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Character and Transformation of Pollutants from Major Fossil Fuel Energy Sources

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MASTER

OAK RIDGE NATIONAL LABORATORY

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Fossil Fuel Energy Sources

David S. Shriner, Samuel B. McLaughlin, and Charles F. Baes¹

ENVIRONMENTAL SCIENCES DIVISION
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ABSTRACT

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This report is concerned with factors influencing ecosystem effects of air pollutants from major fossil-fuel energy sources. Chemical speciation of major effluents, the variations in source term associated with type of source, and other factors which influence the characteristics of the effluent at the source/atmosphere interface are discussed. The major current and potential sources of energy-derived pollutant burdens, and projected future patterns of energy production are reviewed. In addition, factors controlling transformation of pollutants during atmospheric transport are described. The most critical controlling factors are identified, as are the major effluent constituents for which transformation is most significant. The chemical species which ultimately reach the atmosphere/vegetation interface are described with regard to their relative potential for effects on terrestrial ecosystems.

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INTRODUCTION

Pollution from the combustion of coal is not uniquely a twentieth-century problem, but dates from as early as the thirteenth century (Brimblecomb 1976). Great strides have been made in control technology which free us from problems such as the dense smoke, soot, and odors characteristic of London in the 1200's. We must, however, because of changing patterns in the spatial distribution of power generation and increased consumption -- already exceeding consumption levels projected for the year 2000 as recently as 1969 (Cuffe and Gerstle 1967) -- still concern ourselves with the potential environmental consequences of utilizing our abundant fossil resource. Coal combustion in the early years of the twenty-first century may quadruple current levels, depending in large part upon the success, failure, or environmental risk of alternative energy sources (ERDA 1975). A number of questions arise as we contemplate the implications of future energy development for both human and environmental health. Among the more important of these are: Are single pollutant standards adequate to protect environmental quality, or must some appreciation of pollutant interactions be incorporated into future standards? Are monitoring stations located to assure compliance with urban health standards also adequate to monitor for the health of the rural environment? Over what distances might emissions from additional point sources be expected to significantly interact with existing levels of pollutants in the local and regional environment?

The degree to which sulfur and nitrogen oxides produced as a result of fossil-fuel combustion are capable of being controlled depends upon many factors. Currently, standards exist to regulate ambient concentrations of these pollutants and consequently, their associated transformation products, photochemical oxidants, and sulfates. These standards are promulgated on the basis of: (1) human health and (2) environmental quality. Understanding the adequacy of such ambient standards in the light of present and projected energy use patterns is an essential prerequisite to assessing future optimum source densities and acceptable control levels and alternatives.

This report addresses some of the significant factors influencing the relationships between atmospheric emissions from electric energy generating sources powered by fossil fuels, and the subsequent distribution of those effluents to the environment. We overview: factors influencing emissions characteristics, source-related emissions trends, factors affecting pollutant transport and transformation, and implications of pollutant transport and transformation for regional air quality.

FACTORS INFLUENCING EMISSION CHARACTERISTICS

The physical and chemical character of effluents from the stacks of a fossil-fuel energy source are dependent upon a wide variety of source and fuel variables. The intent of this review is to introduce the more important of these variables and to suggest their potential significance in the transformation of effluents during transport from the source. A number of other recent reviews discuss in greater detail potential new advances in technology which may influence the future character of emissions from fossil-fuel sources (Hall and Bowen 1976, Murthy et al. 1976, White 1977, Coates 1976, Leavitt et al. 1976, CTAB 1975, and McDonald 1975).

Source Types

Currently, oil and natural-gas-fired sources contribute approximately 10% and 35% of total sulfur and nitrogen oxide emissions, respectively, from fossil-fuel electric generation (Drysdale and Calef 1976). Based on present and projected use patterns, the major sources of fossil-fuel energy to the year 2000 will increase their use of coal, with a decreased emphasis on petroleum and natural gas. For this reason, coal combustion effluents of major significance to air quality (SO_x , NO_x and particulates) may be expected to continue to contribute significantly to regional pollutant burdens during the coming decades (ERDA 1975). Of the coal conversion options expected to be of

importance in the near future, coal gasification is among the more promising. Growth projections indicate that by 1981 five coal gasification plants will be in operation producing synthetic natural gas (SNG) (Hamilton 1977). On a coal usage basis, emissions of non-methane hydrocarbons, CO, NO_x and particulates from these sources are potentially of the same order of magnitude as those from comparable sized combustion units (Hamilton 1977). Uncontrolled emissions of sulfur dioxide, however, are potentially a factor of 10 less from gasification facilities (Hamilton 1977). Because it is difficult to project air emissions from the limited data base available for such coal conversion processes, our discussion will focus on the combustion technology and on those conversion emissions which are directly comparable (SO_x, NO_x).

Focusing on coal combustion specifically, a number of factors regulate the qualitative and quantitative composition of emissions from any given source. Among these are flame temperature, rate of cooling of decomposition products, amount of excess air required, boiler type, gas velocity, coal heat value, and type of control equipment employed (Smith and Gruber 1966). Table 1 summarizes the influence of boiler design on major emissions from a typical coal-fired power plant.

Fuel Type

Compared to emissions from all sources, total estimated emissions from fuel combustion for electricity generation account for approximately 1% of the carbon monoxide, 25% of the particulates, 60% of the sulfur oxides, 25% of the nitrogen oxides, and 5% of the hydrocarbons (Ballentine 1974). Table 2 illustrates the influence of fuel type on gaseous and particulate effluents from a 1000-MWe power station.

The major fuel variables influencing the quantitative and qualitative relationships of sulfur and nitrogen oxides include % sulfur, organic S/inorganic S ratio, % nitrogen, % volatile matter, moisture content, ash content, heating value (Btu/lb), carbon content of ash, and size of the coal (Slack and Hollinden 1975, Smith and Gruber 1966).

Table 1. Estimated emissions from an uncontrolled 1000-MW fossil-fuel-fired power plant and emissions allowable under new source performance standards

Coal-fired

Assumptions: 10% ash
3% sulfur
11,200 Btu/lb
1 mw-hr = 9×10^6 Etu

Type of furnace	Prevalence	#/hr	Particulates		#/hr	Sulfur dioxide		#/hr	Nitrogen oxides	
			#/ton coal	#/10 ⁶ Btu		#/ton coal	#/10 ⁶ Btu		#/ton coal	#/10 ⁶ Btu
Pulverized,										
Wet bottom	13.4%	52,200	130	5.80	45,900	114	5.1	12,060	30	1.34
Dry bottom	73.8%	68,400	170	7.60	45,900	114	5.1	7,227	18	0.80
Cyclone	9.5%	8,010	20	0.89	45,900	114	5.1	22,050	55	2.45
Other	3.3%									
<hr/>										
Allowable emissions under NSPS.		500	2.24	0.10	10,800	26.9	1.2	6,300	15.7	0.70
Required efficiency (for most prevalent type)		59%			76.5%				13%	

Sources: Polglase 1974, Cowhard et al. 1975.

Table 2. A comparison of gaseous effluents from 1000-MWe power stations

Pollutants, (tons per year)	Coal	Fuel type	
		Oil	Gas
Carbon monoxide	600	9	---
Carbon dioxide	7.0×10^6	5.2×10^6	4.1×10^6
Sulfur dioxide	102,000	54,000	12
Hydrocarbons	240	736	---
Oxides of nitrogen	24,000	24,000	13,000
Particulate	6,000	2,300	465
Totals (not including CO ₂)	132,840	81,945	13,477
Fuel consumed, (tons per year)	2.4×10^6	1.68×10^6	1.45×10^6

Source: Ballentine 1974.

Organic/inorganic sulfur ratios may be used to determine the feasibility of coal cleaning to reduce S emissions. The inorganic pyrites may be physically separated by density difference, while organic sulfur is not affected by cleaning. Ash content is related to the heating value and to the particulate concentration; carbon content of the ash is related to particle density (CNR 1975, Slack and Hollinden 1975).

Various projections for the utilization of the different fuel options depend significantly on future national energy policy. If a nuclear power option is adopted, we would anticipate the relative contributions of coal, gas, and oil to decline in the near term. However, if nuclear power is deemphasized, significant increases in coal utilization will be unavoidable as gas and oil reserves decline. In this case as much as 2.1×10^9 tons/year increased consumption of bituminous coal could result, amounting to a 67% increase over levels that would be expected from present ratios of fossil:nuclear fuel used by year 2000 (ERDA 1975). If improved end-use efficiencies are attained, energy conservation efforts could result in a 30% reduction over the base scenario (no new initiatives), or a 60% reduction in coal consumption over options depending on heavy coal utilization with limited nuclear development (Fig. 1).

Control Variables

There are currently several major strategies employed or proposed for control of sulfur emissions from coal combustion (CNR 1975): (1) coal cleaning, which can reduce sulfur content of the coals used by as much as 40%, depending on the organic/inorganic S ratio; (2) use of low-sulfur, low-ash coal from such processes as solvent refining; (3) gasification; (4) liquefaction; (5) fluidized bed combustion; (6) flue gas desulfurization, scrubbing; (7) tall stacks and intermittent control systems.

For oxides of nitrogen from coal-fired utility boilers, uncontrolled emissions are higher than those for gas and oil (CNR

Fig. 1. Coal consumption scenarios to the year 2000 (Source: ERDA 1975).

1975). Generally, fuel nitrogen contributes roughly 50% of the total emission at full load, the remainder contributed by thermal NO_x (atmospheric N_2 fixed during combustion). Coal moisture content, nitrogen content, burner design, furnace design, and operating conditions are major factors controlling the relative contributions of fuel and thermal NO_x (CNR 1975). For these reasons, techniques such as low excess-air firing and staged combustion have been successful in reducing NO_x emissions from coal-fired units by as much as 37% (Crawford et al. 1974). Fluidized bed combustors, tall stacks, lower peak flame temperature, and intermittent combustion systems are also proposed mechanisms of attaining NO_x standards. However, since stationary-source electric power generation accounts for only about 25% of total NO_x emissions, it is questionable whether significant reductions in stack emissions would have a major influence on overall photo-oxidation reactions, especially under meteorological conditions favoring those reactions (U.S. EPA 1976b).

Combustion control systems only indirectly effect control of photochemical oxidant levels, and as such, oxidant concentrations as a function of control variables will not be discussed additionally.

SOURCE-RELATED EMISSION TRENDS

Historical Perspectives

As a result of the rapid industrial, economic, and population growth in the United States during the past few decades, very dramatic concurrent increases in both total and electric-generating-derived atmospheric releases of air pollutants have been observed. Table 3 summarizes this trend for the two pollutants, SO_x and NO_x . A comparison of changes in estimated total and steam electric emissions of these pollutants from 1940 through 1970 emphasizes the enormous significance of increases in steam electric sources to the nationwide trends in total emissions of air pollution during this 30-year period. While total emissions of SO_x and NO_x increased at rates of

Table 3. Summary of nationwide emission estimates

Emission type	1940	1950	1960	1968	1970 ^a	1972 ^b	1980 ^c	1990 ^c
<u>Emissions (10^6 tons yr^{-1})</u>								
<u>Total</u>								
SO _x	21.5	23.8	23.3	31.3	33.9	32.0	56.2	79.7
NO _x	7.9	10.4	14.0	21.3	22.7	24.0	29.3	33.1
<u>Steam electric</u>								
SO _x	2.8	5.4	10.1	17.4	19.4	17.4	38.8	58.2
NO _x	0.6	1.2	2.3	4.2	4.7	5.8	8.2	8.8
<u>Steam electric percent of total</u>								
SO _x	13	23	43	56	57	54	69	80
NO _x	7	12	16	21	21	24	28	27
<u>Percentage change (based on 1940)</u>								
<u>Total</u>								
SO _x	0	11	8	46	58	49	161	270
NO _x	0	31	77	170	187	204	270	318
<u>Steam electric</u>								
SO _x	0	92	260	521	592	512	1285	1978
NO _x	0	100	283	600	683	867	1273	1380

^a1940-1970 Emissions Trends. (Cavender et al. 1973).

^b1974 EPA-National Emissions Report (U.S. EPA 1974a).

^c180-1990 Estimates cited on p. 140 of CNR 1975.

approximately 2% and 6% per year during the past 30 years, emissions from steam electric sources showed respective increments of approximately 20% and 23% per year during the same interval (Cavender et al. 1973). Latest emission figures (U.S. EPA 1976a) show that over 60% of the total SO_x and over 25% of the total NO_x released to the atmosphere in the United States are currently derived from fossil-fuel combustion by steam electric plants. Furthermore, projections for 1980 and 1990 indicate that if uncontrolled, SO_x emissions may double from 1970 to 1980 and nearly triple by 1990 (CNR 1975). The significance of these emissions to changes in our national air quality can be addressed only by considering the spatial distribution and relative strength of these sources, their relationship to meteorological factors influencing the movement and reaction rates of the pollutants involved, and the presence of pollutants from other sources with which physical, chemical, or biological reactions may occur.

Spatial Distribution of Sources

The spatial distribution of major coal-and oil-fired steam electric generating facilities in the United States as of 1971 (U.S. EPA 1975) is shown in Fig. 2. This figure dramatically emphasizes two points. First, the much higher total number of generating units in the eastern than in the western United States is obvious. Approximately 80% of the U.S. electric generating capacity derived from fossil fuel is in the eastern half of the country. Approximately 50% of the total is in the northeastern states. The second point to be noted from Fig. 2 is the relatively high density of these point-source emissions in the eastern United States and the relative scarcity of areas remote from potential short distance (≤ 100 km) transport of pollutants from these sources. The longest distance of any point in the eastern United States from some fossil-fuel-fired electric plant appears to be on the order of 175 km, with average distances being somewhere in the range of 30 to 60 km. Of additional importance to the presence of larger numbers of plant sites in the Northeast are much higher contributions of

Fig. 2. Location of major coal- and oil-fired power units, 1971 (Source: U.S. EPA 1975).

pollutants from other industrial and urban sources. Total SO_x and NO_x emissions in the north central and northeastern states comprise approximately 50% and 56% of the total SO_x and NO_x emissions for the contiguous United States, respectively (U.S. EPA 1947a). Since atmospheric releases from energy generating facilities cannot be considered apart from these other sources, Fig. 3 is included to illustrate the geographic distribution of emission density of SO_x for the United States. Also indicated are the percentage contributions of energy-derived SO_x and NO_x emissions to the total emissions of these pollutants for each of five EPA-designated data analysis regions (U.S. EPA 1974b) of the United States. From this figure the much higher levels of emissions per unit area as well as the higher ratio of steam electric to total emissions in the eastern United States are readily apparent.

Regional Meteorological Factors Affecting Pollutant Transport

In addition to the emission density, other factors which strongly influence the transport and transformation of pollutants from steam electric plants are the regional meteorological conditions, such as predominant windflow patterns, frequency of air stagnation events, air temperature and humidity, and the presence of chemically reactive species of pollutants such as ozone and other photochemical oxidants.

The regional meteorology of the United States has been classified into 8 atmospheric areas (Federal Register 1968) based on conditions which strongly influence the interchange and diffusion of pollutants in the atmosphere. These include primarily wind speed and direction, and the frequency, persistence, and height variation of stable layers of air. Boundaries of these areas were based on annual averages of low-level inversion frequency, maximum depth of vertical mixing, and the frequency of light winds. The concepts of dilution climatology embodied in this classification system are currently used in the High Air Pollution Advisory System (HAPA) for forecasting regional conditions of high likelihood for accumulation of air pollutants.

TOP NO. = TOTAL SO_2 - NO_2 EMISSIONS/AIR QUALITY REGION ($10^6 \text{ tons yr}^{-1}$)
 BOTTOM NO. = % OF TOTAL CONTRIBUTED BY FOSSIL FUEL UTILIZATION

Fig. 3. Geographic variation in SO_x and NO_x emission density, and percent of total SO_x and NO_x emissions per air quality region (Sources: CNR 1975, U.S. EPA 1974a, 1974b).

Holzworth (1968) delineated high frequencies of occurrence of air stagnation in both the west and east coasts, using the number of HAPA days forecast over a 5 to 8-year period. The Southern Appalachian Mountains and California had the highest frequency of occurrences, averaging 5 to 8 times per year and 8 to 16 times per year, respectively. The central and midwestern states, on the other hand, recorded an annual average of 0 to 2 occurrences per year. The occurrence of air stagnation systems in the heavily populated coastal areas has potential significance not only in the restriction of movement of atmospheric effluents from steam electric power plants, but also in the potential rate at which these compounds may undergo secondary reactions with elevated levels of photochemical oxidants now occurring over large areas of the United States, particularly the Northeast (Westburg et al. 1976).

CHEMICAL CHARACTERISTICS AFFECTING POLLUTANT TRANSPORT

Just as emissions may vary as a function of source parameters and fuel type, ambient environmental conditions play an important role in determining not only rates of secondary reactions, but also the ultimate physical and chemical form of pollutants which will impact biological systems.

The important primary pollutants emitted by fossil-fuel plants - sulfur dioxide, nitric oxide, hydrocarbons, and particulates - interact with one another and with substances already present in the atmosphere to produce a variety of products, many of which are also supplied by other anthropogenic as well as natural sources. The interactions and transformations of greatest interest to us include (1) the oxidation of SO_2 , (2) the conversion of the sulfuric acid produced to sulfate salts, (3) the oxidation of NO and hydrocarbons, which is accompanied by the production of ozone, and (4) the ultimate conversion of nitrogen oxide to nitric acid and nitrate salts. Assessment of the impact of a particular primary pollutant on terrestrial ecosystems requires a proper appreciation of these chemical transformations and interactions.

The Oxidation of Sulfur Dioxide

Sulfur Dioxide (SO₂).

This gas, the principal form of sulfur emission, usually accounts for 98% of the sulfur in the fuel (Cuffe and Gerstle 1967). While it can persist in the atmosphere for days under favorable conditions, it is eventually oxidized to sulfuric acid, which in turn is converted to sulfates. The oxidation can occur by many pathways involving homogeneous reactions with gaseous species, reactions within liquid droplets or films, and reactions at the surfaces of solids.

The homogeneous oxidation of SO₂ by atmospheric oxygen is photochemically induced and relatively slow. From laboratory measurements, Kasahara and Takahashi (1976) have recently estimated an oxidation rate of 0.7% hr⁻¹ at 35°N latitude in the noonday summer sun. The present state of knowledge of this oxidation mechanism has recently been summarized by Sander and Seinfeld (1976).

Perhaps the most important homogeneous oxidation is by hydroxyl (OH) radical. Castleman et al. (1975) estimates for the rate expression

$$-\frac{d[\text{SO}_2]}{dt} = k[\text{SO}_2][\text{OH}] \quad , \quad (1)$$

$k = 4.7 \times 10^4 \text{ ppm}^{-1} \text{ hr}^{-1}$. Since the ambient concentration of hydroxyl radical (a species whose concentration is controlled by other reactions) can reach $2 \times 10^{-6} \text{ ppm}$ (Wang et al. 1975), the rate of this process can be as high as 9% hr⁻¹.

Other as yet unspecified homogeneous reactions may account for enhanced oxidation rates in the presence of nitrogen oxides and hydrocarbons. This is the conclusion reached by Sander and Seinfeld (1976) after a careful review of the available laboratory data and detailed simulations in which all the known homogeneous rate processes were considered.

Before considering the oxidation of SO₂ in aqueous solution, we should note that the gas dissolves to produce sulfurous acid (H₂SO₃)

which undergoes two dissociation steps to produce bisulfite ion (HSO_3^-)

and sulfite ion (SO_3^{2-}). As a result the solubility of SO_2 does not follow Henry's law, but is of course determined by the equilibrium constraints of these reactions. As a result, the solubility and the amounts of the dissociation products formed depend strongly on amounts of other acidic or basic materials that may be present in the solution.

The most intensively studied aqueous oxidation of SO_2 is by oxygen. Beilke et al. (1975) has recently reviewed the data which indicate that the species being oxidized is the SO_3^{2-} ion, the dominant form of SO_2 in basic solution. The mechanism of this process is complex and the rate can be catalyzed by some metal ions and decreased by others. Perhaps a more important oxidation mechanism involves dissolved ozone. The data of Penkett (1972) indicate half-times for this process of only a few minutes in acidic solutions. The fraction of SO_2 dissolved in aqueous droplets or films on particles is usually quite small, however, because of the small total volume fraction of the liquid phase in the atmosphere and the fact that it is usually acidic. Hence, the aqueous oxidation of SO_2 is probably not important except under the most favorable conditions, i.e., high humidity, relatively high aqueous pH, and/or high ozone concentration (Baes et al. 1976).

The oxidation of SO_2 at the surface of solid particles is complicated by the fact that the product of the oxidation, sulfuric acid (see below), alters the character of the surface, either by covering it with an acidic aqueous film or by reacting with the particle. It has been difficult to assess quantitatively the effect of atmospheric particles on the rate of SO_2 oxidation, though there is evidence that it is significant (e.g., Devitofrancesco et al. 1974, Newman et al. 1975).

In summary, for SO_2 oxidation the homogeneous reaction with oxygen and hydroxyl radical are fairly well characterized; the reactions in aqueous solution are less so and need more study; and the reactions at solid surfaces are least well characterized and will be the most difficult to study. Overall oxidation rates seem to be lowest under clear, dry conditions (a few % per hr) and relatively rapid at times of high humidity and aerosol concentrations (> 10% per hr).

Sulfuric Acid ($\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$).

The primary product of SO_2 oxidation is sulfur trioxide (SO_3), the anhydride of sulfuric acid. It reacts essentially instantly and completely with any water available, either gaseous or liquid, to produce aqueous sulfuric acid (Carabine and Maddock 1976). The concentration of acid, either in water droplets or in aqueous films on the surface of particles, is quite high (several molar) at intermediate relative humidities (Fig. 4). In this state the acid is much stronger and more aggressive than sulfurous acid. It will react completely with any ammonia that is present, and if a stoichiometric amount of ammonia is supplied (2 moles per mole of H_2SO_4), it will be converted to ammonium sulfate. It can also react with the metal oxides, silicates, and carbonates present in solid particles to produce other sulfate salts.

"Sulfate".

This term, unfortunately, is frequently used to describe all forms of oxidized SO_2 in the atmosphere, often with the implication that they are uniformly toxic. As we have just seen, however, "sulfate" first appears as sulfuric acid, a very toxic material, and then - as basic materials such as ammonia and particulates react with the acid - is converted to sulfate salts. The most important property of "sulfate" is its acid content. Also important are the cations (e.g., NH_4^+ , Ca^{2+} , Fe^{3+} incorporated into the material as neutralization proceeds. Analytical procedures are being developed and observations made (Tanner and Newman 1976; Askne and Brosset 1972,

Fig. 4. Dependence of the concentration of aqueous sulfuric acid on the relative humidity at 25°C.

Brosset 1976) to characterize the composition and particle size of "sulfates". The sulfate salts produced as end products would appear to be relatively benign compared to the concentrated acid from which they are derived.

The Oxidation of Nitrogen Oxide

Nitric Oxide (NO), Nitrogen Dioxide (NO₂).

Like SO₂, these oxides of nitrogen ultimately are converted by oxidation to an acid (nitric acid, HNO₃) which can, in turn, be neutralized to a salt (nitrates) by basic materials in the atmosphere. The more important role of NO and NO₂ as pollutants, however, involves ozone (O₃) production. In the presence of sunlight the following reactions occur:

and, as a result, a steady state can be established in which the ozone concentration is proportional to the NO₂/NO ratio and to the intensity of illumination (J):

$$[\text{O}_3] = K \cdot J \cdot [\text{NO}_2] / [\text{NO}] \quad (6)$$

(The proportionality constant K contains the rate constants for the above reactions).

While this steady-state condition is often a useful approximation relating the three concentrations [NO], [NO₂] and [O₃] (Calvert 1976a), the chemical processes that fix two of these three quantities

at a given time and place so that the third may be calculated are very complex, involving the oxidation of varied hydrocarbons present in the atmosphere, from natural as well as anthropogenic sources, ultimately to carbon dioxide and/or formic acid (Buffalini et al. 1976). Models have been produced, involving scores of reactions, that simulate reasonably well the behavior observed in urban (Calvert 1976b) and rural (Chameides and Stedman (1976) environments.

Both NO_2/NO ratios and the ozone concentrations in a power plant plume are low near the source. Reactions involving oxidation of hydrocarbons and of NO to NO_2 appear to become important as the plume mixes with the surrounding air (Hegg et al. 1976). The increasing NO_2/NO ratio produces increasing amounts of ozone through the operation of the above steady-state mechanism. It is currently becoming evident that ozone concentrations in excess of primary and secondary standards (> 80 ppb) can thus appear hours later in rural areas far downwind from the sources of nitrogen oxides and hydrocarbons that apparently produced them (Chameides and Stedman 1976, Bantz et al. 1974, Rubino et al. 1976).

Ozone (O_3).

This gas is toxic because of its great oxidizing power. It attacks carbon-carbon multiple bonds to produce reactive compounds and free radicals containing oxygen. Because the gas is so reactive, its concentration in the atmosphere is highly variable, often being determined by the relative abundance of substances that can react to produce it or to consume it. Ozone is produced continuously in the stratosphere (Junge 1963) by U.V. photolysis of oxygen:

It is destroyed there principally by the reactions

In unpolluted air, the concentration can be quite low (< 10 ppb, Bantz et al. 1974), and may come largely from downward mixing of the stratosphere. As we have just noted, reactions involving NO_x and hydrocarbon often produce ozone concentrations exceeding 100 ppb (Frankhauser 1976).

Implications of Pollutant Transformation on Regional Air Quality

Having examined the sources of energy-derived pollutants, some aspects of their atmospheric chemistry, and some regional considerations influencing their distribution and transformation, we will consider the final integration of these factors as evidenced by their impact on air quality. In interpreting trends in regional air quality we must first emphasize, however, the importance of the presence of multiple sources of a variety of types and the fact that distribution patterns change in time. Two additional major considerations are the changing distribution of air quality monitoring stations and heterogeneity in the analytical techniques being used at these stations. Data reported in the latest EPA Air Quality Monitoring Summary (U.S. EPA 1976b) indicate that 8, 7, and 5 different techniques are currently utilized for SO_2 , NO_x , and O_3 , respectively. Because of the present controversy over potential environmental and health effects of sulfur oxides, we will emphasize primarily current trends in sulfur dioxide and sulfate concentrations.

Trends in SO_2 Concentrations

A map of the United States showing a typical geographical distribution of annual urban sulfur dioxide concentrations in 1970-71 (CNR 1975, Fig. 5) effectively illustrates the spatial relationship between areas of highest SO_2 concentrations and the areas of highest emission previously shown in Fig. 3. Concentrations of SO_2 in the eastern United States averaged approximately three times those in the west. More recent air quality summaries by EPA (1976b) indicate that, during the interval 1970-1973, average annual SO_2 concentrations

Fig. 5. Geographical distribution of typical annual urban ambient sulfur dioxide concentrations (Source: CNR 1975).

declined across the United States by approximately 20%. Decreasing concentrations were most notable in the northeast and north central states. Limited data (10 sites) from 10 background locations demonstrated a slightly perceptible decrease during this time in non-urban areas.

Trends in Sulfate Concentrations

Averaged annual urban sulfate concentrations (CNR 1975) showed a similar spatial distribution in 1971 as that indicated for SO_2 . Highest concentrations were again recorded in the industrialized northeast, with eastern sites averaging concentrations about twice those in the west. Analysis of National Air Sampling Network (NASN) sites for 1964 to 1968 by Altshuller (1973) indicates that averaged urban sulfate concentrations were $12.5 \mu\text{g}/\text{m}^3$ for eastern sites, and $6.5 \mu\text{g}/\text{m}^3$ for western sites. In spite of the general agreement between emissions density and sulfate levels, a comparison of trends in sulfate patterns for the whole United States during the interval 1957-1970 showed rather constant urban levels of sulfate of approximately $100 \mu\text{g}/\text{m}^3$ during the period 1957-1970 (CNR 1975). Non-urban levels measured during the interval 1962-1970 showed somewhat more fluctuation (approximate range 5.0 - $7.5 \mu\text{g}/\text{m}^3$) with only a slight observable net increase ($<1 \mu\text{g}/\text{m}^3$). When this comparison was restricted to the 18 stations from which data were available for at least six of the years during this interval, an increase of approximately 50 to 75% was noted. These very limited data indicate that non-urban sulfate trends may reflect the influence of changes in SO_2 emissions much more closely than do urban trends.

The decreases in SO_2 and lack of any observable trend in sulfate concentrations during a time when SO_2 emissions have been increasing represents an apparent anomaly. However, it should be stressed that air sampling has historically been heavily concentrated in densely populated areas with little emphasis on sampling in rural sites where most fossil-fuel power plants are located. A survey of monitoring and

air quality in 1973 (U.S. EPA 1974b) indicates that at that time only approximately 2% of the 213 SO₂ surveillance sites were source-oriented, and 5% were in background areas. The remainder (93%) were in heavily populated areas. An explanation for the observed trends has been discussed in an earlier report (CNR 1975) and is considered to be related to the reductions in sulfate emissions from localized urban sources which resulted from shifting to lower fuel sulfur levels and reductions in space heating. A larger portion of the energy needs of these areas are now being met by rural power plants with tall stacks. Thus, sulfur oxide emissions have merely been shifted from the heavily monitored urban environment to rural sites remote from urban monitoring stations.

The most recent air quality data reported by EPA for 1974 (U.S. EPA 1976b) indicate that declines in urban SO₂ levels ceased during the 1973-1974 interval. This trend was interpreted as indicative that the effects of shifting emission patterns which occurred in the 1960's have largely diminished and that in the future regional air quality may be expected to respond more sensitively to changes in SO₂ emissions.

While recognition of the potential problems associated with long-range transport and transformation of sulfur oxides has engendered much recent concern in regard to both human health effects and the potential ecological consequences of regional scale acidification of precipitation, we should not ignore the possibility of both local and regional scale effects from gaseous mixtures of SO₂, O₃, and NO₂. A considerable body of data has been accumulated (see review by Reinert et al. 1975) to indicate that very low levels (0.05 to 0.15 ppm) of these pollutants may act synergistically to adversely affect vegetation when more than one pollutant occurs simultaneously. The high density of electric power plants in the East combined with high emissions from urban and industrial sources makes the widespread occurrence of potentially phytotoxic levels of combinations of pollutants particularly likely within this region.

To develop a general indicator of the likelihood of chronic air pollution effects to vegetation occurring throughout the United States,

the spatial distribution of occurrences of elevated levels of SO_2 , O_3 , and NO_2 reported in a 1976 summary of monitoring and air quality trends was examined (U.S. EPA, 1976a). In this report the highest 24-hr average SO_2 and NO_2 concentrations, and the highest 1-hr oxidant/ozone concentrations were tabulated for all stations with valid data (reporting at least three 24-hr samples or at least 400 hourly values from a continuous monitor). Stations are identified both by state and designated air quality control region. To provide an index of the occurrence of elevated pollutant concentrations across the United States, the highest concentrations of SO_2 , O_3 -oxidant, and NO_2 (24-hr, 1-hr and 24-hr averages respectively) were tabulated for each region or portion thereof contained within each state. These data were then averaged to provide a single integrated value for each pollutant for each state. Selection of these values required the rejection of data which were considered abnormally high (i.e., a 1-hr oxidant value of 9 ppm reported by New York). Arbitrary levels for SO_2 (≥ 1 ppm for 24 hr), O_3 (≥ 1 ppm for 1 hr), and NO_2 (≥ 1 ppm for 24 hr) were chosen and the occasional data points above these levels were excluded.

Approximate levels at which injury to sensitive species of vegetation might occur as a result of exposure to these pollutants were selected on the basis of data from controlled exposure studies with individual and combined pollutants. The ozone level (1-hr av = 0.15 ppm) was selected on the basis of data summarized by Larsen and Heck wherein some species were injured by 1-hr exposures ≤ 0.15 ppm. SO_2 and NO_2 levels (24-hr av = 0.10 ppm) were selected on the basis of interaction studies reported by Tingey et al. (1971) which showed leaf injury at combined levels of 0.10 ppm of each pollutant for four hours. States were then classified as having 0, 1, 2, or 3 pollutants at occasional concurrent levels sufficient to injure vegetation and mapped accordingly as shown in Fig. 6a. Potentially phytotoxic levels of SO_2 , oxidant- O_3 , and NO_2 were found in 20, 19, and 18 states respectively. Of the 48 contiguous states, elevated levels of 3, 2, 1, and 0 pollutants were found in 8, 13, 8, and 19 states, respectively.

Areas with highest pollutant concentrations occur in a band across the middle of the United States with the greatest density of "3" category states in the industrialized northeastern states. "Cleanest" areas appear to be the northwestern and northern plains states and those on the southern Gulf Coast.

Figure 6b presents an even more conservative scenario, wherein, in addition to the restrictions imposed upon reported values in Fig. 6a, the values reported represent mean values for the three highest recorded values for all stations reporting in a given state. Once again, for those states with few monitoring points, the view may be distorted by limited data; however, for the bulk of the eastern United States, a general picture of overall air quality and potential for pollutant interactions emerges. Comparison with Fig. 6c shows that even with this conservative approach, significant portions of the major forest and crop producing areas of the United States lie within the regions of apparent potential for chronic effects to vegetation as a result of SO_2 , O_3 , and NO_2 pollutant synergisms.

This map is intended only as a very general indicator of potential regional-scale pollution problems. The authors realize that while both rural and urban stations were included, the current distribution of monitoring stations is heavily weighted toward metropolitan areas and hence toward localized emission sources. Other drawbacks are that the data represent a variety of sampling methods and that there are unequal numbers of regions (and hence data points by our method of averaging) for each state. In some cases data did not exist for one or more pollutants within a state. In this situation a non-elevated level was assumed (see number codes in Fig. 6a which indicate the number of data points comprising the average value for each pollutant in each state). Nevertheless Fig. 6a indicates that elevated pollutant levels are being measured at sites representing a broad geographical distribution across the United States. While the role of emissions from steam electric plants in the occurrence of these levels may be debated, there is a high probability of interactions of effluents from steam electric plants with those from adjoining plants and other industrial and urban

Fig. 6b. Potential . . . NO_2), mean of three highest values per reporting station.

MAJOR CROP AND FOREST PRODUCING AREAS

Fig. 6c. Major crop and forest producing areas of the U.S. (Source: Gerlach 1970).

sources. Studies of transport and transformation of pollutants derived from the St. Louis area indicate a definite urban plume could be detected 120 km downwind of the city with maximum concentrations of SO₂ of approximately 0.04 ppm above background (Breeding et al. 1976).

CONCLUSIONS

While the characterizations we have just presented have their obvious limitations, the trend which might be interpreted from them presents some revealing insight into potential patterns of air quality and the way future fossil-fuel consumption levels may influence those patterns. It is conceivable that coal utilization by the year 2000 may have reached levels which will enhance ambient pollutant levels to the point where the pattern developed in Fig. 6a will be as representative of long-term average conditions as Fig. 6b is today.

The 1976 National Air Quality and Emissions Trends report (U.S. EPA 1976a) shows that total emissions have declined slightly from 1972-1975. Ambient levels in the well-monitored urban areas have declined markedly, possibly reflecting largely a shift to a growing number of sources in relatively sparsely monitored, rural areas. Sulfur oxide emissions from electric power generating plants increased during the same period, however. Similarly, NO₂ emissions have increased with increasing amounts of fuel consumed by electric utilities, and hydrocarbon emission trends have remained unchanged.

One might anticipate that with future development of coal resources in regions of the country not currently heavily developed, overall emissions density may not produce changes in ambient air quality directly proportional to the increases in coal utilization. Translated into potential for vegetation effects, one must bear in mind the relative sensitivity of the species of plants common to those regions likely to bear the burden of increased fossil-fuel emissions, as well as the prevalence of environmental factors favorable for conversion of SO₂ to SO₄, for example.

Projected growth in emissions centers around three regions: two in the west, the Four Corners area in New Mexico, and the Southeastern Montana-Northeastern Wyoming coal fields; and the Appalachian Coal fields of the East. Vegetation of the arid western regions is generally much less sensitive to pollutant injury than is that of the more mesic, eastern United States, suggesting that, given current pollution levels in the west, a lower potential for chronic effects probably exists in those regions (Bridgmon and Lang 1976).

As we have discussed, there appear to be few viable energy alternatives to coal in the near term. Environmental scientists will play an important part in determining the role of environmental constraints in any system of checks and balances designed to weight economic and environmental costs as coal assumes an expanded share of the national energy base.

The manner in which future changes in coal utilization, and hence SO_2 emissions, may be expected to influence regional air quality is still the subject of much controversy. The issue is critical to determining not only the level of control of emissions required to meet acceptable levels of air quality, but also the spatial distribution of those emissions relative to improvement of air quality in specific locations. As a result of analysis of urban and non-urban patterns and trends in SO_2 emissions and SO_2 and sulfate air quality in the United States, Altshuller (1976) concluded that long-range transport and conversion of SO_2 to sulfate is a major factor influencing present levels of urban sulfate in the eastern and midwestern United States. He cites as evidence for this the way low variations in sulfate concentrations (approximately 30%) are associated with large (500 to 1000%) variations in localized emissions of SO_2 . The importance of this long-term transport and conversion of SO_2 to sulfate and its influence on both local and regional air quality can be expected to stimulate considerable future research as we attempt to relate emissions to air quality and air quality to environmental quality in the United States. Perhaps even more significant research questions are posed by the apparently broad, regional extent of levels

of one or more pollutants known to interact with one another to effect plant response. Air pollution effects research in the future must address with increasing vigor the implications of low-level pollutant interactions when attempting to assess the significance of levels of any single pollutant entering the environment.

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