Environmental Health Perspectives
Vol. 79, pp. 15-34, 1989

Acidic Sulfate Aerosols: Characterization and Exposure

by Paul J. Lioy* and Jed M. Waldman*

Exposures to acidic aerosol in the atmosphere are calculated from data reported in the scientific literature. The majority of date was not derived from studies necessarily designed to examine human exposures. Most of the studies were designed to investigate the characteristics of the atmosphere. However, the measurements were useful in defining two potential exposure situations: regional stagnation and transport conditions and local plume impacts.

Levels of acidic aerosol in excess of 20 to 40 $\mu g/m^3$ (as H_2SO_4) have been observed for time durations ranging from 1 to 12 hr. These were associated with high, but not necessarily the highest, atmospheric SO_4^{2-} levels. Exposures of 100 to 900 $\mu g/m^3$/hr were calculated for the acid events that were monitored. In contrast, earlier London studies indicated that apparent acidity in excess of 100 $\mu g/m^3$ (as H_2SO_4) was present in the atmosphere, and exposures < 2000 $\mu g/m^3$/hr were possible.

Our present knowledge about the frequency, magnitude, and duration of acidic sulfate aerosol events and episodes is insufficient. Efforts must be made to gather more data, but these should be done in such a way that evaluation of human exposure is the focus of the research. In addition, further data are required on the mechanisms of formation of H_2SO_4 and on what factors can be used to predict acidic sulfate episodes.

Introduction

Animal and human exposure studies in the laboratory indicate that acidic sulfate particles will produce functional changes in the respiratory tract at levels well below lethal ones (*1*). Although the bulk of toxicological data on acidic aerosols involves sulfuric acid (H_2SO_4) or bisulfate (HSO_4^-) particles, the available evidence indicates that the observed irritant responses are likely due to hydrogen ion (H^+) rather than to sulfate (*2*).

The information available on the concentration patterns and human exposure to atmospheric acidic aerosol is meager. Many of the available studies were not designed to measure human exposure but rather were part of a program of research directed at characterizing the ambient atmosphere. Nonetheless, the information is useful for pointing out directions for future work, as well as for estimating the exposure to acidic species for specific conditions. This paper attempts to summarize the data available on acidic aerosol species with special emphasis on acid events. It also includes an analysis of measurement methods used in the reported studies.

Because the occurrences of acidic aerosols are linked to precursor emissions [sulfur dioxide (SO_2) and nitrogen oxides (NO_x)], oxidation, and neutralization, we have included discussions of these factors. In addition, London and California fog data are discussed to provide historical and regional contexts for the data base of largely eastern United States acidic sulfate aerosol measurements.

Despite the toxicological data, there is no epidemiological evidence clearly linking acidic aerosols acting alone with adverse health effects in humans. The body of available research suggests that there is a likely association, but studies aimed at ascertaining this association have been strapped by limited field data. Moreover, more research is needed to satisfactorily resolve the extent that community health is affected by episodic and chronic acidic aerosol exposures.

Methods for Acidic Aerosol Measurement

Because there is no reference method for acidic sulfate species, a major area of concern is the multitude of techniques that have been used to detect various acidic species in the environment. Measurements are generally made by aerosol collection on filters with subsequent analysis or continuous analysis with a real-time detector. From an exposure assessment

---

*Exposure Measurement and Assessment Division, Department of Environmental and Community Medicine, University of Medicine and Dentistry of New Jersey, Robert Wood Johnson Medical School, 675 Hoes Lane, Piscataway, NJ 08854.

standpoint, continuous data offer few advantages to short duration (1–8 hr) filter intervals, although the continuous data allow assembly of any desired integrated-sample schedule. The detection of acidic sulfur species has usually resulted in data being available in one of two forms: the compound H_2SO_4 or the strong acid (free or titratable), H^+. There are no techniques available to exclusively detect the intermediate acid species, ammonium bisulfate, although there have been a few attempts to calculate the ammonium bisulfate concentration in the field (*3–5*).

Filter Collection

Thermal Volatilization. Thermal volatilization schemes were popular for several years for speciation of acidic sulfate compounds in aerosols. Filter samples were heated and H_2SO_4 collected by microdiffusion (*6,7*) or determined directly by flame photometry after volatilization from Teflon filters (*8,9*). In one method, H_2SO_4 was distinguished from other volatile sulfates [e.g., ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$)] and nonvolatile sulfates [e.g., sodium sulfate (Na_2SO_4) by heating consecutively at two different temperatures (*10*). In another technique, 2-perimidinylammonium sulfate is formed from acidic sulfates and thermally decomposed to SO_2 for West-Gaeke analysis (*11*). Due to recovery problems and limited success in distinguishing NH_4HSO_4 and $(NH_4)_2SO_4$ from each other, thermal volatilization from filter samples have fallen into disfavor in recent years. Nonetheless, coupled with a heated denuder system, it is the basis of the continuous H_2SO_4 measurements using real-time flame photometric detectors (see next section).

Filter Extraction with pH Measurement or Titration. Filter samples may be analyzed for strong acid content by extraction into water or dilute mineral acid. The extracted free acid content may be determined by simple measurement of pH and, in the absence of weak acids, equated to the amount of strong acid originally present in the sample. However, this determination can be in error because of the potential presence of buffering agents such as weak carboxylic acids or hydrated forms of heavy metal ions, e.g., Fe(III) and Al(III) (*12,13*). A titration procedure for strong acid based on the Gran titration (*13*) and perfected by Brosset and Ferm (*14*) has been used widely (*15*). Coulometric generation of strong base for Gran titrations has also been used [e.g., Tanner et al. (*16*)]. Dissolution of filter samples in a 0.05 to 0.10 μM mineral acid solution followed by Gran titration with correction for blank allows for titration of micromolar levels of strong acid with precision and accuracy better than ± 10% (*16,17*). All samples must be protected against ammonia.

Filter Extraction with Specific Analysis of Sulfuric Acid. Most efforts in specific extraction of atmospheric acids has been related to H_2SO_4. Benzaldehyde has been shown to be specific for H_2SO_4 in dried acidic aerosol sulfate/nitrate samples with analysis for sulfate in aqueous back-extracts (*10*). Several methods for derivativization of collected H_2SO_4 aerosol have been proposed (*18,19*) but these suffer from interference by sulfate salts. The use of specific extractant methodologies has decreased in recent years in favor of generic strong acid determinations.

Continuous Analysis

H_2SO_4 may be determined using a continuous flame photometric detector (FPD) with a diffusion denuder tube for SO_2 and H_2SO_4 removal attached before the FPD. The temperature of the denuder tube or a zone just upstream from it is cycled between about 20°C and 120°C. At the lower temperature, H_2SO_4 remains in the aerosol phase, but at 120°C it is volatilized and removed as the air flows through the denuder tube. The difference in response at the two temperatures represents ambient H_2SO_4 levels (*20–22*). The minimum cycle time and, hence, time resolution for the technique, is about 6 to 8 min (*23,24*). Sensitivity is found to be enhanced by using sulfur hexafluoride-doped hydrogen gas (*25*).

Acidic sulfates including H_2SO_4 may also be continuously analyzed using the humidograph techniques of Charlson et al. (*26*) or thermidograph variations developed more recently (*27,28*). The latter technique involves heating the aerosol-containing air stream progressively from 20°C to 380°C in 5-min cycles, rapidly cooling it to the dry bulb temperature and measuring the light scattering at 65 to 70% relative humidity with a nephelometer. By comparing this output with the thermidograms of test aerosols, the fractional acidity can be measured and approximate level of H_2SO_4 determined.

Sampling Anomalies

Sampling anomalies have plagued the measurement technologies described previously and generally fall into two classes: reversible or irreversible sorption losses onto filter materials or sampling lines; and equilibrium-driven loss or gain of species due to nonsteady-state conditions in the sampled atmosphere over the time period of the measurement.

Sorption Losses. Studies of sorption losses on filters have centered on three major areas. One area is the loss of strong acid in aerosol particles by reaction with basic sites in the filter matrix used to collect the particles (*29*). Depth-filter matrices used for high-volume samples, in particular glass-fiber filters, are unsuitable for collection of acidic aerosol particles (*16,30,31*). This is true even if glass fiber filters are pretreated with acid and fired to a high temperature, as subsequent rinsing produces additional free basis sites in the glass (*16*). However, high-purity quartz filters can be pretreated to remove basic sites for high-volume samples. Treated quartz and Teflon filter media are generally inert with respect to acidic particles and have replaced glass fiber and cellulose filters for sampling acidic aerosols by high-volume and low-volume techniques, respectively.

Avoiding the use of glass-fiber filters also eliminates a positive source of error in sulfate measurements: The artifact sulfate formed by base-catalyzed oxidation of SO_2 sorbed on the filter surface to form H_2SO_4 (*32*). While the acid formed on reactive filter surfaces is neutralized, the residual sulfate remains and can lead to a substantial measurement bias.

A third problem is the loss of strong acid contents by reactions between co-collected basic and acidic particles on the filter surface. This most frequently occurs as the result of coarse (> 2.5 μm), alkaline, soil-derived particles interacting with fine (< 2.5 μm), acidic sulfate particles (*33,34*). This problem can be eliminated by using a coarse particle preseparator (e.g., a cyclone or impactor inlet). Alternatively, sampling for shorter time durations, in most ambient environments for 4 hr or less, results in low enough surface coverage to prevent topochemical reactions. However, this does not prevent subsequent neutralization during extraction procedure.

Equilibria-Driven Losses. Equilibria involving gas- and particulate-phase species may lead to errors in sampling strong acids, as well as other species in the atmosphere, both under steady-state and nonsteady-state conditions. Thermodynamic considerations suggest that aerosol sulfate/H_2SO_4 mixtures should be in equilibrium with atmospheric ammonia (NH_3) (*35*). NH_3 is the principal neutralizing agent H_2SO_4, and the equilibrium level of NH_3 for even slightly acidic sulfate is much below average ambient NH_3 levels (*36*). Hence, acidic aerosol on filter membranes are subject to neutralization if NH_3 ammonia-laden air is sampled later in the same interval. Another equilibrium-driven filter sampling artifact is the coupled volatility of NH_3 and nitric acid (HNO_3) when ammonium nitrate (NH_4NO_3) is collected with acidic sulfate aerosol (*37*). Denuders are used to scavenge neutralizing species.

Regional Patterns of Precursor Emissions and Aerosol Concentrations

Oxides of Sulfur and Nitrogen

For the eastern United States (EUS), the distribution of SO_2 emissions are highest in the area within the Ohio Valley from the Mississippi River through southwestern Pennsylvania (Fig. 1*A*). Other locales with significant emissions that surround this core area include rural and urban centers. In contrast, the NO_x emissions are centered in the major urban areas of metropolitan New York-New Jersey-Connecticut, Chicago, and Detroit (Fig. 1*B*). However, it can be seen that the distribution of NO_x is more ubiquitous throughout the EUS.

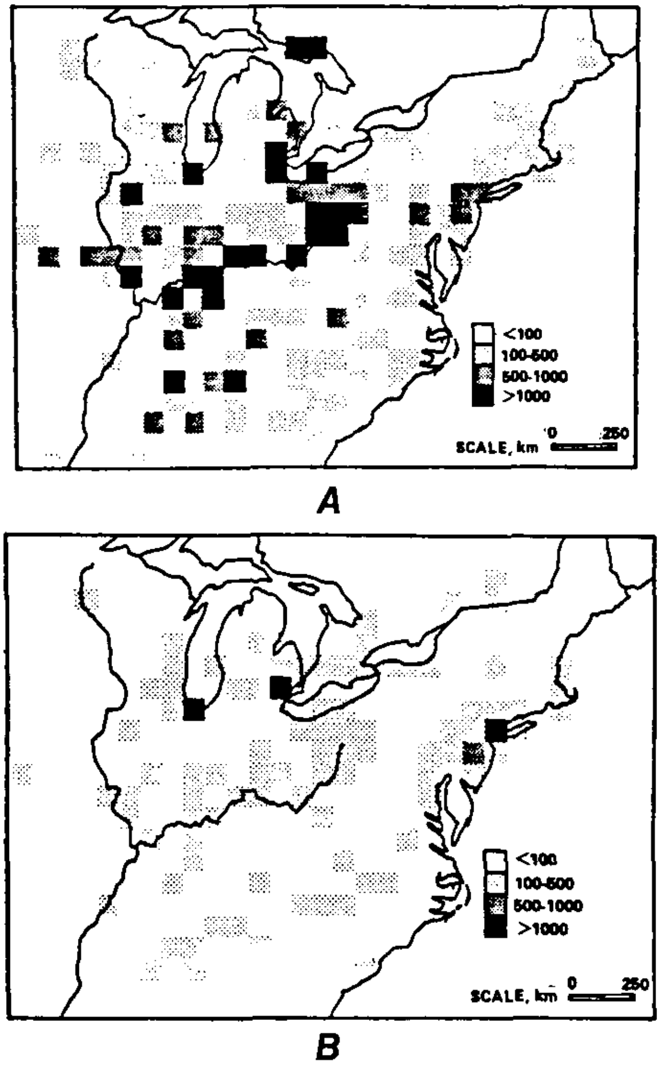


FIGURE 1. Distribution of (*A*) SO_2 emissions and (*B*) NO_x emissions in the SURE area for summer (metric tons/day). Emissions are based on data representative of 1977. From Mueller et al. (*39*).

In the western half of the nation, SO_2 emissions are centered around more isolated, large stationary sources such as smelters. The NO_x emission in the west are distributed much more broadly. The actual emission densities tend to be much lower than in the east, except in the southern and central California urban centers.

Sulfate

While the toxicological data suggest that the SO_4^{2-} is not the biologically active portion of particulate sulfate species (*38*), it has been used as an indicator pollutant in many health studies. In addition, SO_4^{2-} is relatively easy to measure and is a major constituent in the ambient aerosol. Therefore, many studies and monitoring programs have routinely provided data on the SO_4^{2-} ion, and a large data base exists.

However, the presence of high sulfate does not necessarily indicate the presence of a high acidic component in the sulfate aerosol. Knowledge of its distribution, nonetheless, gives some indication of the possible spatial extent of acidic sulfate in the worst possible case (i.e., little neutralization). Figure 2 shows the monthly average SO_4^{2-} concentrations measured in the EUS during the sulfate regional experiment (SURE) project (*39*). The peak values recorded in SURE reached in excess of 25 μg/m^3 during the summer. Lesser peak values were recorded during the winter with the seasonally highest concentrations shifting to the southeast. The data also indicate that a substantial portion of the EUS experienced average sulfate above 8 μg/m^3.

The regional relationship between SO_4^{2-} and SO_2 at the SURE monitoring sites was examined using the ratio of sulfate to total sulfur (SO_4^{2-} plus SO_2). The

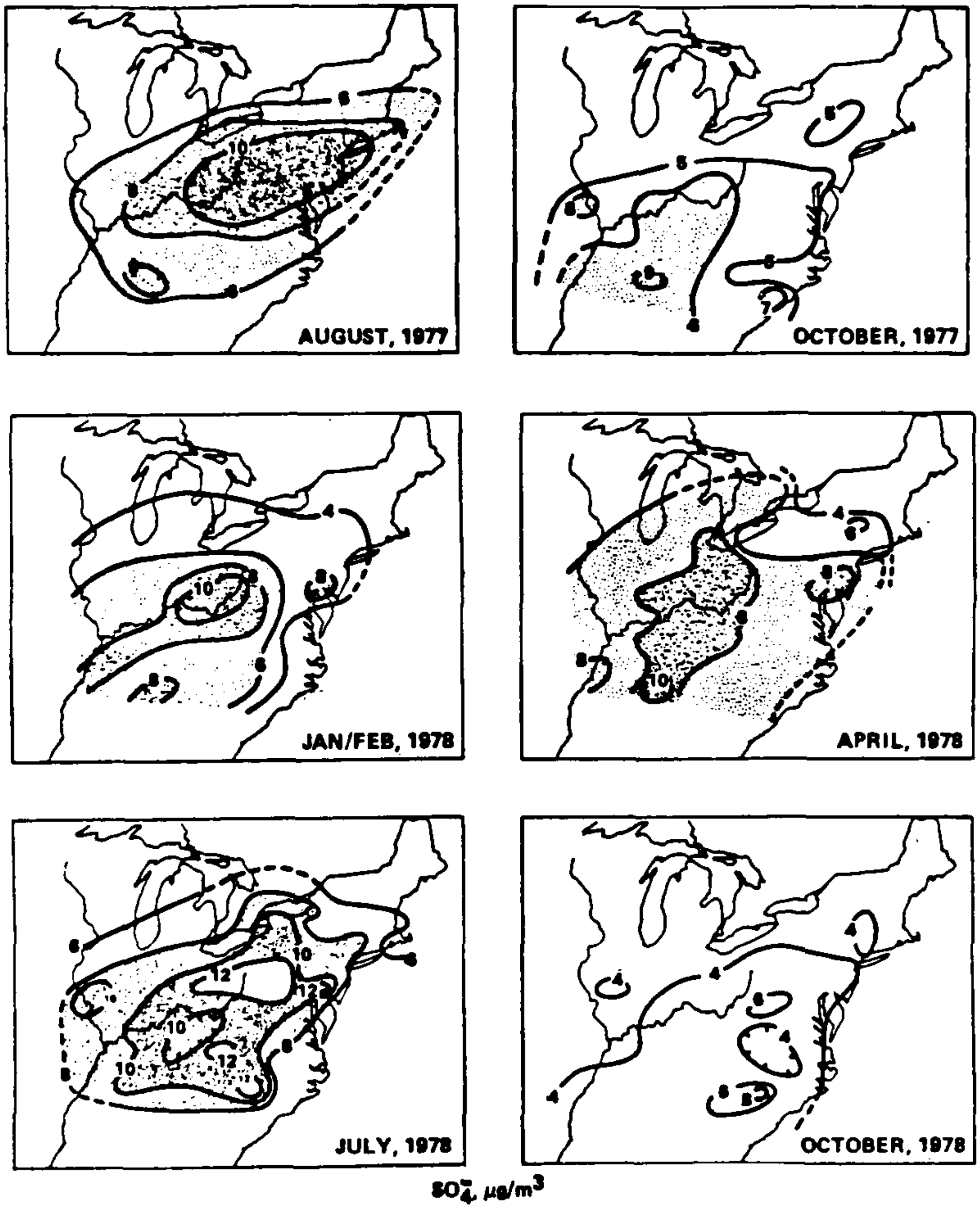
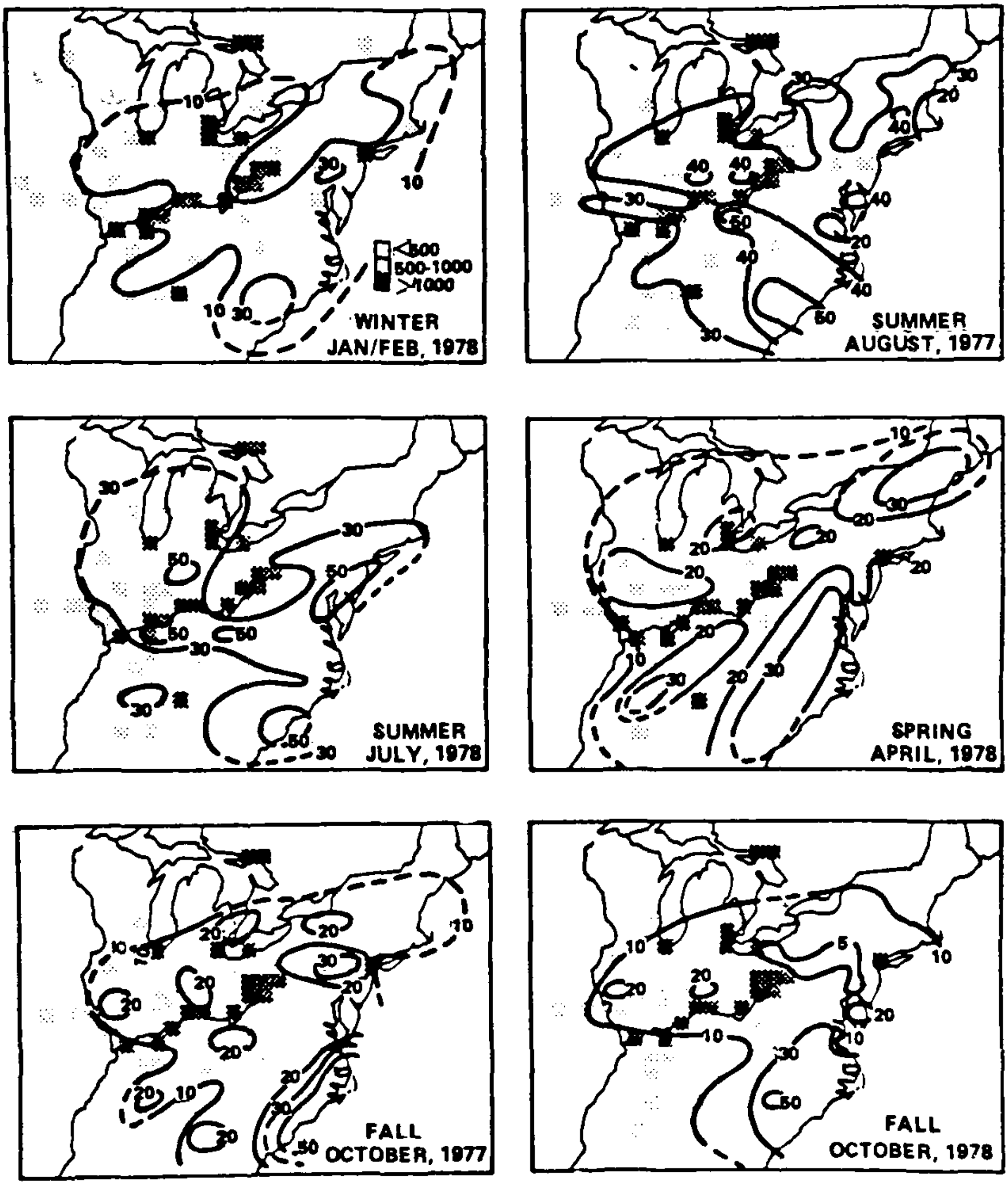


FIGURE 2. Monthly average distribution of 24-hr high volume (HIVOL) particulate sulfate concentrations in the eastern United States. From Mueller et al. (*39*).

results for each season are shown in Figure 3. The findings indicate that the ratios for summer were much higher than for the winter. The ratios were characteristically lower in the northern part of the SURE study area then in the southern and the coastal sections. These differences were consistent with the expectation of both greater rates of SO_2 oxidation and greater losses by dry deposition of SO_2 during the warmer months and in warmer regions.

Formation of Acidic Sulfates

The mechanisms involved with the transformation of SO_2 were reviewed in the Air Quality Criteria for



WINTER JAN/FEB, 1978

SUMMER AUGUST, 1977

SUMMER JULY, 1978

SPRING APRIL, 1978

FALL OCTOBER, 1977

FALL OCTOBER, 1978

FIGURE 3. Geographical distribution of the ratio of sulfate sulfur to total airborne sulfur for different seasonal periods (%). From Mueller et al. (39).

Particulate Matter and Sulfur Oxides (*40*) and are summarized in Table 1. Included are both heterogeneous and homogeneous reactions that produce H_2SO_4 in the gas phase or within the aqueous phase. Additional potential mechanisms involve metal catalysts, carbon, and surfaces. The predicted atmospheric conversion rates range from < 0.5% to > 100% per hour. These reactions do not necessarily occur at the same time. Each will be associated with particular environmental conditions such as near a source, in a plume, or in the general atmosphere. Some of these conditions are mutually exclusive. The importance of particular reaction schemes will be dependent upon insulation and humidity, hence, the season, geographic location, the time of day (night or daylight), and the local or prevailing meteorology.

Ammonia

A key factor in determining the persistence of atmosphere acidic sulfate species is the potential for atmospheric ammonia neutralization. This will be controlled by the reaction of NH_3 with H_2SO_4 and the formation of ammonium salts [NH_4HSO_4 and $(NH_4)_2SO_4$]. The major sources of environmental ammonia appear to be animals and humans, although significant contributions can come from manufacture of fertilizer. For both animals and humans the emissions are a result of excretion through the skin or from urea. Animals are probably a much larger source of ammonia due to the sewage treatment of human excrement. A regional mapping of domestic animal (cattle and pigs) and human ammonium emissions by Husar (*41*) yielded quite different distributions. Animal ammonium emissions centered in the midwest, and human emissions were keyed to the major population centers.

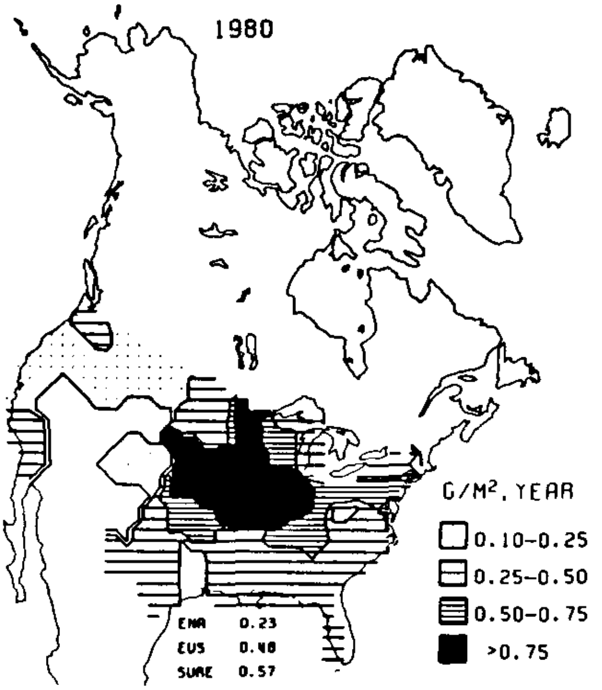


FIGURE 4. Annual average N-NH_4^+ emissions from cattle, hogs, humans, and fertilizer. From Husar and Holloway (*42*).

Husar and Holloway (*42*) also added the emissions inventory for fertilizer production and a combined emissions estimate for ammonium (NH_4^+) is shown in Figure 4. These estimated emissions suggested that ammonia neutralization will be dependent upon the land areas over which a sulfuric acid-ladened air mass travels and the contact time of air mass with the surface.

There are very limited data for ambient ammonia concentrations in the northeastern U.S. An extensive

Table 1. Important reaction rates for oxidation of SO_2.[a]

Reaction	Rate, %/hr			Comments[b]
Gas phase				
HO radical		0.3-1.3		*a*
HO_2 radical		0.4-2.0		*a,b*
CH_3O_2 radical		0.3-1.5		*a,b*
Aqueous phase, pH	1	3	5	
Mn(II) catalysis	1E − 1[c]	1E + 1	1E + 3	*b,c,d,i*
Fe(III) catalysis	5E − 5	5E − 1	5E + 3	*c,e,i*
C (soot) catalysis	3E + 1	3E + 1	3E + 1	*f,i*
O_3, 40 ppb	2E − 8	2E − 6	2E − 4	*c,g*
O_3, 120 ppb	6E − 8	6E − 6	6E − 4	*c,g*
H_2O_2, 1 ppb	2E − 2	3E − 2	3E − 2	*c,h*
H_2O_2, 10 ppb	2E − 1	2E − 1	3E − 1	*c,h*

[a] Source, EPA (*40*).

[b] Comments: *a*: typical range for daytime at northern midlatitudes during the summer; *b*: this reaction rate is not well established; *c*: assumed that liquid water volume of aerosol = $50 \times 10^{-12} m^3/m^3$, $\{SO_2\}$ = 10 ppb; *d*: assumed that Mn(II) mass concentration = 20 ng/m³, also, the Mn(II) is assumed to be uniformly dissolved in the liquid water of the aerosol [Mn(II) = 8.9×10^{-3}M]. Rate calculation used the expression of Neytzell-de Wilde and Taverner (*78*); *e*: assumed that Fe(III) mass concentration = 2 μg/m³, also, the Fe(III) is assumed to be uniformly dissolved in the liquid water of the aerosol [Fe(III) = 0.9 M]. Rate calculation used the expression of Neytzell-de Wilde and Taverner (*78*); *f*: assumed that C mass concentration = 10 μg/m³ and behaves as the soots studied by Chang et al. (*79*), whose expression was used for this calculation; *g*: rate calculation was based on Eqs. 2-39 (*40*); *h*: rate calculation was based on Eqs. 2-43 (*40*); *i*: influence of inhibitors has been ignored, but they are likely to suppress the rate by orders of magnitude.

[c] E denotes exponent to the base 10 (e.g., 3E − 1 = 3×10^{-1}).

monitoring program conducted by the Dutch (*43*) showed that the range in monthly averages for NH_3 reached from 0.2 to 35 $\mu g/m^3$. These concentrations are sufficient to fully neutralize from 0.6 to 100 $\mu g/m^3$ of H_2SO_4 aerosol. This represents an upper range to be expected in the U.S., since the density of livestock breeding is far greater in the Netherlands.

Data on aerosol NH_4^+ are generally linked to measurements of sulfate. The SURE study included aerosol measurements of the two species for nine sites in the EUS over a 2-year period (*39*). The ratios of SO_4^{2-}/NH_4^+ in total suspended particulate (TSP) samples were calculated for all sites and indicated that 40% of the samples were neutralized ammonium salts. The remaining 60% of the samples could have contained unneutralized acidic sulfate. A scatter diagram of the ratios for the SURE data is shown in Figure 5. The distribution of the data indicates that the majority of potentially acidic samples were associated with moderate sulfate concentrations (< 15 $\mu g/m^3$) and not the extremely high sulfate concentrations that are usually measured during the intense portions of a photochemical smog episode. It is likely that the fraction of acidic-to-total sulfate is lower because the air parcels associated with the episodes have greater opportunity to come in contact with local ammonia emissions.

However, these data are likely to underestimate the potential for acidic sulfate. The caveats regarding neutralizing capacity of the coarse fraction described in the methods section applies here to the TSP samples of the SURE study. Nonetheless, other studies have reported similar findings, i.e., the highest H^+/SO_4^{2-} ratios do not occur at the highest sulfate concentrations (*3,44–46*).

Morandi et al. (*3*) examined the distribution of acidic species for a regional smog episode that occurred in the summer of 1980. For measurements made at Tuxedo, NY, the most acidic portion of the smog episode they examined occurred at its beginning, and the acidity decreased with time. This is in contrast with the reported results of a study at Fairview Lake, NJ, in

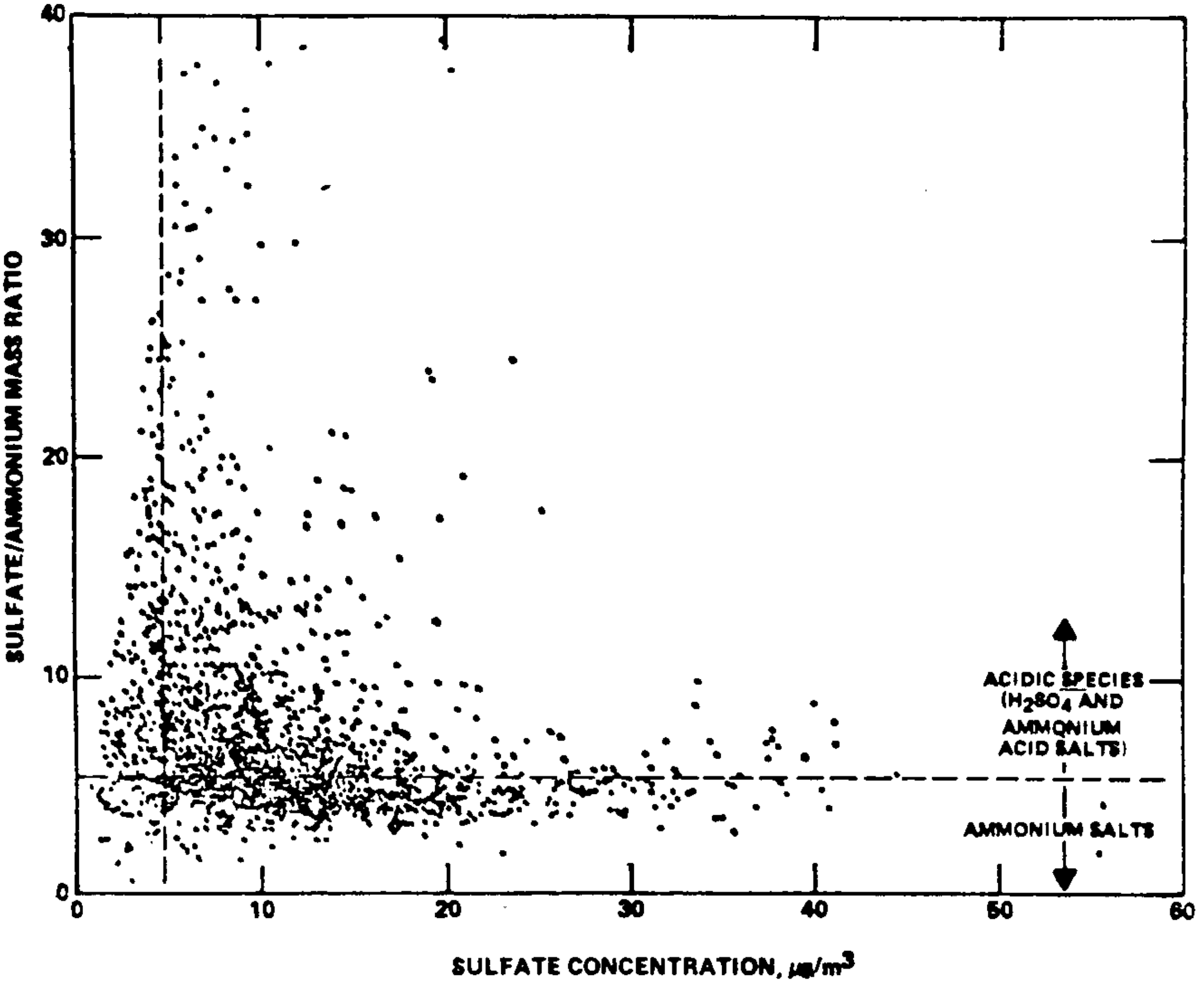


FIGURE 5. Scatter diagram of sulfate to NH_4^+ mass concentration ratios as a function of sulfate concentration for high volume filter samples. From Mueller et al. (*39*).

the summer of 1984 (*4*). It was observed during a 3-day episode that the acidic aerosol was primarily partially neutralized sulfate (i.e., NH_4HSO_4) with no H_2SO_4 measured. However, during the last day of that period, H_2SO_4 increased from approximately 0 to 4 μg/m^3 for 4 hr in the afternoon. These different phenomena must be examined more fully to understand the dynamics of the atmospheric environment when acidic species could be present.

Particle Size of Acidic Sulfate Aerosol

The sulfate particles are generally found in the fine particle size range (> 2.5 μm). The SURE results in the EUS showed that on the average, 80% of the SO_4^{2-} is in the fine fraction with a range of 50 to 100% (*39*). Size distribution data have been acquired for SO_4^{2-} and H^+ by Pierson et al. (*44*) and Keeler (*45*) in two separate investigations at Allegheny Mt., PA, in July and August 1977 and in August 1983. The cumulative mass equivalent size distributions for the respective studies are shown in Figures 6 and 7. The measured mass median diameters were 0.7 to 0.8 μm for both H^+ and SO_4^{2-} in both studies.

In California, two types of size distributions for sulfate aerosol have been noted, illustrated in Figures 8A and 8B (*47*). The size distribution in Figure 8A shows most of the mass centered around 0.5 μm; Friedlander has classified this as a coastal sulfur aerosol, and it reflects the influence of coastal humidity. In Figure 8B, the sulfur mass mode is between 0.1 and 0.2 μm. This has been classified as desert-type sulfur aerosol, which appeared to be formed from homogeneous reaction mechanisms and does not grow appreciably in the arid atmosphere. Recently, measurements of the distribution of H^+ and SO_4^{2-} as a function of particle size were made in Claremont, CA, where H^+ was found only in the range < 1.5 μm (*48*).

Record of Acidic Aerosol Concentrations and Exposures

As stated previously, the available data are based on direct measurements of H_2SO_4 or determinations of free or titratable acidity. To place the results from these studies in context, the concentrations are expressed as μg/m^3 (as H_2SO_4), even when only H^+ measurements were made. These values are probably an overestimate of the actual H_2SO_4 concentration since in both urban and rural areas acidic sulfate particles are usually in a partially neutralized form. However, the data are readily converted to the same scale of strong acid (e.g., nano equivalents/m^3).

London Historical Data

A relationship between air pollution and mortality/morbidity was recognized in England, especially after the severe London fog episode of December 5–8, 1952. Although routine air pollution monitoring conducted by local authorities and other regulatory bodies did not have data for H_2SO_4, it was conjectured that H_2SO_4 was considered to be one of the pollutants potentially responsible for the increased mortality and morbidity (*49*). Apparent H_2SO_4 measurements were

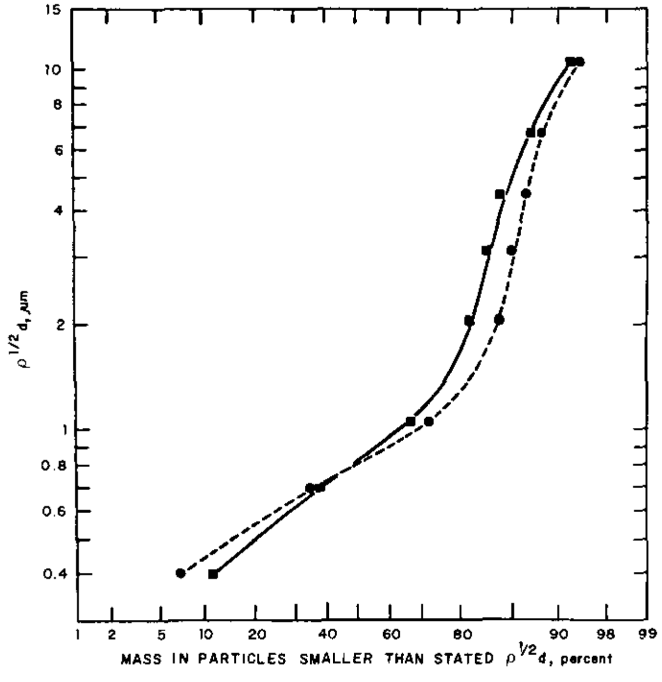


FIGURE 6. Particle size distribution of H^+ (●) and SO_4^{2-} (■) at the tower on Allegheny Mountain, 8:00 P.M. July 24 to 8:00 A.M. August 11, 1977. From Pierson et al. (*44*).

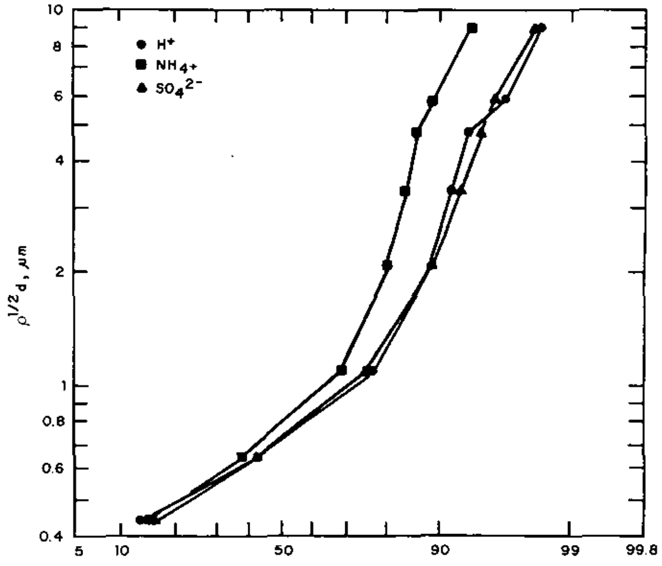


FIGURE 7. Log probability plot of H^+, NH_4^+, and SO_4^{2-} size distribution at the tower on Allegheny Mountain, August 12–17, 19–22, and 28, 1977. From Keeler (*45*).

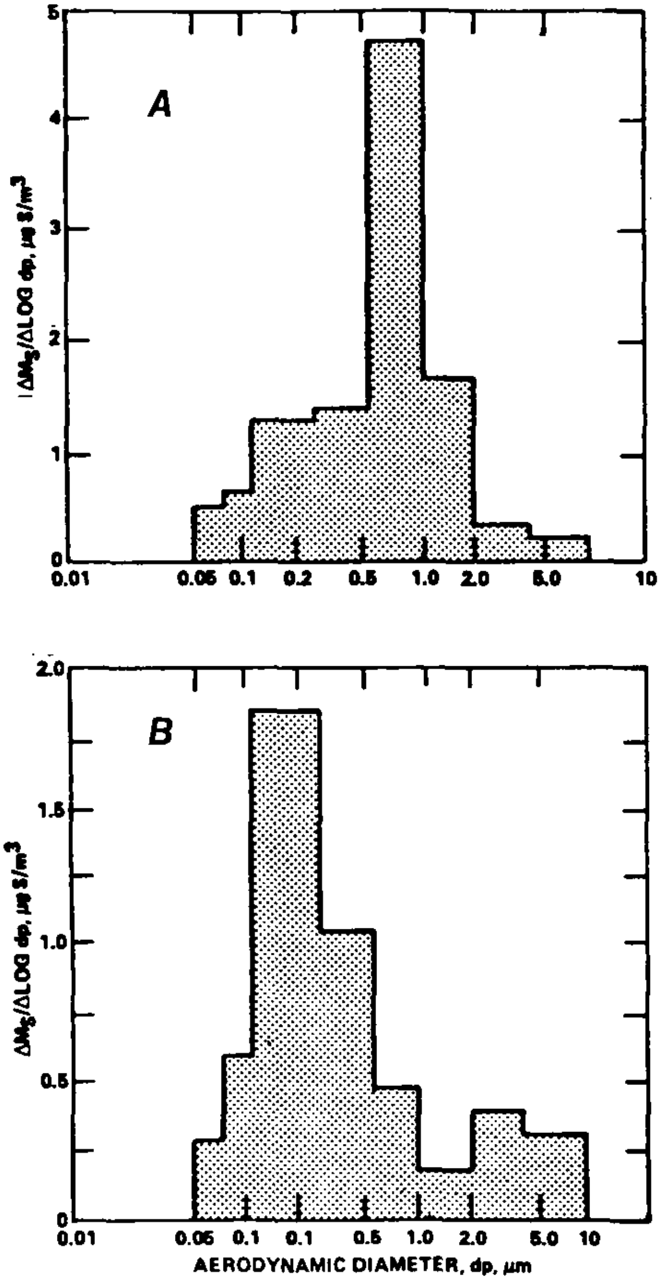


FIGURE 8. Aerosol sulfur mass distribution. (*A*) Pasadena, CA, December 26, 1978. Average of two samples from 2:28 P.M. to 4:00 P.M. Total mass loading was 10.6 μg/m³. (*B*) Trona, CA, May 13, 1978, from 9:46 A.M. to 11:45 A.M. Total mass loading was 1.42 μg/m³. From Freidlander et al. (*47*).

reported for episodes starting in the winter of 1957–1958 using the sodium tetraborate method (*50*). The highest daily and highest hourly apparent acid concentrations were 347 μg/m³ and 678 μg/m³, respectively, recorded in December 1962. Daily measurements began during April 1964 (Fig. 9) (*51*). The sampling site (Bartholomew Hospital) was in a commercial area. Smoke came mainly from domestic heating sources at some distance from the site, while much of the SO_2 came from central heating installations in commercial buildings (*50*). Annual peak concentrations occurred during the winter, probably due to increased heating fuel usage and adverse meteorological conditions. A gradual decrease of acid concentrations during the 10-year record can be observed, as a result of the Smoke Control Order in 1984.

Los Angeles Historical Data

In 1949, a study was conducted in Los Angeles, CA to determine the amount of free H_2SO_4 in the atmosphere during periods of intense fog and clear days (*52*). There were 2 days with levels above 150 μg/m³, and each occurred on days with high relative humidity. The extreme in acidity was corroborated by an independent observation of lesions on leaves during the same period (*53*). A short-term study conducted in Los Angeles in the winter of 1961 recorded a peak concentration of 60 μg/m³ (*54*).

Acid Fog

Fog and clouds are a special type of atmosphere aerosol (*55*). While aerosols are generally comprised of crystalline, aqueted salt, or other solid particles, fogs and clouds are the suspension of liquid water droplets in the air. From condensation nuclei of 0.1 to 1.0 μm, droplets grow to diameters between 2 to 100 μm, although the majority of droplet mass occurs in the range of 5 to 30 μm. The presence of nuclei, composed of both soluble and nonsoluble material, is essential to the formation of atmospheric water droplets.

Fog droplets are highly effective at scavenging pollutant materials present in the air. The overall fraction incorporated into fog droplets depends upon two processes: nucleation scavenging (i.e., activation) of aerosol and gas dissolution. The speciation of pollutant components present prior to fog formation is therefore important. The pollutant species of concern are often present as hygroscopic aerosol (e.g., sulfates and nitrates). Furthermore, *in situ* chemical transformations, such as oxidation of SO_2 to H_2SO_4, alter this speciation and the effectiveness of fog scavenging while the droplet phase is present (*56*).

The study of fog has traditionally remained in the domain of atmospheric physicists, who were principally concerned with its effect on visibility or the mechanisms of cloud formation. Yet, the data of early investigations of fog demonstrate that fogwater can be highly concentrated with respect to a variety of chemical components (Table 2). The high solute concentrations and extremes in acidity found in fogwater are reason for concern. There has been a historical correlation of fog with the most severe air pollution episodes (*57*). Identification of a link between urban fog events and human injury was made even before detailed measurements of fog composition (*58*).

Table 2. Summary of fogwater composition measurements (*56*).

Location	Date	Type[a]	n[b]	pH	NA$^+$	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	Reference
				Concentration, microequivalents/L								
Mt. Washington, NH (1,900 m)	1930–1940	I	35(a)	4.5 3.0–5.9					4 0–34		150 4–1,100	(*80*)
Coastal MA and ME	1930–1940	M	37(a)	4.7 3.5–6.3					940 0–5,800		380 60–2,600	
Germany, Baltic Sea	1955–1965	M	42(a)	3.8	1,500	2,300	750		700	900	1,900	(*81*)
near Dresden	1955–1965	R	12(a)	4.2		2,100	3,200		590	450	780	
Harz Mountain (1,150 m)	1955–1965	I	18(a)	5.1	300	710	220		200			
Japan, Mt. Moribura (3,026 m)	July 1963	I	10(m)	3.9 3.4–4.3	87 45–165	175 115–260			110 75–230	36 25–175	3,300 230–1,250	(*82*)
Mt. Tsukaba (876 m)	Nov 1963	I	5(m)	5.9 5.6–6.5	290 180–435	880 110–965			800 295–1,290	17 5–37	1,600 360–2,100	
Whiteface Mountain, NY	Aug 1976	I[c]	28(a)	3.7	11	89	17	6	31	90	140	(*83*)
(1,500 m)	Aug 1980	I	50	3.2–4.0	1–7	1–200			1–14	7–190	32–800	(*84*)
Los Angeles foothills (780 m)	Spring 1982 and 1983	I	120(m)	2.9 2.1–3.9	240 135–8,700	580 62–7,400	140 5–3,000	80 1–1,800	190 15–9,650	1510 160–16,300	840 130–9,300	(*85*)
Nova Scotia	Aug 1975	M	14(ar)		1,040 600–1,530	33 3–94	45 20–69	100 13–130	87 3–450		250 50–500	(*86*)
California, central coast	Fall 1976	M	8(ar)		320 80–950	190 0–580	55 9–100	68 23–175	400 95–1,240	115 24–235	200 77–490	(*87*)
Los Angeles area	Fall-winter 1980–1982	M, I	11(m)	3.3 2.7–7.1	139 30–620	1,580 420–4,260	168 0–460	54 22–310	223 68–423	110 580–2,980	584 354–1,875	(*88*)
Los Angeles area	Fall-winter 1981–1982	M	24	2.3–5.8	12–2,180	370–7,960	190–4,350	7–1,380	56–1,110	130–12,000	62–5,000	(*89*)
Pt. Reyes, CA	Aug 1982	M	17(m)	4.5 3.5–5.0	190 21–4,700	64 28–330	10 0–240	36 5–1,200	215 34–7,000	23 2–526	186 36–1,281	(*90*)
San Nicholas Island, CA	Aug 1982	M	7(vw)	3.9	6,100	450	450	1,500	5,300	1,580	1,080	(*90*)
San Diego Area, CA	Jan 1983	M	5(vw)	2.9	510	780	49	130		1,850	470	
Albany, NY	Oct 1982	R	24(m)	5.8 4.3–6.4	36 10–100	215 70–350	120 65–350	13 6–47	47 18–175	85 11–220	155 21–1,360	(S. Fuzzi, unpublished data, 1984)
Bakersfield, CA	Winter 1983	R	108(m)	4.2 2.6–7.0	20 1–325	1,440 490–2,330	47 7–3,500	6 1–430	47 1–980	850 200–6,800	1160 10–9,400	(*91*)
Italy, Po Valley	Feb and Nov 1984	R	5(ar)	3.5–4.3	10–110	580–1,620	60–130	10–50	20–120	290–1,100	400–990	(*92*)

[a] Fog type: I, intercepted stratiform cloud; M, marine or coastal fog; R, radiation fog.
[b] Number of samples or events: (a) average; (m) median; (vw) volume-weighted mean of n samples; (av) average and/or range of r events.
[c] Nonprecipitating stratiform cloud data only.

Atmospheric Acidic Sulfate Studies from 1974–1986

Measurement studies of acidic sulfate species in the U.S. and Canada since 1974 have been tabulated with references (Table 3). A variety of sampling strategies and analytical methodologies were used, and the individual sampling times ranged from 1 to 24 hr, although none used glass fiber filters. Most of the studies were conducted during the summer when large scale and prolonged regional O_3 and sulfate smog episodes can occur in the eastern U.S. and Canada (*59*). In addition, photochemical smog episodes are most frequent during the summer in Los Angeles, CA (*60*), and Houston, TX (*61*). The magnitude of the wintertime levels of acidic sulfate species were derived from a more limited data base.

The range of concentrations recorded in the studies outlined in Table 3 is shown in Table 4. It is apparent that a wide range of SO_4 and acid sulfate levels were encountered. The peak H_2SO_4 value, measured with a flame photometric detector (FPD), was 41 μg/m^3 (1-hr average) in 1984 at a site in St. Louis, MO (*62*). Pierson et al. (*63*) completed a study at both Allegheny Mountain and Laurel Mountain in 1983, and they observed peak H^+ concentrations of 30.4 and 42.0 μg/m^3 (as H_2SO_4) at the respective sites.

An H^+ concentration of 39 μg/m^3 (as H_2SO_4) was

Table 3. A summary of representative North American atmospheric studies during which acid sulfate or total acidity was measured.

Location	Acid species measured	Dates	Method for acid determinations	Reference
St. Louis, MO	Inferred acid sulfates	Aug.-Oct. 1973	Humidographs/light scattering	*(26)*
Glasgow, Il	H^+	July 20-30, 1975	Titration	*(64)*
Research Triangle Park, NC	H^+	July 27-31, 1977	Titration	*(15)*
St. Louis, MO	H_2SO_4	July 1977-June 1978	Flame photometry detection	*(93,94)*
High Point, NJ	H^+	Aug 1-15, 1977	Titration	*(66)*
New York City	H^+	Aug 1-15, 1977	Titration	*(95)*
Allegheny Mountain, PA	H^+	July-Aug 1977	Titration	*(44)*
Great Smoky Mountains, TN	H^+	Aug 20-26, 1978	Titration	*(70)*
Lennox, CA	H_2SO_4, H^+	July 12-19, 1979	Titration (H^+) extraction (H_2SO_4)	*(68)*
Shenandoah Valley, VA	H^+	July-Aug 1980	Titration	(R. K. Stevens, personal communication, 1983)
Houston, TX	H^+	Aug 1980	Titration	(R. K. Stevens, personal communication, 1983)
Tuxedo, NY	H^+	Aug 1980	Flame photometry detection/titration	*(3)*
Mendham, NJ	H^+	July-Aug 1982	4 and 8 hr titration	*(71)*
St. Louis, MO	H_2SO_4	Aug 3-19, 1979	Flame photometry detection	*(65)*
St. Louis, MO	H_2SO_4	Nov 1983-Mar 1984	Flame photometry detection	*(62)*
Los Angeles, CA	H^+	Aug 1983	Titration	*(69)*
Harriman, TN	H_2SO_4	Mar-Dec 1984	Flame photometry detection	*(67)*
Watertown, MA	H_2SO_4	1984	Flame photometry detection	*(67)*
Fairview Lake, NJ	H^+, H_2SO_4	July-Aug 1984	Flame photometry detection/titration	*(71)*
Warren, MI	H^+	June 1981-1982	Titration	*(72)*
Whiteface Mountain, NY	H^+	Jan-Dec 1984	NA[a]	*(73)*
Nova Scotia, Canada	H^+	Aug 18-Sept 11, 1983	Titration	*(74)*
		May 23-July 9, 1984	Titration	
Toronto, Canada	H^+	June 30-Aug 10, 1986	pH by addition	*(46)*
Allegheny Mountain and Laurel Mountain, PA	H^+	Aug 1983	Titration	*(63)*

[a] Method not specified.

observed in 1975 just northeast of St. Louis in Glasgow, IL *(64)*. Important features of the Glasgow data were: (a) that the H^+ was measured in the submicrometer size range; (b) the measurements were 12-hr duration samples; and (c) the visibility maps indicated the development of an urban plume from St. Louis. The measured levels of aerosol NH_4^+ on July 29, 1975, indicate that the aerosol in Glasgow, IL, contained both NH_4HSO_4 and H_2SO_4. A number of other studies also indicated the presence of both species *(3,64,65)*.

Morandi et al. *(3)* included an attempt to actually infer the distribution of acidic species from coincident instrumental FPD measurements of H_2SO_4 and filter analyses for H^+. From their data, there was no evidence of the presence of strong acids ($pK_a \leq 2$) other than NH_4HSO_4, or H_2SO_4. Their results also showed that the species H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$ can occur simultaneously. Thurston and Waldman *(5)* showed that although the sulfate aerosol measured in Toronto was as high as 30% acidic at times, the measured H_2SO_4 was less than 2% of the total sulfate composition.

For most of the summertime studies, peaks of H_2SO_4 and/or H^+ were associated with the presence of a slow-moving high pressure system. For example, a major acidic sulfate event occurred in the EUS during early August 1977 *(66)*. The daily variation of the 6-hour particulate sulfate and H^+ concentrations and the daily maximum O_3 concentrations are shown in Figure 10. Samples for this period measured at High Point, NJ, and Brookhaven, NY (separated by 160 km), showed peak excursions of H^+ at the two sites with the passage of pollutant-laden air masses *(66)*.

Samples collected in New York City for the same period were reported by Tanner et al. *(34)*. The

Table 4. Concentration ranges of acidic species measured in various locations.

Study	Sample duration, hr	Concentration range, μg/m^3		Reference
		SO_4^{2-}	H_2SO_4	
Glasgow, Il	12	7–48	0–39	*(64)*
St. Louis, MO				
1977 Summer	1	5–60	0–28	*(94)*
1978 Winter	1	3–24	0–12	
Lennox, CA	2–8	1.2–18	0–11	*(68)*
Smokey Mountains, TN	12	6.2–17.4	2.8–9.6	*(70)*
High Point, NJ	6	3.0–36.6	2.2–17.8	*(66)*
Brookhaven, NY	3	1.0–23.7	0.3–10.2	*(66)*
Research Triangle Park, NC	2,4	3.6–19.8	0–9.8	*(15)*
Allegheny Mt. PA	12	1–32.5	0–20	*(44)*
Shenandoah Valley, VA	12	2–40	0–23	(R. K. Stevens, personal communication, 1983)
Tuxedo, NY	1–12	1–41	1–8.7	*(3)*
Mendham, NJ	4,20	1–37.3	0–6.3	*(71)*
Houston, TX	12	2–32.4	0–7.6	(R. K. Stevens, personal communication, 1983)
New York City	6		NM^a	*(66)*
St. Louis, MO	QC^a	3–25	0–7	*(65)*
St. Louis, MO	QC	5–43	0–34	*(62)*
Los Angeles, CA	12	3–10	0.6–3.2	*(69)*
Harriman, TN	QC	9–47	0–18	*(67)*
Watertown, MA	QC	5–31	0–14	*(67)*
Fairview Lake, NJ	QC,4	13–27	0–12	*(71)*
Warren, MI	24	0.4–36.7	0.8–8.7	*(72)*
Whiteface Mt., NY	24	0–58.9	0–14	*(73)*
Nova Scotia	24	0–26	0–9	*(74)*
Toronto, Canada	8,16	0–75	0–19.4	*(46)*
Allegheny Mt., PA	7,10	1.7–45.4	0.4–30.5	*(63)*
Laurel Mt., PA	7,10	2.2–55.5	0.5–42.0	*(63)*

^{a}QC, quasi-continuous; NM, not in measurable quantities.

trajectory analysis indicated that air parcels passed from High Point to New York City or Brookhaven (i.e., southeasterly). However, no aerosol acidity was observed in New York City on any of the sampling days, even when acidity was recorded in High Point. This would indicate that the flux of NH_3 emanating from the metropolitan area was sufficient to neutralize the acid-laden air parcels. Values of H^+ at Brookhaven (80 km to the east of New York City) were consistently lower than the values reported at High Point. This suggests that there was partial neutralization and/or fresh acid production over the metropolitan area.

In 1984, Spengler et al. *(67)* indicated H_2SO_4 studies at two of the Harvard Six-Cities Health Study sites: Harriman, TN (coal-burning area), and Watertown, MA (suburb of Boston). Using the continuous FPD system for H_2SO_4 measurements, they classified acid events. Those that occurred in the coal burning area of Harriman, TN, were of longer duration and higher in concentrations than observed at Watertown, MA. In another investigation by Harvard, an H_2SO_4 concentration of 41 μg/m^3 was observed in St. Louis *(62)*. In this case wintertime conditions were studied, and the results suggested an association with a power plant plume.

In a July 1979 study at Lennox, CA, a 4-hr maximum of 11 μg/m^3 of H_2SO_4 was observed *(68)*. This was apparently associated with the daytime oxidation of local SO_2 emissions. Only three other acid events were measured, although elevated levels of sulfate were measured throughout the week-long study. A later study in Los Angeles found lower concentrations of acidity *(69)*. Of the two sites monitored, the downwind location, east of Los Angeles, recorded the higher acid concentrations.

Studies in the Great Smoky Mountains, TN *(70)*, in the Shenandoah Valley, VA (R. K. Stevens, personal communication, 1983), and in Mendham, NJ *(71)*,

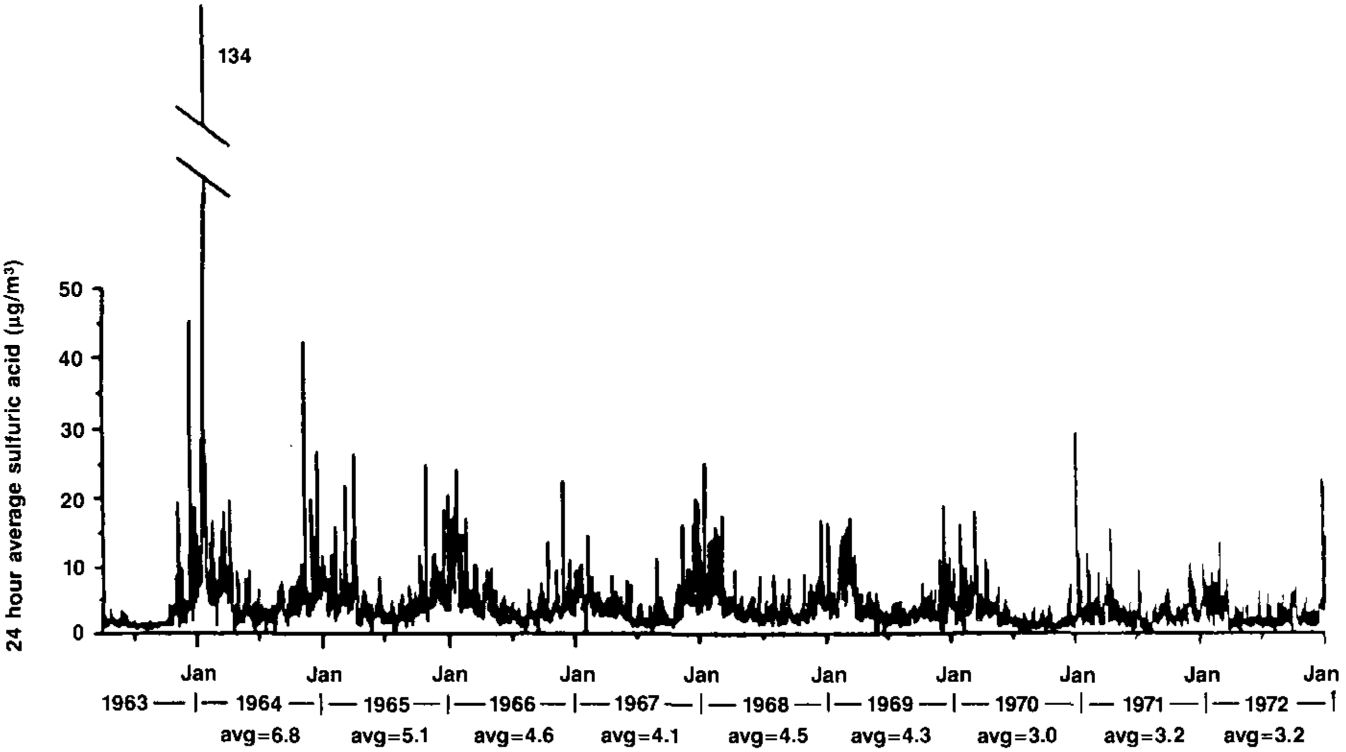


FIGURE 9. Historical London daily aerosol acidity data, total H^+ as H_2SO_4. From Ito and Thurston (*51*).

showed the presence of acidic species in nonurban areas of the EUS. Cadle (*72*) reported the results of H^+ made at a suburban site in Warren, MI, from June 1981 through June 1982. The most frequent excursions occurred during the summer, with six 24-hr samples exceeding 4 µg/m³. However, the highest H_2SO_4 concentration Cadle reported occurred during the wintertime.

Rural investigations, one in Whiteface Mt., NY (*73*), and the other in Nova Scotia, Canada (*74*), focused on acidic sulfate aerosol. In each case there was at least one period during which the acid concentration exceeded 9 µg/m³.

To date, there have been only two studies in which the acidic sulfate species were measured simultaneously at several nearby (less than 50 km) sites (*46,63*). A study in Toronto, Ontario, was conducted during the summer of 1986 using three sites within the metropolitan area (*46*). Separate filters were run during the day (9:00 A.M.. to 5:00 P.M.) and night (5:00 P.M. to 7:00 A.M.). During several episodes, the nighttime period was broken further by sampling from 7:00 P.M. to 9:00 P.M. (evening) and from 9:00 P.M. to 9:00 A.M. The peak concentrations for the major species (H^+, NH_4^+, and SO_4^{2-}) occurred on the July 25–26 sampling periods. While the 24-hr values for sulfate were quite uniform at the three sites (34, 34, and 35 µg/m³), H^+ concentrations were 9.4, 8.3, and 5.9 µg/m³ H^+ (as H_2SO_4) (Fig. 11), respectively. The highest concentrations occurred during the brief evening period on July 25 (broken out of the nighttime period at sites 1 and 2 only); these were 48 and 75 µg/m³ SO_4^{2-} and 14.4 and 19.4 µg/m³ H^+ (as H_2SO_4). During this episode, the degree of sulfate neutralization was between 70 and 75% at sites 1 and 2, which were located north 30 km northeast and northwest of downtown. However, for samples collected at the third site, located in the urban downtown area, the sulfate aerosol samples were 80 to 85% neutralized.

Acidic Sulfate Exposure and Events

The ambient atmosphere studies measured a wide range of acidic sulfate concentrations in the atmosphere. Most of the H_2SO_4 or H^+ (as H_2SO_4) values were below 5 µg/m³, although events with higher values occurred occasionally (at least once) over the course of each study. It is not appropriate, based on the available data, to equate an acid event with a sulfate episode, since periods of high acid concentrations do not necessarily coincide with periods with the highest SO_4^{2-}, e.g., photochemical haze or smog. Therefore, the definition of an acidic sulfate event is somewhat arbitrary. For this discussion, a pollution event for acidic sulfate will be defined as an event when the measurement of H_2SO_4 or H^+ (as H_2SO_4) reached levels ≥ 5 µg/m³ for at least 1 hr.

With the preceding criterion, some of the studies listed in Table 4 were selected for estimating the frequency of events and the potential exposure to acidic sulfates [as (µg/m³)-hr]. Event exposures calculations

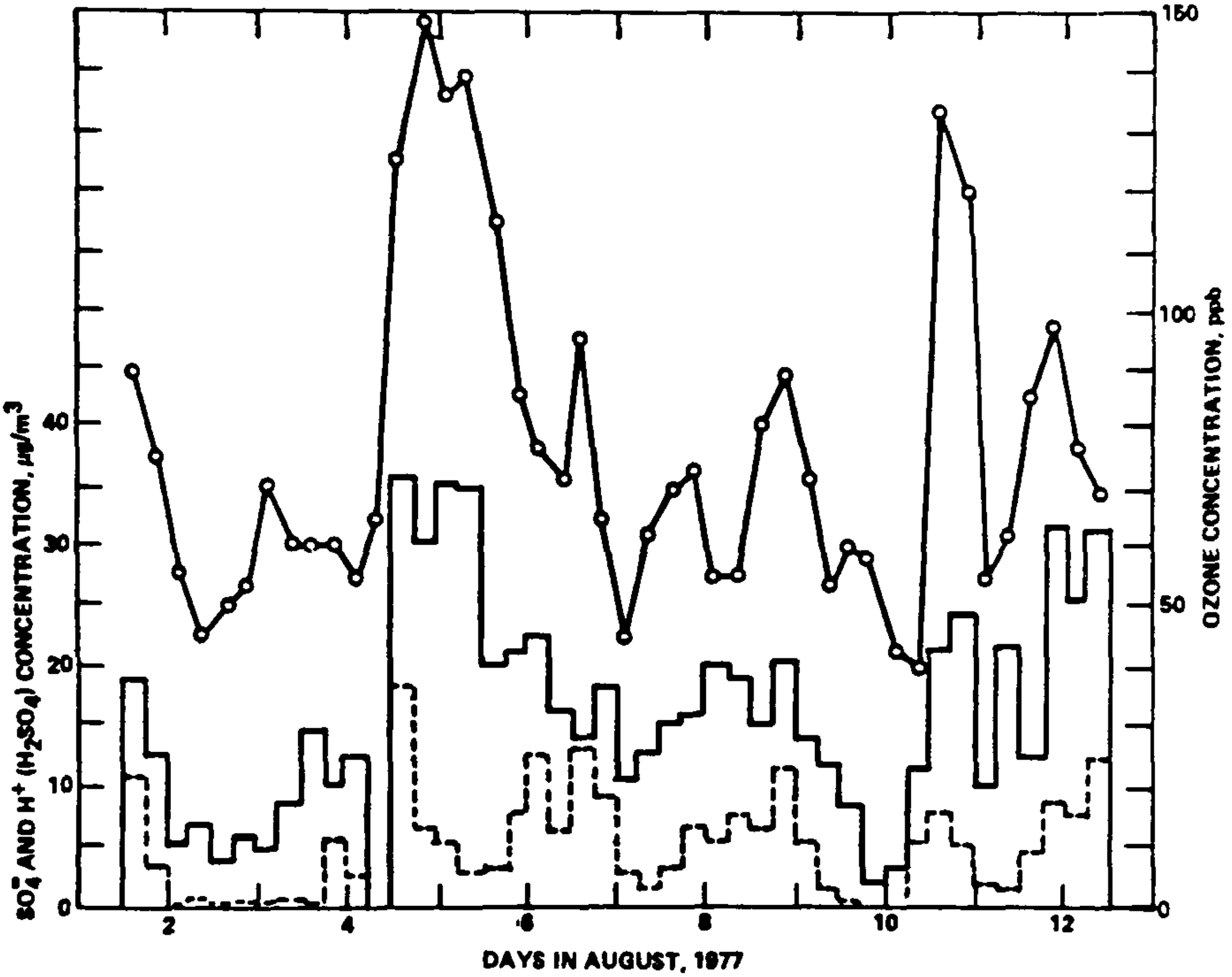


FIGURE 10. Six-hour SO_4^{2-}(—) and H^+ (---) and 6-hr maximum. O_3 (-o-) samples collected during August 1977 at High Point, NJ.

may be of some biological significance since it has been shown in a controlled human study that the effects of exposures as low as 100 µg/m³ H_2SO_4 for 2 hr enhance the effects of mucociliary clearance observed for 1-hr exposures (*75*). For the purposes of the following discussion, however, the exposure values (µg/m³)-hr should be interpreted as the maximum potential exposure during an event, and not as the biologically effective dose to an individual. It should be emphasized that the exposure calculation (concentration × time) will only be applied for determination of exposures that can occur during an event. For example, annual average calculations of exposure are to be avoided.

The exposure and event results shown in Table 5 and are divided into representative studies with sample collection times of 24 hr, 12 hr, 6 hr, 1 hr, and a combined sampling time. This was done because the length of reported events is different for the various collection times. For the 24-hr studies (Table 5), the events lasted a maximum of 24 hr, which was the sample duration. This may be an underestimate of the length of the event since the portion of the next or preceding 24-hr period may have been above 5 µg/m³ and could not have been detected. The exposures for the 24-hr episodes ranged from 120 to 336 (µg/m³)-hr and were isolated instances of high acidic sulfate.

The acidic sulfate events for the 12-hr samples reached 36 hr in duration and recorded peak exposures of 510 and 925 (µg/m³)-hr. An interesting feature of the 12-hr values (Table 6) was that for studies conducted for a period of 1 month or less, each had at least one event with acidic sulfate exposure above 100 (µg/m³)-hr. Obviously, the frequency of acid events in each location cannot be described since longer duration studies would be required.

The two examples of 6-hr samples (Table 7) had exposure above 100 (µg/m³)-hr during intervals of sampling that encompassed less than 2 weeks. The intensity and duration of the High Point, NJ, expo-

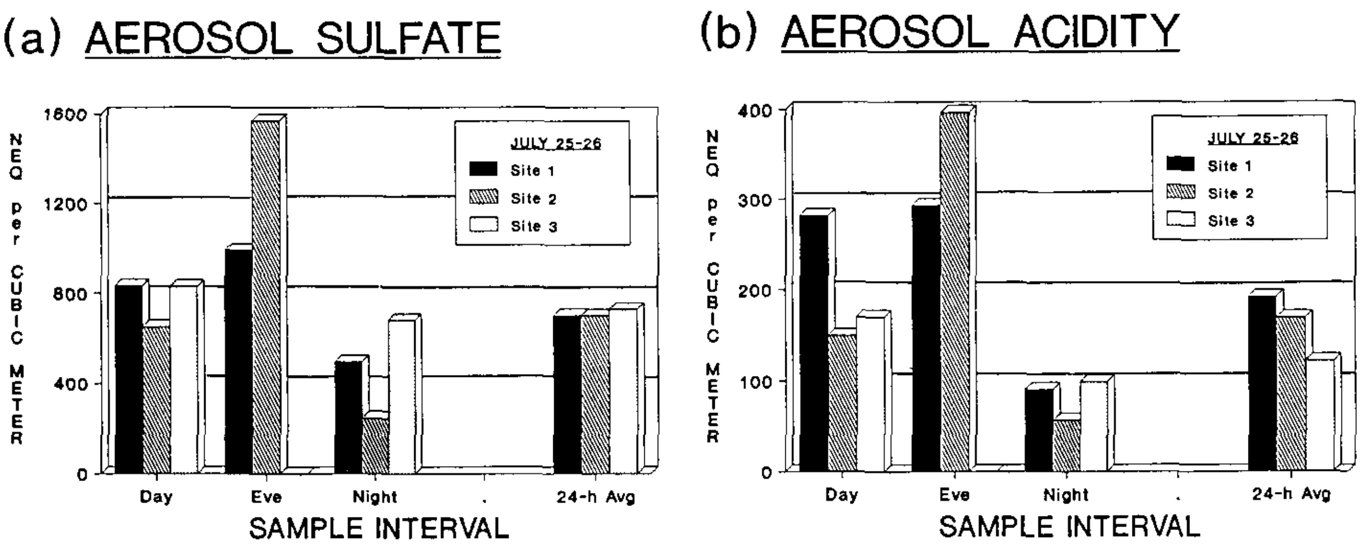


FIGURE 11. Aerosol concentration for individual sampling intervals during July 25–26, 1986, episode (*46*).

sures were quite different (*66*). In the period from August 5 through 12, there were almost daily exposures to acidic sulfate above 100 (µg/m^3)-hr.

All studies reporting 1-hr sample intervals used direct measurements of H_2SO_4 by FPD, and the exposure results are found in Table 8. The duration of episodes ranged from 1 to 20 hr. For St. Louis, there were only two instances during which exposures to H_2SO_4 were above 100 (µg/m^3)-hr and three above 80 (µg/m^3)-hr. This is puzzling since the sampling included an entire year, and there are major sources of SO_2 in the area (*76*). However, the work of Ellestad (*77*) and the previously cited work of Tanner and Marlow (*64*) may explain the lack of frequent high excursions in H_2SO_4. Particle light scattering was measured during the 1975 MISST study at Glasgow, IL, 17 km downwind of St. Louis urban and power plant plumes (*77*). Those data indicated aerosol production during the summer. H^+ measurements made in summer 1975 at the same location indicated very high exposures [> 900 (µg/m^3)-hr] (*64*). Thus, the main acid impact from the urban plumes are likely to be more sub-

Table 5. Episodic acidic aerosol data and estimates of exposure from 24-hr sampling acid sulfate studies.[a]

Study (period)	Date	Mean, µg/m³	Duration, hr	Exposure, (µg/m³)-hr
Whiteface Mt. (*73*)	1984			
(85 samples	July	8.2	24	197
collected over 1 year)	Aug	10.0	24	240
	Aug	14.0	24	336
Nova Scotia (*74*)	1983			
(23 days)	Sept 6	9.0	24	216
Warren, MI (*72*)	1981-1982			
(1 year)	July	9.0	24	216
	July	6.5	24	156
	July	7.5	24	180
	July	6.7	24	160
	Aug	5.0	24	120
	Aug	5.0	24	120
	Nov	6.5	24	156
	Feb	10.0	24	240
St. Louis, MO (*96*)	1985-1986			
(9 months)	Sept	6.1	24	146
Kingston, TN (*96*)	1985-1986			
(9 months)	May 30	7.7	24	184
	June 3	5.9	24	141
	July 6	5.4	24	135
	July 17	11.1	48	509
	July 22	8.3	48	384
	Aug 5	6.1	24	146
	Aug 18	14.3	24	343

[a] Only periods where concentrations exceeded 5 µg/m³ H_2SO_4 were considered episodes.

Table 6. Episodic acidic aerosol data and estimates of exposure from 12-hr sampling acid sulfate studies.[a]

Study (period)	Date	Peak, $\mu g/m^3$	Mean, $\mu g/m^3$	Duration, hr	Exposure, $(\mu g/m^3)$-hr
Tuxedo, NY (*3*)	1980				
(31 days)	Aug 2	8.0	8.0	12	97
	Aug 8	8.0	8.0	12	97
	Aug 27	20.1	14.2	36	511
Glasgow, Il (*63*)	1975				
(8 days)	July 22	9.3	9.3	12	112
	July 26	5.2	5.2	12	62
	July 28,29	36.0	25.7	36	925
Smoky Mts. (*70*)	1978				
(6 days)	Sept 20,21	5.64	5.6	12	68
	Sept 21,22	8.2	8.2	12	98
	Sept 24-26	9.6	8.6	36	308
Houston, TX	1980				
(R. K. Stevens, personal	Sept 11	6.4	6.4	12	76
communication, 1983)	Sept 12	6.7	6.7	12	81
(9 days)	Sept 13	7.6	7.6	12	91

[a]Only periods where concentrations exceeded 5 $\mu g/m^3$ H_2SO_4 were considered episodes.

stantial at downwind locations. In the future, studies will require careful consideration of topographical and meteorological data to determine where major plume impacts will occur and their potential for producing high acid concentrations and exposures.

In the Toronto study (*46*), the exposure analyses completed for the three sites showed that there was one period during which exposures at two of the three sites were above 100 $(\mu g/m^3)$-hr (Table 9). At the third site, the acid levels were much lower, which was probably due to local neutralization. Thus, across this metropolitan area of 2.5 million people (and probably other areas, too), the potential for local differences in acidic sulfate must be examined in order to define the locations of maximum potential exposures.

Summary

High exposures to acidic aerosol in the atmosphere were calculated from data reported in the scientific literature. The majority of data was not derived from studies necessarily designed to examine human exposures. Most of the studies were designed to investigate the characteristics of the atmosphere. However, the measurements were useful in defining two potential exposure situations: regional stagnation and transport conditions and local plume impacts.

Levels of acidic aerosol in excess of 20 to 40 $\mu g/m^3$ (as H_2SO_4) have been observed for time durations ranging from 1 to 12 hr. These were associated with high, but not necessarily the highest, atmospheric SO_4^{2-} levels. Exposures of 100 to 900 $(\mu g/m^3)$-hr were calculated for the acid events that were monitored. In contrast earlier London studies indicated that acidity in excess of 100 $\mu g/m^3$ (as H_2SO_4) were present in the atmosphere, and exposures > 2000 $(\mu g/m^3)$-hr were possible.

It is apparent that at least two types of conditions mentioned can lead to a number of possible situations for epidemiological and human exposure studies. The

Table 7. Episodic acidic aerosol data and estimates of exposure from 6-hr sampling acid sulfate studies.[a]

Study (period)	Date	Peak, $\mu g/m^3$	Mean, $\mu g/m^3$	Duration, hr	Exposure, $(\mu g/m^3)$-hr
High Point, NJ (*66*)	1977				
(11 days)	Aug 1	11.6	11.6	6	69
	Aug 3	5.8	5.8	6	35
	Aug 4,5	17.6	9.0	24	215
	Aug 5,6	13.8	10.1	30	304
	Aug 7-9	11.6	7.4	36	264
	Aug 10	8.2	6.5	18	118
	Aug 11,12	12.6	8.3	24	198
Shenandoah Valley	1980				
(R. K. Stevens, personal communication, 1983) (7 days)	Aug 29-Sept 1	21.3	14.6	24	350

[a]Only periods where concentrations exceeded 5 $\mu g/m^3$ H_2SO_4 were considered episodes.

Table 8. Episodic acidic aerosol data and estimates of exposure from 1-hr sampling acid sulfate studies.[a]

Study (period)	Date	Peak, μg/m^3	Mean, μg/m^3	Duration, hr	Exposure, (μg/m^3)-hr
St. Louis, MO (*93*)	1977				
(61 days)	July 15	12.2	7.0	3	21
	July 16,17	18.4	9.2	7	64
	July 17	27.6	13.0	4	52
	1978				
(59 days)	Feb 9,10	10.5	7.0	13	91
	Feb 10	8.0	6.0	1	6
	Feb 10	9.0	7.0	3	21
	Feb 11	9.0	7.5	4	30
	Feb 11	13.7	8.5	20	170
St. Louis, MO (*94*)	1984				
(8 days)	Aug 4	7.4	7.4	1	7
	Aug 5	9.8	9.8	1	10
	Aug 6	7.4	7.4	1	7
	Aug 7	12.3	12.3	1	12
	Aug 8	8.3	8.3	1	8
Harriman, TN (*62*)	1984				
(7 days)	Aug 13	8.0	6.0	7	42
	Aug 14	10.0	6.5	13	85
	Aug 15	18.0	8.5	16	136
	Aug 16	9.0	6.3	4	25
	Aug 17	7.0	5.8	5	29
	Aug 18	14.0	8.0	11	88
	Aug 19	6.0	5.2	2	10
Watertown, MA (*62*)	1984				
(7 days)	Aug 9	14.0	7.0	6	42
	Aug 10	14.0	7.5	12	90
	Aug 12	11.0	7.0	8	56

[a]Only periods where concentrations exceeded 5 μg/m^3 H_2SO_4 were considered episodes.

Table 9. Episodic acidic aerosol data and estimates of exposure from multiple-hour sampling acid sulfate studies.[a]

Study (period)	Date	Peak, μg/m^3	Mean, μg/m^3	Duration, hr	Exposure, (μg/m^3)-hr
Toronto (*46*)	1986				
(6 weeks) (Site 1)	July19	7.8	6.4	12.4	86
(Site 1)	July 25	14.4	14.1	18.8	264
(Site 2)	July 25	19.4	13.4	25.3	338
(Site 3)	July 25	8.3	8.3	7.5	62

[a]Only periods where concentrations exceeded 5 μg/m^3 H_2SO_4 were considered episodes.

first would be studies conducted during major summertime haze episodes, where large populations in the eastern U.S. could be affected periodically by high acidic sulfate levels. The exposure could be manifested by high H_2SO_4 and/or NH_4HSO_4 accumulated over periods of 1 hr or more throughout a day or sequence of days. Because these episodes occur in the summer, large segments of the population will be participating in outdoor activities in the rural and suburban areas. These individuals would be most at risk during regional episode and would be the focus of opportunities for epidemiological studies.

The second type of exposure would be confined to places downwind of a power plant plume or urban plume during any season of the year. Obviously, the greatest potential for population exposure would still be the summer; however, exposures could still occur during all of the other seasons. The latter would be confounded by variable levels of outdoor activity and degree of penetration of the acidic sulfate into the home. It should be noted that the highest acid concentrations observed in the cited studies appear to be associated with direct plume impacts. Therefore, these types of locations warrant considerable attention in future epidemiological studies.

Our present knowledge about the frequency, magnitude, and duration of acidic sulfate aerosol events and episodes is insufficient. Efforts must be made to gather more data, but these should be done in such a way that evaluation of human exposure is the focus of the research not just to establish a routine monitoring network. In addition, further data are required on the mechanisms of formation of H_2SO_4 and on what factors can be used to predict acidic sulfate episodes.

We are very grateful for the exhaustive literature searches conducted by Timothy Buckley, a doctoral student in the Exposure Assessment joint curriculum of Rutgers University Department of

Environmental Science and UMDNJ-Robert Wood Johnson Medical School Department of Environmental and Community Medicine. We thank Dr. Roger Tanner of Brookhaven National Laboratory who supplied us with a thorough review of the analytical methodology for use in preparing the EPA Critical Issues Document. Arlene Bicknell and Theresa McShane diligently and patiently typed the manuscript. This work was partially supported by EPA Contract No. 7DIZ16NANX, Research Triangle Park, NC, Lester Grant, Project Officer.

REFERENCES

1. Wolfe, R. F. Effects of airborne pollutants on mucociliary clearance. Environ. Health Perspect. 66: 223–237 (1986).
2. Schlesinger, R. B. Comparative irritant potency of inhaled sulfate aerosols—effects on bronchial mucociliary clearance. Environ. Res. 34: 268–279 (1984).
3. Morandi, M., Kneip, T., Cobourn, J., Husar, R., and Lioy, P. J. The measurement of H_2SO_4 and other sulfate species at Tuxedo, NY, with a thermal analysis of flame photometric detector and the analysis of simultaneously collected quartz filter samples. Atmos. Environ. 17: 843–848 (1983).
4. Lioy, P. J., Spektor, D., Thurston, G., Citak, K., Lippmann, M., Bock, N., Speizer, F. E., and Hayes, C. The design considerations for ozone and acid aerosol exposure and health investigations: The Fairview Lake summer camp—photochemical smog case study. Environ. Internat. 13: 271–283 (1987).
5. Thurston, G. D., and Waldman, J. M. Acid aerosol transport episodes in Toronto, Ontario. Proceedings of the 80th Annual Meeting of the Air Pollution Control Association, New York City, 87–89.9, 1987.
6. Scarengelli, F. P., and Rehme, K. A. Determination of atmospheric concentrations of sulfuric acid aerosol by spectrophotometry, coulometry, and flame photometry. Anal. Chem. 41: 707–713 (1969).
7. Dubois, L., Baker, C. J., Teichman, T., Zdrojewski, A., and Monkman, J. L. The determination of sulphuric acid in air: A specific method. Mikrochim. Acta 2: 269–279 (1969).
8. Richards, L. W., and Mudgett, P. S. Methods and Apparatus for Sulfuric Acid Aerosol Analysis. U.S. Patent No. 3, 833, 972, October 1, 1974.
9. Richards, L. W., Johnson, K. R., and Shepard, L. S. Sulfate Aerosol Study. Rockwell International, Newbury Park, CA, Report AMC8000.13FR, August 1978.
10. Leahy, D., Siegel, R., Klotz, P., and Newman, L. The separation and characterization of sulfate aerosol. Atmos. Environ. 9: 219–229 (1975).
11. Maddalone, R. F., Shendrikar, A. D., and West, P. W. Radiochemical evaluation of the separation of H_2SO_4 aerosol by microdiffusion from various filter media. Mikrochim. Acta 3: 391–401 (1974).
12. Commins, B. T. Determination of particulate acid in town air. Analyst 88: 364–367 (1963).
13. Junge, C., and Scheich, G. Determination of the acid content of aerosol particles. Atmos. Environ. 5: 165–175 (1971).
14. Brosset, C., and Ferm, M. Man-made airborne acidity and its determination. Atmos. Environ. 12: 909–919 (1978).
15. Stevens, R. K., Dzubay, T. G., Russworm, G., and Rickel, D. Sampling and analysis of atmospheric sulfates and related species. Atmos. Environ. 12: 55–68 (1978).
16. Tanner, R. L., Cederwall, R., Garber, R., Leahy, D., Marlow, W., Meyers, R., Phillips, M., and Newman, L. Separation and analysis of aerosol sulfate species at ambient concentrations. Atmos. Environ. 11: 955–967 (1977).
17. Phillips, M. F., Gaffney, J. S., Goodrich, R. W., and Tanner, R. L. Computer-Assisted Gran Titration Procedure for Strong Acid Determination. Brookhaven National Laboratory, Upton, NY, Report BNL 35734, October 1984.
18. Huygen, C. A simple photometric determination of sulfuric acid aerosol. Atmos. Environ. 9: 315–319 (1975).
19. Penzhorn, R. D., and Filby, W. G. Eine methode zur spezifischen bestimmung von schwefelhaltigen sauren in atmospharischen aerosol. Staub-Reinhalt Luft 36: 205–207 (1976).
20. Huntzicker, J. J., Hoffman, R. S., and Ling, G. S. Continuous measurement and speciation of sulfur-containing aerosols by flame photometry. Atmos. Environ. 12: 83–88 (1978).
21. Cobourn, W. G., Husar, R. B., and Husar, J. D. Continuous, in situ monitoring of ambient particulate sulfur using flame photometry and thermal analysis. Atmos. Environ. 12: 89–98 (1978).
22. Tanner, R. L., D'Ottavio, T., Garber, R., and Newman, L. Determination of ambient aerosol sulfur using a continuous flame photometric detection system. I. Sampling system for aerosol sulfate and sulfuric acid. Atmos. Environ. 14: 121–127 (1980).
23. Allen, G. A., Turner, W. A., Wolfson, J. M., and Spengler, J. D. Description of a Continuous Sulfuric Acid Sulfate Monitor. Presented at the Fourth National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources, Raleigh, NC, May 1984.
24. Slanina, J., Schoonebeek, C. A. M., Klockow, D., and Niessner, R. Determination of sulfuric acid and ammonium sulfates by means of a computer-controlled thermodenuder system. Anal. Chem. 57: 1955–1960 (1985).
25. D'Ottavio, T., Garber, R., Tanner, R. L., and Newman, L. Determination of ambient aerosol sulfur using a continuous flame photometric detection system. II. The measurement of low-level sulfur concentrations under varying atmospheric conditions. Atmos. Environ. 15: 197–204 (1981).
26. Charlson, R. J., van der Pohl, A. H., Covert, D. S., Waggoner, A. P., and Alquist, N. C. $H_2SO_4/(NH_4)_2SO_4$ background aerosol: Optical detection in the St. Louis region. Atmos. Environ. 8: 1257–1267 (1974).
27. Larson, T. V., Ahlquist, N. C., Weiss, R. E., Covert, D. S., and Waggoner, A. P. Chemical speciation of $H_2SO_4/(NH_4)_2SO_4$ particles using temperature and humidity controlled nephelometry. Atmos. Environ. 16: 1587–1590 (1982).
28. Rood, M. J., Larson, T. V., Covert, D. S., and Ahlquist, N. C. Measurement of laboratory and ambient aerosols with temperature and humidity-controlled nephelometry. Atmos. Environ. 19: 1181–1190 (1985).
29. Appel, B. R., Wall, S. M., Haik, M., Kothny, E. L., and Tokiwa, Y. Evaluation of techniques for sulfuric acid and particulate strong acidity measurements in ambient air. Atmos. Environ. 14: 559–563 (1980).
30. Appel, B. R., Tokiwa, Y., Wall, S. M., Haik, M., Kothny, E. L., and Wesolowski, J. J. Determination of Sulfuric Acid, Total Particle-Phase Acidity and Nitric Acid in Ambient Air, Air and Industrial Hygiene Laboratory, Berkeley, CA, Report CA/DOH/AIHL/SP-18, June 1979.
31. Coutant, R. W. Effect of experimental variables on collection of atmospheric sulfate. Environ. Sci. Technol. 11: 873–878 (1977).
32. Pierson, W. R., Hammerle, R. H., and Brachaczek, W. W. Sulfate formed by interaction of sulfur dioxide with filters and aerosol deposits. Anal. Chem. 48: 1808 (1976).
33. Camp, D. C. An intercomparison of results from samplers used in the determination of aerosol composition. Environ. Intern. 4: 83–100 (1980).
34. Tanner, R. L., Garber, R., Marlow, W., Leaderer, B. P., and Leyko, M. A. Chemical composition of sulfate as a function of particle size in New York summer aerosol. Ann. N.Y. Acad. Sci. 322: 99–114 (1979).
35. Stelson, A. W., and Seinfeld, J. H. Relative humidity and temperature dependence of the ammonium nitrate dissociation constant. Atmos. Environ. 16: 983–992 (1982).
36. Jacob, D. J., Waldman, J. M., Munger, J. W., and Hoffmann, M. R. The H_2SO_4-HNO_3-NH_3 system at high humidities and in fogs: 2. Comparison of field data with thermodynamic calculations. J. Geophys. Res. 91: 1089–1096 (1986).
37. Russell, A. G., McRae, G. J., and Cass, G. R. Mathematical modeling of the formation and transport of ammonium nitrate aerosol. Atmos. Environ. 17: 949–964 (1983).
38. U.S. Environmental Protection Agency. An Acid Aerosols Critical Issues Paper: Health Effects and Aerometrics. ECAO, Research Triangle Park, NC, 1987.
39. Mueller, P. K., and Hidy, G. M. The sulfate regional experiment: Report of findings, Volumes I–III. EPRI EA-1901, EPRI, Palo Alto, CA, March 1983.
40. U.S. Environmental Protection Agency. Air Quality Criteria for

Particulate Matter and Sulfur Oxides. EPA-600/8-82-029b, ECAO, Research Triangle Park, NC, December 1982.

41. Husar, R. B. Ammonia over North America: Sources, sinks, and flow rates. CAPITA Report, Washington University, St. Louis, MO, 1982.
42. Husar, R. B., and Holloway, J. M. Sulfur and Nitrogen over North America, Ecological Effects of Acid Deposition. National Swedish Environment Protection Board, Report PM 1636, 95–115, 1983.
43. Erisman, J. W., Wevmetten, A. W. M., Pinksterboer, E. F., Asman, W. A. H., Waijer-Ypelaan, A., and Slanina, J. Atmospheric ammonia: Distribution, equilibrium with aerosols and conversion rate to ammonium. Proceedings on the EURASAP Symposium on Ammonia and Acidification (W. A. H. Asman and H. S. M. A Diederen, Eds.) Bilthoven, Netherlands, 13–15 April 1987, pp. 59–72.
44. Pierson, W. R., Brachaczek, W. W., Truex, T. J., Butler, J. W., and Korniski, T. J. Ambient sulfate measurements on Allegheny Mountain and the question of atmospheric sulfate in the northeastern United States. In: Aerosol: Anthropogenic and Natural Sources and Transport (T. J. Kneip and P. J. Lioy, Eds.), Ann. N. Y. Acad. Sci. 338: 145–173 (1980).
45. Keeler, G. J. A Hybrid Approach for Source Apportionment of Atmospheric Pollutants in the Northeastern United States. Ph. D. Dissertation, University of Michigan, Ann Arbor, MI 1987.
46. Waldman, J. M., Lioy, P. J., Thurston, G. D., and Lippmann, M. Analyses of spatial patterns in sulfate aerosol acidity within a metropolitan area. Atmos. Environ., submitted.
47. Friedlander, S. K. Future aerosols of the Southwest: Implications for fundamental aerosol research. In: Aerosol: Anthropogenic and Natural Sources and Transport (T. J. Kneip and P. J. Lioy, Eds.). Ann. N.Y. Acad. Sci. 338: 588–598 (1980).
48. California Air Resources Board. The Fourth Annual Report to the Governor and Legislature on the Air Resources Board Acid Deposition Research and Monitoring Program. Sacramento, CA, 1986.
49. Ministry of Health, Mortality and Morbidity during London Fog, December 1952. Reports on Public Health and Medical Subjects, No. 95 Her Majesty's Stationary Office, London, 1954.
50. Commins, B. T., and Waller, R. E. Observation from a ten-year study of pollution at a site in the city of London. Atmos. Environ. 1: 49–68 (1967).
51. Ito, K., and Thurston, G. D. The estimation of London aerosol exposures from historical visibility records. Presented at the 80th Annual Meeting of the Air Pollution Control Assoc., New York, Paper 87–42.2, 1987.
52. Mader, R. P., Hamming, W. J., and Bellini, A. Determination of small amounts of sulfuric acid in the atmosphere. Anal. Chem. 22: 1181–1183 (1950).
53. Thomas, M. D., Hendricks, R. H., and Hill, G. R. Some impurities in the air and their effects on plants. In: Air Pollution: Proceedings of U.S. Technical Conference (L. McCabe, Ed.), McGraw-Hill, New York, 1952, pp. 41–47.
54. Thomas, M. D. Sulfur dioxide, sulfuric acid aerosol and visibility in Los Angeles. Int. J. Air Water Pollut. 6: 443–454 (1962).
55. Pruppacher, H. R., and Klett, J. D. Microphysics of Clouds and Precipitation. D. Reidel Publishing, Dordrecht, Holland, 1978, pp. 9–55.
56. Waldman, J. M., and Hoffmann, M. R. Pollutant behavior in fog. In: Source and Fates of Aquatic Pollutants (R. A. Hites and S. J. Eisenriech, Eds.), ACS Adv. Chem. 216: 79–129 (1987).
57. Hoffmann, M. R. Comment on Acid Fog. Environ. Sci. Technol. 18: 61–64 (1984).
58. Firket, J. Fog Along the Meuse Valley. Trans. Faraday Soc. 32: 1192–1197 (1936).
59. Wolff, G. T., Kelley, N. A., and Ferman, M. A. On the sources of summertime haze in the eastern United States. Science 211: 703–705 (1981).
60. Hidy, G. M., Mueller, P. K., Grosjean, D., Appel, B. R., and Wesolowski, J. J. The Character and Origins of Smog Aerosols. John Wiley and Sons, New York, 1980.
61. Beck, W. B., and Tannahill, G. K. An overview of the Houston area oxidant study. Proceedings of the 71st Annual APCA Conference No. 78–30.1, June 1978.
62. Ferris, B. G., Jr., and Spengler, J. D. Problems in estimation of human exposure to components of acid precipitation precursors. Environ. Health Perspect. 63: 5–10 (1985).
63. Pierson, W. R., Brachaczek, W. W., Grose, R. A., Jr., Japar, S. M., Norbeck, J. M., and Keeler, G. J. Atmospheric acidity measurements on Allegheny Mountain and the origin of ambient acidity in the northeastern United States. Atmos. Environ., submitted.
64. Tanner, R. L., and Marlow, W. H. Size discrimination and chemical composition of ambient airborne sulfate particles by diffusion sampling. Atmos. Environ. 11: 1143–1150 (1977).
65. Huntzicker, R. S., Hoffman, J. J., and Cary, R. A. Aerosol sulfur episodes in St. Louis, MO. Environ. Sci. Technol. 18: 962–967 (1984).
66. Lioy, P. J., Samson, P. J., Tanner, R. L., Leaderer, B. P., Minnich, T., and Lyons, W. The distribution and transport of sulfate species in the New York metropolitan area during the 1977 summer aerosol study. Atmos. Environ. 14: 1391–1407 (1980).
67. Spengler, J. D., Allen, G. A., Foster, S., Severance, P., and Ferris, B. J., Jr. Sulfuric acid and sulfate aerosol events in two cities. In: Aerosols: (S. D. Lee, T. Schneider, L. D. Grant, and P. J. Verkerk, Eds.), Lewis Publishers, Chelsea, MI, 1986, pp. 107–119.
68. Appel, B. P., Hoffer, E. M., Tokiwa, Y., and Kothny, E. L. Measurement of sulfuric acid and particulate strong acidity in the Los Angeles Basin. Atmos. Environ. 16: 589–593 (1982).
69. John W., Wall, S. M., and Ondo, J. L. Dry acid deposition on materials and vegetation: Concentration in ambient air. California Air Resources Board Interagency Agreement A1-160-32, February 1985.
70. Stevens, R. K., Dzubay, T. G., Shaw, P. W., Jr., McClenny, W. A., Lewis, C. W., and Wilson, W. E. Characterization of the aerosol in the Great Smoky Mountains. Environ. Sci. Technol. 14: 1491–1498 (1980).
71. Lioy, P. J., and Lippmann, M. Measurement of exposure to acidic sulfur aerosols. In: Aerosols (S. D. Lee, T. Schneider, L. D. Grant, and P. J. Verkerk, Eds.), Lewis Publishers, Chelsea, MI, 1986, pp. 743–752.
72. Cadle, S. Seasonal variations in nitric acid, nitrate, strong aerosol acidity, and ammonia in an urban area. Atmos. Environ. 19: 181–188 (1985).
73. Kelly, T. J., Tanner, R. L., McLaren, S. E., and DuBois, M. V. Seasonal variation in atmospheric chemistry in the Adirondacks Presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, MI, June 16–21, 1985.
74. Palmer-Smith, T., and Wentzell, B. R. Ambient acid aerosols in rural Nova Scotia. Water Air Soil Pollut. 30: 837–843 (1986).
75. Spektor, D. M., Yen, B. M., and Lippmann, M. Effect of concentration and cumulative dose of inhaled sulfuric acid on lung clearance in humans. Environ. Health Perspect. 79: 167–172 (1988).
76. Husar, R. B., Lodge, J. P., Jr., and Moore, D. J., Eds. Sulfur in the Atmosphere. Pergamon Press, Oxford, 1978.
77. Ellestad, T. G. Aerosol composition of urban plumes passing over a rural monitoring site. In: Aerosols: Anthropogenic and Natural, Sources and Transport (T. J. Kneip and P. J. Lioy, Eds.) Ann. NY Acad. Sci. 338: 202–218 (1980).
78. Neytzell-de Wilde, F. G., and Taverner, L. Experiments relating to the possible production of an oxidating acid leach liquor by autooxidation for the extractions of uranium. In: Proceedings of the 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy, Volume 3, Geneva, Switzerland, September 1–13, 1958. United Nations, Geneva, Switzerland, 1958, pp. 303–317.
79. Chang, S. G., Brodzinsky, R., Toossi, R., Markowitz, S. S., and Novakov, T. Catalytic oxidation of SO_2 on carbon in aqueous solutions. In: Proceedings of Carbonaceous Particles in the Atmosphere (T. Novakov, Ed.), National Science Foundation and Others, Berkeley, California, March 20–22, 1978. LBL-9037, University of California, Lawrence Berkeley Laboratory, Berkeley, CA, June 1979, pp. 122–130.
80. Houghton, H. G. On the chemical composition of fog and cloud water. J. Meteorol. 12: 355–357 (1955).
81. Mrose, H. Measurement of pH and chemical analyses of rain-, snow-, and fog-water. Tellus 18: 266–270 (1966).
82. Okita, T. Concentration of sulfate and other inorganic metals in fog and cloud water and in aerosol. Jpn. Meteorol. Soc. Jpn. 46: 120–126 (1968).

83. Castillo, R. A., Jiuso, J. E., and McLaren, E. The pH and ionic composition of stratiform cloud water. Atmos. Environ. 17: 1497–1505 (1983).
84. Falconer, P. D., Ed. Cloud Chemistry and Meteorological Research at Whiteface Mountain: Summer 1980. Atmospheric Sciences Research Center, State University of New York, Albany, Publ. No. 806, 1981.
85. Waldman, J. M., Munger, J. W., Jacob, D. J., and Hoffmann, M. R. Chemical characterization of stratus cloudwater and its role as a vector for pollutant deposition in a Los Angeles pine forest. Tellus 37B: 91–108 (1985).
86. Mack, E. J., and Katz, U. The Characteristics of Marine Fog Occurring off the Coast of Nova Scotia. Calspan Corp., Buffalo, NY, Report CJ-5756-M-1, 1976.
87. Mack, E. J., Katz, U., Rogers, C. W. An Investigation of the Meteorology, Physics, and Chemistry of Marine Boundary Layer Processes. Calspan Corp., Buffalo, NY, Report CJ-6017-M-1, 1977.
88. Brewer, R. L., Ellis, E. C., Gordon, R. J., and Shepard, L. S. Chemistry of mist and fog from the Los Angeles urban area. Atmos. Environ. 17: 2267–2271 (1983).
89. Munger, J. W., Jacob, D. J., Waldman, J. W., and Hoffmann, M. R. Fog water chemistry in an urban atmosphere. J. Geophys. Res. 88C: 5109–5121 (1983).
90. Jacob, D. J., Waldman, J. M., Munger, J. W., and Hoffman, M. R. Chemical composition of fogwater collected along the California coast. Environ. Sci. Technol. 19: 730–735 (1985).
91. Jacob, D. J., Waldman, J. M., Munger, J. W., and Hoffmann, M. R. A field investigation of physical and chemical mechanisms affecting pollutant concentrations in fog droplets. Tellus 36B: 272–285 (1984).
92. Fuzzi, S., Castillo, R. A., Juisto, J. E., and Lala, G. G. Chemical composition of radiation fogwater at Albany, N. Y. and the relationship to fog microphysics. J. Geophys. Res. 89D: 7159–7164 (1984).
93. Cobourn, W. F. In Situ Measurements of Sulfuric Acid and Sulfate Aerosol in St. Louis. Doctoral Dissertation, Washington University, St. Louis, MO, 1979.
94. Cobourn, W. G., and Husar, R. B. Diurnal and seasonal patterns of particulate sulfur and sulfuric acid in St. Louis, July 1977–June 1978. Atmos. Environ. 16: 1441–1450 (1982).
95. Tanner, R. L., Leaderer, B. P., and Spengler, J. D. Acidity of atmospheric aerosols: A summary of data concerning their chemical nature and amounts of acid. Environ. Sci. Technol. 15: 1150–1153 (1981).
96. Koutrakis, P., and Spengler, J. D. A nine month study of acid aerosol in St. Louis, MO, and Kingston, TN. Atmos. Environ., in press.