}(e^{-ct}-e^{-(a\ b)t})$		$SO_4^=$ dry deposition 0.3 percent/h
Wet deposition, SO_2	Expressed as a percent deposited deposited per hour	$D(t)= \frac{b}{a+b}(1-e^{-(a+b)t})$		SO_2 wet deposition 0.175 percent/h
Wet deposition, SO_4	Expressed as a percent deposited per hour	$W(t)=P(c=0)-P$ where $P(t)= \frac{a}{a+b-c}(e^{-ct}-e^{-(a+b)t})$		$SO_4^=$ wet deposition 1.2 percent/h
Conversion $SO_2 \rightarrow SO_4^=$	Expressed as a percent converted per hour	$P(t)= \frac{a}{a+b-c}(e^{-ct}-e^{-(a+b)t})$		$SO_2 \rightarrow SO_4^=$ conversion 1.3 percent/h
NO_x contribution	NO_x mechanisms are similar to those for SO_x	N/A	N/A	$NO \rightarrow NO_2$ rate 10 percent/h or total $NO_2 \rightarrow HNO_3$ 2-6 percent/h $NO_2 \rightarrow PAN$ 1-3 percent/h NO_2 removal 1 percent/h HNO_3 removal 4-5 percent/h PAN removal 0.1-4 percent/h
Sources considered	Emissions from inventoried sources are assigned to pseudo sources of quantum emissions of 6.1×10^7 kg/yr each. Puffs are released every 3 hours equal to 2.1×10^4 kg per source	N/A	N/A	All sources whether point or area are assigned to pseudo sources of equal size
Pollutant emissions considered	Considers emissions of NO and SO_2. NO may be converted to NO_2 instantly as an option	N/A	N/A	N/A
Conversion $SO_4^= \rightarrow pH$	The model is adaptable to predict H^+ mass as HN_4HSO_4 and HNO_3. This must still be converted to pH	N/A	N/A	Model does not directly predict pH
Terrain	Terrain not considered	N/A	N/A	N/A

[a] The dispersion equations were not contained in the documentation reviewed by PEDCo.

N/A = Not applicable.

Other characteristics of the Monte Carlo model are listed below:

- Emissions are biased towards major source regions and reflect only annual average rates.
- Stack parameters or primary $SO_4^=$ emissions are not considered. There is no discrimination between emissions from coal- and oil-fired units.
- Advection is based on modified surface winds, with 24-hour interpolation. There is no explicit vertical component.
- Diffusion is a perturbation applied to the trajectory at each 3 hour time step, unvarying in magnitude.
- Kinetics do not vary geographically or diurnally.
- Wet deposition is calculated from average continental rates rather than from episodic action.
- The scale height used to relate vertical column mass to surface concentrations is constant across the eastern U.S.
- Only regional phenomena are simulated. Urban scale mechanisms are not included.