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BRIAN WELLS GALUSHA

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MASTER OF SCIENCE IN METEOROLOGY

NORTH CAROLINA STATE UNIVERSITY

SYNOPTIC-SCALE VARIABILITY IN ATMOSPHERIC SUSPENDED SULFATE CONCENTRATIONS

by

BRIAN WELLS GALUSHA

A thesis submitted to the Graduate Faculty of
North Carolina State University at Raleigh
in partial fulfillment of the
requirements for the Degree of
Master of Science

METEOROLOGY

RALEIGH

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ABSTRACT

GALUSHA, BRIAN WELLS. Synoptic-Scale Variability in Atmospheric Suspended Sulfate Concentrations. (Under the direction of GERALD F. WATSON).

The spatial variation in atmospheric suspended sulfate concentrations are studied for evidence of meteorologically linked sulfate transformation and transportation. Low frequency (every 12-14 days) data from 41 National Air Surveillance Network stations as well as higher frequency (every 2-3 days) data available from two special studies are examined. Variations in high frequency data with wind direction for St. Louis, Missouri, are compared to local and regional sources of precursor pollutants for two one-year periods; January-December 1969 and April 1975-March 1976. Spatial variations in low frequency sulfate concentrations during the spring season (March-May) for the six-year period 1969-1974 are compared with synoptic weather and wind circulation patterns. These comparisons indicate that regional and local sulfate transport can largely account for large-scale sulfate variations. Sulfate transformation due to humidity, temperature and sunlight intensity do not adequately explain observed variations, but may be of secondary importance.

The existence of regionally high concentrations of sulfate in the northeastern United States and of a general summertime peak in sulfate values is confirmed.

BIOGRAPHY

Brian W. Galusha was born October 13, 1943 in Granville, New York. He was educated in public schools, graduating from Granville Central High School in 1961.

He received a Bachelor of Arts degree with a major in Chemistry from Syracuse University, Syracuse, New York. He also received a commission in the United States Air Force through AFROTC.

The author has served the Air Force in the career fields of Ballistic Missiles and Meteorology. In the course of his duties in the latter career field, he has held positions as Weather Forecaster, Staff Weather Officer, and as Detachment Commander. While in the Air Force he has obtained an additional Bachelor of Science degree with a major in Meteorology from Pennsylvania State University and a Master of Arts degree with a major in Business Management from Central Michigan State University. The author entered North Carolina State University in the fall, 1976, to undertake a course of study leading to the Master of Science degree in Meteorology.

Mr. Galusha is married to the former Miss Carol Elizabeth Cooke of Auburn, New York.

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The author wishes to express sincere appreciation to the Meteorology Division of the Environmental Sciences Research Laboratory, Environmental Protection Agency at Research Triangle Park, North Carolina, and to its personnel for providing facilities, assistance and the data for this study. A special acknowledgement is extended to Mr. George C. Holzworth for his assistance and encouragement.

The author wishes to thank the Air Force Institute of Technology for providing the scholarship which permitted the accomplishment of this study, and Dr. Gerald F. Watson whose knowledge and assistance were essential.

Finally, the author wishes to thank his wife, Carol, and children, Heather and Jeffrey, whose encouragement, patience and sacrifices have been an inspiration throughout the course of this study.

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INTRODUCTION

Description of Atmospheric Sulfates Effects

Atmospheric suspended sulfates have been identified as a significant pollution problem by the Environmental Protection Agency (EPA). These sulfates have been related to adverse health effects (EPA, 1974c), reduced visibilities (Wilson *et al.*, 1977), and the corrosion, discoloration, and deterioration of materials (EPA, 1976).

The term "sulfates" applies collectively to a large class of sulfur compounds. Any single physical property which characterizes all is difficult to define. One of the major distinctions is that some sulfates are hygroscopic and others are not. Although some researchers have found it convenient or necessary to assume homogeneity, generalizations about sulfates are often invalid. Thus, results of studies conducted in one section of the country may not be applicable to other regions. Adding complexity to the problem is the fact that sulfates are usually secondary pollutants transformed chemically from the precursor agents such as sulfur dioxide (SO_2) and hydrogen sulfide (H_2S).

The health effects of atmospheric sulfates have been well documented by epidemiologic studies of the EPA's Community Health and Environmental Surveillance System (CHESS) Program. These studies provide dose-response relationships between sulfur oxides and health effects. The report concluded that pollution thresholds for adverse health effects were 8-15 micrograms per cubic meter ($\mu g/m^3$). The usual adverse effect was on the human cardio-pulmonary system.

Sulfate Sources

Atmospheric sulfates originate from both natural and anthropogenic (manmade) sources. Natural sources include, primarily, volcanic activity, biological decay, and sea-salt crystal formation. Anthropogenic sources, including precursor sources, are automobile exhaust products, fossil fuel power plant effluents and by-products of various industrial processes. Of the anthropogenic sources, power plant emissions are deemed the most important and automobile exhaust products the least important. However, local conditions can rank these sources in a different order.

Natural sources are believed to contribute a background sulfate concentration in the range of 2-4 $\mu g/m^3$ depending upon location (Kurosaka, 1976). Sampling of ambient atmospheric sulfates from all sources has produced averages of 5-21 $\mu g/m^3$ with individual samples over 150 $\mu g/m^3$ being reported in the data analyzed during this study. Because of the considerable variation in sulfate concentration both in time and space, restraint must be exercised in making generalizations about real cause and effect relationships.

As stated previously, anthropogenic sulfates are thought to be formed predominately from SO_2 and H_2S. To date, both the chemistry and the exact relationships between the primary precursor, SO_2, and the end sulfate are not clearly understood. Table 1 shows some of the chemical reactions thought to be important, although their relative importance is not yet known. Possible meteorological influences enter these reactions through dependence on atmospheric humidity and liquid water, and on sunlight intensity which depends significantly on cloud

Table 1. Mechanisms that convert sulfur dioxide to sulfates (after EPA, 1974b).

Mechanism	Overall reaction	Factors on which sulfate formation primarily depends
1. Direct photo-oxidation	$SO_2 \xrightarrow[\text{water}]{\text{light, oxygen}} H_2SO_4$	Sulfur dioxide concentration, sunlight intensity.
2. Indirect photo-oxidation	$SO_2 \xrightarrow[\text{organic oxidants, hydroxyl radical } (OH^-)]{\text{smog, water, } NO_x} H_2SO_4$	Sulfur dioxide concentration, organic oxioxidant concentration, OH^-; NO_x
3. Air oxidation in liquid droplets	$SO_2 \xrightarrow{\text{liquid water}} H_2SO_3$	Ammonia concentration
	$NH_3 + H_2SO_3 \xrightarrow{\text{Oxygen}} NH_4^+ + SO_4^=$	
4. Catalyzed oxidation in liquid droplets	$SO_2 \xrightarrow[\text{heavy metal ions}]{\text{oxygen, liquid water}} SO_4^=$	Concentration of heavy metal (Fe, Mn) ions
5. Catalyzed oxidation on dry surfaces	$SO_2 \xrightarrow[\text{carbon, water}]{\text{oxygen, particulate}} H_2SO_4$	Carbon particle concentration (surface area)

cover. Air temperature may have some role since reaction rates are often temperature sensitive.

In addition to the effects of transformation, transportation of sulfates from source regions, sometimes for hundreds of miles, has been proposed as a reason for widespread variability of sulfate concentration. This may be a particularly significant factor since a large portion of atmospheric sulfates are submicron in size. Figure 1 shows the bimodal volume and mass distribution of atmospheric particles reported by Whitby and Liv (1974). They have examined these two modes and concluded that the accumulation mode, between 0.1 and 1.0 micron, is occupied by particles that have been formed as a result of chemical and physical processes that convert gases to particles. The mode near 11 microns consists of coarser particles formed by mechanical processes such as weathering, grinding or rubbing. The EPA (1975) has found that typically 80% of the atmospheric sulfates are found in the accumulation mode, that portion of the size spectrum that is associated with visibility reduction. Furthermore, because of their slow settling velocity (10^{-3} centimeters per second) these particles can be transported great distances from their place of formation (EPA, 1975). Eventually the sulfates will fall out or be rained out producing an acid rainfall. This polluted rainfall often has significant consequences to surface biology but this problem will not be considered here.

Two recent studies indicate how the dual problem of transformation and transportation interface. In a recent report on the Midwest Interstate Sulfur Transformation and Transport (MISTT), Wilson _et_ _al_., (1977) reported that for power plant plumes, most sulfate formation occurred between 30 and 50 km from the source. Further, sulfate formation in

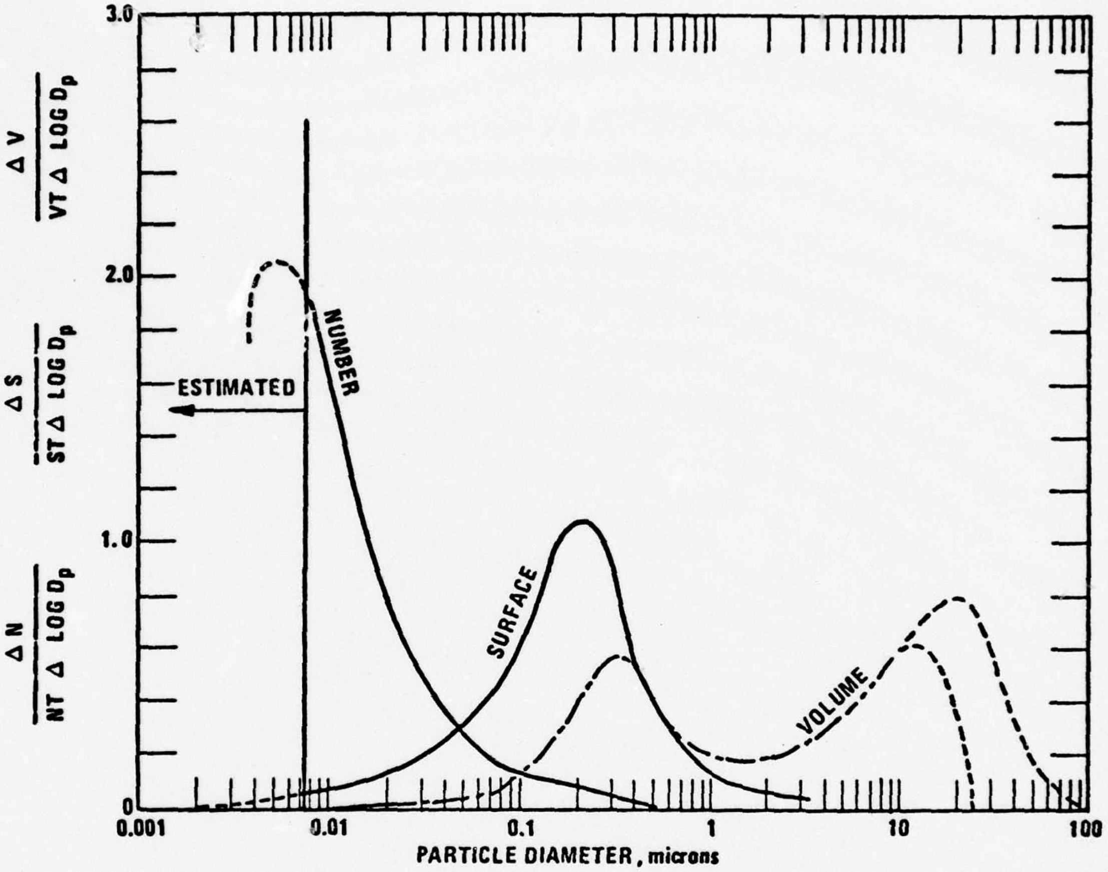

Figure 1. Bimodal distribution of atmospheric particles (after Whitby and Liv, 1974).

urban plumes began after a 1-2 hour aging time. These conclusions indicate that the effect of transformation is a greater problem at a few hours transport distance than close to the source. In a report relating atmospheric visibility and aerosols, Auer (1977) has also found that visibility reductions of 50% occurred at distances 2-3 hours downwind of St. Louis, Missouri, for air parcels moving at a mean transport speed. The above writer further found that these reductions were coincident with increasing concentrations of particles in the 0.1-2.5 micron size range.

Previous Studies

Epidemiologists have attempted to relate sulfates and suspended particulates to health effects. Chemists have attempted to isolate, both in the laboratory and in the atmosphere, the chemical reactions that predominate the sulfate transformation. Electric utility corporations have sponsored several studies to determine the environmental impact of power plant emissions. Statisticians have analyzed sulfate data for means and trends both spatially and temporally. It appears to the present writer that many studies have not fully accounted for sulfate data shortcomings mentioned earlier, and that the meteorological factors controlling the relevant chemistry and transport are yet to be appreciated. The following is a brief review of pertinent studies of the sulfate problem undertaken to define the spatial and temporal distributions.

Wagman, Lee and Axt (1967) evaluated the influence of some atmospheric variables on sulfate concentration. The authors examined the diurnal variability at several city locations, and concluded that the variability for different locations was not consistent. Rodhe et al. (1972) examined the regional transport of sulfate into southern Sweden. Among his conclusions was the revelation that sulfate sources as distant as 1000 km could contribute significantly to local sulfate burden of the atmosphere. Frank (1974) provided the first comprehensive spatial and temporal examination of sulfates. The northeastern United States was found to display the highest annual average sulfate levels, a result verified by other researchers. In addition, Frank determined that while sulfur dioxide and total suspended particulate concentrations have decreased between 1964 and 1970, the same has not occurred with sulfates.

Garvey (1975) conducted a study to examine sulfates in Huntington, New York. It was concluded that sulfates peaked in the summer months, were not highly correlated with sulfur dioxide, nor with any single meteorological variable except visibility. When sulfate concentrations were paired with the prevailing wind no influence of a nearby power plant was discernable. Garvey was also unable to support the hypothesis that moisture in the air is a primary factor in sulfate formation. Garvey's analysis for diurnal cycles indicated peak concentrations in the morning from 08-10 EDT and minimum concentrations at night from 00-02 EDT.

A study of sulfates in the eastern United States was undertaken by Tong, Battel and Bachelder (1976). They generally confirmed the results of Frank mentioned above in regards to the high concentrations characteristic of this region. They also found that maritime tropical air masses were generally associated with periods of high sulfate concentrations. Frank and Possiel (1976) produced a follow-up study which further supported the presence of particularly high concentrations in the northeastern United States, and third calendar quarter peak concentrations. Additionally, they indicated that annual concentrations of sulfate were increasing in non-urban as well as in urban areas of previously low sulfate concentration.

Lipfert _et al_., (1977) examined the spatial and temporal variations of sulfates in the northeastern United States. Lipfert generally agreed with Frank, but reported that the long-term trend of sulfate was constant, despite the fact that power plant emissions had increased in the study area some 90% from 1960-1970. It was further concluded that the data do not clearly evidence the significance of long-range sulfate transport.

Although many of the above studies used similar approaches, major conclusions often differ. One point of agreement, however, is the recognized need for further information on the chemistry and meteorology of the sulfate problem.

Scope of Present Study

The present study is undertaken with the hope that a more detailed meteorological investigation can provide a better understanding of the mechanisms involved in sulfate transport and transformation. In particular, this study proposes to determine whether the sulfate concentrations display well-defined patterns over areas resolvable by the normal meteorological surface observation network. This implies areal extents of a few hundred kilometers (synoptic-scale). If such patterns of sulfates are found, what then is their relationship to patterns of meteorological variables? This question and others will be answered in the remaining sections of this study.

SULFATE DATA

Data Sources and Description

The basic data set used in this study was obtained from the EPA's National Aerometric Data Bank. These data were collected by the National Air Surveillance Network (NASN), a network of local and state agencies who perform ambient air sampling.

The complete sulfate data file was requested and received in January 1977. An examination of that file showed that sulfate data had been archived since 1955. Until about 1963, sulfate data were only sporadically reported. Later, sulfate values were reported more uniformly on a modified biweekly schedule. As reported by Akland (1977), the schedule was modified to insure an equal distribution of sulfate values for each day of the week. Since 1972, the sampling frequency has been increased to once each 12 days, thereby eliminating the requirement to modify the schedule.

Sulfate concentrations are obtained by a chemical fractionation of the Total Suspended Particulate (TSP) sample, a procedure further described below. The TSP sample is obtained using a high volume sampler (Hi-Vol). Ambient air is drawn through a glass-fiber filter at a rate of approximately 1.5 cubic meters per minute. The sampling period period is 24 hours beginning at midnight local time. The result is a 24-hour averaged concentration.

Although nearly 250 sampling sites have been involved in the collection of these data, changing priorities, budgets, and short-term projects have limited the number of continuously reporting sites to approximately one hundred.

Sulfates, as defined by the EPA (1975) and used throughout this paper, are water soluable sulfates which include acid-sulfates, neutral metallic sulfates, adsorbed sulfur dioxide and sulfites.

The chemical analysis of the TSP sample for sulfate concentration is begun by cutting a portion of the glass fiber filter and dissolving the soluable portions of the TSP sample in a small quantity of water. The chemical analysis for sulfates is then conducted on this filtrate with auto-analyzers using the methylthymol blue method. Briefly, this method involves reactions of the filtrate with methylthymol blue dye and barium chloride. By adjusting the pH of the solution, the unreacted blue dye turns yellow and the intensity of the yellow dye is then measured colorimetrically. Since this excess dye is proportional to the sulfate ions present, sulfate concentration can be determined. The concentrations are reported in $\mu g/m^3$ of air at 25°C and 760 mm Hg. A more detailed description of the chemical method may be found in several references including Appendix C of the EPA (1974c) report.

Data Selection for the Present Study

The data employed in this study were selected from the basic file using the following criteria:

a. Only urban, population-oriented sampling sites in close proximity to reporting National Weather Service (NWS) stations were selected.

b. Only the eastern portion of the United States was considered.

c. Since it is imperative that similar chemical analyses be performed, only those data analyzed by the methylthymol blue method were considered. (In earlier years several methods were in use at various times.)

Additional restrictions were imposed to insure that the annual data for each station were valid:

a. To be valid, each station must have at least five samples from each season during any year.

b. If any month had no samples, then each of the other months in that season must have at least two samples each.

c. No month should have more than three samples. Data were selectively chosen, based upon date, in a few cases to meet this criteria.

d. Each station must have four valid years of data out of the six-year period.

After applying these criteria, 41 stations were selected. Station locations are shown in Figure 2; they are listed together with the data years in the Appendix.

To examine the transport of sulfates, supplemental data sets were used. The first of these was included among the NASN data and consists of higher frequency samples taken every two to three days at St. Louis, Missouri; Houston, Texas; and Washington, D. C. A second supplemental data set was also taken at St. Louis as part of the Regional Air Pollution Study (RAPS) project. Again, observational frequency was approximately every three days. In each of these supplemental data sets, the method of obtaining and analyzing the sample was the same as that employed for the main data set.

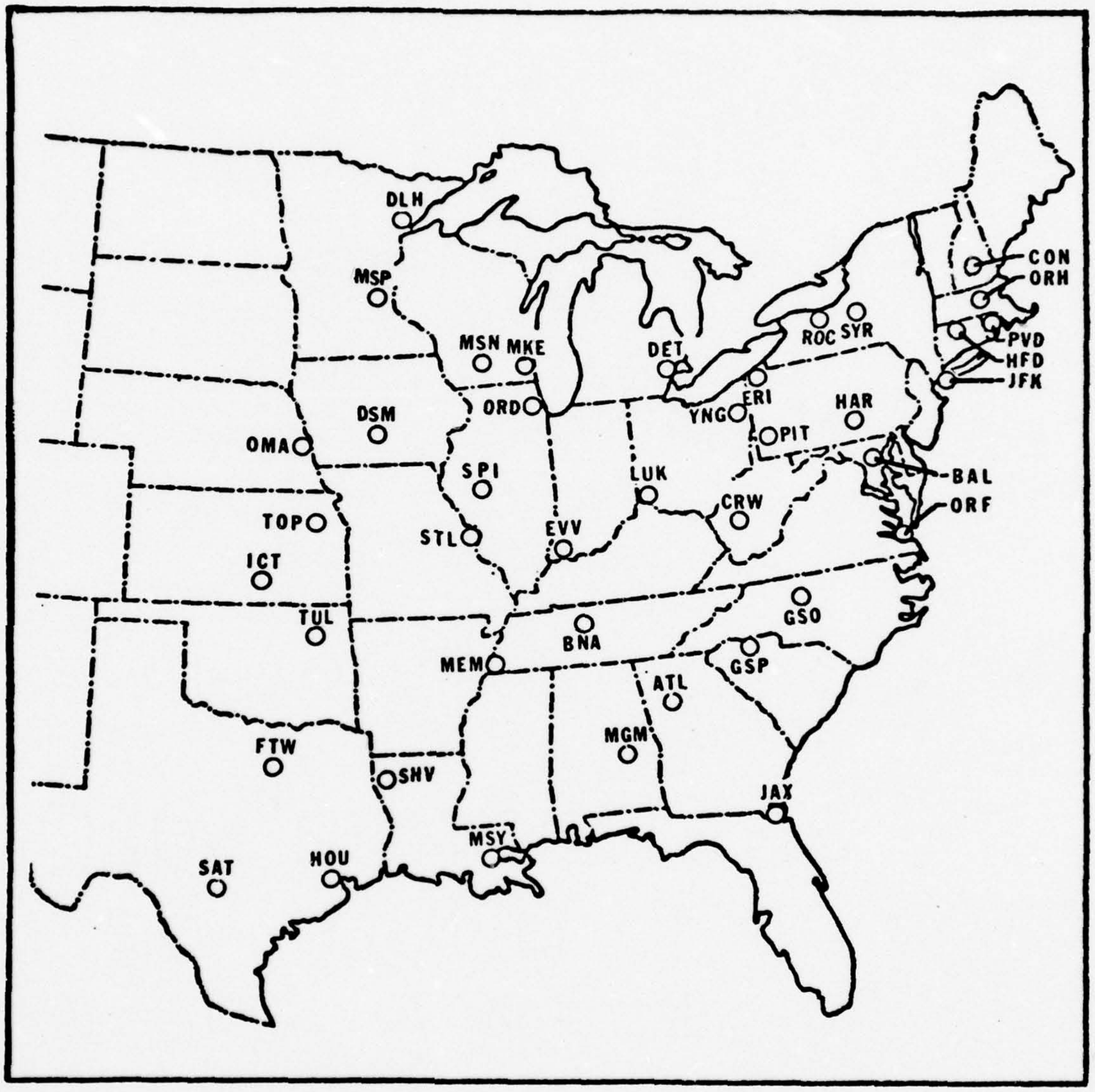

Figure 2. National Air Surveillance Network stations whose data are employed in the present research.

Error Analysis

Sulfate data have been severely criticized by many researchers as being error-ridden. Although the quality of the data is certainly subject to question and readily admitted to be non-optimum by the EPA, it should be remembered that there was no effort to establish a network specifically to sample for sulfates. The sulfate values are obtained from TSP samples by trace analysis techniques. It would seem inappropriate to be overly critical of the sampling method when used for purposes other than its intent. With this data limitation in mind the errors in the data are now discussed.

The most critical errors in the sulfate data have been analyzed by Wagman et al., (1967). They reported that substantial amounts of sulfate were formed on the glass-fiber filter due to the basicity of the filter itself. They estimated that as much as 16 per cent inflation of the concentration value could be attributed to this cause. Further study indicated that the amount of artifact sulfate generated in this manner usually occurred in the first few hours of sampling. After this time period, the pH of the filter was low enough so that no further sulfate would form.

Coffer (1974) has further investigated this problem considering sulfate formation with various aerosol and humidity combinations. A positive correlation with both relative humidity and aerosol amount was noted, which would lead to a significantly larger (50 per cent or more) percentage of artifact sulfate formation. This formation of sulfate on the filter media is the largest known source of systematic error. Because of these effects, it is doubtful that the absolute value of sulfate concentration error can be stated. This study, however, does not depend on the actual concentration values in the ambient air so much as on variances from the mean, spatially and temporally. One might expect variations in concentrations to be more reliable than absolute values.

Errors which arise from the chemical analysis are also present in the data. Akland (1977) assigns a percentage error of 6.3 ± 10% (95% confidence limits) as due to this effect. This is the repeatability error. Since all samples were analyzed automatically in one laboratory this error reasonably represents that associated with chemical analysis of filters.

There are undoubtedly other errors, both systematic and random, present in the data caused by siting problems and equipment calibration. These, however, are difficult to specify in any given data set.

In summary, the errors involved in sampling and analyzing the sulfate concentrations are appreciable. The large artifact error, however, should only result in overestimating the magnitude of sulfate present. This study has attempted to minimize the effect of this error by working with values expressed as deviations from the mean. Other errors cannot be so easily minimized and consequently any deviation value of magnitude less than 1 $\mu g/m^3$ is certainly not significant.

METEOROLOGICAL ASPECTS OF LARGE SCALE SULFATE VARIABILITY

Some Statistical Aspects of Sulfate Variability

The data for this study were selected to provide a representative base for the large scale sulfate variability. This same scale in meteorology is represented by synoptic weather patterns. Although smaller scale variations exist, this study only examines the broader scale and relationships attributable to such variations.

The NASN low frequency data for the 41 stations in this study were treated according to standard statistical analysis techniques.

First, time series were plotted for a few representative sites and analyzed. Figure 3 is an example of such a time series for Nashville, Tennessee. The most remarkable characteristic of the time series was the large sample-to-sample variance. As can be seen in Figure 3, this variation is often a factor of 2 or more between samples. A second characteristic of these time series was the evidence of seasonal variations. In the case of Nashville, this variation was indicated by lower sulfate values in winter and spring than in summer and fall.

To examine this seasonal variation further, both short-term (one year) and long-term (six years) seasonal means were calculated and evaluated. The short-term means evidenced strong variance with some stations showing consistent seasonal variations but most showing inconsistent year to year peaks. The long-term seasonal means were far more consistent between stations and Figure 4 shows the regionally representative seasonal variations by means of bar graphs. The predominate seasonal peak occurs in summer.

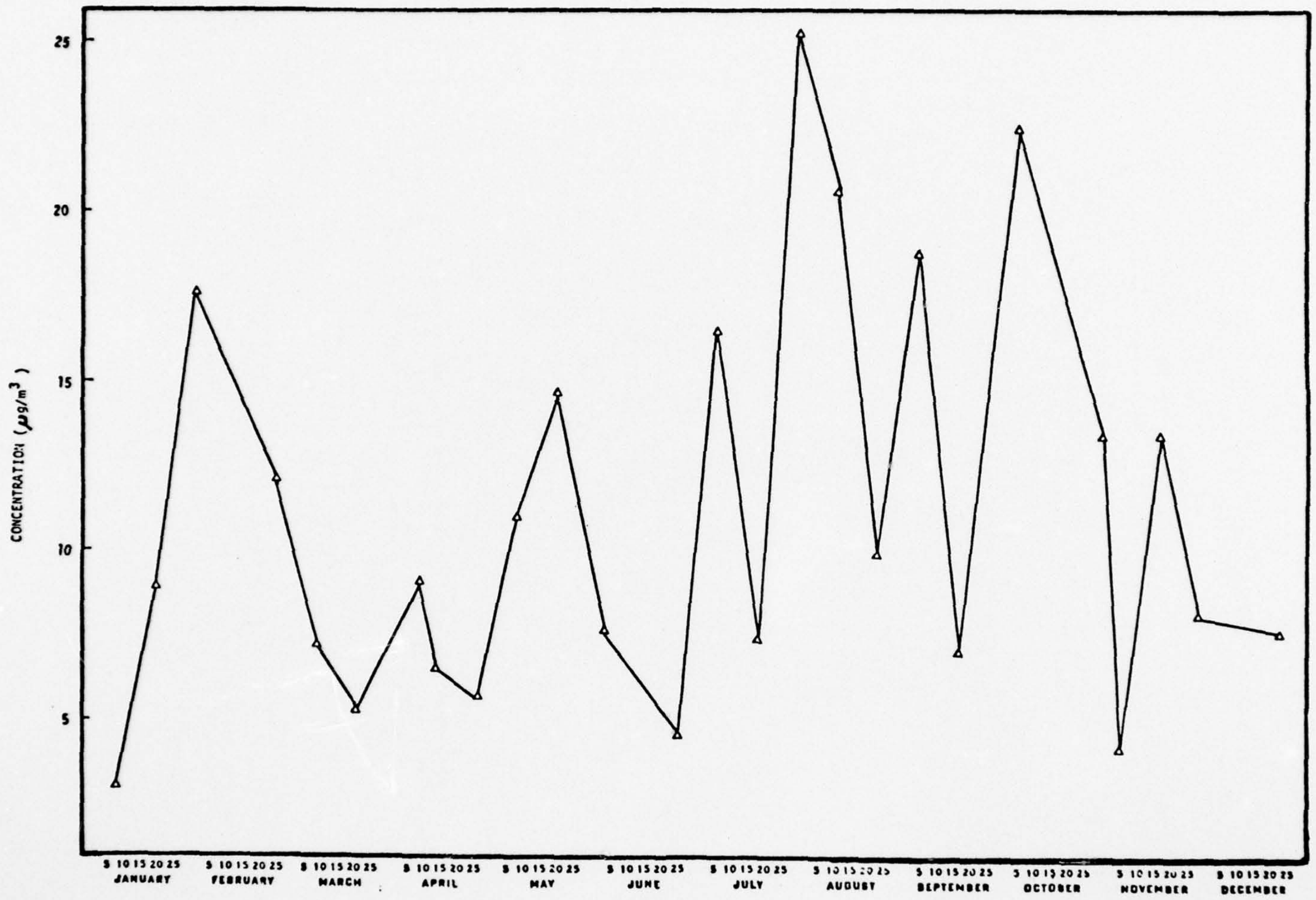

Figure 3. Time Series of one year's sulfate data (1972) for Nashville, TN.

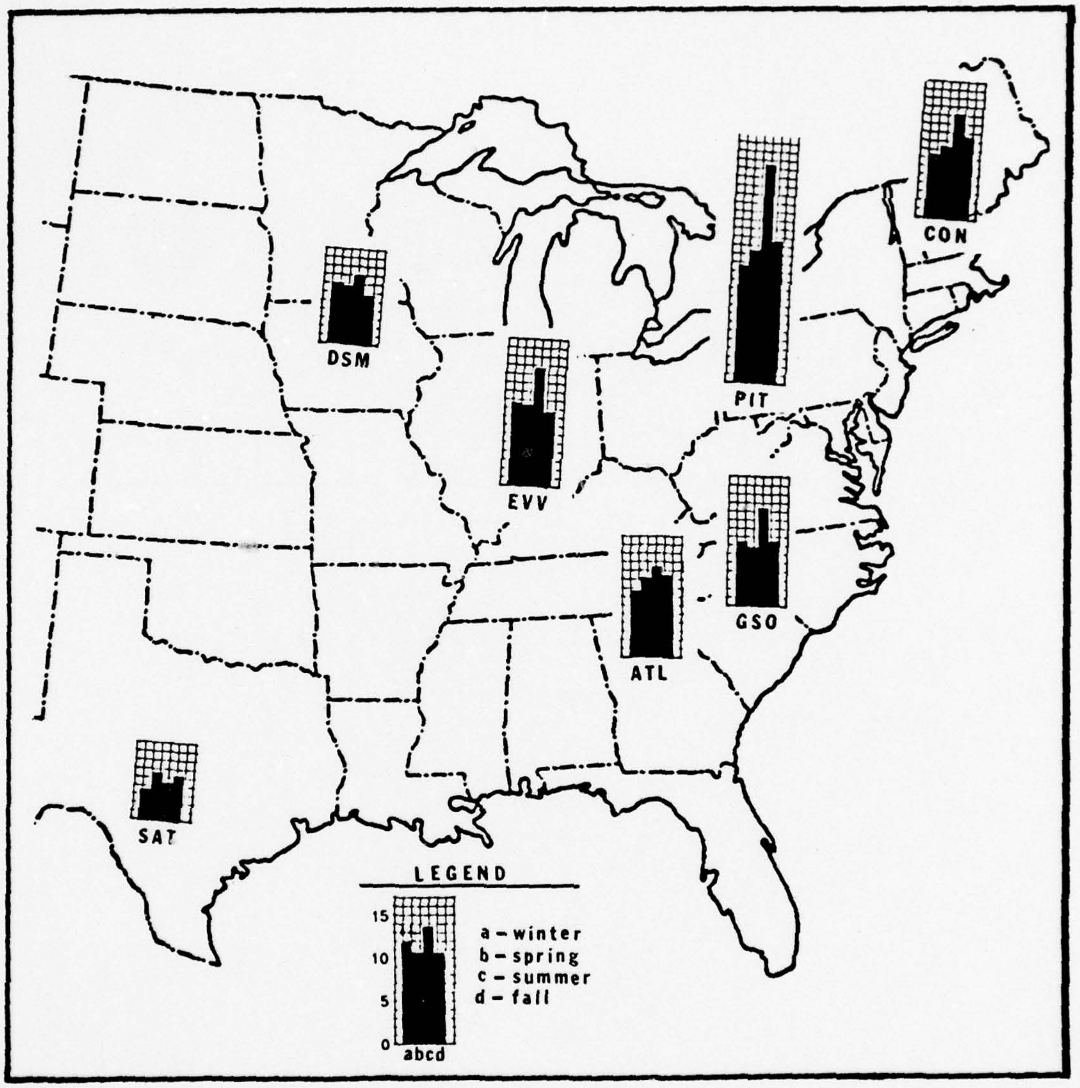

Figure 4. Regionally representative seasonal means (1969-1974). Each bar in the graph represents a mean seasonal value. Vertical scales are in units of μg/m^3.

The magnitude of this summer peak increases from the U. S. midwest to the east, and from south to north. In the midwest and south the amplitude of the summer peak is only about 2 $\mu g/m^3$ whereas in the upper Ohio Valley region it is about 10 $\mu g/m^3$. The New England region displays a drop in the peak to about 4 $\mu g/m^3$. This agrees with results reported by other researchers including Frank (1974), Frank and Possiel (1976) and Lipfert et al. (1977).

Tong, Battel and Batchelder (1976) have attributed the summertime peak to the stagnating anticyclone systems and the general higher humidity and temperature regimes of the accompanying maritime tropical air masses. When one considers the generally slower wind speeds and stable conditions associated with the summer high pressure areas, their hypothesis seems reasonable.

Portions of the Texas and Gulf Coast region are an exception to the general pattern of summertime peaks. This area displays a springtime peak. No reason is offered here for this anomoly, however, it is plausible that the chemical nature of the sulfates in this region may be different from those at more inland stations. Possibly sea salt nuclei or biologically derived sulfates from salt marshes are responsible for this anomoly. The spring season is noted for frequent and strong onshore flow in this region.

Arithmetic and logrithmic frequency distributions were prepared for each station to determine which distribution was best for further statistical treatments. Geometric frequency distributions, as those in Figure 5, display a great deal of variability. Although some stations do not show a clear-cut single modal distribution (Omaha, Nebraska), many

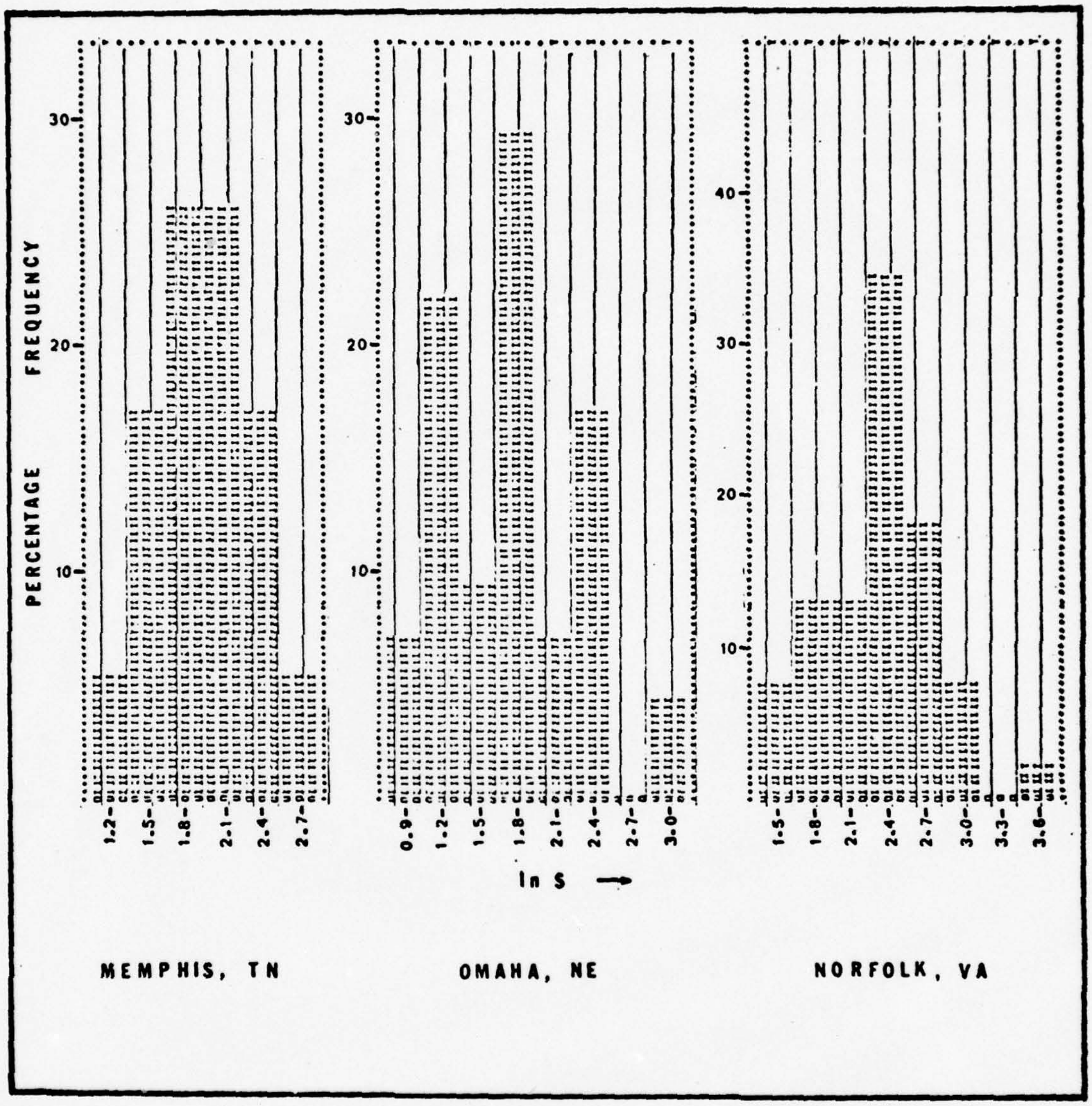

Figure 5. Representative examples of geometrically plotted histograms of sulfate concentration (S). Scaling of vertical axes in these computer plots was based upon the number of data points in each class interval. The abscissa values are plotted at the midpoint of the class interval.

distributions can be reasonably well represented by a lognormal distribution function. This result was anticipated and is in general agreement with previous work on pollutant frequency distribution functions (Larsen, 1971).

Annual means were also calculated for each year and the entire study period for each station. Inter-annual variability of means was quite large at many stations, a variance about the six-year mean of about 20 per cent occurred frequently. A spatial plot, Figure 6, of the long-term annual mean produces excellent agreement with Frank and Posseil (1976).

This spatial distribution of sulfate concentrations has several important characteristics. The most significant point is that there is a large area of significantly above normal sulfate concentration in the relatively populus and industrialized northeastern states. This area is well related to power plant density patterns as reported by the EPA (1975). In addition, the magnitude of the annual average in this area is greater than the best estimate of the pollutant threshold value for adverse health effects as reported in the CHESS study (1974c).

Synoptic-Scale Sulfate and Weather Distributions

The weather-active spring season (March-May) was chosen for a more detailed analysis of the synoptic-scale distribution of sulfates. In order to examine the variability associated with weather and circulation systems, it was first necessary to remove the seasonal variability from the data.

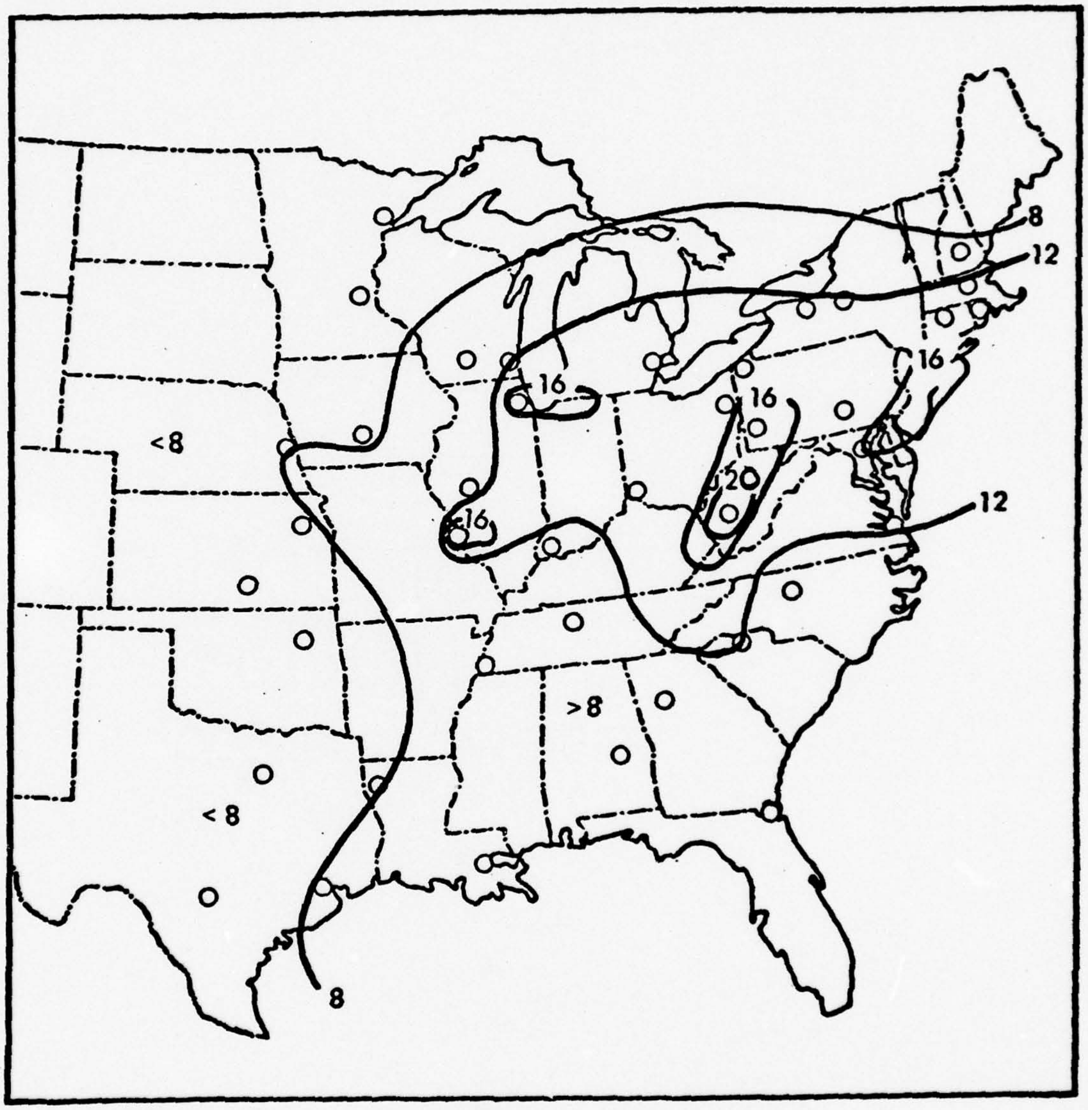

Figure 6. Distribution of annual average sulfate concentrations ($\mu g/m^3$), 1969-1974.

Springtime sulfate values were averaged for the entire six-year period and the long-term geometric average obtained for each station. This mean value was then subtracted from the station's daily sulfate values and the resulting deviations from the mean were output in chronological order for plotting on charts. The sampling schedule provided for 39 days of sampling during these six spring periods.

When plotted on a surface chart, these values often exhibited clearly defined areas of greater or less than normal amounts of sulfate presumably due to synoptic-scale variability of atmospheric variables and processes.

Synoptic weather features were next added to the surface charts in an attempt to identify the weather/sulfate association. Once again, 24-hour averaged sulfate values presented problems. During the spring period, weather systems are usually rapid moving and may travel a thousand or so miles in a day. Some sort of daily average weather chart would be most appropriate for comparison with the sulfate data. It was decided that the 12 GMT surface chart be used as this was readily available, and the time roughly representative of the middle of the 24-hour sulfate sampling period.

The prior review of sulfate formation chemistry (Table 1) led to the hypothesis that sulfate concentrations might be correlated to sunshine, humidity and temperature. As the 39 cases of weather/sulfate patterns were examined, however, it became apparent that there were no well-defined weather features consistently associated with either low or high values of sulfates. Apparent correlations on one map were contradicted on another. Figures 7 and 8 are examples. In these figures, sulfate values are plotted as deviations from the seasonal mean to the nearest whole $\mu g/m^3$. Values of $\pm$ 1 $\mu g/m^3$ are not plotted since they may not be significantly different from zero.

In Figure 7a, large positive values over the Carolinas and Virginia are correlated to cloudy skies and warm temperatures. In Figure 7b, large positive values over the same geographical area are related instead to mostly clear skies and near freezing temperatures. Figure 7a shows large negative values over Nebraska and Kansas correlated to nearly clear skies and warm temperatures whereas Figure 7b relates large negative values to cloudier skies and sub-freezing temperatures.

In Figure 8a, large positive values over the southeastern United States are associated with a high pressure system off the South Carolina coast. In Figure 8b a similar high pressure system is related to large negative values in the same geographical area. In contrast, positive values are located near the low pressure center over Iowa on that same map.

Sulfate Variability and Transport

Some higher frequency data were available from special studies, and would prove valuable in checking the nebulous weather/sulfate associations discussed above. Data taken every 2-3 days at St. Louis, Houston, and Washington in connection with the EPA's Continuous Air Monitoring Program (CAMP) were also examined. Inspection of these data again indicated no definitive relationship of sulfate concentration with temperature, relative humidity or cloud cover. However, significant insight into the transport aspects of the sulfate problem were revealed.

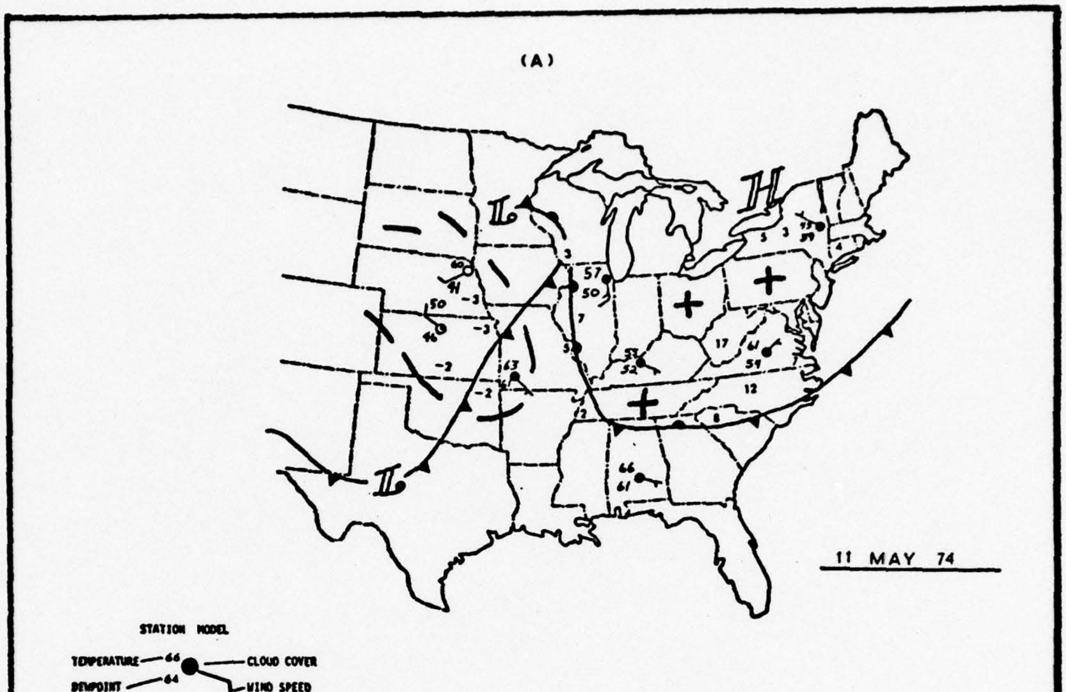

Figure 7. Patterns of synoptic weather (12GMT) and sulfate concentration. Sulfate concentrations are expressed as deviations from the seasonal mean. Only deviations greater than 1 μg/m^3 are plotted.

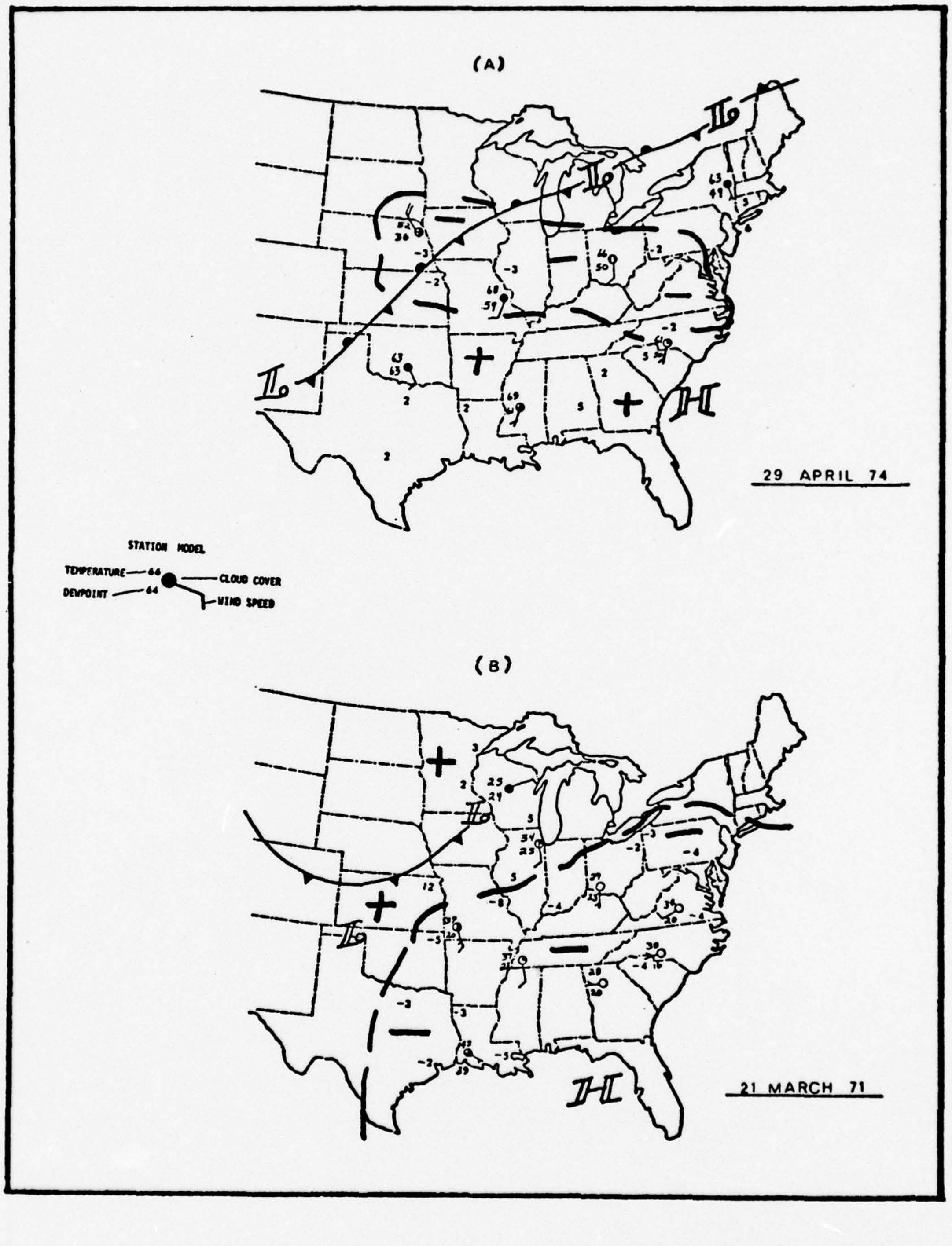

Figure 8. Patterns of synoptic weather (12GMT) and sulfate concentration. Sulfate concentrations are expressed as deviations from the seasonal mean. Only deviations greater than 1 μg/m^3 are plotted.

The 1969 data at St. Louis were stratified by wind direction with a class interval of 10 degrees. It was then noted that sulfate values more than one standard deviation away from the seasonal mean were very highly correlated with wind direction.

The wind data were then analyzed for persistence. Persistence is defined by the following equation (Panofsky and Brier, 1968).

$$\text{PERSISTENCE} = \frac{\text{Speed of the Resultant Wind}}{\text{Mean Wind Speed}} \times 100\%$$

A high persistence indicates that the wind direction is nearly constant, a low persistence indicates that wind direction is variable. Even with the rather severe 85% persistence criteria, a sizable number of data points remained. Those days on which the wind was at least 85% persistent for the 24-hour sampling period had their average sulfate values in each wind direction determined. The resulting averages were plotted as a smoothed graph, using a five-point moving average (Figure 9). Considerable variability is shown and a strong relationship to wind direction implied.

The location of local point sources that might produce precursor agents are shown at the wind direction corresponding to their direction from the sulfate measurement site. High sulfate values are strikingly related to fetches with upwind point sources; low sulfate values to fetches with no nearby point sources.

Regional transports are also reflected in the figure. High sulfate values are mainly related to wind directions with an easterly component. Low sulfate values are generally found with westerly winds. Comparison with the spatial distribution of the annual mean sulfate concentrations,

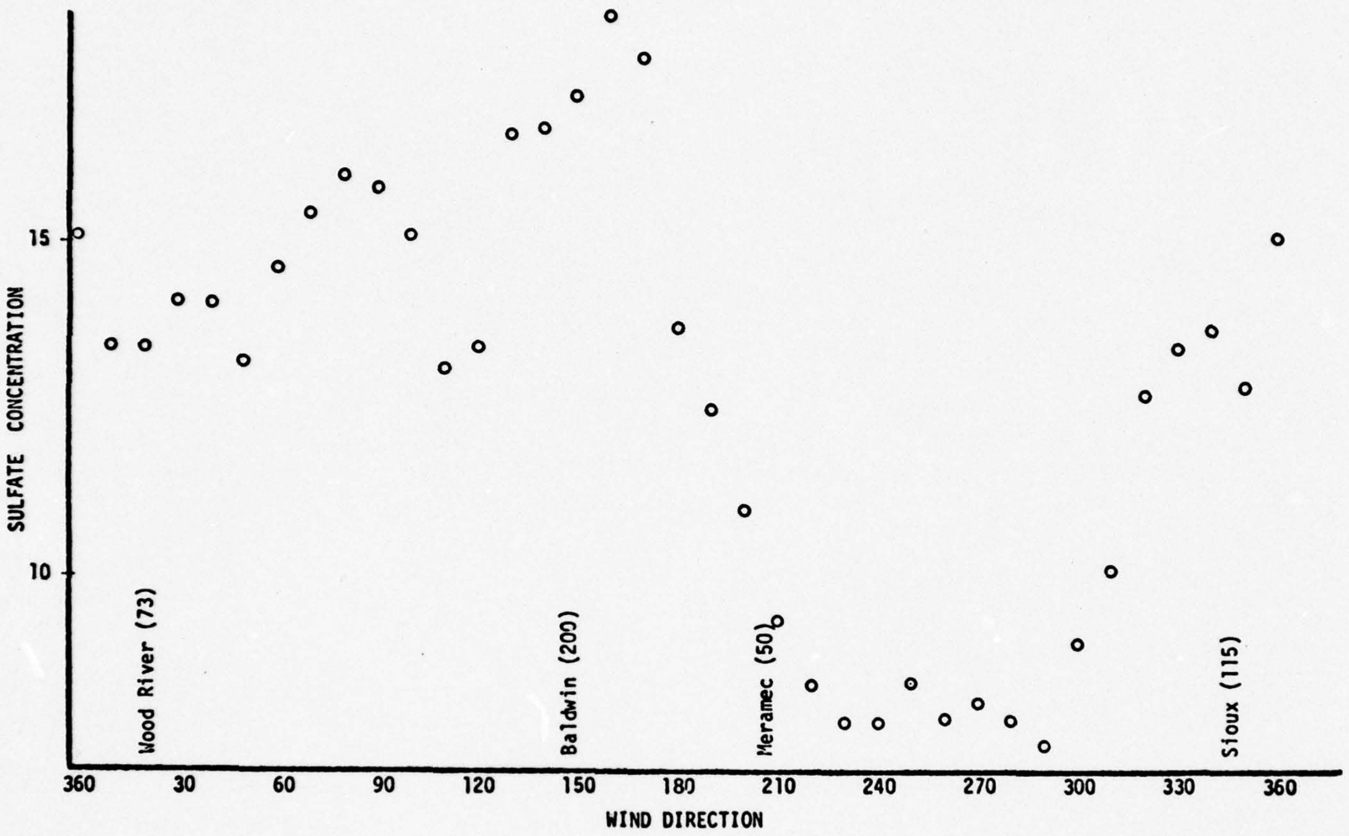

Figure 9. Sulfate concentration (μg/m^3) versus wind direction at St. Louis, MO, January-December 1969. The concentrations shown are 5-point running averages for those days with wind persistence ≥ 85 per cent. Annual SO_2 emissions in 1000 tn/yr (in parentheses) are noted with source name.

Figure 6, confirms that regional transport of sulfates would result in just such a pattern.

While examining another period (April 1975-March 1976) of St. Louis high frequency data, it was noted that the generally low sulfate values from 220^{o}-270^{o} directions in Figure 9 were replaced by quite high values. Examination of sulfate sources for this latter period showed that a new power plant (Labadie) had been built and placed into operation in 1970. By 1975 this plant was producing in excess of 300 thousand tons of sulfur dioxide emissions per year. Although the data are too sparse to say that the new power plant was responsible for the higher sulfate values, it is strongly implied. The data for the 12-month period, April 1975-March 1976, was analyzed in the same manner as the 1969 data and is presented in Figure 10.

Both of these figures tend to confirm the requirement of an aging time or transport distance prior to significant sulfate formation (Wilson _et al_., 1977). The Mermec power plant, shown on these figures at near 210^{o}, produces a significant amount of emissions, yet does not appear to affect the sulfate level. Its relatively nearby location to the sampling site (17 miles from the 1969 sampling site and 15 miles from the 1975-76 site) is suggested as a reasonable explanation for this apparent discrepancy, and as confirmation of the requirement for a minimum aging time/distance. Table 2 provides emission levels and directional information for major SO_2 point sources.

Visibility has been strongly linked to sulfate concentrations. The variation of sulfate values with wind direction should also be indicated in the visibility curves for St. Louis if such a visibility/sulfate relationship exists.

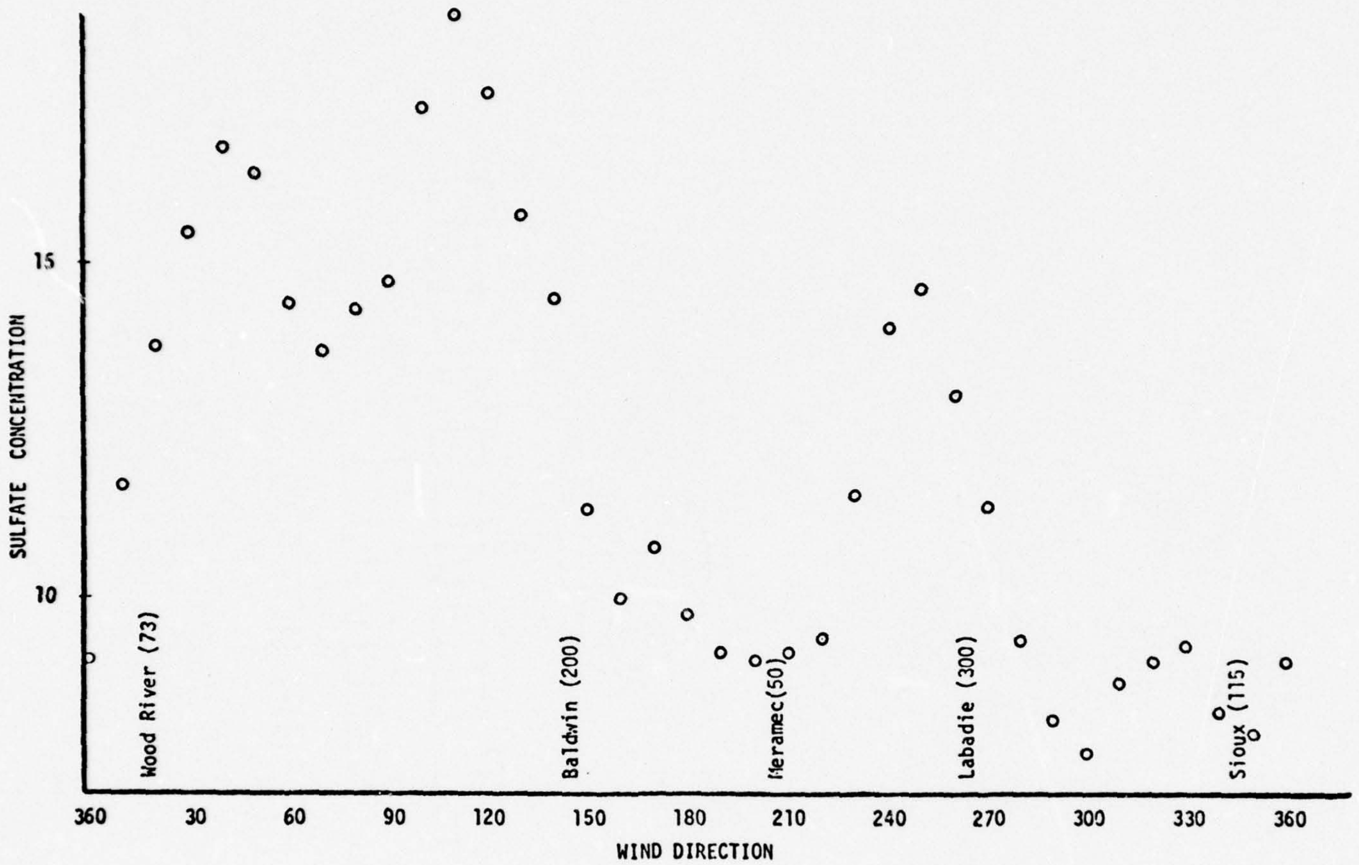

Figure 10. Sulfate concentrations ($\mu g/m^3$) versus wind direction at St. Louis, MO, April 1975-March 1976. The concentrations shown are 5-point running averages for those days with wind persistence $\geq$ 85 per cent. Annual SO_2 emissions in 1000 tn/yr (in parentheses) are noted with source name.

Table 2. SO_2 point sources, emission levels, directions and distances from various observation sites near St. Louis, Missouri.

SO_2 Point source	Emission level (1000 tn/yr)	Direction (degrees)/Distance (miles) from observation site		
		Airport (wind and visibility)	12th Street (1969 sulfate data)	Site 105 (1975-76 sulfate data)
Sioux	115	19/12	345/21	347/23
Wood River	73	57/15	12/17	13/19
Baldwin	200	145/46	148/34	146/33
Meramec	50	178/26	208/17	208/15
Labadie	300	243/31	Not operating in 1969	265/34

Foster (1978) obtained averaged daytime visibility curves for several cities. His directionally stratified visibility curve for St. Louis is presented in Figure 11 along with the location of point sources for comparison with Figures 9 and 10. Note that the visibility and sulfate observation sites are not the same thus placing source locations differently in Figure 11.

The coincidence of lower visibilities with easterly winds and higher visibilities with westerly winds is prominent. In addition, the correlation with local point sources is also striking. Interestingly, even the aging requirement appears to be evident. The Souix power plant, correlated with good visibility, is only 12 miles distant from the observation point, whereas the Mermec power plant is 26 miles distant and may be expected to have greater influence.

The strong effect of wind direction upon St. Louis sulfate values led to a reanalysis of the previously discussed weather/sulfate charts. Analysis of local sources was not feasible due to lack of sufficiently detailed information, however, the broader, regional effects were examined. Figure 6, which shows the distribution of annual average sulfate concentrations, was used as a reasonably representative regional pattern. Although trajectories are most correct for examining transport, a simpler qualitative examination using surface wind directions and mean winds of 10-20 knots to imply transport was conducted to examine the effects of transport.

Figure 12a shows transport of high sulfate values from the regionally polluted area of New York-New Jersey into the cleaner Carolina region. The positive values in Tennessee and Wisconsin could be explained in the same way. In contrast, negative values over Nebraska and Kansas are

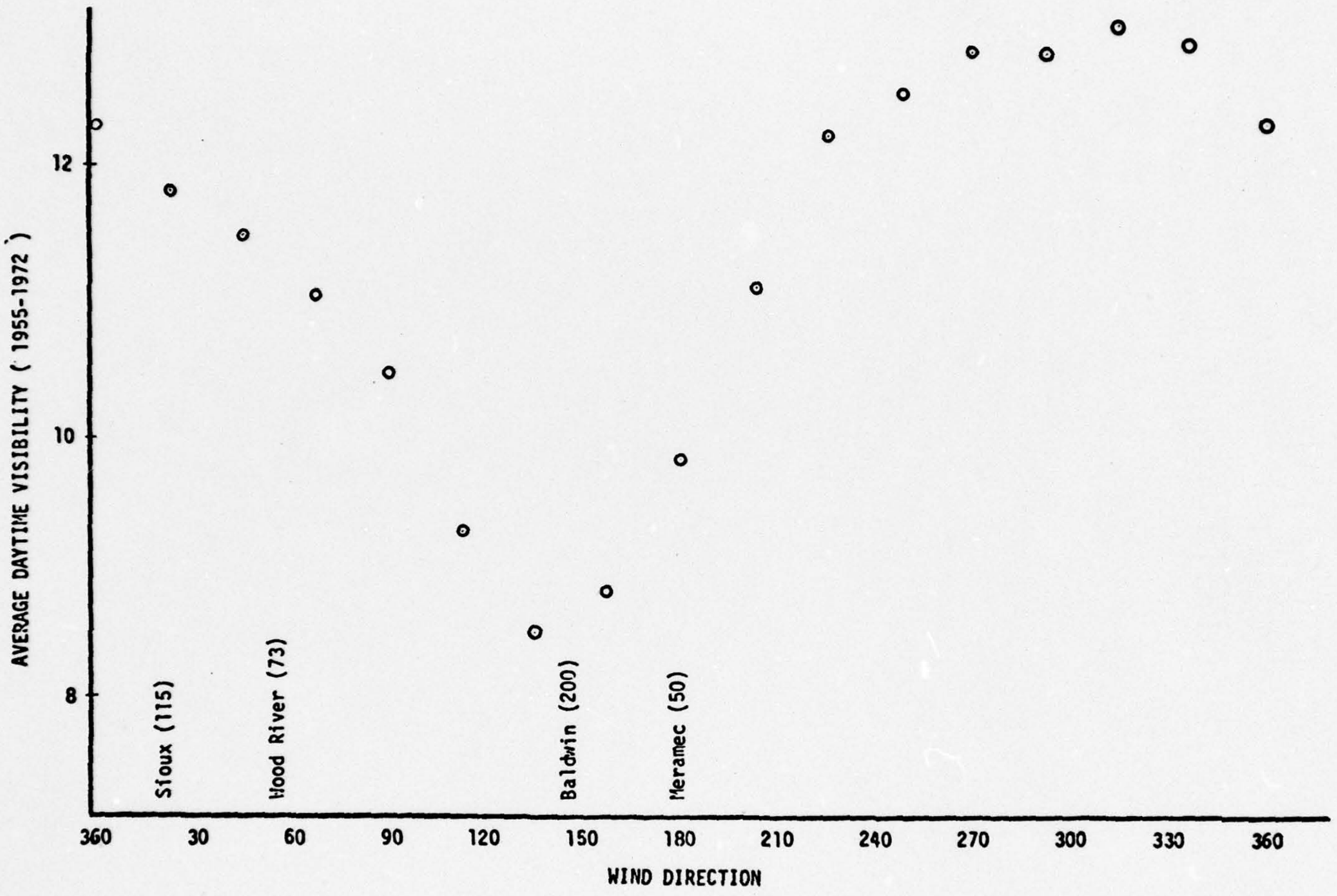

Figure 11. Average daytime visibility (miles) versus wind direction at St. Louis, MO. Annual SO_2 emissions in 1000 tn/yr (in parentheses) are noted with the source name (after Foster, 1978).

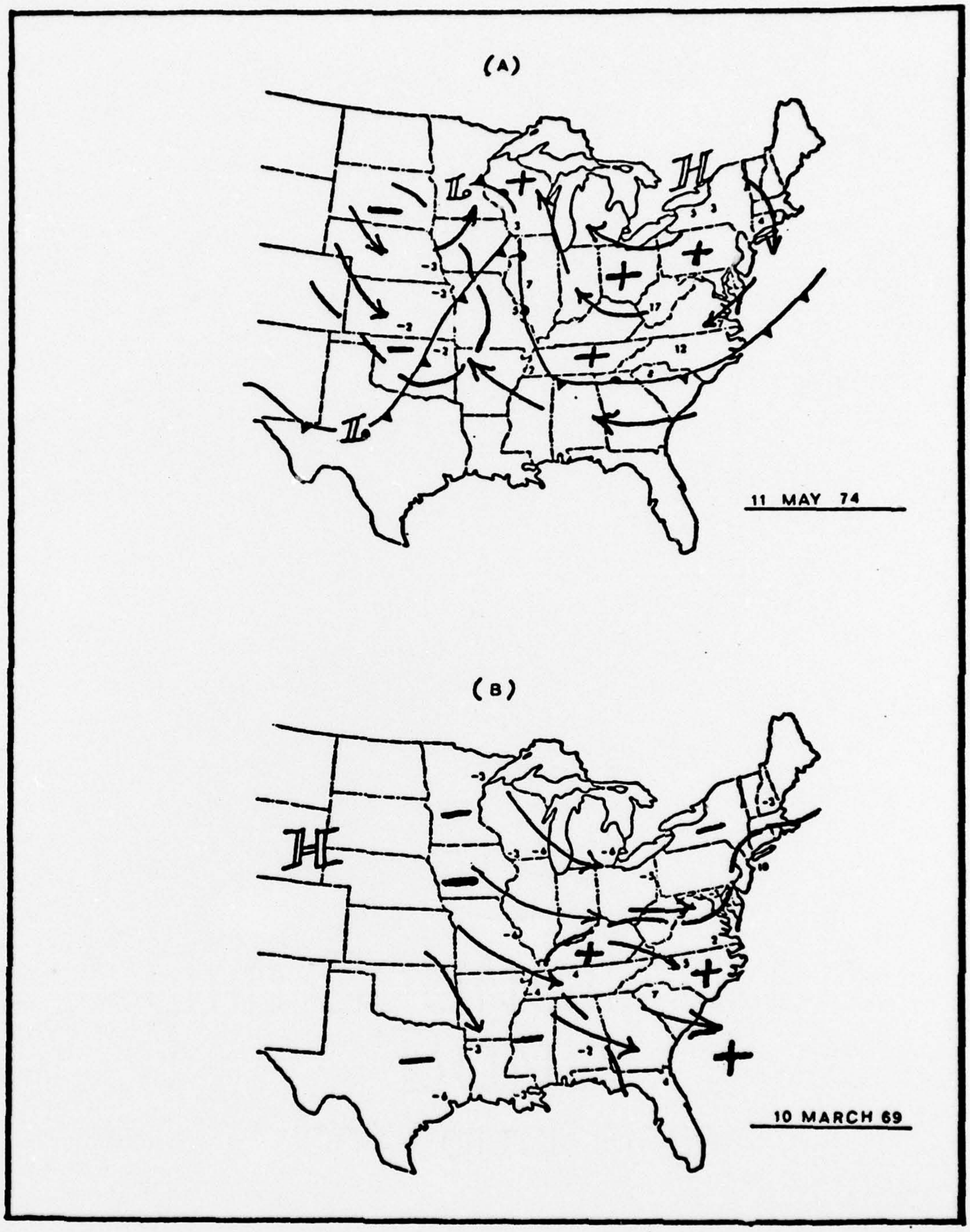

Figure 12. Patterns of synoptic weather (12GMT) and sulfate concentrations. Streamlines (arrows) suggest sulfate transport. Synoptic stations are the same as in Figure 7, but have been omitted for figure clarity.

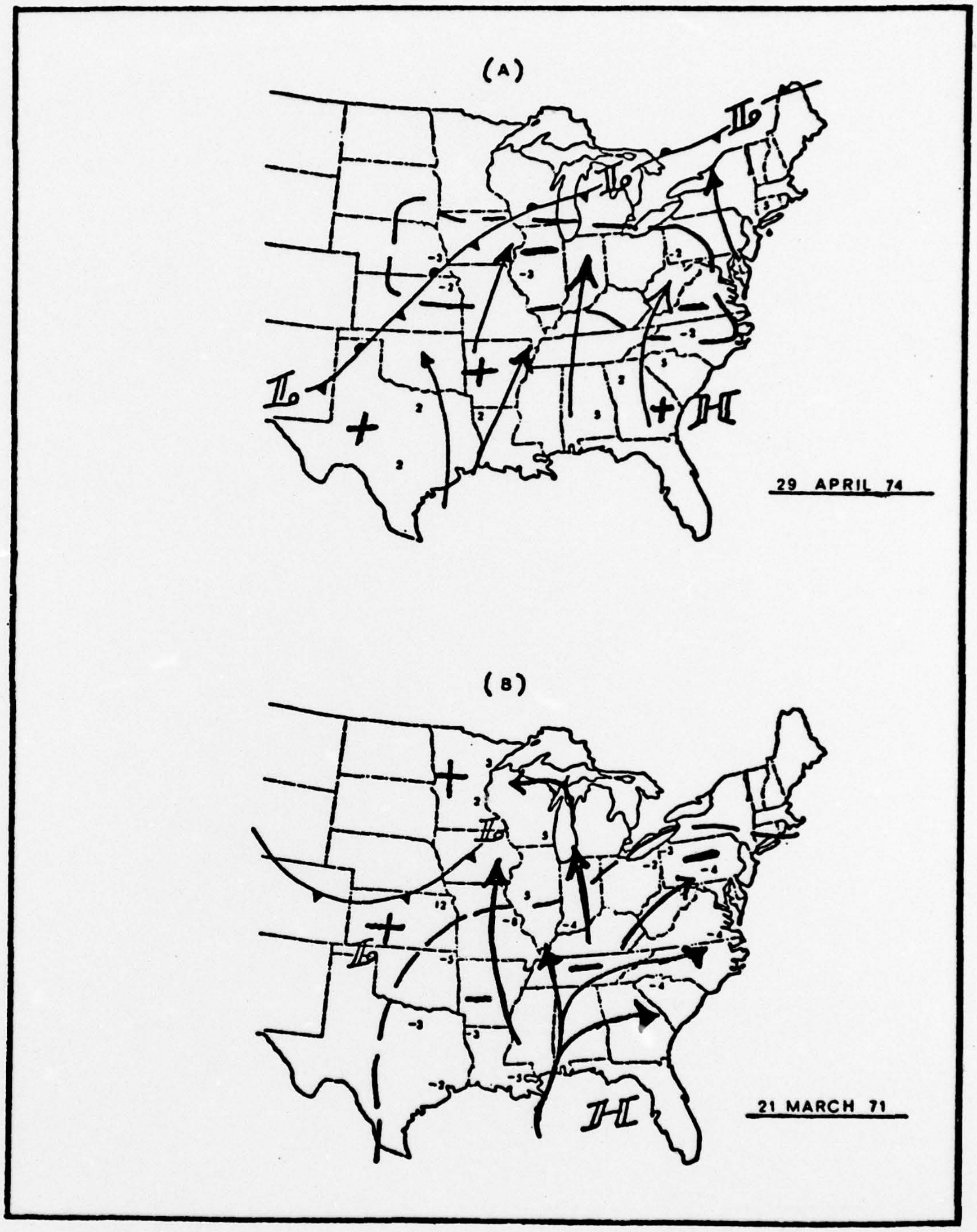

Figure 13. Patterns of synoptic weather (12GMT) and sulfate concentrations. Streamlines (arrows) suggest sulfate transport. Synoptic stations are the same as in Figure 8, but have been omitted for figure clarity.

indicated to be associated with transport from the cleaner Plains areas. Figure 12b also shows the Carolinas receiving transported high values from the more polluted Ohio Valley region. Large negative values are again associated with transport from the cleaner western areas.

Figure 13a depicts a large high pressure system with generally southerly winds across the eastern United States. The negative values in Pennsylvania and Illinois could be explained by the transport of relatively cleaner air from the southeastern United States. Figure 13b is similar to the last although more variability in the winds are evidenced. Negative values can again be explained by transport of cleaner air masses into the normally high sulfate concentration areas. The positive values in Minnesota and Wisconsin can likewise be explained since a shift in the concentration patterns would move the highest values over that region.

Thus the geographical distribution of sulfate sources together with large scale wind patterns combine to explain most of the synoptic-scale sulfate variability uncovered in this report.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

This study has arrived at a number of conclusions. Some conclusions must be considered tentative due to the marginally acceptable sulfate data presently available. Future researchers, utilizing data of better quality and quantity, may be able to determine whether these conclusions remain valid.

When sulfate values are represented as deviations from seasonal means and plotted on maps, synoptic-scale patterns emerge. Although expected correlations with temperature, moisture, and sunshine were not clearly evident, these are still thought to exist. Apparently, such relationships are overshadowed by sulfate transport which seems to explain most of the synoptic scale variability.

The importance of sulfate transport was most readily demonstrated at St. Louis, Missouri where sufficient data were available and sources of sulfate or precursor agents are nonuniformly distributed around the horizon. Similar results were apparent at other stations with relatively high frequency observations. Recognition of the dominance of the transport process led to a re-examination of previously puzzling sulfate distributions in which no obvious correlation with other meteorological variables was evident. Reinterpretation of these distributions in terms of regional sulfate distribution and wind circulation convincingly demonstrates the primary role of long-range transport. This confirms and strengthens the conclusions of Spirtas and Levin (1970).

The strength of the sulfate source/wind relationship can be expected to depend on the general sulfate environment of a station. Stations in a rather extensive area of more or less uniform sulfate background might show less variability with wind direction than, say St. Louis. Such a station might allow the unmasking of relationships with other meteorological variables.

Some complications to any interpretation of sulfate variability include such local effects as terrain and proximity to water bodies. For example, Lyons (1977) showed that large bodies of water can affect low-level atmospheric stability which in turn produces unexpected pollution problems. Additional problems can occur in analyzing sulfate pollution near the sea since sea salt nuclei are often sulfate crystals.

Because large scale sulfate concentrations depend upon wind direction, annual means, interannual trends, and inferences about intrinsic sulfate variability based on such data (Frank, 1974) should be reevaluated. The present monitoring network with 12 or so days between measurements may not be adequate to remove through averaging preferential wind directions which in turn may bias the derived annual mean. Furthermore, such means may be expected to vary from year to year because of shifting storm tracks and flow patterns associated with the planet's general circulation.

The results of this study suggest topics for further research. In some instances these new efforts may not be practicable without an improved sulfate sampling network or firmer knowledge of sulfate chemistry.

The direct measurement of sulfate concentration needs to be performed as a separate sampling process, not merely as a by-product of the total particulate evaluation. A separate sampling method for sulfate would eliminate much of the systematic error incurred by artifact production on the intake filter in the presence of other pollutants. Furthermore, the laboratory analysis would be simpler and more reliable if it were not first necessary to separate sulfates from the mixture of various substances. If and when this improvement becomes available shorter sampling periods and more frequent observations would be justified. Such data would help resolve some of the weather/sulfate relationships suspected but not detected in this study.

Research into appropriate ways of filtering out the influence of wind direction in annual means and variability is needed if underlying variations due to source effluxes are to be determined. This might be accomplished by taking into account changes in annual wind roses and significant changes in regional sulfate sources. These filtered data would aid the Environmental Protection Agency in establishing meaningful sulfate standards, as well as providing data that could be subjected to analysis for relationships with other meteorological variables.

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APPENDIX

Appendix. Stations location index.

City and SAROAD No.	Abbreviation* used in study	Data used from years (X)					
		1969	1970	1971	1972	1973	1974
Montgomery, AL 012460001A01	MGM	X	X		X		X
Hartford, CT 070420001A01	HFD	X	X	X	X	X	X
Jacksonville, FL 101960002A01	JAX	X	X		X	X	
Atlanta, GA 110200001A01	ATL	X	X		X	X	X
Chicago, IL 142200001A01	ORD	X	X	X	X		
Springfield, IL 147280001A01	SPI	X	X	X	X		X
Evansville, IN 151300001A01	EVV	X	X	X	X		
Des Moines, IA 161180001A01	DSM	X	X	X	X	X	X
Topeka, KS 173560001A01	TOP	X	X	X	X		X
Wichita, KS 173740001A01	ICT	X	X	X		X	X
New Orleans, LA 192020002A01	MSY	X	X	X	X		
Shreveport, LA 192740001A01	SHV	X	X	X	X		X
Baltimore, MD 210120001A01	BAL	X	X		X	X	
Worchester, MA 222640001A01	ORH	X	X	X	X		

Appendix (Continued).

City and SAROAD No.	Abbreviation* used in study	Data used from years (X)					
		1969	1970	1971	1972	1973	1974
Detroit, MI 231180001A01	DET	X	X	X	X		
Duluth, MN 241040001A01	DLH	X	X	X	X		X
Minneapolis, MN 242260001A01	MSP	X	X	X	X		
St. Louis, MO 264280001A01	STL	X		X	X	X	X
Omaha, NE 281880001A01	OMA	X	X	X	X	X	X
Concord, NH 300120001A01	CON	X	X	X	X		
New York, NY 334680001A01	JFK	X	X		X	X	X
Rochester, NY 335760001A01	ROC	X	X	X	X		X
Syracuse, NY 336620001A01	SYR	X	X	X	X		X
Greensboro, NC 341740001A01	GSO	X	X		X	X	X
Cincinnati, OH 361220001A01	LUK	X	X	X	X		
Youngstown, OH 367760001A01	YNG	X	X	X	X		
Tulsa, OK 373000001A01	TUL	X	X	X		X	X
Erie, PA 393060002A01	ERI	X	X	X	X	X	

Appendix (Continued).

City and SAROAD No.	Abbreviation* used in study	1969	1970	1971	1972	1973	1974
Harrisburg, PA 39388001A01	HAR	X	X	X	X		
Pittsburgh, PA 397140001A01	PIT		X		X	X	X
Providence, RI 410300001A01	PVD	X	X	X	X		
Memphis, TN 442340001A01	MEM	X	X		X	X	X
Nashville, TN 442540001A01	BNA	X	X		X	X	
Ft. Worth, TX 451880001A01	FTW	X	X	X	X	X	X
Houston, TX 452560001A01	HOU	X	X	X	X	X	X
San Antonio, TX 454710001A01	SAT	X	X	X	X		X
Norfolk, VA 48214001A01	ORF	X	X	X	X	X	X
Charleston, WV 500280001A01	CRW	X	X	X	X	X	X
Madison, WI 511860001A01	MSN	X	X	X	X		X
Milwaukee, WI 512200001A01	MKE	X	X	X	X		

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* The station abbreviations have been used by the author to aid in plotting synoptic and sulfate data. Sulfate sampling sites are not collocated with synoptic weather observation sites.