

Transport and Fate of Gaseous Pollutants Associated with the National Energy Program*

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The experimental evidence related to the long-range transport and transformations of sulfates has been critically reviewed. It has been concluded that sulfate emissions from various sources can be superimposed on each other during long-range transport to create episodes far from the contributing sources. Sulfates are important contributors to degrading visibility through the United States including relatively pristine areas in the western United States. Acid sulfate components, along with nitric acid, may increase the problem of acidity in precipitation on soils, vegetation, and lakes in certain areas of the eastern United States. Improvements in monitoring of these pollutants are required to follow changes in air quality caused by long-range transport.

Introduction

The National Energy Plan (NEP) projects the need for substantial increases in coal production and utilization by 1985. There is a strong commitment of the NEP to protect the environment and insure that pollution control goals will be attained. An independent committee, the Committee on Health and Ecological Effects of In-

creased Coal Utilization, has been established by the Department of Energy to assess whether the commitment is adequate to provide protection of public health and environmental effects. Both DOT (Department of Transportation) and EPA have substantial involvements in the issues to be considered. To aid in meeting these objectives, groups of papers have been prepared to identify areas of consensus and areas requiring further research.

The present paper is concerned with the transport and fate of gaseous pollutants and their atmospheric reaction products from coal-fired facilities. The physical, meteorological and chemical processes involving dispersion, transport, transformations and removal of these pollutants form the vital link between the pollutants as emitted and their ultimate impact on receptors.

These processes determine the distribution of pollutants between the atmosphere and the surfaces of crops, forests, soil, lakes, and materials of construction and in a variety of other uses. The same processes determine the airborne concentra-

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tion and composition of gaseous and aerosol products impacting on the health status of affected populations.

Increased use of coal will have potentially adverse incremental effects on a number of regions of the United States where coal is already used extensively as a fuel. Its use in regions where other fuels have previously been utilized may be anticipated to cause absolute increases in the concentrations of the pollutants particularly associated with burning of coal. The effects may be on a local scale because of fall-out of aerosols or because of meteorological conditions causing plumes containing the emissions to reach the ground relatively near the source. Other meteorological conditions may lead to movement of the plumes aloft over longer distances. Depending on the time interval and atmospheric conditions, substantial conversions may occur of the originally emitted gaseous pollutants to other gases or aerosols having increased potential for adverse effects. Examples are the conversion of sulfur dioxide to sulfuric acid and other sulfates or the conversion of nitric oxide to nitrogen dioxide and to nitrates. The opportunities for such conversions are increased when the emissions occur from tall stacks which should often reduce local effects, but increase the potential for contribution to effects on a regional scale because of longer range transport of pollutants.

Finely divided sulfates are formed during combustion of sulfur-containing fuels. Atmospheric chemical reactions are even more important sources of finely divided sulfates. The finely divided sulfates can be transported for long distances because these particles are much less readily removed from the atmosphere than sulfur dioxide or nitrogen dioxide.

Sulfates formed during combustion can contribute to ground-level sulfate concentrations near power plants, particularly under adverse meteorological conditions. However, this "locally" formed sulfate is only an increment to the sulfate also present, but formed in the atmosphere during transport of sulfur dioxide from more distant power plants, as well as from industrial and urban sources. Similar considerations probably also apply to nitrates.

Sulfates and nitrates are of particular concern in health effects, acid precipitation, and corrosion effects when present as acid sulfates and nitric acid. Finely divided sulfates in all chemical forms can contribute significantly to visibility degradation and turbidity. This latter effect is of particular concern in the western U.S., where large coal-

fired sources can cause visibility to be reduced substantially.

The following sections of this report are concerned first with the experimental evidence for long-range transport of pollutants from sources, particularly coal-fired sources. The status of the measurement techniques available and their use in characterizing the pollutants in the source, plume and ambient atmosphere are considered. The laboratory investigations concerned with the chemical and physical mechanisms by which aerosols are formed, particularly sulfur-containing aerosols, is reviewed. The experimental studies of the concentrations and composition of the pollutants as emitted from sources and in the subsequent behavior downwind in plumes are discussed. The current status of the various source and air quality models available for use in predicting the distribution of pollutant species is also considered. In addition, one particular modeling approach is applied to provide a general indication of the potential impact of the NEP upon air quality in the various geographic subdivisions of the U.S. Finally, the conclusions and pertinent recommendations are presented.

Evidence of Long-Range Transport

Meteorological Conditions

There are five basic meteorological conditions that produce long-range transport of pollutants like sulfates in the atmosphere, namely: (1) prevailing winds at the typical altitudes (150m to 600m above ground) of steam electric and industrial plant plumes; (2) strong and persistent winds near the ground; (3) spatial correlation between winds at the surface or aloft between adjacent observation stations (trajectories); (4) vertical temperature variations that cause effluent plumes to be trapped in a well mixed layer that extends to the plume altitude or to be embedded in a stable layer that is isolated from the ground; (5) relative movements of adjacent high and low pressure weather systems.

The purpose of this section is to illustrate each of these five basic meteorological conditions especially for a high emission density region due to steam electric and industrial plants, namely the Ohio River Basin, and to set the stage for the dispersion modeling approach which uses one of these five basic conditions in estimating the potential impact on the NEP upon air quality in 10 selected regions of the country.

Prevailing Winds. The prevailing winds at

the typical altitudes of steam electric and industrial plant plumes are available (1) at the 70 locations. The wind direction frequencies and most frequent wind speed ranges at 600m for the summer season show the following significant features. The prevailing (most frequent) wind direction in the northern and southern (Nashville) portions of the basin is westerly (toward the east) and the most frequent wind speed range is next to the highest (5.1-10m/sec). The frequencies of southerly (toward the north) winds at Salem and Peoria are nearly as great as for the prevailing (easterly) direction. The results for the mid-eastern portion of the region (Huntington) show the lowest frequencies and speed ranges probably due to the blocking effect on the winds aloft by the Appalachian Mountains and the frequent air mass stagnation centered over this location.

The Ohio River Basin region experiences a definite maximum in sulfate levels during the summer season (2). The highest sulfate levels in this region are found to the north of the lower Ohio River Basin (west-central Indiana) and to the northeast of the upper Ohio River Basin (north-central Pennsylvania) in agreement with these prevailing wind features (3).

Strong-Persistent Surface Level Winds.

Strong and persistent winds near the ground have been recognized recently as being related to regional sulfate (3) and air quality problems. The direction of the most frequent persistence sectors in the Ohio River Basin are generally to the north or northeast. The specifics for the sectors at the 10 locations used in dispersion modeling will be discussed later in this paper. The conditions associated with extreme persistence in surface winds are those that generally produce good vertical coupling between the flow at all levels in the lower 500 - 1000 m above ground. Hoxit (4) has found that the vertical wind direction shear is smallest under strong wind conditions and to the west of the center of the high pressure cell.

The use of surface weather data to augment upper air data in long-range transport analyses is important because the latter is generally too coarse in space (200 km) and time (12 hr) scales to be adequate for dispersion modeling of local and subregional scale sulfate episodes.

Trajectories. When a strong spatial correlation exists between winds at the surface or aloft between adjacent observation stations then air mass trajectories can be constructed with greater confidence than when only a weak correlation exists. Air mass trajectories to simulate the long-

range transport of effluents have been computed by Wendell (5), Gage et al. (6), and many other researchers. The most relevant air mass trajectory calculations for the NEP analyses are those that originate from the major emission source regions of importance and the 10 subregional locations being analyzed in this paper.

Vertical Temperature Variations. The vertical temperature variations that cause effluent plumes to be trapped in a well mixed layer that extends to the plume altitude or to be embedded in a stable layer that is isolated from the ground have been analyzed recently (7,8). The inversion height of 251-500 m would generally cause shorter stack plumes to be trapped below the elevated inversion layer and taller stack plumes to be embedded within the elevated inversion layer. The inversion height of 751-1000 m would generally cause both shorter and taller stack plumes to be trapped below the elevated inversion layer. The frequencies of trapping short stack plumes and embedding taller stack plumes are highest at Buffalo and Peoria and are lowest at Dayton. The frequencies of trapping both shorter and taller stack plumes are highest at Dayton and Salem and are lowest at Pittsburgh. Taller stack plumes in the vicinity of Salem appear to be embedded in inversion layers aloft which contain high relative humidities more often than at the other six locations. These conditions are thought to be very effective in promoting the long-range transport-transformation of SO_x emissions from tall stacks (9).

Movements of Large Weather Systems. The relative movements of adjacent high and low pressure systems has been analyzed recently (10,11). The summer season distribution of atmospheric stagnation show two areas with the maximum number of cases centered over Georgia and West Virginia. The Ohio River Basin has experienced about one-half the maximum number of cases of extended stagnation in the summer season during the past 40 years than that of Georgia and West Virginia. The average tracks of summer season stagnating anticyclones are very important to long-range transport analyses. The average track of these systems in the summer season is generally parallel to the Ohio River Valley for the limited sample of cases, namely those with an absence of fronts and precipitation during their 4 days or more lifetime, and the average track is generally curved in a clockwise direction for the full sample of cases. The stationarity of the high pressure centers near Pittsburgh for the limited sample of cases is especially noteworthy.

It has been observed (12) that two main types of weather patterns are associated with rainwater sulfate episodes as follows: a slow moving active frontal system (cold or warm) where convergence of moist air at low levels usually enhanced by mountains produce heavy and prolonged rainfall; and a stagnating anticyclone over a high SO₂ emission density area which eventually moves on thereby allowing the pollutant air mass to reach the periphery of the high pressure cell where it can be drawn into an active frontal system.

In the first instance, the ambient sulfate concentrations need only be average to produce high sulfate concentration in the rainwater levels, whereas in the second instance only a relatively small amount of rain could produce high sulfate concentration in the rainwater.

Finally, another evidence of long-range transport in meteorological data comes from analyses of conventional visual range observations at weather stations (13). A comparison of trajectories with the large areas of visibility degradation suggests that elevated sources such as fossil steam plants probably contributed more to visibility degradation via long-range transport than did lower-level sources. However, the relative contributions to visibility degradation of elevated and low-level sources within the areas of degradation remain to be determined as do the relative contributions from long-range transport versus local production in general.

Summary. The five basic meteorological conditions discussed above suggest the following preferred long-range transport paths associated with adverse dispersion conditions: to the north of the lower Ohio River Basin extending into Canada; to the northeast and to the south of the upper Ohio River Basin; to the north of Washington and New York; to the southwest of Georgia; and to the north and northwest of east-central Texas.

Experimental Evidence: U.S.

Evidence for long-range transport of sulfates began appearing in the U.S. literature in 1973. The large background of sulfates measured at eastern nonurban locations was attributed to long distance transport of sulfate formed by atmospheric oxidation of sulfur dioxide (14). Several instances were reported of satellite observations of industrial plumes visible for 150 km over water (15). An observation of synoptic scale air pollution transport was also reported (16) during which a massive pall of hazy, smokey air drifted from the Ohio River Valley into the Great Plains.

However, it was generally felt that such situations were unusual and that plumes, especially over land, would be sufficiently dispersed by 50 to 100 km as to be undetectable.

However, a number of studies during 1974 and 1975 led to an increased interest in the long range transport of pollutants. Scandinavian scientists attributed increases of acid rain in their country to long-range transport of SO₂ and sulfuric acid aerosol from tall utility stacks in England and western Europe. In attempting to explain why urban sulfate levels have stayed generally constant, while SO₂ concentrations decreased due to SO₂ control, EPA scientists hypothesized long-range transport of sulfate from rural power plants with tall stacks (17). Measurements of light scattering aerosols 50 km southwest of St. Louis indicated no discernible increase in scattering when the air mass had passed over St. Louis. This suggested high regional background rather than an urban source for light scattering aerosol (18).

Studies performed as part of EPA's Midwest Interstate Sulfur Transformation and Transport Program (MISTT) during 1975 and 1976 demonstrated that on a number of days, power plant and urban plumes could be followed for 300 km by measuring SO₂, sulfate, ozone, or light scattering aerosols (9,19). Contributing to such long-range transport are stable meteorological conditions.

During nighttime, or other periods of low vertical turbulence, plumes remain cohesive for hundreds of kilometers and can travel long distances and still give high concentrations when mixed to ground level. Under certain conditions, the nocturnal jet, an air stream at about plume height which moves at about twice the ground wind speed, will form and increase the distance traveled by the cohesive, nighttime plume. During the daytime vertical turbulence mixes plumes throughout the boundary layer (approximately 1000 m high) and wind shear (the change in wind speed and direction with altitude) increases the horizontal spreading of plumes. However, conditions are sometimes such that the wind shear is low and then plumes will show little horizontal dispersion over a distance of 200 to 300 km. Such conditions occurred about one-fourth of the time during MISTT sampling periods of one month each summer.

Such long-range transport can be very important when one plume is emitted into another dispersed plume from an upwind source. The frequency at which this "source intensification" occurs in various parts of the northeast United States has been examined (6). This phenomenon has been shown experimentally to be responsible

for very high sulfate concentrations. Sulfate measurements made during the design phase of SURE (Sulfur Regional Experiment sponsored by the Electric Power Research Institute) indicated an air pollution episode in West Virginia during which sulfate levels at Wheeling reached $80 \mu\text{g}/\text{m}^3$ (2). An analysis using weather maps, visibility profiles, long-range trajectories, and emission inventories was undertaken to determine if the episode was due to local sources or long distance transport. The high concentration occurred when the air mass had traveled over several high emission regions in succession but did not occur during similar meteorological conditions when the air mass had traveled over less polluted regions (20). Thus, the analysis confirms the importance of long-range transport.

Other studies have focused on larger-scale phenomena. Under certain meteorological conditions, such as high-pressure, stagnating anticyclones, pollutants can build up in regions with dimensions of several hundred miles. Satellite imagery and visibility isopleths, prepared from National Weather Service visibility observations, have been used to examine these hazy air masses or "blobs" (21). These "blobs" of polluted air, which correlate closely with sulfate levels (22), can be identified as they move over extended distances. Long-range air mass trajectories have been used to confirm that the blob actually travels as a cohesive air mass. Inspection of visibility isopleths for June, July, and August of 1975 revealed six blobs with an average duration of 8 days over various multistate regions of the midwestern and eastern United States. During the period June 25 to July 5 an air mass entered the U.S. over Louisiana and moved north somewhat east of St. Louis, crossing the high emission areas TVA and stagnating for several days over the Ohio River Valley. It then moved south again over the TVA area, west across St. Louis, north to St. Paul-Minneapolis, and east across the Great Lakes. It then moved south and east, causing visibilities of less than 4 miles over Atlanta, Birmingham, and Tallahassee before moving out to sea (23).

The contribution of local, advected and chemical converted sulfate during transport was estimated for the eastern U.S. on an annual average basis (24). Comparisons of urban and nonurban sulfur dioxide, sulfate, and vanadium made by using sulfur dioxide and vanadium as tracers result in the association of about $1 \mu\text{g}/\text{m}^3$ with locally formed sulfate, $2 \mu\text{g}/\text{m}^3$ with advected urban sulfate, and the remainder of the 6 to $10 \mu\text{g}/\text{m}^3$ of sulfate with sulfate formed by chemical conversion of SO_2 during transport.

Experimental Evidence: Europe

In 1968, a first detailed analysis of approximately 15 years of data from the European Air Chemistry Network showed that an area of highly acid precipitation (pH 3-4) located in the industrial heart of Europe was steadily expanding. This finding was of great concern to Scandinavians, since it coupled with their own observations that rivers and lakes in southern Norway and Sweden were becoming increasingly acidic. This was believed to be causing lower fish population and reduced forest production in those areas. It was suspected that long-range transport of sulfur emissions to Scandinavia from source areas in the U.K. and other Western Europe countries was responsible for this increasing acidity.

This concern led to the initiation in 1972 of a comprehensive five-year research program called the Long Range Transport of Air Pollutants (LRTAP) study, which had the goal of determining the relative importance of local and distant sources of sulfur compounds within European countries. Special attention was focused on the question of precipitation acidity. The project was sponsored by the OECD and 11 European countries participated actively. A leading role was taken by the Norwegian Institute for Air Research, which prepared the recently issued final report of the project (25,26). These results have also been summarized by Barnes (27). In general, the study confirmed that airborne sulfur compounds do travel long distances (several hundred kilometers or more), and has shown that the air quality in any one European country is measurably affected by emissions from other European countries.

The LRTAP experimental program involved the measurement of sulfur compounds—both air concentrations and deposition in precipitation—at a network of 76 ground stations and by aircraft. In addition, mathematical dispersion modeling was used to estimate concentrations and depositions using SO_2 emissions and meteorological data.

In general, the measured concentrations and the derived total deposition of sulfur compounds were found to be at a maximum in the major emission areas and to decline with increasing distance from them. However, certain localized areas (e.g., southern Scandinavia and Switzerland) have higher total deposition figures than would be expected by their distance from the major sources. This situation is brought about by high amounts of wet deposition due to a large amount of terrain-induced precipitation in these areas.

It was found that acidity is principally introduced to the precipitation as sulfuric and nitric acid. A limited number of measurements showed clearly that the contribution of oxides of nitrogen to the acidity in precipitation in Northwest Europe is substantial, and in some cases as large as that from sulfur oxides.

Several of the participating countries used instrumented aircraft to obtain data on above-surface concentrations of air pollutants. Flights were usually made under specific meteorological conditions and never at night or in clouds. The results confirmed that under these conditions, sulfur compounds are normally transported in the lowest 2 km of the atmosphere, generally with a peak concentration a few hundred meters above ground level and a progressive decline above that height. The average mixing height under flight conditions was found to be 1200-1300 m, although individual vertical profiles varied considerably. The flights also showed that under certain conditions distinct plumes of pollutants existed several hundred kilometers downwind of major source areas.

A sector analysis was performed on the surface measurements. Using 850 mbar (1200-1500 m altitude) trajectories, the data were allocated to six directional arcs and a mean value was calculated. The results showed that the sectors with high mean concentrations and/or depositions were not randomly oriented, but were directed towards the main areas of emission. The sector analysis did not, in general, give a clear indication of which sources give rise to what fraction of the concentrations in a given sector. Hence, mathematical modeling was employed in conjunction with the measured data to give more definitive estimates of interregional and transnational sulfur exchanges, as well as to obtain a more complete pattern of concentration and deposition in Europe.

The resulting overall picture showed a considerable transport of sulfur pollutants over the national borders in Europe. The total deposition in a given country due to foreign emissions of SO_2 was found to depend on the size and geographical position of the country in relation to the major emission sources. From the model estimates countries were grouped roughly into net receivers or donors of sulfur pollution. For 1974, the estimates showed that there were countries with depositions almost three times their emissions while others had emissions three times their depositions. In about half of the countries in the study, the total deposition estimated for 1974 exceeded the indigenous emissions. The model results also indicated that, within Western and Central Eu-

rope as a whole, about 50% of the sulfur emitted is dry deposited and 30% is wet deposited, with the balance leaving the region.

The results of the LRTAP study showed clearly that if some European countries find it desirable to reduce substantially the total deposition of sulfur within their borders, individual national control programs can achieve only a limited improvement. At the same time, these national programs will result in reductions in pollution received in other countries.

Measurement and Characterization

The measurement of the pollutants produced by combustion of coal should take into consideration the impact of the following aspects on pollution concentration and composition: effect of control devices on flue gases; chemical and physical changes in flue gases when they are cooled and diluted initially in the plume; chemical and physical changes as pollutants are dispersed and transported downwind in plume; air quality at ground level when the plume touches the ground.

Coal-fired sources produce substantial concentrations of sulfur dioxide, nitric oxide and particulates. The gaseous pollutants also include sulfur trioxide, carbon monoxide, hydrogen chloride, and organics including aldehydes (28). The particulate fraction also contains sulfur, aluminum, silicon, iron, potassium, and sodium as major constituents (29,30). The trace elements, including sodium, magnesium, phosphorus, titanium, vanadium, chromium, manganese, nickel, copper, zinc, bromine, cadmium, tin, antimony, barium, mercury, lead, arsenic, gallium, thallium, beryllium, selenium, and cobalt will be considered in another paper (29,30). The more abundant elements in the flyash excepting sulfur are of limited interest.

In the plume, sulfur trioxide can be converted to sulfuric acid. To the extent that the ammonia mixes into the plume varying amounts of neutralization will occur. The nitric oxide can be converted to nitrogen dioxide in the plume (31). This process occurs particularly rapidly if sufficient ozone is available to mix effectively throughout the plume. Larger particles or liquid aerosols can fall out of the plume near the stack.

Sulfur dioxide, sulfuric acid, and particulate sulfur have been of great interest in the emissions from coal-fired facilities. Sulfur dioxide and sulfate can be analyzed by modifications of EPA method 6 and method 8 determinations (32).

Opacity is a physical characteristic of plumes regulated by opacity emission standards (33).

While opacity standards apply to the opacity of plumes, opacity monitoring measurements are made in stacks or ducts (34). In-stack measurements are made by transmissometers with a folded optical path through a probe. Plume opacity also can be measured by a trained observer, lidar unit or sun photometer (34). In-stack and plume opacity measurements usually agree satisfactorily. However, if substantial amounts of sulfuric acid aerosol in the light scattering range should form as the stack emissions cool and condense in the plume the plume opacity will exceed the in-stack opacity. Although such differences have been observed in plumes from some oil-fired facilities (34), similar effects have not been reported to date in plumes from coal-fired facilities.

Considerable effort has gone into the development and evaluation at emission sources of continuous monitoring instruments for sulfur dioxide, nitric oxide and other gaseous pollutants in combustion sources (35-40). Instruments have been developed to operate in extractive, in situ and remote sensing modes with particular emphasis on sulfur dioxide. A considerable fraction of the effort has been on adapting continuous monitoring instruments to which samples are brought through probes and transport systems. Appropriate operation of such instruments (38). In situ instruments also are available which can be directly mounted in a stack access port (35,36,38). Several operational ground-based remote-sensing techniques are available for measurement of pollutants in plumes (40). This type of equipment can be used to obtain the flux of pollutant species in plumes. The correlation spectrometer (COSPEC) 14 has been used to obtain flux measurements in power plant plumes progressing downwind (40).

Instrumented aircraft are used to obtain pollutant profiles at various distances downwind in plumes. Most of the equipment used involves the faster response commercially available continuous ambient air monitors for sulfur dioxide, nitrogen oxides, ozone condensation nuclei, and meteorological visual range measurements (41). Special filter procedures have been developed especially to measure particulate sulfur in aircraft operations (42,43). An electrical mobility analyzer and optical particle counters also have been successfully operated in aircraft to obtain aerosol size distributions (41).

Ground level sampling for transport and fate studies does not typically utilize unique techniques compared with other ambient air monitoring activities. However, there often is available a high level of analytical capability so more complex and advanced techniques and instrumen-

tation often are used along with more conventional instrumentation. Ground level installations also provide the opportunity for intercomparison of interrelated techniques. Since the rapid response needs for plume studies do not apply, techniques involving time integrated samples can be conveniently utilized. In aircraft operations the concentration of effort for aerosols has been on sulfate or total particulate sulfur, aerosol size distribution and visual range. In ground level operations it is possible to analyze for acid sulfates, nitrates, ammonium and many elements after particulate sizing. A large number of chemical and spectroscopic techniques have been proposed for differentiating sulfate species (44). However, many of these techniques have a limited capability to distinguish sulfate species in ambient air, cannot be readily quantitated, lack adequate sensitivity, or the procedures are extremely tedious. Most of these approaches have received relatively limited evaluation. The most impressive efforts have been by Brosset et al. using Gran titration (45,46).

Most analytical methods for sulfates are preceded by collection on filters. Some filter materials such as glass fiber, particularly when alkaline convert sulfur dioxide to sulfate. This artifact, although recognized some years ago (47), has been the subject of much recent laboratory investigations (48,49) and field sampling projects (50,51). Based on both laboratory and ambient air comparisons, an artifact of from less than $1 \mu\text{g}/\text{m}^3$ to 4 or $5 \mu\text{g}/\text{m}^3$ can occur, owing to oxidation of SO_2 to sulfate on the filter medium.

An intercomparison study on ambient air particulates in Charleston, W. Va. using a large number of different samplers and analytical methods provides results on the variability of sulfate measurements (52). For total sulfates, total sulfur, finely divided sulfate, and finely divided sulfur, the average standard deviations on a set of 16 samples was as follows: 16%, 15%, 19%, and 11%. These differences are reasonably satisfactory, considering the diversity of samplers and analytical techniques used. When the same type of dichotomous sampler was used in triplicate with the same analytical technique, typical concentrations of total particulate sulfur measured were as follows: 2.3, 2.2, $2.3 \mu\text{g}/\text{m}^3$; 6.1, 5.9, $6.0 \mu\text{g}/\text{m}^3$; 11.3, 11.3, $11.3 \mu\text{g}/\text{m}^3$.

An integrated measurement system with particle size separation into coarse and fine fractions on a dichotomous sampler has been coupled to x-ray fluorescence analysis (EDXRF) for particulate sulfur and about 20 other elements (51). After EDXRF, extracted samples can be analyzed

for sulfate, nitrate, ammonium, and hydrogen ions by use of ion exchange chromatography, the spectrophotometric thorin method, the ion selective electrode and Gran titration (51). Other anions such as sulfite, if present, also can be measured. Total fine and coarse fraction mass also can be determined. An extensive evaluation and research monitoring program has been conducted using many of the components of this system (51).

Laboratory Results on Reaction Kinetics of Sulfur Oxides

In order to understand the formation, transport and removal of sulfate it is necessary to understand both the chemical reactions leading to the conversion of SO_2 to sulfate and to the aerosol dynamics that govern the size distribution of the resulting aerosol particle. This research involves laboratory studies of basic kinetics, chemical kinetic model predictions of oxidation rates, smog chamber studies which simulate atmospheric behavior, and small and large field studies of atmospheric phenomena.

Transformation Mechanisms

The mechanisms by which SO_2 is oxidized to sulfates are important because they determine the

rate of formation of sulfate, the influence of the concentration of SO_2 and other species on the reaction rate, and, to some extent, the final form of sulfate. Atmospheric SO_2 may be oxidized in the gas phase to sulfur trioxide (SO_3) and subsequently be converted to sulfuric acid aerosol, or it may dissolve in aqueous solution to form sulfite ions which are then oxidized to sulfate. Subsequent to the oxidation, sulfuric acid or sulfate may interact with other materials to form other sulfate compounds. The most important sulfate formation mechanisms identified to date are summarized in Table 1.

A key concern for air pollution control strategy is to determine whether SO_2 conversion is first-order or zero-order in SO_2 . If the conversion is first-order, then an 80% decrease in SO_2 emissions could lead to an 80% decrease in sulfate. If, on the other hand, the conversion is zero-order in SO_2 and if we assume that at the present time 10% of emitted SO_2 is converted to sulfate, then it could require a 98% reduction in SO_2 emissions to produce an 80% reduction in sulfate. In the latter case it becomes very important to determine if there are other pollutants that influence SO_2 conversion and that could be more easily controlled. For example, if heavy metal catalysis is important (mechanism 5), better fly ash controls to limit primary aerosol emissions could be used to reduce sulfate.

Table 1. Mechanisms by which sulfur dioxide is converted to sulfates.

Mechanism	Overall reaction	Factors on which sulfate formation primarily depends
Direct photooxidation through electronic excitation	$\text{SO}_2 \xrightarrow[\text{water vapor}]{\text{sunlight, oxygen}} \text{H}_2\text{SO}_4$	Sulfur dioxide concentration, sunlight intensity
Indirect photo oxidation or photochemically induced oxidation	$\text{SO}_2 \xrightarrow[\text{water vapor, hydroxyl radical (OH), HO}_2\text{CH}_3\text{O}_2\text{radicals}]{\text{smog, sunlight}} \text{H}_2\text{SO}_4$	Sulfur dioxide concentration, sunlight intensity, OH, HO_2 , CH_3O_2 concentration
Air oxidation in liquid droplets	$\text{SO}_2 \xrightarrow[\text{oxygen}]{\text{liquid water}} \text{H}_2\text{SO}_4$	Ammonia concentration
Catalyzed oxidation in liquid droplets	$\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NH}_4^+ + \text{SO}_4^{2-}$ $\text{SO}_2 \xrightarrow[\text{heavy metal ions}]{\text{oxygen, liquid water}} \text{SO}_4^{2-}$	Concentration of heavy metal (Fe, V, Mn) ions or carbon particles
Oxidation in liquid droplets by strong oxidants	$\text{SO}_2 \xrightarrow[\text{H}_2\text{O}_2]{\text{ozone}} \text{SO}_4^{2-}$	Ozone or hydrogen peroxide concentration
Catalyzed oxidation on dry surfaces	$\text{SO}_2 \xrightarrow[\text{fly ash, carbon or other particles}]{\text{oxygen, water}} \text{H}_2\text{SO}_4$	Particle concentration and surface area

Mechanisms 1 and 2 are first order in SO_2 and in sunlight. Mechanism 2 also depends on the composition of the background air because this will influence the concentration of reactive species such as OH , HO_2 , and CH_3O_2 . Mechanisms 3, 4, 5, and 6 may be near zero-order in SO_2 , but depend strongly on the concentration of ammonia, oxidants, soluble catalytic metal ions, or particulate surface area. Mechanisms 3, 4, and 5 will be important only when liquid droplets can exist, i.e., under conditions of high water vapor content and high relative humidity.

Reaction Rates

A number of recent studies of the reaction rates of both gas and liquid phase reactions were summarized and reviewed at the International Symposium on Sulfates in the Atmosphere (ISSA) held in Dubrovnik, Yugoslavia, September 1977. During the ISSA workshop, further discussions led to substantial agreement on what is known and what additional questions most urgently need to be answered.

The direct photooxidation of SO_2 by way of electronically excited states of SO_2 , mechanism 1, is relatively unimportant for most conditions that occur within the troposphere (53).

The indirect photooxidation, mechanism 2, is a major mechanism for the conversion of SO_2 to sulfate in the troposphere. Early smog chamber studies showed that SO_2 was converted to sulfate somewhat faster when irradiated in the presence of hydrocarbons and nitrogen oxides (up to 5%/hr in an auto exhaust/air mixture) than when irradiated in "clean" air (1 to 2%/hr in charcoal-filtered air). However, the presence of SO_2 had only a minor influence on the gross parameters of the smog reactions such as the rate and quantity of NO_2 and ozone formation (54). More recently, smog chamber experiments with improved instrumentation have been conducted to determine the relationship between SO_2 oxidation and the gaseous precursors common in polluted air (55). A mixture of 17 nonmethane hydrocarbons (NMHC), which simulates the ambient urban atmosphere, was used with various concentrations of NO_x and SO_x in a series of solution irradiation experiments. The oxidation of SO_2 to sulfate aerosol was found to be first-order in SO_2 . The maximum rate of oxidation was strongly related to the initial NMHC/ NO_x ratios, but over the 6-hr irradiation period, the total conversion of SO_2 to aerosol was only weakly related to the initial NMHC/ NO_x ratio. For constant NMHC/ NO_x ratios, the maximum rate of SO_2 conversion was essentially

independent of precursor concentrations (55). Typical SO_2 oxidation rates for polluted air ranged from 2% to 8%/hr, but the high rates were sustained for only a few hours. Outdoor smog chamber studies, in which SO_2 was added to St. Louis urban air, also gave conversion rates in this range (55). SO_2 half-lives of 1 to 2 days are predicted from these experiments in accordance with half-lives derived from kinetic simulations of photochemical smog and from tropospheric measurements.

An evaluation has been made of the existing kinetic data related to the elementary homogeneous reactions of SO_2 within the troposphere (53,56). During the last decade laboratory and field evidence has been obtained which indicates that the gas phase oxidation of SO_2 is a significant path for the formation of sulfate in the atmosphere. Among the most important reactions are those of SO_2 with OH , HO_2 , and CH_3O_2 free radicals. Reactions involving RCHOO , CH_3O , and $\text{O} (^1\text{P})$ are of lesser importance. The direct photooxidation of SO_2 is not important. The radicals and atoms are produced in the NO_x - O_3 -hydrocarbon-sunlight photochemical cycle and are found in polluted urban air, "clean" rural air, and in stack gas plumes. Rate constants for most of the important reactions have been measured, with general agreement among reported values. Of fundamental importance to the confirmation and improvement of present homogeneous reaction mechanisms of SO_2 oxidation is the direct observation of the reactive transients (OH , HO_2 , CH_3O_2 , etc.) within the various atmospheres.

Computer simulations for typical urban mixtures of pollutants (53,56) indicate an SO_2 oxidation rate of about 2-4%/hr for a sunny summer day, in good agreement with atmospheric measurements of 1-5%/hr. Computer simulations also suggest that in clean air, the SO_2 oxidation rates are somewhat slower than in the urban environment. The present level of understanding of homogeneous SO_2 oxidation justified incorporation in model calculations of rate expressions beyond simple first order, linear dependence on SO concentration.

Experiments on the conversion of SO_2 to sulfate in liquid droplets have been made on both bulk and dispersed systems. Eight experimental studies of mechanism 3, the uncatalyzed conversion of SO_2 to sulfate by dissolved oxygen in liquid droplets, were analyzed (51). Six independent studies found that this reaction was unimportant in the troposphere. However, two other groups obtained rate constants approximately two orders of magnitude larger. If these are correct, this mechanism

could be significant. Additional studies are needed to resolve this discrepancy. Such studies are difficult because traces of organic pollutants in the water will greatly reduce the reaction rate while traces of catalysts can substantially increase the reaction rate. The only role that ammonia appears to play is to reduce the pH of the droplet and thus permit more SO_2 to be dissolved into the solution.

Mechanism 4, in which the oxidation of SO_2 by dissolved oxygen is catalyzed by transition metal ions, has also received considerable study. (57,58) This mechanism may be important for high concentrations of ions ($10^{-5}M$) which may occur in urban plumes of smogs but probably will not occur in background rural air. However, one study has reported that when two transition metal ions are present in solution the reaction rates are perhaps an order of magnitude higher than for the same concentration of a single ion. This synergistic interaction requires further study. There are two different situations in which this mechanism might be important. In clouds the droplets will be relatively dilute. However, in other situations where the droplets result from the deliquescence or hygroscopicity of ambient aerosols highly concentrated solutions will occur. Further studies are needed to determine the composition and concentrations of dissolved species in both cloud water droplets and liquid urban aerosols.

A third type of liquid phase mechanism involves the solution of strong oxidants such as ozone or hydrogen peroxide into a liquid droplet containing dissolved SO_2 (58). Two studies of the reaction of ozone give rate constants varying by a factor of 10. If the higher rate constant is correct, background ozone concentrations of 50 ppb would lead to significant conversion of SO_2 to sulfate in liquid droplets. Further studies are needed to determine the correct reaction rate. The reaction of hydrogen peroxide is faster than that of ozone. The one measurement reported indicates that hydrogen peroxide at an ambient concentration level of 1 ppb would yield significant conversion rates. It therefore becomes important to be able to make direct measurements of the hydrogen peroxide concentration in the troposphere (57,58). Recent studies suggest that carbon particles, formed during all combustion processes, if dispersed in liquid droplets could also catalyze the conversion of SO_2 to sulfate (59).

The catalytic oxidation of SO_2 to sulfate on dry surfaces appears to be controlled by the number of absorption sites and therefore depends on the surface area of the particle. It appears that once SO_2 is absorbed it is slowly converted to sulfate and stays on the surface so that only a limited

amount of sulfate can be formed by this mechanism (60).

It is clear that the homogeneous photochemical mechanisms, first order in SO_2 , are sufficient to account for a substantial conversion of SO_2 to sulfate. Therefore any control mechanism to reduce sulfate formation will have to include reduction in SO_2 emissions. The liquid phase reactions are not as well understood. However, there is some qualitative evidence that the liquid phase reaction does occur and may indeed under certain circumstances be much faster than the homogeneous conversion. It is observed experimentally that when very high ambient concentrations of sulfate are found, they are usually associated with clouds of high relative humidity. Liquid phase conversion might be reduced by control of precursors or reactants other than SO_2 . Further studies are needed to define the contribution and specific mechanisms involved in the liquid phase reaction mechanism.

Aerosol Dynamics

In order to predict the rate of removal of aerosol particles by dry deposition, the amount and location of particles deposited in the lung, and the effect of aerosols on visibility, weather and climate, it is necessary to understand the processes governing the formation and growth of aerosol particles and their changes in size with changes in relative humidity.

Studies (61,62) over the past five years of the size distribution of particles in both sulfate aerosols and general atmospheric aerosols have led to important changes in our understanding of the behavior of aerosols such as sulfates in the ambient atmosphere. There are three principal modes (particle-size ranges). Particles in the Aitken nuclei mode $< 0.08 \mu\text{m}$ diameter, are formed by condensation of vapors produced either by high temperatures or chemical processes. The accumulation mode, which includes particles from 0.08 to $2.0 \mu\text{m}$ in diameter, is formed by coagulation of particles in the nuclei mode and by growth of particles in the nuclei mode through condensation of vapors onto the particles. Coarse particles, $> 2.0 \mu\text{m}$ are formed by mechanical processes such as grinding or rubbing—for example soil, street dust, and rubber tire wear—and by evaporation of liquid droplets. Accumulation mode particles do not continue to grow into coarse particles, however, because the more abundant small particles have a higher gas-aerosol collision rate and dominate the condensational growth process. Sulfates formed by the conversion of SO_2

are found in the accumulation mode; MgSO_4 from sea salt, Na_2SO_4 from paper pulping, and CaSO_4 from gypsum are found in the coarse particle mode.

The processes governing aerosol dynamics are understood qualitatively and some effort has been made to interpret aerosol dynamics in smog chamber studies (63). Models of aerosol dynamics have been developed but these need to be tested quantitatively with chamber and ambient data (64). The aerosol growth laws predict different aerosol sizes for the different reaction mechanism. If the model is confirmed, these differences could be used to determine whether growth is by condensation of vapors formed by homogeneous gas phase reactions, reaction in liquid droplets, or absorption on particle surfaces.

Field Investigations

Direct Emissions

Emissions from combustion sources are characterized in terms of particulate matter and gases. The physical and chemical properties of these emissions include: organic and inorganic particulate matter and gases, particles of varying size distribution, and particulate matter with optical properties and trace element content. Measurements have been conducted to quantify and to characterize emissions that result from different operating conditions. Operations that potentially impact in a significant manner on the emission and that are being addressed in various field studies are: emission control systems, excess oxygen for combustion, combustion modification, type of fossil-fuel (gas, lignite coal, and oil), and the sulfur and trace metal content in the fuel. Coal utilization will involve fuel switching, mainly from gas and oil to coal. A selected but limited number of field studies have been conducted to date to measure and characterize emissions from combustion sources under different operating conditions. The data resulting from such studies will provide insight on the impact on emissions as a result of fuel switching from oil to coal, particularly for various levels of sulfur content.

Characterization of Emissions. Data characterizing emissions from coal-fired sources, are presented with emphasis on particulate mass loading, particle size distribution, particle composition, SO_4 , SO_2 , NO_x , and polynuclear organic matter (POM).

Particulate. Mass emission rates for particulate matter have been measured for a number of combustion sources with three different types of

particulate control equipment (65). The range of emissions for the various control systems were as shown in Table 2.

Particle Size Distribution. Both monomodal and bimodal size distributions have been reported for emissions from coal-fired combustion sources with and without electrostatic precipitators (66-68). Monomodal peaks appear in the 1-10 μm range. It is probable that the use of an impactor without calibration of the upper stages failed to provide adequate data to resolve a second peak (68). An impactor with calibrated upper stages gave a bimodal distribution with a peak in the submicron range (0.7 μm) and another peak at 5 μm . Additional data for emissions from industrial and utility boilers showed bimodal distributions for all given sources measured. Again, the upper size peak was in the 1 to 10 μm range and the lower size peak was in the 0.1-1.0 μm range (66).

Electrostatic precipitators (ESP) have a collection efficiency curve as a function of particle size that shows a minimum in the 0.1-1 μm size range (69). In effect, an ESP can tend to smooth out an incoming bimodal distribution, especially if the minimum in the distribution coincides with the peak penetration of the ESP. The percent penetration is increased with a decrease in the sulfur content of the coal (69).

Field studies on coal of particulate emissions downstream of conventional venturi scrubbers on coal-fired boilers have shown efficient (98%) collection of large particles down to about 2 μm . The efficiency drops off rapidly, to 90% at 1 μm and about 10% at 0.3 μm (70).

Baghouses are very efficient particulate control devices, having efficiencies in excess of 98% for particles down to and less than 0.3 μm (71,72).

Particle Composition. Field studies have characterized particulate composition on bulk samples (73-75) and on size-fractionated samples (30,74,76). As many as 60 elements have been measured in the flyash (76). The concentration distributions for a number of elements showed bimodal distribution with a distinct minima in the region $0.3 \leq d \leq 1.0 \mu\text{m}$ (30). The elements predominating in concentration $\geq 1\%$ included Si, Al, Na, K, Ca, Fe, C, and S. Trace elements ($\geq 0.01\%$)

Table 2. Range of emissions for various control systems

Control system	Particulate emission rate, lb/million BTU input
Electrostatic precipitators	0.01-0.26
Baghouses	0.0014-0.1
Venturi scrubbers	0.019-0.19 (used with FGD controls)

included Mg, Ti, Ni, Cr, Mn, Ba, Cu, and Sr (75).

Polynuclear organic material (POM) measurements were conducted on emissions from three large coal-fired power plants (77). Total POM concentration was in the range of 28 to 30 ng/Nm³; and the BAP fraction was 0.2 to 0.3 ng/Nm³.

Nitrogen Oxides (NO_x). Studies have been made on the control of nitrogen oxides emissions by combustion modifications (78-80) and the impact on emissions for large coal-fired steam generators (200 MW output) and for smaller industrial boilers. For the large utility boilers, the NO_x emissions under normal operating conditions (4-7.3% O₂) range from 0.56 to 0.85 lb/million BTU input (78). With combustion modifications, the range of emissions is 0.25 to 0.66, depending upon the reduced level of combustion air (2 to 5% O₂), burner design, and configuration of firing in the boiler. Reductions of 30 to 50% in NO_x emissions from industrial boilers have been achieved (79). Combustion modification can be made on both utility and industrial boilers without significant impact on concurrent emissions of (HC, CO, SO₂) gaseous pollutants (78,79). However, measurements made of fine particulate emissions showed that NO_x control caused an increase of particles in the submicron size range (79,80) and the presence of carbonaceous particles (predominating in the sizes <0.4 μm) as compared to the normal combustion condition (80). The reduction in NO_x emissions from industrial boilers was accompanied by an increase in particulate loading of 5 to 50% (79).

Sulfur Dioxide (SO₂). Field studies conducted on combustion sources that burned low (1.5%) and high (4.2%) sulfur coal gave a range of SO₂ emissions of 2.1 to 6.7 lb/million BTU input. These sources had ESP particulate control but no SO₂ controls. Data are being collected currently on sources with SO₂ controls and burning coals of various sulfur content.

Sulfate-Sulfur Trioxide (SO₃). Sulfuric acid (H₂SO₄), and sulfate compounds are measured in combustion source emissions as total water soluble sulfates (TWSS) (81). Field studies on coal-fired boilers without SO₂ controls but with ESP

particulate control substantiate that emissions of TWSS are in the range of 1 to 2% of the sulfur in the fuel (82) as presented in the EMISSIONS HANDBOOK (83). The ESP control reduces the TWSS emissions by a factor of about 2 (82). A few measurements of emissions downstream of wet scrubbers for SO₂ control show qualitatively that TWSS penetrate these controls (84). More studies are needed to establish quantitatively the impact of SO₂ control on TWSS emissions. Use of high sulfur fuel on the basis that flue gas desulfurization (FGD) will keep SO₂ emissions within bounds may, in effect, permit a significant increase in TWSS emissions, proportionate to the increase of the sulfur in the fuel.

Visible Emissions. Emission standards on visible emissions are 20% opacity on plumes from coal-fired power plants (85). The presence of sulfuric acid (H₂SO₄) in the gas phase at stack gas temperatures has no impact on in-stack opacity measurements but it may impact on plume opacity as it condenses at ambient temperatures. In oil-fired combustion sources, the impact of H₂SO₄ in plume opacity is significant (23-54% in the plume versus 13% in the stack) (86). In sources burning low sulfur coal (>2.5%S) and having electrostatic precipitators, plume and stack opacity measurements have not shown significant differences. Measurements are currently underway on sources burning high sulfur coal (>3%S) with ESP control and on similar sources with wet scrubbers. The impact of H₂SO₄ on plume opacity is affected by the relative concentration of other particulate matter which is a function of the ash content of the fuel and the presence and efficiency of any particulate control system.

Impact on Emissions with Fuel Switching to Coal. Results of recent field studies with emphasis on SO_x emissions from oil- and coal-fired combustion sources are summarized in Table 3. Low particulate, SO₂, and SO₄ emission rates are associated generally with low sulfur fuel and similarly, high emission rates for high sulfur fuels. Switching from low sulfur oil (1.2%) to coal of about the same sulfur level (≈1.5%) shows about a factor of 6 increase in the particulate emission

Table 3. Data on particulate, SO₃, and SO₄⁻ emissions from oil- and coal-fired combustion sources.

Fuel			Emissions			
Type	S, %	V, ppm	Particulate matter	SO ₂	SO ₄	Remarks
Oil	1.2-2.5	10-50	0.014-0.17	0.77-2.5	0.02-0.33	No particulate or SO ₂ control
Coal	1.5-4.2	10-35	0.019-0.17	2.1-6.7	0.03-0.25	Particulate control but no SO ₂ control

rate, a factor of about 3 in SO_2 , and about the same SO_4 emission rate. Switching from high sulfur oil (2.5%) with high vanadium content to high sulfur coal (4.2%) shows the same particulate emission rates (0.17), about a factor of 2 increase in SO_2 , and a slight decrease in SO_4 .

Data on coal-fired sources with SO_2 controls are needed to provide a more complete picture on Table 3. Also, the limited data in Table 3 at this time provide more of a qualitative indication than a comprehensive quantitative measure. The variations in operating parameters are not adequately represented to indicate the effect of switching under optimum conditions for each type of fuel.

Plume Transport

Reductions in urban SO_2 emissions have been accompanied by increases in rural SO_2 emissions from new power plants located outside cities. Sulfur dioxide from these power plants may be transformed to sulfate in the atmosphere and transported over long distances to urban areas. Interest in the transformation-transport theory led to a major expansion of existing studies by establishing Project MISTT (Midwest Interstate Sulfur Transformation and Transport). The technical approach of Project MISTT was to study the transformations of SO_2 to sulfate in polluted air masses undergoing transport. The intent was to measure pertinent chemical and meteorological parameters with sufficient accuracy so that they may be used with physical and mathematical models to derive rate parameters which characterize the transformation processes. This research gave insight into transformation mechanisms and serve as a guide for related laboratory studies.

Results on Power Plants Plumes. A small amount of conversion of SO_2 to sulfate appears to result from adsorption of SO_2 onto plume particulate matter. The amount depends on surface area and ceases as soon as active adsorption sites are covered or the liquid coating becomes acidic (60). For plumes from modern power plants with efficient particle removal equipment this amounts to the order of 1% of the SO_2 emitted (86). Further reaction of SO_2 in the cohesive plume is inhibited because the particles are too acidic to dissolve more SO_2 and NO_x is preferentially oxidized to NO_2 . As the plume disperses, O_3 in the background air mixes into the plume and converts the NO_x to NO_2 . The background air may also bring in NH_3 to neutralize acid droplets. In the dispersed plume therefore both gas and liquid phase reactions may begin to convert SO_2 to sulfate. In the power plant plumes which have been completely analyzed, the

rate of conversion was 0.5%/hr or less at night and in early morning and late evening (87,88). During the middle of the day, however, plume conversion rates increase to as high as 5%/hr (87). Since both dispersion and photochemically-generated radicals (OH , HO_2 , RO_2) increase with sunlight intensity it is not possible to definitely state whether gas phase or liquid phase reactions were rate controlling. However, condensation nuclei counts and aerosol size distribution profiles suggest that the major pathway is a homogeneous reaction, first order in SO_2 , and probably involving the OH , HO_2 , and RO_2 radicals. The reaction rate certainly depends on sunlight intensity and appears to also depend on water vapor concentration, background ozone levels, and the extent to which the plume has mixed with background air. The pollutant profiles, in both power plant and urban plumes, resemble those observed in chamber studies and suggest that the current chemical kinetic models can be used to calculate sulfate formation.

Heterogeneous reactions may be important at night, in clouds, or other conditions during which high water vapor content and high relative humidity may lead to the existence of liquid droplets. Attempts to make nighttime measurements during the summer of 1975 were frustrated by difficulties in locating the plume. The use of lidar during the summer of 1976 made it possible to locate the plume but usually dry conditions led to nighttime relative humidities substantially lower than normal. Therefore, the data analyzed to date does not allow any conclusions regarding heterogeneous reactions. There are, however, several qualitative indications suggesting that under proper conditions heterogeneous reactions may be important and may lead to rates significantly greater than the 5%/hr maximum found for homogeneous reactions. The key parameters governing heterogeneous reactions, in addition to high relative humidities and high water vapor content, are thought to be ozone and ammonia concentrations, concentrations of catalytic species in aerosol form, and the extent of mixing with background air.

Transport Distances. The time and distance over which an air mass maintains its integrity depends on its initial size and the meteorological conditions. Power plant and urban plumes have been tracked for 300 km. These plumes maintain their integrity and high pollutant concentrations for much longer times and farther distances than originally expected. During stable nighttime conditions, the cohesive-plume is frequently caught in a nocturnal jet which carries it along at as

much as twice the normal wind speed. Gaussian plume models are satisfactory for the first few 10's of kilometers, but, beyond that, wind shear seems to play the dominant role in determining dilution. In urban plumes, wind shear is clearly the determining factor.

Models. Models, of several levels of complexity, have been developed for calculating secondary pollutant concentrations in power plant and urban plumes. These include a multistep chemical kinetic model and a reacting plume model with relatively simple mixing parameters but with provisions for aerosol formation, coagulation, and growth. In addition, a model has been developed using a sulfate formation rate that is a function of sunlight intensity and that has more sophisticated meteorological terms including multilayers for vertical diffusion and dry deposition.

Future Work. The present study has concentrated mainly on sulfate, ozone and light scattering. Plans call for extending the EPA plume studies to include measurements of organics and nitrate aerosols and vapors such as nitric acid. To determine the importance of heterogeneous reactions, more work is needed under conditions of high relative humidity and high water vapor content, which are conducive to heterogeneous reactions. In general more information is needed to provide better statistics on the parameters that influence reaction rates in power plant and urban plumes.

Summary. Power plant and urban plumes have been sampled out to 300 km from their sources. Sampling at these distances revealed that sulfate, generated from SO_2 in power plant plumes, and ozone, generated from hydrocarbons and nitrogen oxides in urban plumes, may be transported at least hundreds of km and may cause air pollution episodes far from the source of pollution. Air pollution, caused by secondary pollutants such as sulfates and ozone, cannot be controlled by the government entity where the air pollution impact actually occurs. Therefore, current concepts of air quality control regions must be revised to take into account the long-range transport of secondary pollutants.

Effect of NEP on Source Emissions

The purpose of this section is to analyze the potential effect of NEP on the magnitude and location of emissions from both steam electric and industrial plants in the eastern U.S. and to develop the emissions inputs to the regional dispersion modeling in the following section.

Projections of the magnitude and locations of steam electric plant emissions have been made for a range of potential energy and environmental control policies (89). These emission projections have been analyzed as part of the Air Quality Impact Assessment Model (AQIAM) of the ITA (11). In that analysis, it was found to be convenient and appropriate for long-range transport analyses to aggregate the emissions over individual steam electric units in each county and designate the county as a "hot spot" if those aggregate SO_2 emissions were greater than 5×10^7 kg/yr.

A high comparison of SO_2 "hot spots" projected the AQIAM under a reference and a high coal use energy policy and under environmental controls mandated by the 1977 Clean Air Act Amendments is presented in Figure 1, which shows the following significant features:

(1) the highest density of "hot spots" under both scenarios and both years is in the Upper Ohio River Basin; (2) ten "hot spots" which disappear after 1985 under both scenarios are generally scattered around the eastern U.S. except for the St. Louis area, where two such "hot spots" are



FIGURE 1. Comparison of SO_2 "hot spot" counties under scenarios REF-CAR and HCU-CAR in 1985 and 1995 from the impact assessment model. Counties with high SO_2 emissions ($\geq 5 \times 10^7$ kg) under: (■) both scenarios in both years; (▲) both scenarios in 1985 only, (★) only one year of one scenario or all years except HCU-CAR 1995; TVA plants (●) > 1500 MW and (○) 800-1500 MW (included because the first-year ITA data base did not include TVA or publicly owned utilities)

found; and (3) eight other "hot spots" which appear in different combinations of scenarios and years are also scattered around the eastern U.S.

The ITA high coal use scenario is nearly the same as the NEP at this date except for a slight difference in the assumed growth rates from 1975 to 1985 and a more significant difference in assumed growth rates from 1985 to 2000. In addition, the publically owned utilities and the states of Nebraska and Tennessee were omitted in the version of the AQIAM used here.

Unfortunately, there is currently no impact assessment model (IAM) for the industrial sector—that is, there is no model capable of predicting the magnitude and locations of industrial plant emissions using the same basic "from the individual unit up" methodology of the electric utility ITA. However, future industrialsource emissions have been projected by using the EPA/ERDA Technology Assessment Modeling Program (TAMP) for the NEP scenario. No formal descriptions of analysis of these TAMP outputs are currently available, so their use here is considered preliminary. TAMP provides only a very limited amount of disaggregation of the nationwide emission projections, namely just for the Federal regions and individual states. The methodology used to disaggregate the state-level TAMP industrial emissions to the county level for use in primary air quality impact analyses has been described previously (3). Briefly, the ITA county siting weights for future steam electric plants are used also for the locations of new coal fired industrial plants.

Generally, the state TAMP emissions were divided by the total number of highly probable siting weights for all fuel types plus the number of FEA/ESECA plant orders unless specific emissions for the latter were available. In that case,

these specific conversions or new plant emissions were subtracted from the TAMP and IAM emissions before dividing by the number of county siting weights plus the number of FEA/ESECA plant orders for which specific plant emissions were unavailable at the time of this paper.

It is of interest to compare the emissions from TAMP, NEDS, and the IAM since the dispersion model calculations are most sensitive to the emissions inputs.

The comparisons of emissions in the state of Ohio for electric utilities and industrial combustion are presented in Tables 4 and 5, respectively. The comparisons in Table 4 show that generally all the similar or newly similar categories of electric utility emissions compare quite well for both sulfur dioxide and particulates.

The comparisons in Table 5 show that generally the similar or nearly similar categories of industrial combustion emissions are different by about a factor of 2 or both pollutants.

Source Air Quality Relations

Short-Range Relations

In considering the short-range (within 20 km of the source) impact from combustion sources, the direct emission of pollutants is of concern rather than the formation of secondary pollutants. Considering the direct emission of sulfur dioxide, national ambient air quality standards exist for both the annual average ($80 \mu\text{g}/\text{m}^3$) and 24-hr maximum not to be exceeded more than once per year ($365 \mu\text{g}/\text{m}^3$). For moderate (stacks 50 to 100 m. high) to large (stacks greater than 100 m) combustion sources, the 24-hr standard is generally the one that is the most difficult to meet.

Air quality dispersion models of the Gaussian

Table 4. Comparison of emissions from electric utilities in Ohio

Data source	Scenario	Year	Pollutant, kg/yr ^a	
			SO ₂	TSP
TAMP	NEP	1975	1.82×10^9	3.59×10^8
		1985	1.65×10^9	8.99×10^7
		2000	1.31×10^9	7.11×10^7
NEDS	—	1972	1.83×10^9	3.27×10^8
		1973	1.90×10^9	3.87×10^8
IAM	REF-BAU	1975	1.93×10^9	3.70×10^8
		1980	1.54×10^9	4.51×10^7
	REF-CAR	1985	1.46×10^9	4.83×10^7
		1995	1.30×10^9	4.91×10^7
	HCU-CAR	1985	1.47×10^9	5.06×10^7
		1995	1.30×10^9	5.80×10^7

^a 1 ton = 907.18 kg.

type (assume time averaged plume concentrations to be distributed normally, Gaussian, bell-shaped, in the crosswind and vertical) can be used to estimate ground level concentrations of directly emitted pollutants for various meteorological conditions. The magnitude of the maximum concentration and the distance to the maximum can usually be determined quite well.

Estimates from a dispersion model (90) indicate that for combustion sources with stacks in the vicinity of 70-100 m, the highest 24-hr concentrations seem to occur for days with a high wind direction persistence (not much wind direction variation), with moderate wind speeds (4-10 m/sec), and neutral to slightly unstable atmospheric stability (related to turbulence level). For combustion sources with stacks in the vicinity of 200 m, the highest 24-hr concentrations seem to occur with 2 or 3 hr with wind from nearly the same direction, with light wind speeds (1.0-2.0 m/sec) and with moderately to extremely unstable conditions.

Concentrations are directly proportional to emission rates. Thus if emissions are reduced by 50%, concentrations are decreased by 50% if other things are equal. An example is a fuel containing half the pollutant of that in a previously used fuel. However, changes in amount of fuel fired will alter the effluent volume flow altering plume rise. Because of this plume rise factor, calculations have indicated only small changes in maximum hourly concentrations in spite of rather large changes in emissions due to fuel rate changes (91).

The impact of direct emissions of sulfates from combustion sources may be estimated using dispersion models in the same way that the impact of sulfur dioxide can be estimated. This assumes that the sulfates are fine particulates or liquid droplets (less than 20 μm).

The areas of short-range impact for the 24-hr averaging time will generally be in the vicinity of 1 to 20 km from the source. Due to meteorological variation the area of impact will shift location

from day to day. Conversion of fuel type at a source will cause areas of impact under given meteorological conditions to expand or contract dependent upon change in emissions. Establishment of new combustion sources must consider that additional new areas of short-range impact will result.

Although greater utilization of coal is likely to occur at new combustion facilities rather than conversion at old facilities, it may be of interest to take information from an actual facility, that previously burned coal and presently burned residual oil of Venezuelan origin, and make estimates of 24-hr SO_2 and directly emitted sulfate for adverse meteorological conditions (representative of once a year). The source is in a river valley and therefore there are some terrain complications. For these estimates a similar source is assumed to exist in gently rolling terrain with no topographical complications.

The engineering information on the source is shown in Table 6 along with the projected concentration estimates. The engineering information is qualified by superscripts to indicate whether information was obtained by stack sampling, from the owner of the source, from engineering estimates, or speculative assumption. Note that because of the heat content, 65% more coal by weight than oil is burned for the same electricity.

On considering the physical height of the source is 108 m, a 24-hr scenario of hourly meteorological conditions was selected from those presented (90). This period (day 20) has moderate winds (3.1-6.2 m/second), quite persistent wind direction (varying only from 230° to 310°) and stability ranging from moderately unstable (Pasquill B) in the daytime to moderately stable (Pasquill F) for one nighttime hour.

It was apparent from the meteorological data that receptor locations centered around an azimuth of 290° from the source would be appropriate. Models from the source of receptors, were used to evaluate the distance to maximum concentration for different meteorological conditions.

Table 5. Comparison of emissions from industrial combustion in Ohio.

Data source	Scenario	Year	Pollutant, tons/yr ^a	
			SO_2	TSP
TAMP	NEP	1975	4.81×10^5	2.29×10^5
		1985	6.28×10^5	6.12×10^4
		2000	8.54×10^5	6.24×10^4
NEDS	—	1972	8.36×10^5	1.08×10^6
		1973	8.58×10^5	1.08×10^6

^a 1 ton = 907.18 kg.

(Table 6 gives the source characteristics and the results of the dispersion modeling performed to estimate the maximum 24-hr concentration). These concentration estimates from the dispersion model are considered accurate to within a factor of two. Note that cooler stack temperatures with lower plume, associated with 80% control of the sulfur dioxide emissions with flue gas desulfurization results in a 75% decrease in 24-hr ground level sulfur dioxide.

The estimated 24-hr SO₂ concentration contributions from this one source for all three situations ranging from 7 to 116 µg/m³ are well below the primary national ambient air quality standard of 365 µg/m³. However, influences from other local sources or the general pollutant levels in the air mass have not been considered. Concentration estimates of sulfur dioxide for other sources will vary considerably dependent upon all of the following: stack height, stack gas temperature, amount of fuel fired, sulfur content of the fuel, and efficiency of any desulfurization equipment.

Regional Impacts

Previous integrated analyses of emission, air quality, and meteorological data suggested that an extension of the sector-box model approach originally used on the congressionally directed analysis entitled Air Quality and Stationary Source Emission Control (92) would be appropriate for this initial evaluation of NEP. Improvements in the basic sector-box model—for example, the provision for treating multiple sources—have been described elsewhere (6); a schematic diagram of the new model is provided in Figure 2. This "sector-box model with source intensification" (SBSI) applies at distances after emissions from individual sources have been well mixed horizontally and vertically by the stronger winds and near-neutral stability conditions associated with the most frequent extreme-persistence conditions under the relaxed criteria.

The direction and width of the extreme persistence sectors are used to specify the emission sources downwind which should be included and

Table 6. Estimates of maximum 24-hr concentrations from a combustion source (oil vs. coal).

	Oil-fired	Coal-fired	
		Without FGD	With flue gas desulfurization (FGD)
Production of electricity, MW	100 ^a	100 ^b	100 ^b
Fuel firing rate, kg/sec	6.3 ^a	10.4 ^b	10.4 ^b
Fuel sulfur content (by weight), %	1.6 ^a	2.7 ^{a,c}	2.7 ^{a,c}
Fuel heat content, BTU/lb	18572 ^b	12383 ^b	12383 ^b
Emission rates, g/sec			(80% control) ^e
SO ₂	195 ^d	498 ^d	100
			(20% control) ^e
Sulfate	8 ^d	8 ^{d,f}	8
Stack parameters			
Height, m	108 ^a	108 ^a	108 ^a
Diameter, m	4 ^a	4 ^a	4 ^a
Exit gas velocity, m/sec	10.5 ^b	16.2 ^b	14.8 ^b
Effluent gas volume flow, m ³ /sec	132 ^b	204 ^b	186 ^b
Effluent gas temperature, °K	453 ^b	433 ^a	395 ^{e,g}
Estimated max. 24-hr concentration	28 ^h	58 ^h	14 ^h
(Adverse meteorology) of directly emitted sulfur dioxide, µg/m ³	(14-56) ⁱ	(29-116) ⁱ	(7-28) ⁱ
Estimated max. 24-hr concentration	1.2 ^h	1.1 ^h	1.1 ^h
(Adverse meteorology of directly emitted sulfates, µg/m ³	(0.6-2.4) ⁱ	(0.6-2.2) ⁱ	(0.5-2.2) ⁱ
Estimated distance to maximum concentration, km	2.25	2.75	2.25

^a From owner of source.

^b From engineering estimate.

^c 10% of fuel sulfur in ash, therefore 90% of fuel sulfur available for conversion to SO₂ or sulfate.

^d Based on stack sampling.

^e Assumption.

^f Measured conversion of 0.5%-2.5% of fuel sulfur to sulfate, assumed 1.25% converted.

^g 38°K (100°F) drop assumed with FGD.

^h Dispersion estimate accurate within a factor of two.

ⁱ Factor of two range of answer.

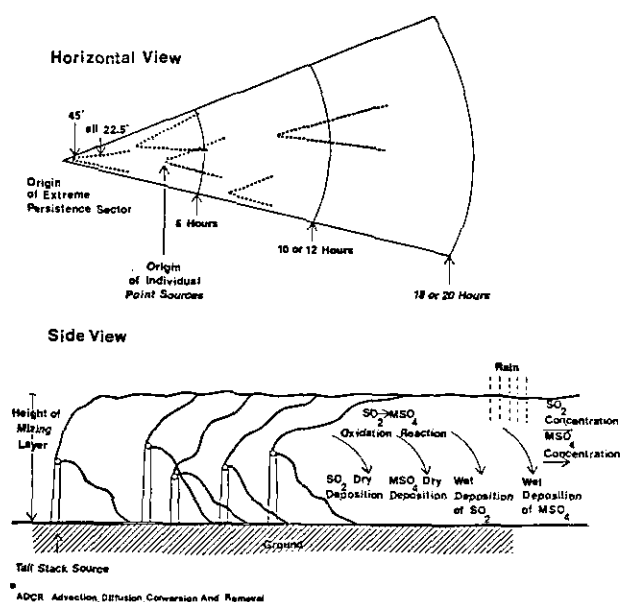


FIGURE 2. Schematic diagram of the Teknekron sector box with source intensification of SO_2/MSO_4 ADCR model, Advection, diffusion, conversion, and removal. Tall stack source.

the rate of horizontal diffusion of each emission sources within the sector. This extensive use of meteorological data to infer diffusion parameters for longer range transport is considered superior to the other techniques currently used in trajectory and grid type models (92). The conversion and removal chemistry in the SBSI is assumed to be linear and is specified in a manner similar to that in current trajectory and grid models (94). The SBSI model inputs selected were as follows: (1) mixing height was 1000 m and the transport speed was 7.1 m/sec; (2) the rate of conversion of SO_2 to MSO_4 was 2%/hr, and the rates of dry deposition of SO_2 and MSO_4 were 1 and 0.1 cm/sec, respectively. (3) The sector width was 22.5° . (4) The short-range cutoff was made at 1 hr of travel time or approximately 25 km. (5) The long-range cutoff was made at 12 hr of travel time for approximately 300 km for six of the locations and at 18 hr of travel time or approximately 450 km for Athens, Kansas City, and Pittsburgh.

The source emission information for the over 200 counties under the most frequent wind persistence sectors at the nine locations required over 2000 input cards to the SBSI model. These model predictions should generally be divided in half to produce conservative 24-hr SO_2 and MSO_4 concentrations since the wind conditions used in the SBSI model generally only persist for 12 hr. These model predictions should be viewed as esti-

mates of the SO_2 and MSO_4 levels above those levels produced by other sources upwind of the sector origin and from urban and area sources within the sectors.

The maximum incremental SO_2 and MSO_4 concentrations for the reference and the high coal use (NEP) scenarios in 1985 for the nine selected locations are presented in Table 7. The only differences which appear to be significant are those for the New York location. The large SO_2 concentration predicted for the Huntington sector under RED-CAR is due to the influence of one large SO_2 emission whose influence is much less under the HCU-CAR scenario.

The maximum incremental SO_2 and MSO_4 concentrations for the reference and the high coal use (NEP) scenarios in 1995 for five of the nine selected locations are presented in Table 8. The maximum SO_2 concentrations under REF-CAR are greater than those under HCU-CAR at the Athens and Washington locations while the maximum under REF-CAR at the other three locations are either equal to or less than the maximum under HCU-CAR. The maximum MSO_4 levels under the two scenarios are the same or nearly the same at these five locations.

Since one of the most important input parameters to the SBSI model is the SO_2 to MSO_4 conversion rate, it is of considerable interest to examine the sensitivity of the predictions to expected variations in the conversion rate. The variations in conversion rate could be the result of

Table 7. Incremental maximum SO_2 and MSO_4 concentrations for reference and the high coal use (NEP) scenarios in 1985 for nine selected locations

Scenario	Area	Maximum concentrations, $\mu\text{g}/\text{m}^3$	
		SO_2	MSO_4
REF-CAR	Dallas, Tex.	11	1
	Kansas City, Mo.	14	1
	Athens, Ga.	53	6
	Detroit, Mich.	22	3
	Washington, D.C.	22	2
	Peoria-Springfield, Ill.	36	5
	Huntington, W. Va.	112	7
	Pittsburg, Pa.	55	7
	New York, N. Y.	30	4
HCU-CAR	Dallas, Tex.	11	1
	Kansas City, Mo.	14	1
	Athens, Ga.	53	5
	Detroit, Mich.	22	3
	Washington, D.C.	21	2
	Peoria-Springfield, Ill.	36	5
	Huntington, W. Va.	55	7
	Pittsburg, Pa.	55	7
	New York, N. Y.	41	6

Table 8. Maximum incremental SO₂ and MSO₄ concentrations for reference and high coal use (NEP) scenarios in 1995 for five selected locations.

Scenario	Area	Maximum concentrations, $\mu\text{g}/\text{m}^3$	
		SO ₂	MSO ₄
REF-CAR	Dallas, Tex.	8	1
	Kansas City, Mo.	13	2
	Athens, Ga.	43	5
	Detroit, Mich.	19	3
	Washington, D.C.	26	2
HCU-CAR	Dallas, Tex.	9	1
	Kansas City, Mo.	13	2
	Athens, Ga.	39	4
	Detroit, Mich.	23	3
	Washington, D.C.	18	2

changes in solar radiation, background air quality, humidity, etc.

The differences in the maximum SO₂ and MSO₄ concentrations under HCU-CAR in 1985 at the Huntington and Pittsburgh locations for various SO₂ and MSO₄ conversion rates are presented in Table 9. It may be seen that the maximum SO₂ concentrations are influenced insignificantly while an 8-fold increase in rate from 0.5% to 4%/hr results in a 7-fold increase in sulfate concentrations. This essential proportionality between rate and sulfate increases occurs because of the initial assumption of first-order chemistry.

Acidity in Precipitation

This section is concerned with the deposition of pollutants with precipitation, the composition of precipitation samples and relationships to sources of emission. The environmental effects of acid precipitation are considered in a separate paper on that subject.

The acidity in precipitation has increased substantially over the last two decades (95, 96). The area impacted also has increased over this period (95, 96). The lowest pH values are reported in the Northeastern United States particularly at sites in the mid-Atlantic states and lower New England (95). The geographic profiles for the regions of lower pH measurements resemble in some respects the profile for sulfate concentrations in the United States (97).

The chemical species measured in precipitation by the several networks operational in the United States include sulfate, nitrate, chloride, fluoride, phosphate, ammonium, calcium, sodium, magnesium, potassium, aluminum, iron, other trace metals, and organic acids (98). However, it appears that the strong acids, sulfuric acid and nitric acid,

account for almost all of the free acidity (pH) on a regional basis (96, 99). Hydrochloric acid may contribute to acidity in precipitation downwind of sources burning high chlorine content coals but not on a regional scale (95, 96).

Deposition of acid sulfate species in precipitation occurs because of oxidation of sulfur dioxide to sulfate in water droplets as well as from washout by rain or snow of acid sulfate aerosols and nitrate acid. The former processes are likely to be slow except in highly contaminated atmospheres where concentrations of the ammonia, and soluble iron and manganese species can be high (100). The rates predicted for conversion of sulfur dioxide in droplets are shown (0.2%/hr), so extended periods of oxidation appear to be necessary for in-cloud processes to be important in sulfur dioxide oxidation (100). Yet another possibility is oxidation of sulfur dioxide by oxygen and ozone in water droplets particularly during nighttime (57). One important source of the ozone is the atmospheric photooxidation reactions to be discussed next.

Homogeneous processes of oxidation of sulfur dioxide to sulfuric acid in the present organic vapors, nitrogen oxides, and sunlight are effective processes for oxidation of sulfur dioxide, and theoretical rates of up to at least 4%/hr are possible (53). Nitric acid also is formed from these homogeneous photooxidation reactions (101, 102). The removal of a water-soluble vapor such as nitric acid by washout should be quite effective. Acid sulfate can be emitted directly from coal and oil-fired sources (81) and thus can be washout downwind of either urban sources or large point combustion sources. Therefore, both direct emissions of acid sulfates and secondary formation by homogeneous and heterogeneous atmospheric reac-

Table 9. Differences in the maximum SO₂ and MSO₄ concentrations under HCU-CAR in 1985 at the Huntington and Pittsburgh locations for various SO₂ to MSO₄ conversion rates.

Conversion rate, %/hr	Location	Maximum concentrations, $\mu\text{g}/\text{m}^3$	
		SO ₂	MSO ₄
0.5	Huntington, W. Va.	57	2
	Pittsburg, Pa.	56	2
1.0	Huntington, W. Va.	56	4
	Pittsburg, Pa.	56	4
2.0	Huntington, W. Va.	55	7
	Pittsburg, Pa.	55	7
4.0	Huntington, W. Va.	52	14
	Pittsburg, Pa.	53	14

tions of sulfuric acid and nitric acid in plumes downwind of sources can provide strong acids in precipitation.

Acid precipitation in the northeastern United States can be associated with washout of acids from air following trajectories through the mid-western states and on to the mid-Atlantic-New England areas several days later. Some trajectory analyses indicate that rainfall associated with trajectories passing the Mississippi and Ohio Valleys north to the Great Lakes arriving in upper New York State 1-2 days later was more acidic than the rainfall associated with trajectories crossing from areas further southwest (95). Such results would be consistent with the large, increasing emissions of sulfur oxide and nitrogen oxides from tall stacks associated with the multitude of large coal-fired facilities in the midwest ultimately contributing to acid precipitation in the northeast.

The relative contribution of acid sulfates and nitric acid reported are in the ratio of about 3 to 2. (96, 99). In comparison, the ratio of nitrogen oxide to sulfur oxides in emissions from coal-fired facilities reported for a number of individual mid-western AQCR's range from 2:1 to 8:1 with most of the ratios between 3:1 and 6:1 (103). Variability is such that ratios will be expected if the relative proportions of different types of combustion units varied among AQCR's. The smaller ratio of the sulfuric to nitric acid in precipitation may well relate to differences in the rates of formation and removal of nitric acid compared to acid sulfates. That is, nitric acid may be formed and removed more effectively than sulfuric acid. The contribution of nitric acid to precipitation also has increased relative to that of sulfuric acid during the last 20 years (95, 96, 98). This increase in aqueous nitrate levels appears to correlate better than do aqueous sulfate levels with decreased pH in precipitation during this period (98).

A procedure for relating increases in acidity in precipitation to changes in emissions has been proposed (95). The approach involves a large number of assumptions which can be briefly summarized as follows: the total amount of sulfates and nitrates deposited in precipitation will vary in proportion to tall stack emissions of SO and NO; the proportion of acid will remain at about one-quarter of total sulfates and nitrates, but if emissions increase substantially the neutralizing capacity in the atmosphere may be exhausted, so all additional sulfates and nitrates produced would be in the form of strong acid; the geographical distribution of sources in the eastern U.S. would not shift significantly enough in the future

to effect long-range downwind precipitation removal; changes in the stack heights for emission and use of control systems will not affect the fractions of emitted sulfur dioxide and nitrogen oxide ultimately converted to acids.

The results are most sensitive to the assumption on the proportion of sulfate and nitrate in strong acid from (95). If the fraction of strong acid remained about constant, each 1% increase in emissions would lead to about a 1% increase in acid in precipitation. However, if neutralization capacity should be exhausted, each 1% increase in emissions could lead to about a 4% increase in acid in precipitation over the base case. The increases to a good approximation are for tall stack emissions but include contributions from all fossil fuels. However, increments in fossil fuel capacity from 1977 or for the source regions of concern are about 90% coal-fired (104). Several studies have been made on the downwind effects of individual power plants on acidity in precipitation (105-108). The results are not consistent in that some of the work indicates only a small fraction of the sulfur removed by precipitation while other work indicates substantial losses. These differences may be explained at least in part by differences in rainfall rates (108). Rapid depletion of acidic components can occur in heavy showers as experienced in one of the studies, but not for low rainfall rates (108). It also is possible that the substantially varying amounts of directly formed particulate acid sulfate were emitted from the several sources investigated because of differences in fuels and operating conditions. If so, the concentration, composition and particle size distribution might have varied sufficiently to contribute to differences in precipitation profiled downwind.

More effort is needed on analysis of samples from individual precipitation events over a broader geographical area. Local impacts need to be better differentiated from regional scale effects. If the neutralization capacity of the atmosphere for acid sulfates and nitric acid in the eastern United States is marginal or if it varies with season or meteorological trajectories over varying terrains, these variations need to be understood. They contribute about a fourfold uncertainty to the estimate of the relationship between source emissions and acidity in precipitations. Much more extensive results are needed also on the effects of precipitation immediately downwind of large coal-fired facilities.

Assessment of the emission levels (109, 110) of sulfur oxides and nitrogen oxides for 1985 and 2000 compared to 1975 suggests much larger in-

crements in nitrogen oxides than sulfur oxides. This result underscores the need to better understand the chemical transformation of nitrogen oxides to nitrates and the role of nitrates in acid precipitation.

Finally, it should be emphasized that dry deposition processes also are important in the transfer of pollutants to the surfaces of plants, soil and water. In terms of some types of effects the impact of dry deposition may be as important as precipitation. Therefore, it is critical that the separate and combined effects of precipitation and dry deposition be understood.

Adequacy of Current Data Bases for Atmospheric Distribution

Throughout the Eastern U.S., EPRI's SURE program has fielded 54 stations aimed at measuring sulfate. While this network will be the source of much data on sulfates, all stations measure only total suspended particulate sulfate, except nine multi-instrument stations which measure fractionated particulate matter; hence information on fine particulates is based on inference. Also, spatial resolution is fairly gross and the network, except for the nine highly instrumented stations, operates for approximately one month each quarter.

In the Rocky Mountain States and Northern Great Plains, EPA's Engery/Environment Program has 76 stations which analyze TSP for sulfate/nitrate. Spatial resolution is poor, but in this area the large distances between sources and lack of complex sources tend to offset the problem. Six fine particulate test sites are operational in the Southwest under this study. About 20 dichotomous samplers are in use in the United States.

Present efforts will not be able to supply definitive, concrete data on the regional distributions of secondary fine particulates across the U.S. Such a data base is a requirement for a rational multi-regional pollution control strategy associated with any National energy plan.

Given the above discussion of the atmospheric transformation, transport and fate of gaseous pollutants from coal combustion and given that the NEP will markedly increase such emissions even with improved control technology, it is certain that the NEP will result in increased atmospheric levels of secondary aerosols (sulfuric and nitric acid) and fine particulate (sulfur, nitrogen and organic compounds). This will be manifested as reduced visibility, broader ecological impacts due to acid rain and more numerous and more severe cases of deleterious health effects.

The locations of the initial measurements would be in the area of the Ohio and Tennessee Valleys, extending eventually to most of the Eastern half of the U.S.; and in the Northern Great Plains and Rocky Mountain States. These are areas which will radically increase coal combustion capacity under any coal-based NEP.

In the Northern Great Plains and Rocky Mountain States, utility capacity is planned to treble during the next eight years. In the Ohio River Valley utility capacity will also increase significantly in 10-15 years.

The secondary pollutants in question are fine particulate matter analyzed for sulfur, nitrogen and organic compounds as well as sulfuric acid and nitric acid aerosols with associated measurements of visibility reduction and acid rainfall being taken as is appropriate to various "regional" situations.

Spatial distribution of measurements would ideally be less than a few hundred kilometers apart to give adequate spatial resolution of regional fine particulate levels downwind of source groupings while stations would be more densely situated near clusters of sources.

Temporal resolution in the secondary pollutant measurements acquired must be sufficient to define daily and seasonal variations as well as intermediate variations (on the order of a few days) associated with changing weather patterns.

The establishment at this point in time of such a scientifically validated data base is a prerequisite to unambiguously determining the geographical distribution of secondary pollution levels associated with existing coal combustion and the alterations and trends in the distribution of secondary pollution levels due to the changes in the geographical pattern of coal combustion due to new sources and to associated increased primary pollutants resulting from NEP.

Conclusions

Emission controls should keep the short-range impacts of gaseous pollutants below the levels of ambient air quality standards. Likewise sulfate emissions from individual sources probably will not, by themselves, create an air quality problem. Short-range impacts can be minimized by judicious local siting that can be justified on the basis of ambient air quality standards.

Sulfates can be transported hundreds of kilometers. Sulfate emissions from diverse sources can, as a result of long range transport, be superimposed on each other to create episodes of air pollution far from the contributing sources.

Emissions from large coal-fired facilities present the risk of degrading visibility particularly in relatively pristine areas in the west.

An increase in emissions of sulfates and nitrates may increase the problem of acidity in rainfall in selected areas of the country.

Laboratory studies have indicated that the photochemical conversion of SO_2 to sulfates is a first order homogeneous reaction in SO_2 and these rates are consistent with rates observed in plumes.

Existing monitoring capabilities are inadequate to provide a base line from which future changes regional air quality owing to long-range transport can be evaluated.

Recommendations

The siting decisions for large coal burning facilities should take into account potential sulfate pollution owing to long-range transformation and transport.

The potential pollution problems resulting from long-range transport transcend the boundaries of existing air quality control regions. Attention should be given to the creation of an institutional mechanism for integrating siting and control decisions to minimize the pollution impacts of regional transport.

In view of the many gaps that still exist in our ability to understand and predict the impact of the NEP on ground level sulfate concentrations, visibility, and acidity in rainfall, a dichotomous sampler monitoring network should be established to record air quality changes over time and to signal any anticipated untoward impacts.

Because of the particular importance of acid sulfates and nitric acid in causing health effects, acid precipitation effects and materials damage much more extensive baseline measurements are needed for these particular species along with other sulfates and nitrates. Such baseline measurements also are essential to air quality model validations.

It is essential that health and welfare effects studies incorporate the most advanced measurement systems for evaluating pollutant dosages of sulfate and nitrate species as soon as these techniques are adequately verified.

Improved rapid response instrumentation is needed for sulfates and nitrates particularly instruments for aircraft measurement of plume characteristics.

The potential for neutralization for acid species by ammonia as a function of season, location and meteorological conditions is poorly understood.

Since the proportion of sulfates and nitrates in acid form is critical, selected baseline measurements also are essential on neutralization phenomena. The study of this phenomenon should be one element of a coordinated research program to deal with the problem of acidity in rainfall.

The measurements of the rates of conversion of sulfur dioxide to sulfate are limited to data as functions of season of year, geographical location and various environmental parameters. An intensified program of research is needed over the next several years to insure that this parameter is available for regional air quality simulation models for sulfates.

Current regional air quality simulation models usually do not contain mechanistic submodels. They are not able to predict effects of varying precursor concentration or neutralization effects. Development of such improvement models should keep pace with the acquisition of the baseline data.

Studies should be carried out to assess the significance of emissions of sulfates from sources equipped with flue gas desulfurization units to insure that such second order effects that may exist can be properly factored into sulfate transport predictions.

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