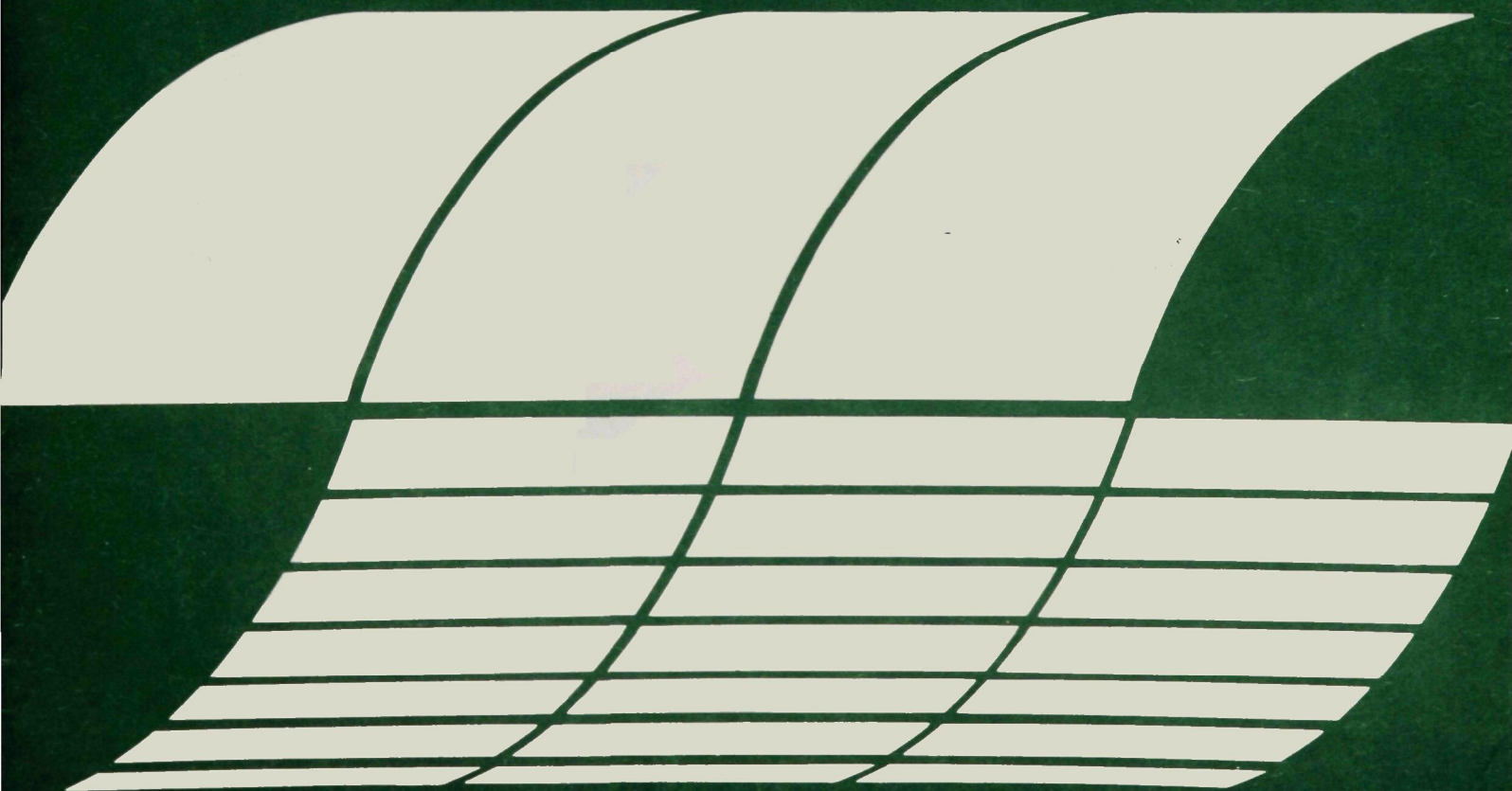


SULFATES IN THE ATMOSPHERE

A Progress Report on Project MISTT

Interagency
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SULFATES IN THE ATMOSPHERE
A Progress Report on Project MISTT
(Midwest Interstate Sulfur Transformation and Transport)

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ABSTRACT

The size and sulfate content of atmospheric aerosols and the rate and mechanisms for sulfate formation from sulfur dioxide in power plant plumes are reviewed. Emphasis is given to results from the recent USEPA study, Project MISTT (Midwest Interstate Sulfur Transformation and Transport rate of conversion of sulfur dioxide to sulfate aerosol in power plant plumes is low near the point of emission, but increases to several percent per hour as ambient air mixes with the plume. Tall stacks reduce ground-level concentrations of sulfur dioxide, resulting in a reduction of the amount removed by dry deposition. In urban plumes, which are well-mixed to the ground near the source, sulfur dioxide is removed more rapidly by dry deposition. Thus, tall stacks increase the atmospheric residence time of sulfur dioxide, which leads to an increase in atmospheric sulfur formation. These sulfate aerosols may be transported over distances of several hundred kilometers and produce air pollution episodes far from the pollution source.

This report covers a period from June 1974 to June 1976 and work was completed as of June 1976.

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SECTION 1

INTRODUCTION

Sulfate is a pollutant of note, having been linked in epidemiological and laboratory studies with adverse effects on human health (1,2). Epidemiological studies have, in fact, indicated that sulfate may be more toxic than sulfur dioxide or total suspended particulates. Sulfates are also known to be major contributors to reductions in visual range caused by atmospheric aerosols (3). Studies of acid precipitation in Scandinavia (4) have implicated sulfuric acid in a variety of adverse ecological effects.

The known adverse health effects of sulfur dioxide (SO_2) led to the control of this pollutant (5). Reduction in urban SO_2 emissions and concentrations effected by the mandatory use of low-sulfur fuels, however, were not accompanied by a proportional decrease in urban sulfate (6).

The observed lack of a proportional decrease has four possible explanations: (1) sulfates can be biogenic in origin, resulting from transformations of hydrogen sulfide, methyl disulfide, and methyl mercaptans, which are natural products; (2) measured sulfate values are not real but anomalous, resulting from conversion of SO_2 to sulfates on filters used in sampling; (3) observed sulfates are primary pollutants produced from the combustion of high-vanadium oil or from combustion in small, inefficient furnaces; and (4) observed sulfates may be explained by the transformation-transport theory. Reductions in urban SO_2 emissions have been accompanied by increases in rural SO_2 emissions from new power plants located outside cities. SO_2 from these power plants may be transformed to sulfate in the atmosphere and transported over long distances to urban areas.

The fourth possibility, the transformation-transport theory, is supported by Scandinavian (4) and U.S. studies (7) and could account for the increased sulfate levels observed in rural areas and the static sulfate

levels observed in urban areas in the U.S. (6). Early information on the rate of conversion of SO_2 to sulfate in power plant plumes suggested that the rate of conversion was too low to result in significant formation, and subsequent transport, of sulfate (7). However, studies of the flux of sulfur out of various areas, e.g., studies by Smith and Jeffrey (8) and of Waggoner et al. (9), successfully showed that some of the sulfur transported from source areas like the United Kingdom arrived in Scandinavia as sulfates.

The transformation-transport theory remains, then, a viable hypothesis for the US and is the subject of this paper.

SECTION 2

TRANSFORMATION MECHANISMS

Though they are not well understood, the mechanisms by which SO_2 is oxidized to sulfates are important because they determine the rate of formation and, to some extent, the final form of sulfate. Atmospheric SO_2 may be oxidized to sulfur trioxide (SO_3) and converted to sulfuric acid aerosol, or it may form sulfite ions that 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.

TABLE 1. MECHANISMS BY WHICH SULFUR DIOXIDE IS CONVERTED TO SULFATES (10)

Mechanism	Overall reaction	Factors on which sulfate formation primarily depends
1. Direct photo-oxidation.	$\text{SO}_2 \xrightarrow[\text{water}]{\text{light, oxygen}} \text{H}_2\text{SO}_4$	Sulfur dioxide concentration, sunlight intensity.
2. Indirect photo-oxidation.	$\text{SO}_2 \xrightarrow[\text{organic, oxidants, hydroxyl radical (OH)}]{\text{smog, water, NO}_x} \text{H}_2\text{SO}_4$	Sulfur dioxide concentration, organic oxidant concentration, OH, NO _x .
3. Air oxidation in liquid droplets.	$\text{SO}_2 \xrightarrow{\text{liquid water}} \text{H}_2\text{SO}_3$ $\text{NH}_3 + \text{H}_2\text{SO}_3 \xrightarrow{\text{Oxygen}} \text{NH}_4^+ + \text{SO}_4^{=}$	Ammonia concentration.
4. Catalyzed oxidation in liquid droplets.	$\text{SO}_2 \xrightarrow[\text{heavy metal ions}]{\text{oxygen, liquid water}} \text{SO}_4^{=}$	Concentration of heavy metal (Fe, V, Mn) ions.
5. Catalyzed oxidation on dry surfaces.	$\text{SO}_2 \xrightarrow[\text{carbon, particulate}]{\text{oxygen, water}} \text{H}_2\text{SO}_4$	Carbon-particle concentration (surface area).

SECTION 3

SIZE DISTRIBUTION

Studies (11) over the past 5 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. A schematic diagram of a typical atmospheric aerosol size distribution is shown in Figure 1. The three principal modes (particle-size ranges), the main sources of mass for each mode, and the principal processes involved in inserting and removing mass from each mode are shown. Particles in the Aitken nuclei mode, 0.005 to 0.05 μm diameter, are formed by condensation of vapors produced either by high temperatures or chemical processes. The accumulation mode, which includes particles from 0.05 to 2 μm 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 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."

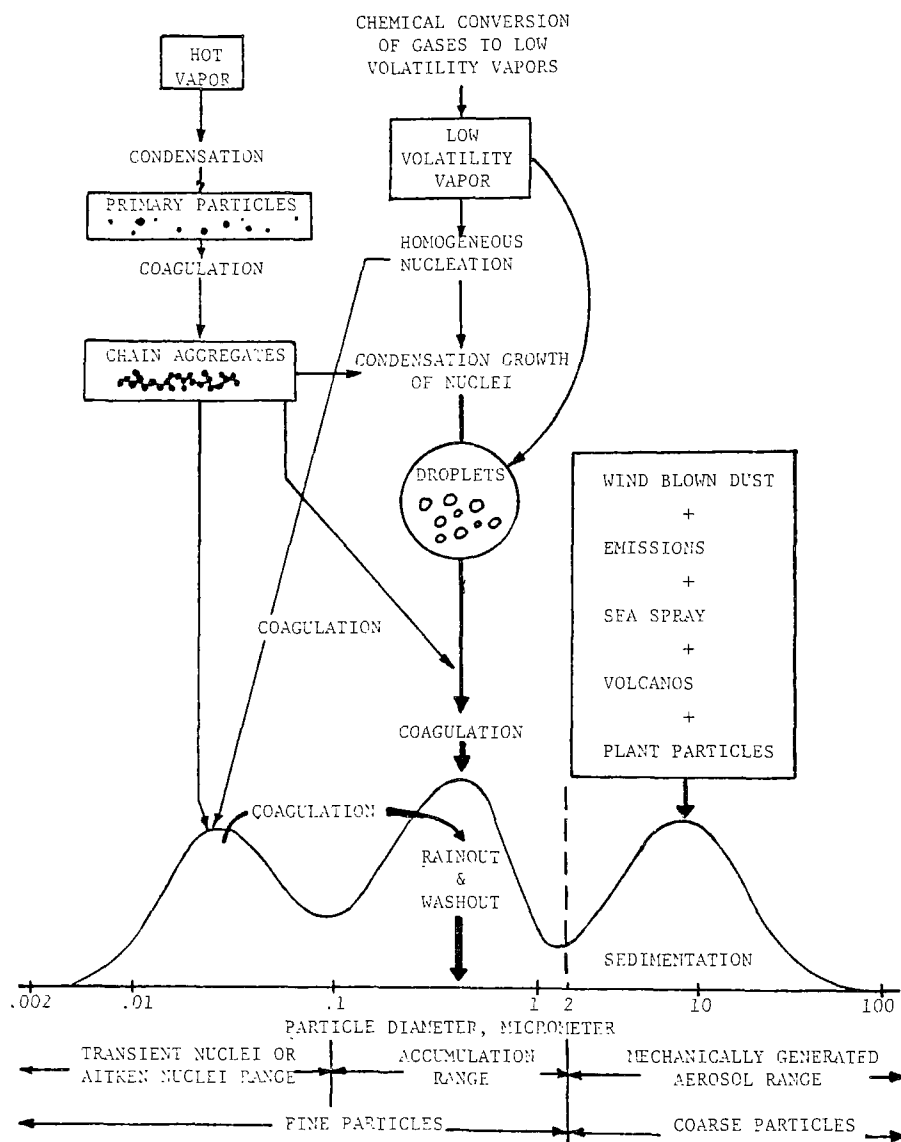


Figure 1. Schematic of a trimodal atmospheric aerosol size distribution showing the principal modes, main sources of mass for each mode, and the principal processes involved in inserting mass and removing mass from each mode.

SECTION 4

CHEMICAL FORMS OF SULFATE

Several different sulfates are among the molecular forms naturally produced as sulfur is cycled through the atmosphere. Table 2 is a list of sulfate forms known to exist in air, along with some of their more outstanding chemical characteristics. As the table shows, sulfate per se is not a single molecular form, and several sulfates are known to be produced from the oxidation of SO_2 . All seven compounds listed are sensed as "sulfate," but they have radically different chemical properties dictated by their molecular nature. They will also have different sizes, depending largely on their mode of formation. Sulfates in the fine-particle size range are respirable and also reduce visibility. Sulfates are also found in the coarse particle mode.

Sulfates are either produced and emitted into the air as such, or they are formed in the atmosphere from gas-particle conversions. The first four substances in Table 2 (H_2SO_4 and its products of neutralization with NH_3) seem to be formed from SO_2 oxidation. The remainder of the sulfates are emitted directly by industrial or by natural sources; that is, they are primary rather than secondary pollutants. The chemical nature of these substances varies from the strongly acid nature of H_2SO_4 and NH_4HSO_4 to the relatively inert salts. Water solubility and hygroscopicity and/or deliquescence vary from extremely high (H_2SO_4) to quite low (CaSO_4).

TABLE 2. KNOWN ATMOSPHERIC SULFATES

Formula	Names	Sources	Notable chemical properties	Probable Size class by mass particle Diameter, D_p
H_2SO_4	Sulfuric acid (oil of vitrol)	Atmospheric oxidation of SO_2 ; direct from manufacturing.	Strong acid, very hygroscopic (drying agent at low RH).	0.1 - 1.0 μm
NH_4HSO_4	Acid ammonium sulfate	Oxidation of SO_2 with NH_3 addition.	Strong acid, hygroscopic.	0.1 - 1.0 μm
$(NH_4)_3H(SO_4)_2$	Triammonium acid disulfate (Letovicite)	Oxidation of SO_2 plus NH_3 .	Acidic, deliquescent (?) at ~65% RH.	0.1 - 1.0 μm
$(NH_4)_2SO_4$	Ammonium sulfate (Mascagnite)	Oxidation of SO_2 plus NH_3 .	Weak acid, water-soluble, deliquescent at 80% RH.	0.1 - 1.0 μm
Na_2SO_4	Sodium sulfate (Glauber's salt)	Paper pulping by kraft process.	Water-soluble, deliquescent at 84% RH; relatively inert.	$D_p > 0.5 \mu m$ (uncontrolled pulp mill)
$CaSO_4$	Calcium sulfate (gypsum)	(1) Wind-blown dust. (2) Manufacture of gypsum products.	Low solubility in H_2O ; relatively inert	$D_p > 1 \mu m$
$MgSO_4$	Magnesium sulfate (Epsom salts)	(1) Sea spray. (2) Paper pulping.	Very hygroscopic; relatively inert and non-toxic.	$D_p > 1 \mu m$ (sea spray) $D_p > 0.5 \mu m$

SECTION 5

REVIEW OF PLUME STUDIES

Information on the rate of conversion of SO_2 to sulfate in power plant plumes was needed to quantify the contributions of power plants to atmospheric sulfates. A critical review of plume studies (7) revealed no reliable information on conversion rates, and only two studies that provided information on the amount of SO_2 converted to sulfate. The early work of Gartrell et al. (12) indicated little conversion of SO_2 to sulfate except at relative humidities greater than 75 percent. However, at high relative humidity, conversion of SO_2 to sulfate may occur either on the filter surface or within the aerosol particles collected on the filter. Therefore, Gartrell's results cannot be accepted unless verified by other techniques.

Investigators at the Brookhaven National Laboratory used two techniques to study sulfate formation in power plant plumes (13,14): the sulfur isotope technique and direct measurements of SO_2 and sulfate. The isotope technique is considered erroneous because of the presence of several competing reactions having different isotope effects (7). The direct measurement of SO_2 and sulfate is considered experimentally valid. The Brookhaven workers measured conversion from 0 to 8.5 percent per hour in coal-fired power plant plumes (13) and 0 to 26 percent per hour in oil-fired power plant plumes (14). The Brookhaven work has previously been interpreted to indicate an average conversion rate in coal-fired plumes of 1 percent per hour or less and a substantially higher rate in oil-fired plumes. However, a careful analysis of the data, after discarding the isotope results, indicates that no difference has been established between oil- and coal-fired plumes and that, depending on conditions, conversion rates of substantially greater than 1 percent per hour are possible (7). The sampling techniques and flight patterns used were such that an accurate measurement of the conversion rate could not be obtained (7).

SECTION 6

EPA PLUME STUDIES

PROGRAM PLAN

In order to obtain a better understanding of the physical and chemical processes occurring in power plant plumes, a new series of field studies were undertaken. During July, August and February of 1975, extensive studies involving three-dimensional mapping of large plumes were carried out in the St. Louis area as part of the Midwest Interstate Sulfur Transport and Transformation Study (MISTT). Preliminary studies were conducted during July and August of 1973 and 1974.

These plume studies differed from earlier ones in that: (1) more gas and aerosol parameters were measured; (2) horizontal and vertical profiles were measured; (3) data were interpreted in terms of mass flows instead of ratios; (4) the background air mixing with the plume was characterized; (5) the chemical composition and size distribution of the aerosols in the plume were determined; and (6) measurements were made in approximately the same air mass as it moved downwind.

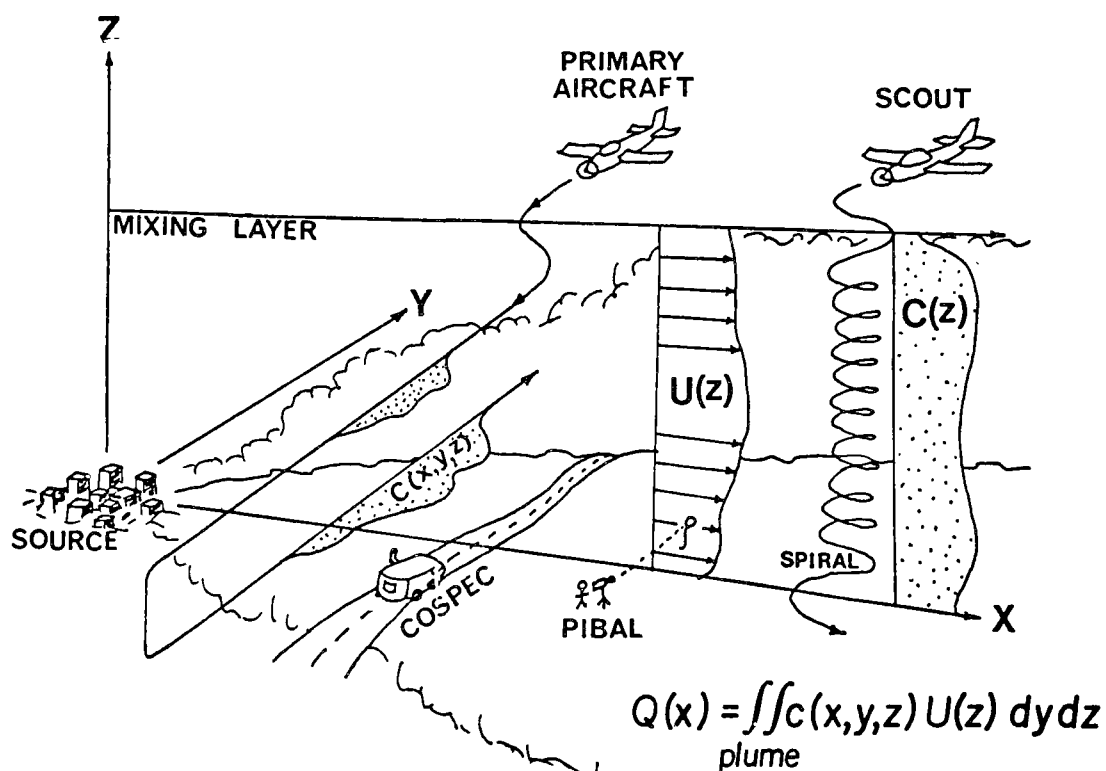
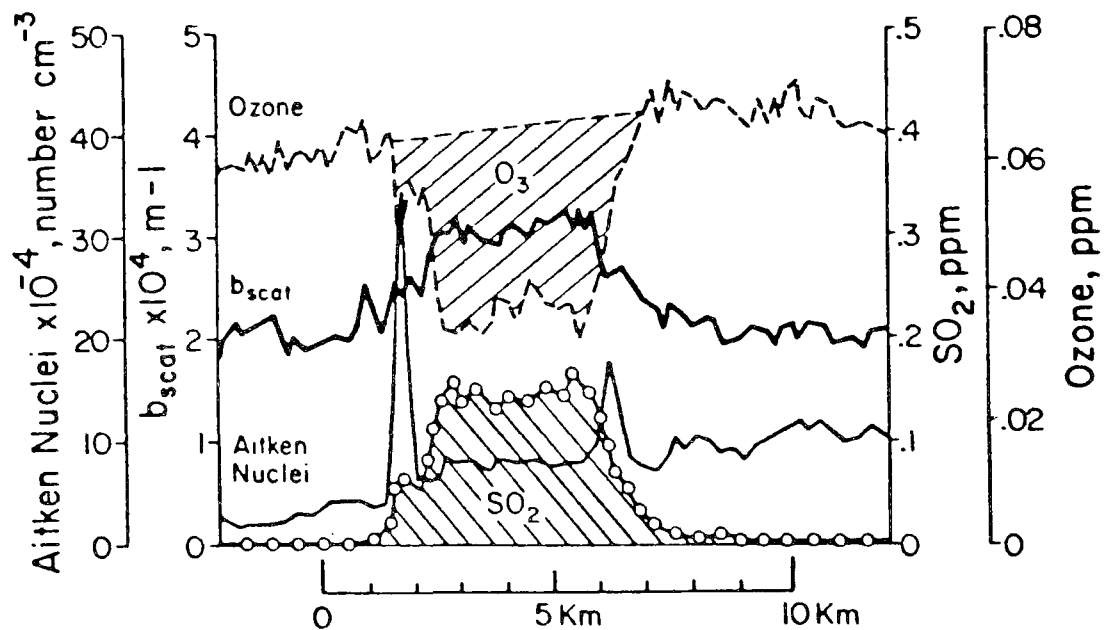
In previous studies, the fractional conversion of SO_2 to sulfate was calculated from the ratio of SO_2 to sulfate collected as integrated filter samples while circling in random portions of the plume at various downwind distances. This technique can overestimate conversion if any SO_2 is removed by dry deposition to ground surfaces. For this reason and because of the need to collect large amounts of SO_2 , samples were usually collected in cohesive plumes which had undergone minimal dilution with background air. This technique can also lead to errors if conversion varies in different parts of the plume or if conversion is influenced by the extent to which the plume has been diluted by background air. That this can indeed be the case is demonstrated in Figure 2, in which the nuclei formation rate is seen to

be much greater at the edges of the plume than in the center. Although such a dramatic difference was not often observed, current interpretation of sulfate formation mechanisms suggests that the conversion rate will be higher in those portions of the plume, such as the edges, in which dilution has led to conversion of plume NO to NO₂ by background O₃ (15). To overcome these problems the EPA plume mapping studies were designed to measure SO₂ and sulfate mass flow rates at increasing distances from the source in both cohesive and well-mixed plumes. From the change in flow rate with distance, it is possible to calculate transformation and removal rates for individual pollutants (16,17).

In the EPA study, the SO₂ mass flow rates were determined by a continuous SO₂ monitor. A two-dimensional plot of SO₂ concentrations in a plane perpendicular to the plume axis was constructed from the horizontal and vertical profiles. The mass flow of SO₂ was calculated from the SO₂ concentration and the wind speed and direction. Since no continuous monitor for sulfate was available, the continuous light-scattering (b_{scat}) measurement was used as an indication of the sulfate concentration distribution. Sulfate, collected in filter samples during each pass through the plume, was analyzed by the flash vaporization-flame photometric detection method--a new, highly sensitive technique modified for aircraft use (18,19). The sulfate flow was calculated from the b_{scat} /sulfate concentration ratio, integrated over a pass, and the b_{scat} flow. Similarly, b_{scat} -to-aerosol volume ratios were used to calculate an aerosol volume flow.

PLUME MAPPING PROGRAM

Two instrumented aircraft, an instrumented van, and three mobile single-theodolite pilot-balloon units were used in a coordinated measurement program (Figure 3). The primary sampling platform was a single-engine aircraft (20) equipped for continuous monitoring of the gaseous pollutants (O₃, NO, NO_x, SO₂); three aerosol parameters (condensation-nuclei count, light-scattering coefficient, and aerosol charge); several meteorological variables (temperature, relative humidity, dew point, and turbulent dissipation); and navigational parameters. Particulate sulfur samples were gathered by a sequential filter tape sampler equipped with a respirable-particle size separator. An



array of four cascade impactors collected size-differentiated aerosol samples for later chemical and microscopic analyses. An optical counter and an electrical-mobility analyzer provided details of the in situ particle-size distribution of grab samples.

An instrumented "scout" aircraft located the plume, laid out the sampling path of the primary aircraft, and directed the three mobile pilot-balloon (pibal) units to their respective positions in the center and at the edges of the plume. Coordinated with the aircraft sampling, a van equipped with a correlation spectrometer (COSPEC) made lateral traverses under the plume and measured the integrated overhead burden of SO_2 and NO_2 (21). Data collected aboard the two aircraft and in the van were recorded automatically at 1- to 10-second intervals on magnetic tapes for subsequent computer processing. The operations headquarters coordinated the mobile units by radio communication.

The flight pattern of the primary aircraft was designed to enable characterization of the plume at discrete distances downwind from the source. At each distance, horizontal traverses were made in the plume perpendicular to the plume axis at three or more elevations. These were supplemented by vertical spirals within and outside the plume. The continuous instruments monitored the distribution of pollutants along each pass, and the sequential filter samples, analyzed later by a sensitive flash-vaporization, flame-photometric technique (17), yielded the average particulate sulfur concentration for each pass. From the three-dimensional pollutant concentration field obtained in this manner, together with the vertical profiles of wind velocity measured every half-hour by the three pibal units, the horizontal flow rates of pollutants at each downwind distance were directly calculated. Under well-defined wind conditions (unidirectional, steady wind field), the reproducibility of the pollutant flow measurement was ± 20 percent.

POWER PLANT PLUME CHARACTERISTICS

Aerosol Volume (22)

An electrical aerosol analyzer and an optical particle counter were used to measure, in each of a number of size ranges, the number of particles per cm^3 of air. By assuming spherical particles, the volume of aerosol material in μm^3 per cm^3 of air may be calculated (volume concentration, $\mu\text{m}^3/\text{cm}^3$). Thus

from size distribution measurements made during horizontal passes and from upwind spirals, as shown in Figure 4, and at the distances given in Tables 3 and 4, it was possible to calculate aerosol volume flows. Wind velocities at each distance were measured with pilot balloons.

Size distributions were also measured, usually near the plume center, as shown in Figure 4. In contrast to the bi- or tri-modal distributions found at ground level (Figure 2), the size distributions at plume height (Figure 5) were unimodal, nuclei apparently having been removed by coagulation and coarse particles by sedimentation. Therefore, these distributions were characterized by fitting them with a single log-normal distribution. The resulting geometric mean diameters and geometric standard deviations are tabulated in Table 3. These show that, although the mean size increased from 0.24 μm at 10 km to 0.29 μm at 45 km, particle sizes in the plume are not significantly different from the average found in the upwind, background spiral.

The flow rates, $Q(x)$, of light-scattering aerosols (b_{scat}) and Aitken nuclei (AN) were obtained for each plume cross section from the double integral of the concentration (x,y,z), and wind velocity, $U(z)$ (17). Since the aerosol volume concentrations calculated from the size distributions could only be determined at discrete points in the plume, the aerosol volume integrals were estimated using the ratios of aerosol volume to b_{scat} determined at discrete points. The assumption that the aerosol volume integral is proportional to b_{scat} implies that the aerosol size distribution is constant along a traverse. This is thought to be an acceptable assumption because of the consistency of the size distribution along the plume as shown in Figure 4 and Table 3. Wind velocities at each distance were calculated from pilot balloon observations. The flow rate for each aerosol parameter is the sum of that due to the background plus that contributed by the plume. The background was measured on both sides of the plume in order to separate the two flow rates.

Plume-associated flow rates for b_{scat} , AN, and aerosol volume measured in the Labadie power plant plume on 4 and 14 August 1974 are shown in Figure 6. The volume flows are also given in Table 3. From Figure 6 it is seen

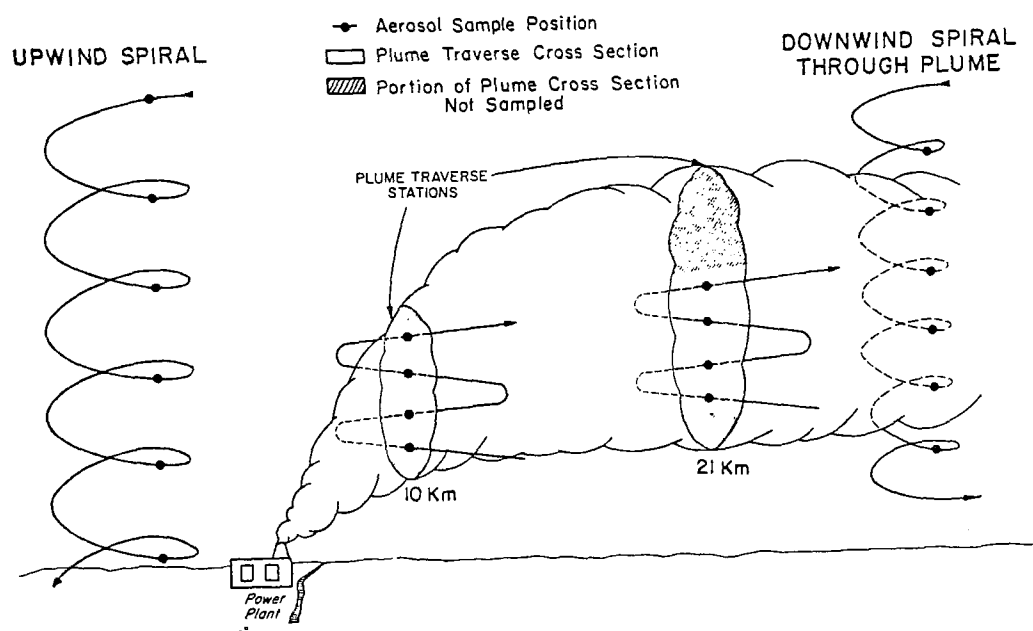


Figure 4. Flight plan of the research aircraft through the plume showing the four altitudes at which passes were made, the upwind and in-plume spirals, and the points at which aerosol size distributions were measured. Only two traverses out of four are shown.

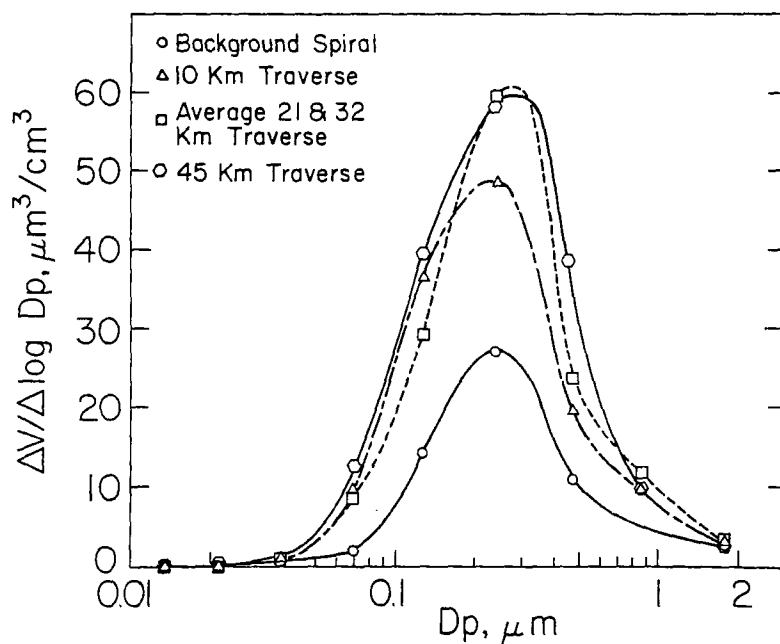


Figure 5. Volume size distribution of aerosol measured within the Labadie power plant plume and background air on August 14, 1974.

TABLE 3. AEROSOL SIZE DISTRIBUTION CHARACTERISTICS

<u>Date</u>	<u>Location</u>	<u>Geometric mean diameter, μm</u>	<u>Geometric standard deviation</u>	<u>Avg. vol., $\mu\text{m}^3/\text{cm}^3$</u>
8-5	Background (upwind) spiral	$0.20 \pm .04$	$2.09 \pm .13$	19.3 ± 5.2
8-5	2-km traverse	$0.20 \pm .01$	$1.95 \pm .04$	22.1 ± 1.6
8-5	4-km traverse	$0.22 \pm .006$	$1.93 \pm .06$	36.5 ± 4.2
8-5	18-km traverse	$0.21 \pm .001$	$1.90 \pm .06$	42.3 ± 7.6
8-14	Background spiral (upwind)	$0.30 \pm .04$	$2.19 \pm .2$	17.9 ± 4.6
8-14	10-km traverse	$0.24 \pm .05$	$2.14 \pm .14$	35.8 ± 9.3
8-14	Avg. 21 and 32-km traverse	$0.28 \pm .04$	$2.31 \pm .12$	38.7 ± 9.0
8-14	45-km traverse	$0.29 \pm .06$	$2.20 \pm .19$	47.0 ± 16.7

TABLE 4. PLUME AEROSOL FLOW RATES AND CALCULATED
SULFUR CONVERSION, 14 AUGUST 1974^a

<u>Distance, km</u>	<u>Time hr</u>	<u>Aerosol volume flow above background, cm^3/sec</u>	<u>SO₂ converted,^b %</u>	<u>SO₂ conversion rate, %/hr</u>
0	0			
10	0.70	185	1.1	1.5
21	1.49	388	2.3	1.8
32	2.29	640	3.7	4.9
45	3.17	1378	8.0	

^aAssuming the aerosol is H_2SO_4 in equilibrium with water vapor.

^bBased on the average SO_2 flow of 4.08 kg/sec and a relative humidity of 75%.

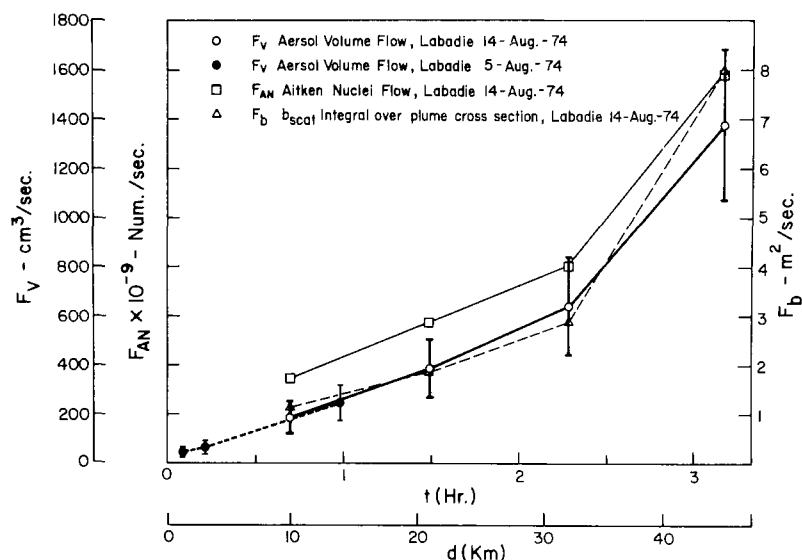


Figure 6. Aerosol volume flows in the plume as a function of time and distance traveled compared with light scattering and Aitken Nuclei flows. Excess aerosol flow due to the plume has increased seven times from 10 to 45 km. Note also the four fold increase in the rate of aerosol formation after 2 hours.

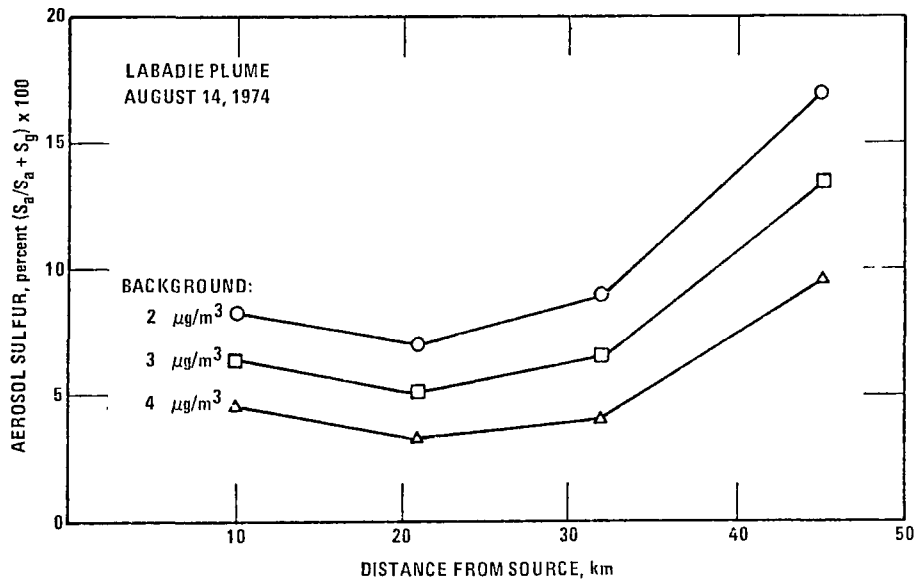


Figure 7. Percentage of sulfur concentration due to aerosol sulfur for several estimated background concentrations of aerosol sulfur.

that on 14 August the growth was two-stage, the growth rate increasing by a factor of 4 after about 2 hours, at a distance of about 30 km.

One of the chief objectives of this study was to determine the rate at which SO_2 is converted to sulfate in plumes. It was assumed that the excess aerosol formed in the plume was sulfuric acid in equilibrium with water vapor at the ambient humidity. The fraction converted and the rate of conversion was determined from the ratio of the calculated sulfur in the aerosol to the total sulfur flow calculated from the SO_2 measurements and the estimated sulfuric acid. These results, presented in the last two columns of Table 4, show that at 45 km 8 percent of the SO_2 was converted to aerosol and that the conversion rate varies from 1.5 percent/hr at 10 km to 4.9 percent/hr at 45 km.

Sulfate Measurements

During these experiments, the concentration of soluble sulfate was also measured with a filter apparatus. These filter samples were integrated from one plume edge to the other during the four passes at each distance. The actual conversion rate determined by the sulfate flow rate method will depend on the sulfate background. Figure 7 shows the pattern for several background concentrations. Adequate background sulfate concentrations were not obtained during this experiment. The drop in percent converted between 10 and 21 km may be due to fall out of large particles which escaped the electrostatic precipitator or it may be due to measurement errors. Measurements of SO_2 in the plume are most difficult nearest the stack because of the high concentration gradients and plume inhomogeneity.

URBAN PLUMES

Similar techniques were used to map the three-dimensional flow of aerosols and trace gases in the air leaving the St. Louis area. It was found that under certain summer, daytime meteorological conditions the aggregate pollutant emissions from metropolitan St. Louis often formed a cohesive, well-defined "urban plume" downwind of the city (16,17,23,24). Such a plume can be identified in Figure 8, which shows ozone concentrations and light-scattering coefficients measured within the mixing layer northeast of St. Louis on 18 July 1975 (24).

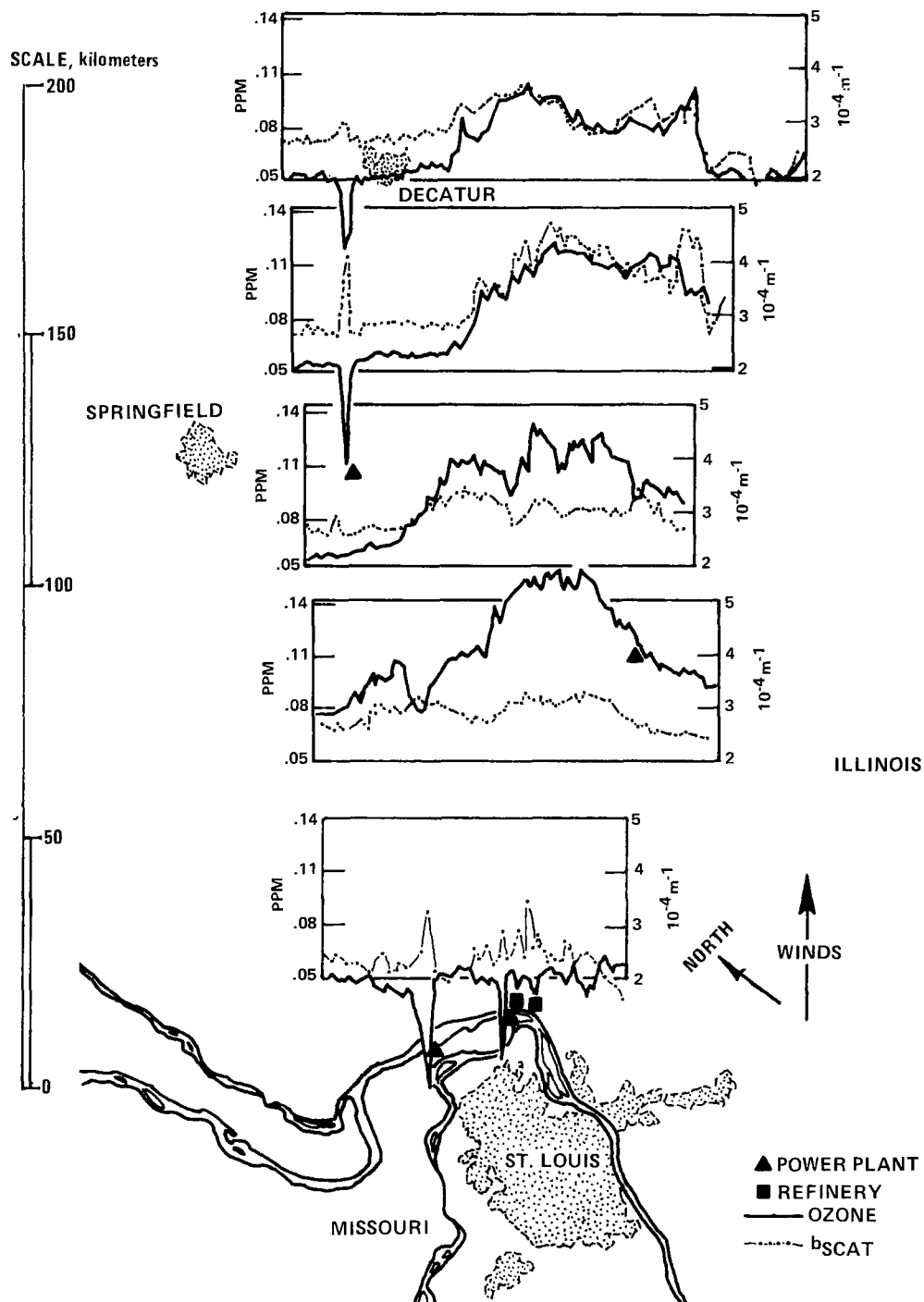


Figure 8. Ozone concentration and aerosol light-scattering coefficient (bscat) downwind of St. Louis on 18 July 1975. Data is taken from horizontal traverses by instrumented aircraft at altitudes between 460 and 760 m msl. Sampling paths are along graph baselines; note that baseline concentrations are not zero (24).

On that day, the St. Louis plume incorporated the emissions of major coal-fired power plants at Labadie (Mo.) and Portage des Sioux (Mo.) and of a refinery complex near Wood River (Ill.), in addition to emissions from industries and automotive traffic of the St. Louis-East St. Louis urban area itself. The concentrated individual plumes immediately downwind of large combustion sources can be identified in Figure 8 by their ozone "deficits"; the depressed concentrations of O_3 in these plumes reflect the high concentration of NO in effluents.

The width of the plume, approximately 40 km, did not change much along its 150-km-length. Apparently, horizontal diffusion at the boundaries of the urban plume was by means of a rather slow dilution mechanism. It appears likely that the elevated ozone concentrations in this plume and the reduced visibility caused by the plume were exported well beyond Decatur (Ill.).

Unlike the primary pollutants NO and SO_2 , ozone and light-scattering aerosols attained their maximum concentrations well downwind of St. Louis on 18 July 1975. The ozone and most of the aerosol were not emitted but were products of chemical and physical transformations in the atmosphere; their secondary origin is evident in Figure 9, which shows flow rates of ozone and aerosol in the St. Louis plume increasing with distance from the city. The flow rates in Figure 9 represent only the contribution of the St. Louis plume, and are calculated from the measured winds within the plume and from the difference between pollutant concentrations inside and outside the plume.

Based on a number of experiments in 1974 and 1975, the following features of the urban plume were observed to be typical: 1. The St. Louis plume significantly degraded the air quality of communities as far as 150 km from the city. 2. The most conspicuous components of the St. Louis plume 50 km or more downwind of the city were the reaction products formed along the way. 3. Most of the aerosol responsible for the high b_{scat} and resulting decrease in visibility within the St. Louis urban plume was formed in the atmosphere.

The sulfate concentrations in the 18 July 1975 urban plume attained a maximum of $20 \mu\text{g}/\text{m}^3$. This is not an extremely high value. On 29-30 July 1975 the urban plume was followed for 18 hours and measurements were made both in the evening and the following morning. During this experiment sulfate con-

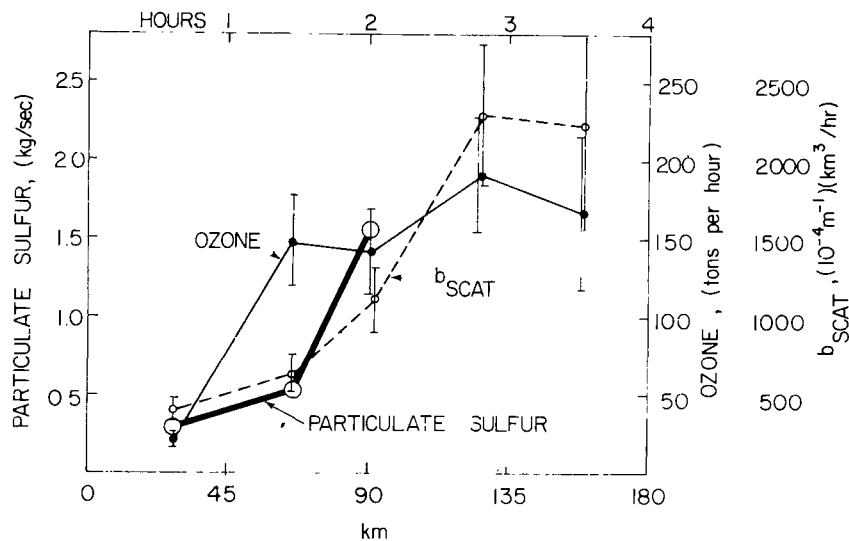


Figure 9. Flow rates and related data for St. Louis plume on 18 July 1975. Values are plotted against distance downwind of the St. Louis Gateway Arch, with equivalent travel times for a constant mean wind speed of 45 km/hr shown for comparison. The mass flow rate of ozone and the flow rate of the aerosol light-scattering coefficient (b_{scat}) are shown.

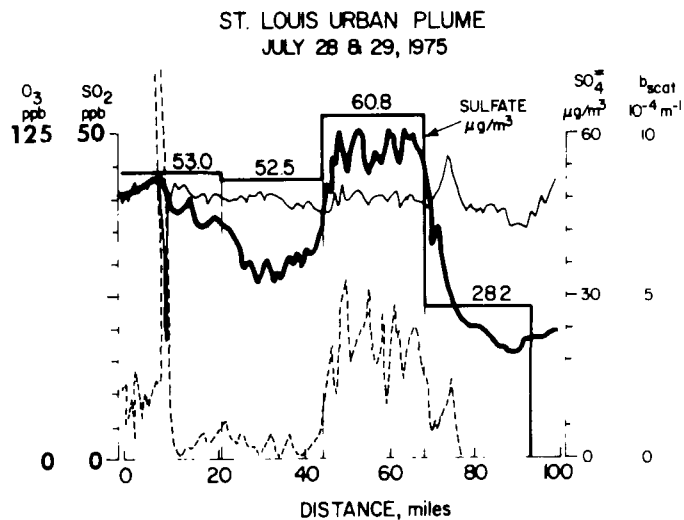


Figure 10. A profile of the St. Louis urban plume taken early in the morning of July 30, 1975, after following the plume for 18 hours. Profiles are shown for ozone (—), sulfur dioxide (---), b_{scat} (—), and aerosol sulfate.

centrations of $60 \mu\text{g}/\text{m}^3$ were measured, as shown in Figure 10. This set of measurements demonstrates that at least under some conditions sulfate formation can exceed removal and dilution and can lead to the accumulation of very high sulfate concentrations.

SULFATE BUDGET

By examining the total flow of sulfur--both SO_2 and sulfate--we can draw some interesting conclusions regarding the transformation and removal of SO_2 in the two classes of plumes, that is, power plant plumes and urban plumes (17).

The experimental results representing pollutant flow data for gaseous and particulate sulfur are shown in Figures 11 and 12. Pollutant flow measurements in urban plumes are shown in Figure 11. Data are reported here only for those days in which the wind direction was such that the plumes of the rural power plants (tall stacks, > 700 ft.) were well separated from the urban plume which contained emissions from low stacks (< 350 ft.) and near ground level sources. In such plumes, the total sulfur flow rate (gaseous plus particulate) has been found to decrease with distance. The pollutant flow rate, as determined from both the aircraft-measured concentrations and correlation spectrometer data, shows a decay in excess of the estimated experimental uncertainty of the methods (± 20 percent).

Sulfur depletion in the urban plumes appears to be equivalent to an exponential rate of decay with a characteristic $(1/e)$ decay time of 3 to 4 hours. Our results show, therefore, that in such plumes only about one-third of the original emissions are transported beyond a radius of 100 km and that formation of new sulfate aerosol is undetectable up to a distance of 50 km. There is evidence that during the daytime the formation of aerosol, including sulfate in an urban plume, begins after an aging time of 1 or 2 hours.

In power plant plumes (Figure 12), total sulfur flow measurements showed no loss of sulfur within the limits of experimental uncertainty. The aerosol fraction of total sulfur flow on 14 August 1974 was 6 percent at 10 km and 13 percent at 40 km from the source. As seen in Figure 10 and 11, most of the particulate sulfur formation occurred between 30 and 50 km from

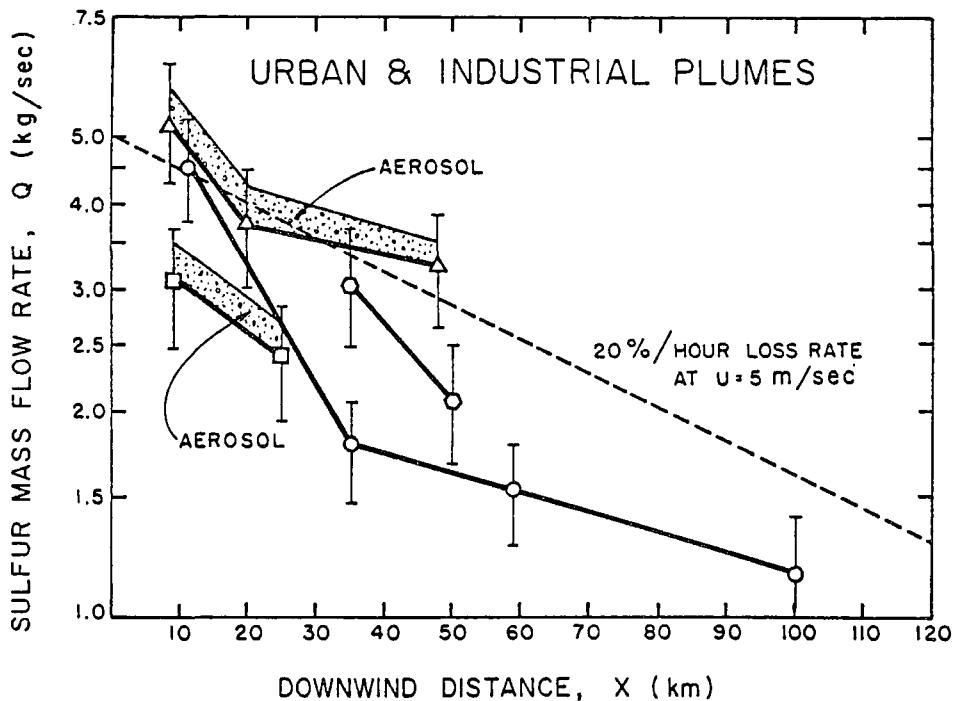


Figure 11. Sulfur budget in urban-industrial plumes. The shaded area represents the particulate sulfur contributions, the solid lines are gaseous sulfur.

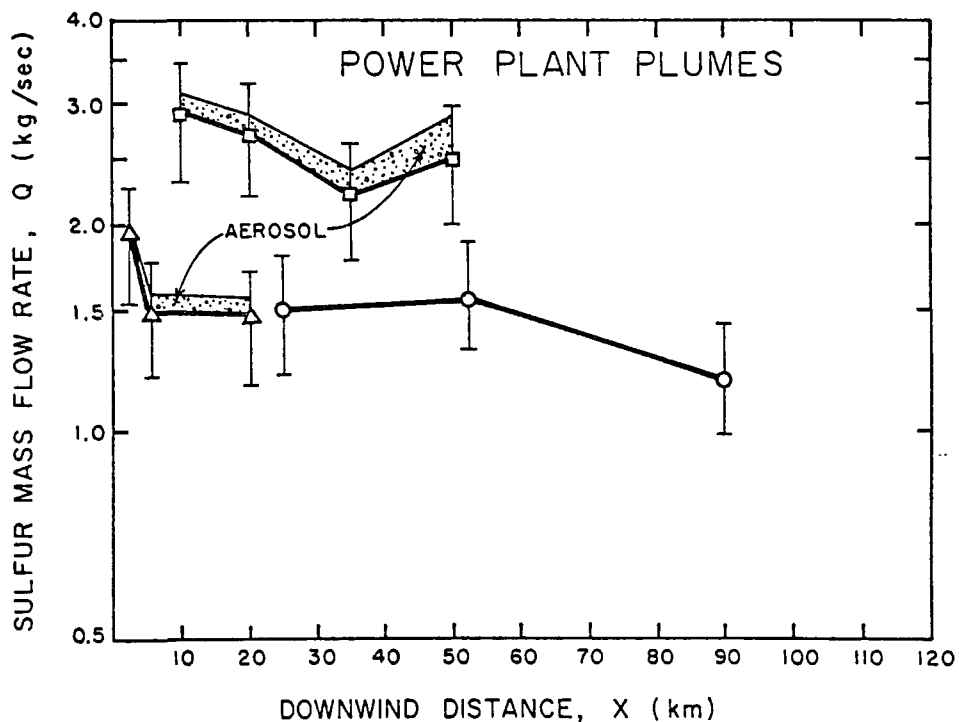


Figure 12. Sulfur budget in power plant plumes. \square 8.14.1974; Δ 8.5.1974; \circ 7.29.1975 (COSPEC). Note the increase of particulate sulfur between 30 and 50 km on 8.14.1974.

the source. The SO_2 flow data for 30 July 1975 were obtained by the correlation spectrometer, unaugmented by particulate sulfur measurements. These power plant plume measurements, all performed during daytime conditions, demonstrate that there is little removal of the sulfur emitted from tall stacks within a region of 50 to 100 km from the plant. During these measurements, dry deposition was minimal either because the plumes had not touched the ground or because they were very dilute at ground level.

REMOVAL PROCESSES

It is important to understand that most sulfate aerosol is secondary, i.e., formed by gas-to-particle conversion in the atmosphere after emission, and occurs in the accumulation mode. Particles in this size range have very long lifetimes. Some confusion has existed regarding the relative removal rates for SO_2 and sulfate aerosol by deposition. The deposition velocity of aerosols depends on the particle size and reaches a minimum in the accumulation size range of 0.1 to 1.0 μm . The deposition velocity of gaseous SO_2 depends on the chemical reactivity of the surface. Both deposition velocities depend on the friction velocity and the surface roughness. However, since the diffusion of accumulation mode aerosols through the surface boundary layer (0.001 to 1 cm) is much slower than the diffusion and surface reaction of an SO_2 molecule, the deposition velocity of sulfate aerosol is always significantly smaller than for gaseous SO_2 (25,26,27). Consequently, though SO_2 is removed fairly rapidly by dry deposition on soil, vegetation, and other surfaces, the removal processes become slower once the SO_2 has been converted to sulfate. Therefore, sulfates can travel long distances before their removal by fallout, rainout, or deposition.

EFFECTS OF TALL STACKS

These aspects of reaction mechanisms, aerosol size, and deposition rates are critical to an understanding of the possible effects of tall stacks. When SO_2 is emitted near the ground, as from home heating units, the SO_2 can be removed by surface removal mechanisms (dry deposition). When SO_2 is emitted higher in the air, as from the tall stacks of fossil-fuel-fired electric power plants, the SO_2 is diluted before it reaches the ground, and the surface removal rates are reduced. Emissions may, in fact, be trapped above an

inversion layer and remain trapped for hours. Thus, elevated stacks theoretically permit a longer residence time in the ambient atmosphere for SO_2 and promote fine particulate sulfate formation by the mechanisms discussed previously. On the other hand, they provide for increased dilution of the sulfate and SO_2 and thus reduce the impact of emissions in the vicinity of the source.

SECTION 7

SUMMARY

Earlier work had shown that the rate of conversion of SO_2 to sulfate in power plant plumes was slow except at very high relative humidity. In the recent EPA program, consistent conversion of several percent per hour at normal levels of relative humidity has been measured. The conversion of SO_2 to sulfate aerosol in power plant plumes is slow in the early part of the plume; that is, close to the point of emission. As ambient air mixes with the plume, the rate of conversion increases. Thus tall stacks reduce ground-level concentrations of SO_2 but increase sulfate aerosol formation by reducing surface losses of SO_2 and by increasing the atmospheric residence time, which results in increased SO_2 -to-sulfate conversion. In urban plumes, which are well-mixed to the ground, SO_2 may be removed by reaction with plants and by deposition. The SO_2 dry deposition rates vary with vegetation, with the nature of the surface, and with time of year.

Urban plumes have been sampled out to 250 km from their sources and power plant plumes out to 60 km. Sampling at these distances revealed that sulfate, generated from SO_2 in power plant and urban 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 and other problems far from the source of pollution. These air pollution problems cannot be controlled by the government entity where the air pollution impact actually occurs.

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