

On the Concentration of Sulfate in Precipitation

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(Manuscript received 21 October 1977, in final form 6 November 1978)

ABSTRACT

Two case studies are used to examine the relationship of the sulfate concentration in surface precipitation to the microphysical characteristics of the precipitating cloud systems. The data from one case study support the contention that existing sulfate aerosol was incorporated into cloud water by the nucleation process and accounted for nearly all of the observed cloud and precipitation water sulfate concentration. These activated sulfate particles comprised nearly 60% of the clear-air sulfate mass concentration. Once nucleated, the sulfate particles accumulated water through the condensation process and were subsequently deposited at the surface after accretion on large snowflakes. The presumption of aqueous phase sulfate oxidation of SO₂ was not necessary to account for the observed sulfate concentrations.

The data from the second case study are more limited and difficult to interpret. Nucleation and below cloud washout appeared to be the main contributors to the surface sulfate concentration in precipitation water.

1. Introduction

The determination of wet removal characteristics for a variety of atmospheric pollutants can proceed only so far without the availability of simultaneous surface and cloud level observations of aerosol, gas and water chemistry. Our present precipitation scavenging program in Muskegon, Michigan, has provided an opportunity to obtain such samples. The following paper presents data from two of the storm events encountered during March 1977. In subsequent sections, changes in the chemical characteristics (notably sulfate) of surface precipitation are related to the aerosol and cloud characteristics determined from aircraft samples and from weather radar observations. However, at this point it is appropriate to present some general background information in order to familiarize the reader with those concepts concerning sulfur transformation, nucleation and wet removal considered in this paper.

2. Background

The sulfate concentration in surface precipitation is the consequence of several cumulative processes occurring within and beneath the clouds. Should a large fraction of the sulfate aerosol be greater than 1.0 μm ,¹ then below-cloud scavenging could account for a significant fraction of the sulfate concentration in precipitation. Indeed, if the data of Kadowaki (1976) and Meszaros (1968) are representative of typical

aerosol spectra, then as much as 10% of the atmospheric sulfate mass could exist as aerosol large enough to be removed by inertial impaction by snowflakes or raindrops.

Brownian diffusion appears to play a less important role than inertial impaction in sulfate removal. Although significant numbers of sulfate aerosol <0.1 μm may be attached to cloud and hydrometeor particles (see, e.g., Young, 1974), the accumulated mass of the attached sulfate aerosol would be considerably smaller than that usually observed (1–10 mg ℓ^{-1}). Similarly, the phoretic attachment of sulfates cannot account for sulfate concentrations typically found in precipitation.

Sulfates, however, are generally soluble with the majority of the mass size distributed over diameters <1.0 μm (Harrison *et al.*, 1975). Thus they should be effective as cloud condensation nuclei. If, as Weiss *et al.* (1977) claim, the major portion of the aerosol between 0.1 and 1.0 μm are sulfate particles, then the sulfate aerosol could be responsible for nearly all of the cloud droplets appearing in continental clouds.

Once a cloud has formed, the possibility exists for the generation of additional sulfate mass through oxidation of SO₂. Indeed, long-lasting non-precipitating clouds, fog or haze droplets may be prolific sources of sulfate aerosol. Generally, however, the lifetime of an individual cloud or raindrop is small in comparison to the lifetime of an entire cloud. Thus, for significant SO₂ conversion to SO₄ to occur in the water being removed from precipitating clouds, the time scale for conversion must be comparable in magnitude to the lifetime of those cloud particles involved in the precipitation process.

¹ All dimensions refer to the maximum particle dimensions.

To estimate the lifetime of individual cloud droplets in a precipitating system, we consider a single collector particle (raindrop or snowflake) with cross sectional area A , and fallspeed v , in a cloud containing n_d cloud droplets per unit volume. This collector particle will sweep out a number of cloud droplets in time δt equal to $A\bar{v}n_d\delta t$. If the total number of collector particles per unit volume is denoted by n_c , and \bar{A} and \bar{v} represent an average cross-sectional area and fallspeed, respectively, for the collector particle population, then the cloud droplet population will be reduced by collisions according to

$$\frac{\delta n_d}{\delta t} = -\bar{A}\bar{v}n_d n_c. \quad (1)$$

By taking any reasonable values for \bar{A} , \bar{v} and n_c (e.g., $4 \times 10^{-7} \text{ m}^2$, 3 m s^{-1} and 10^3 m^{-3} , respectively) one can establish that most cloud droplets will be collected and removed from the cloud well within one hour of their formation, provided that precipitation is steady over the collection interval.

The formation of the collector particles, themselves, is a relatively rapid process and generally takes less than one hour (Scott, 1978). Thus, 1 h is felt to be a representative upper limit for the lifetime of individual precipitation particles or cloud droplets within precipitating clouds. Therefore, aqueous phase conversion of SO_2 within individual liquid phase elements of such clouds could proceed for no more than 1 h before the elements are deposited upon the surface.

Based on this time restriction, large conversion rates of SO_2 are required to explain observed sulfate concentrations in precipitation water. It seems reasonable to suggest, therefore, that the majority of sulfate in the precipitation reaching the ground probably already existed as sulfate aerosol before the precipitating cloud formed.

To illustrate the above suggestions about sulfate in precipitation water, assume that the sulfate aerosol is primarily $(\text{NH}_4)_2\text{SO}_4$ or H_2SO_4 . Then cloud supersaturations as low as 0.2% should activate a major portion of the airborne sulfate aerosol mass.² With typical sulfate concentrations of $5 \mu\text{g m}^{-3}$ (Alkezweeny and Powell, 1977), nearly all of the $5 \mu\text{g m}^{-3}$ of sulfate should be placed into the cloud water at nucleation. Airborne SO_2 concentrations are typically near $30 \mu\text{g m}^{-3}$ (e.g., Alkezweeny and Drewes, 1977). Thus, sulfate concentration added to cloudwater by oxidation of SO_2 would approach that incorporated by nucleation only if transformation rates are sustained at a rate exceeding 10% per hour for an hour or more.

Transformation rates in excess of 10% per hour are possible by the O_2 or O_3 oxidation mechanisms provided

the pH of cloud water remains above 5 (Harrison *et al.*, 1976). Usually, however, the pH in precipitation over much of the eastern United States is nearer 4.5 (Likens, 1976). The oxidation rate of SO_2 by H_2O_2 is much more rapid and nearly independent of pH (Penkett *et al.*, 1977), but the total amount of SO_2 that is oxidized is limited by the available H_2O_2 . Assuming that one mole of SO_2 is oxidized for every mole of H_2O_2 , then values of H_2O_2 would have to exceed 1 ppb in the lower troposphere before the sulfate produced in the cloud by this mechanism would equal the amount of sulfate nucleated at the cloud edges. Presently no observations of airborne H_2O_2 exist in the lower troposphere.

While the data presented in this paper are too limited to resolve these uncertainties about in-cloud conversion of SO_2 , some details of precipitation scavenging of sulfates have been revealed. The data are from experiments performed in Muskegon, Michigan, in March 1977.

3. Observations

Aircraft observations of trace gas concentrations and aerosol size distributions were obtained on several occasions during March 1977 at Muskegon, Michigan. On one day (5 March) penetrations of precipitating clouds provided supplemental determinations of droplet size distribution and cloud water concentration. Samples of cloud water were also collected for analysis on 5 March. On two days (5 and 17 March) surface samples of precipitation and SO_2 were obtained simultaneously with the aircraft samples.

The aircraft was equipped with a Thermo-Systems electrical aerosol (Whitby) analyzer and a Royco optical particle counter for determining aerosol size distribution, an integrating nephelometer for indication of particles $>0.1 \mu\text{m}$, a GE Aitken Nuclei Counter for indication of total particles, and a thermal-diffusion chamber (Radke and Turner, 1972) for determination of cloud condensation nuclei. Giant aerosol $>5 \mu\text{m}$ were impacted on glass slides, tested for deliquescent properties, and chemically analyzed with a scanning electron microscope (Hindman, 1975).

High-volume filter samples were obtained aboard the aircraft at ~ 40 min intervals and were used to determine concentrations of SO_2 , SO_4 and total atmospheric ammonia. A Whatman GF-82 filter treated with oxalic acid was used for total ammonia measurements. Sulfur concentrations were obtained with a filter pack combination. A quartz filter (Pallflex, QAO 2500) was used for sulfate collection and was followed by two carbonate-glycerine impregnated cellulose papers (Schleicher and Schuell Fast flow SS-2w) to absorb SO_2 . Ozone concentrations were obtained with a Bendex ozone monitor. A Teco model 14 monitor was used for NO/NO_x concentrations.

Cloud droplet size distributions and liquid water concentration (LWC) were obtained with a Knollenberg

² Most numerical convective cloud models predict supersaturations exceeding 0.2% during the growth and mature stage of the cloud lifetime (see Arnason and Greenfield, 1972).

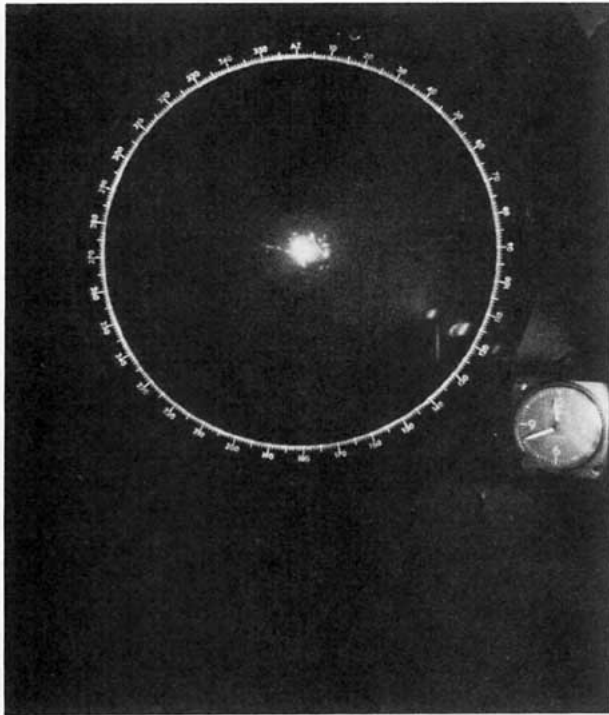


FIG. 1. Muskegon radar PPI display on 5 March 1977.
Range contours are at 50 km intervals.

axially scattering optical probe and a Johnson-Williams (JW) cloud water meter, respectively. Bulk cloud water samples were obtained by accreting supercooled cloud droplets onto a nylon wand inserted into the airstream through a hole in the fuselage.

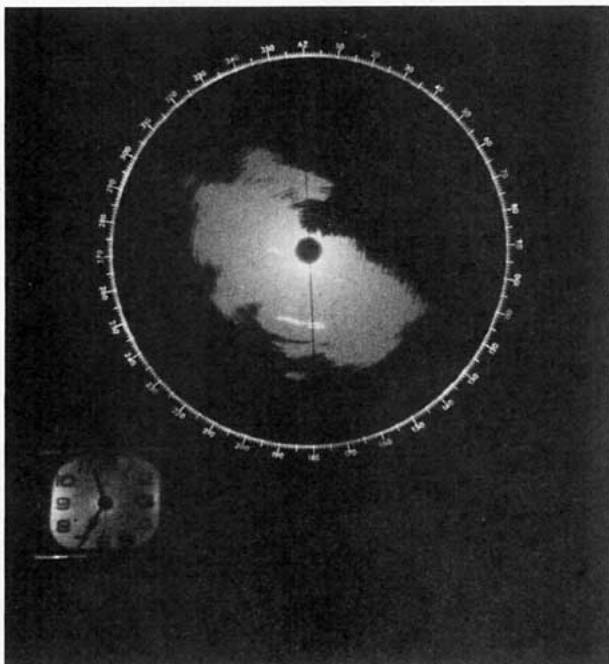


FIG. 2. As in Fig. 1 except on 17 March 1977.

At the surface, snow was collected on 3.3 m² polyethylene sheets, Formvar replicas of ice crystals were obtained, and SO₂ air concentrations were determined with a Casella SO₂ analyzer.

Both the cloud water samples and the surface precipitation samples were analyzed for SO₄, NO₃, Cl, Na and K with an ion chromatograph. Atomic absorption was used to obtain Ca and Mg, a Technicon Auto Analyzer was used for NH₄, and pH was determined with an Orion model 801A pH meter.

4. Results

This paper presents primarily the data obtained during the storm periods of 5 and 17 March. These two days represent widely varying synoptic situations as illustrated by the PPI displays in Figs. 1 and 2. On 5 March data were collected in a (snow) showery, post-frontal air mass. The only cloud echos appearing on the radar display in Fig. 1 were associated with a thin line of convective activity extending ~50 km to the west of Muskegon (center of scope). This thin band of convective activity was roughly 2 km wide and was oriented parallel to the prevailing winds at 1500 m. The band moved from west to east and passed almost directly over the surface sampling location.

Fig. 3 shows computed 12 h constant-level trajectories for air arriving at Muskegon during the 5 March sampling interval. The sampled air mass had passed over rural regions and appears to have eluded larger urban areas for at least 18 h prior to its arrival at Muskegon. Indeed, in terms of total number concentration, this was the cleanest air mass encountered during the experimental period in March. However, the sulfate and SO₂ concentrations of 6 and 15 μg m⁻³, respectively, are higher than would be expected from a clean-air mass. The 460 m MSL trajectory passed over a 400 MW fossil fueled power plant at Sheboygen, Wisconsin, where significant sulfur input into the sampled air mass could have occurred.

By contrast, the storm of 17 March was related to a synoptic-scale low center passing to the south of Muskegon. The associated precipitation shield extended north from a warm front and contained embedded bands of heavier precipitation (see the radar display in Fig. 2). The majority of precipitation falling from extratropical cyclones is felt to be associated with the passage of similar banded structures. Bands similar in appearance to those of Fig. 2 have been reported by Houze *et al.* (1976) and others who relate them to convective activity. The bands illustrated in Fig. 2 were moving from south to north and were oriented roughly perpendicular to the 850 mb wind direction.

Computed 12 h constant-level trajectories for air arriving at Muskegon during the sampling periods on 17 March (Fig. 4) illustrate considerable vertical wind shear. The heavy line in Fig. 4 represents a crude approximation of an actual 12 h trajectory of air

originating near the surface in northern Ohio and Indiana and arriving at cloud base (~1500 m MSL) at the beginning of the precipitation period (the trajectory assumes an average ascent rate of 0.02 m s⁻¹).

Table 1 presents the basic meteorological parameters associated with these two sampling periods. The below-cloud observations represent averages over ~1 h of sampling. The in-cloud observations on 5 March represent averages of several passes through (and roughly parallel to the long axis of) the convective line shown in Fig. 1. Each pass through the 5 March cloud lasted about 3 min, and the in-cloud data represent an average over ~10 km. The in-cloud observations of 17 March represent 30 min of flight in a solid cloud layer. Accuracy of the humidity measurements is estimated at ±10%.

For the 5 March cloud penetrations, substantial amounts of liquid water were observed. Indeed, at one point icing was so severe that the Johnson-Williams liquid water probe was encased in ice shortly after peak LWC values of 0.32 gm⁻³ were recorded, suggesting that even higher values of LWC prevailed in the cloud. The heavily rimed aggregates of columns collected at the surface are consistent with ice particles riming in an environment with large liquid water content.

By contrast, on 17 March no liquid water was detected with the JW meter, and no icing was observed on the aircraft extremities or on the bulk water probes. Although "cloudiness" obscured the ground from the aircraft during the penetration, the sampled region was subsaturated, even with respect to ice. Large, wet flakes were observed at the ground but the temperature was too warm (1-4°C) for replication.

Below-cloud relative humidity (RH) exhibited similar contrasts on each day. On 5 March high humidities (87%) were encountered, while on 17 March the air was considerably drier below cloud base (humidities of 50%).

Table 2 summarizes the aerosol distributions determined during the two storm periods, and for comparison, during a fair weather day (11 March). All data reported in Table 2 were computed from observations

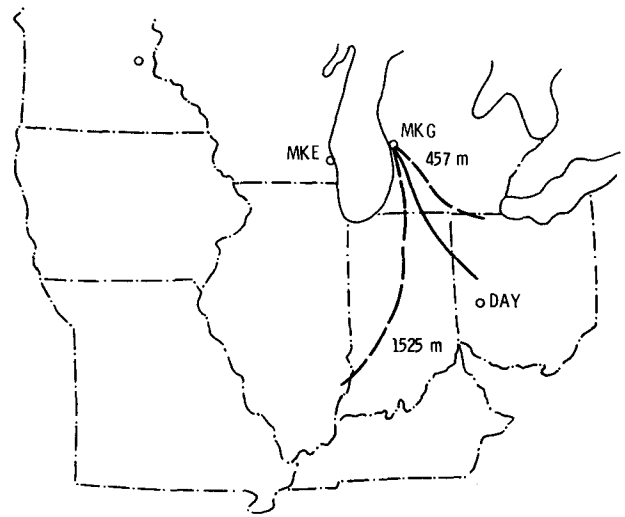


FIG. 4. 12 h trajectories for air arriving at MKG at 1800 EST 17 March 1977.

taken in the well-mixed boundary layer below cloud-base level (if clouds existed). Flights in this boundary layer exceeded an hour in duration. Grab samples were used to compute aerosol concentration while continuous samples were used for determination of CCN supersaturation spectra, concentration of deliquescent particles and gas concentrations.

The aerosol number concentration was determined from an EAA analysis of bag samples. The number concentrations in Table 2 represent average concentrations while the range of values are indicated by the plus-minus notation. As seen in the table, the aerosol number concentration on 5 March was one-third to one-half of the concentration recorded on 11 and 17 March; the discrepancy resulted from a deficiency of particles <0.1 μm on 5 March.

The high ambient humidities (87% on 5 March and 50% on 17 March) made determination of aerosol size distributions difficult. For example crystalline (NH₄)₂SO₄ deliquesces at 81% RH (Twomey, 1953) while H₂SO₄ exists as a solution droplet at all humidities, ≥30% (Charlson *et al.*, 1974). At humidities near 90%

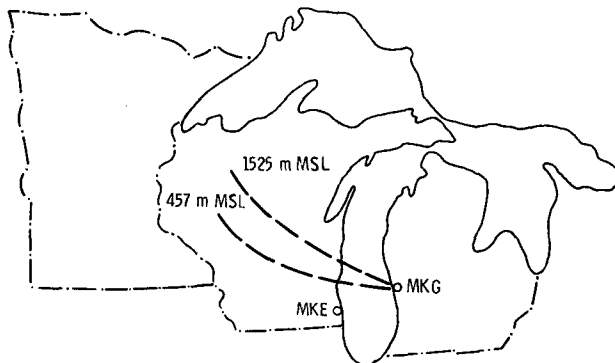


FIG. 3. 12 h trajectories for air arriving at MKG at 1800 EST 5 March 1977.

TABLE 1. Meteorological parameters.

Date	5 March			17 March	
Altitude (m MSL)	335	670	1525	700	1525-1700
Cloud liquid water concentration (g m ⁻³)					
Average	none	0.10	0.16	none	none
Maximum	none	0.16	0.32*	none	none
Air temperature (°C)	-1	-4	-9	0	-6
Relative humidity (%)	87±10	100	100	50±10	80±10
Cloud base (m MSL)	610			1550	
Type of snow crystal at the ground	heavily rimed aggregates of columns; snow grains			large flakes—no replicas (too warm)	

* Maximum value before probe iced up.

TABLE 2. Aerosol characteristics.

Date	5 March	11 March	17 March
Altitude of sample (m MSL)	335	900	700
Total number of particles >10 ⁻² μm	4100 ± 1100 7-bag average	14900 ± 2700 3-bag average	9200 ± 5500 6-bag average
Total mass of aerosol with dimensions between 10 ⁻² and 1 μm (μg m ⁻³)	5.7–11.5	14.9–29.8	4.1–8.1
CCN spectra (valid for 0.2 < S < 1.5%) (cm ⁻³)	N = 2400S ^{0.71}	N = 980S ^{0.46}	N = 636S ^{1.35}
Deliquescent particles >5 μm at 95% RH (m ⁻³)	No sample	<50	~100
Mass of airborne sulfate (μg m ⁻³)			
Range	5.7–6.3	7.7–10.3	2.2–2.8
Mean	5.9	9.1	2.4
Ratio of sulfate mass to aerosol mass	0.46–0.92	0.27–0.54	0.27–0.53

solution droplets of (NH₄)₂SO₄ or H₂SO₄ can roughly double their dry sizes due to condensation of water vapor (Tang and Munkelwitz, 1977). However, the temperature differential between the ambient air and the cabin air was 25–30°C. Therefore, the sampled particles were assumed to have dried by the time they were sized by the Whitby and Royco instruments.

The total mass of aerosol between 0.01 and 1.0 μm was approximated by multiplying the observed average number concentration in each sampling interval by the geometric mean volume of that interval and summing the product over all intervals up to 1.0 μm. The bulk density of the aerosol particles was assumed to vary between 1000 kg m⁻³ (to give the lower mass value in Table 2) and 2000 kg m⁻³ (to give the higher mass value in Table 2). Notice that in spite of differences in number concentration, the total aerosol mass concentration for 5 March was comparable to the mass concentration computed for 17 March.

The cloud condensation nuclei (CCN) spectra presented in Table 2 were obtained from an eyeball fit to all CCN data collected during several scans over supersaturations between 0.2 and 1.5% during a 20–30 min leg of each flight. Cloud supersaturations between 0.2 and 1.5% activate aerosols with dimensions roughly between 0.02 and 0.10 μm if they are completely soluble. However, natural aerosol often contain insoluble components. For example, should the aerosol be only 30% soluble, then supersaturations between 0.2 and 1.5% would activate particles with dimensions roughly between 0.03 and 0.15 μm. Thus, there is some uncertainty about the size of the aerosol activated at particular supersaturations. Assuming that particles as small as 0.02 μm are activated at 1.5% supersaturations, then on 11 and 17 March between 15 and 20% of the aerosol >0.02 μm acted as CCN, while on 5 March nearly 100% of the aerosol >0.02 μm appeared to be CCN. Hindman (1975) has also reported cases

where the majority of aerosol appears to be effective CCN.

An additional uncertainty in number of CCN exists. Theoretical calculations by Alofs and Carstens (1976) indicate that for aerosol with CCN spectra characteristics similar to those given here, the CCN counter may underestimate the correct value of cloud condensation nuclei by 50% at cloud supersaturations of 1%. Corrections have not been made to the above estimates. Thus, the above stated fractions of active aerosol could be a factor of 1.5 too low.

Each mean value of SO₄ in Table 2 (and SO₂ or ammonia in subsequent tables) represents the average of two hi-volume filters samples weighted by the sample volume of each. Sample volumes ranged from 13 to 26 m³. Sulfate filter concentrations from the high-volume samples always exceeded blank filter concentrations by factors of 30 or more.

In order to estimate the ratio of submicron sulfate mass to total submicron aerosol mass, 90% of the observed sulfate mass was assumed to be distributed in particles <1.0 in diameter (Kadowaki, 1976; Meszaros, 1968). Based on this assumption, the sulfate ion was found to account for a considerable fraction of the total aerosol mass in each of the three sets of data presented here—ranging from 27–54% on 11 and 17 March to 46–92% on 5 March.

Summaries of various air and water chemistry measurements are shown in Table 3. Both the range- and volume-weighted averages are presented for surface precipitation chemistry data. The data are from sequential precipitation samples taken at roughly half-hour intervals at single sites during the storms of 5 and 17 March. The averaged value is comprised of three samples for 5 March and five samples for 17 March. Roughly 0.3 mm of (melted) precipitation fell during the sampling interval for each storm. The first sample on each day was taken at the beginning of the storm. Snow continued to fall after the last sample was taken.

Cloud penetrations were at the predicted upwind source regions of the precipitation arriving at the surface. Chemical analyses of the liquid cloud water collected during these penetrations are also presented in Table 3. Each cloud water probe was left in the airstream until rime ice was visible on it. The cloud water entries in Table 3 represent data from a single probe at each altitude.

The most notable data in Table 3 illustrate the differences in pH and sulfate concentrations that occurred during the two storm periods. The precipitation (and cloud liquid water) on 5 March were quite acidic (3.7 < pH < 4.8) and contained large amounts of sulfate (11–33 mg ℓ⁻¹), while on 17 March, the precipitation contained much less sulfate (~2 mg ℓ⁻¹) and was much less acidic (pH ≈ 6.2).

Also of interest in Table 3 is the high concentration of inorganic components in the cloud base liquid water. In addition, the cloud liquid water near cloud base was

TABLE 3. Values for air and water chemistry measurements.

	pH	SO ₄ (mg l ⁻¹)	NO ₃ (mg l ⁻¹)	Cl (mg l ⁻¹)	NH ₄ (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	Total ammonia (μg m ⁻³)	O ₃ (μg m ⁻³)	SO ₂ (μg m ⁻³)	SO ₄ (μg m ⁻³)
5 March													
(a) Surface precipitation	4.0-4.8	11.2-12.8	10.8-11.7	0.6-0.9	4.3-5.9	0.1-0.6	0.1-0.4	0.5-1.9	0.2-1.0				
(b) Clear air	4.1	12.0	11.2	0.8	5.3	0.5	0.2	1.2	0.5		135	16.2	5.9
1. 335 m MSL										3.4		13.8	
2. Surface													
(c) Cloud water	4.0	32.9	29.6	1.9	14.6	1.3	1.3	2.9	0.2				
1. 670 m MSL								0.6	0.03				
2. 1525 m MSL	3.7	12.0	10.2	0.4	2.7	0.1	2.1						
17 March													
(a) Surface precipitation	5.8-6.8	0.6-4.3	1.2-2.9	0.1-0.4	0.3-0.6	0.1-1.0	0.1-6.3	0.6-1.8	0.2-0.6				
(b) Clear air	6.2	1.9	2.0	0.3	0.5	0.5	1.4	1.2	0.4		130	12.4	2.4
1. 700 m (MSL)										1.3		6.0	
2. Surface													
(c) Cloud water	No liquid cloud water detected												

less acidic than the cloud top water—suggesting a neutralization of the low-level aerosol by ingested ammonia or basic subcloud particles.

It is unclear what role the nitrates played in determining cloud-water/precipitation-water acidity or in influencing the aerosol size distribution or solubility. When the sulfate concentrations were high as on 5 March, the nitrate and hydrogen ion concentrations were also high. Low nitrate concentrations on 17 March corresponded to low sulfate and hydrogen ion concentrations.

5. Discussion of data

a. 5 March

On 5 March comparisons between surface chemistry data and cloud liquid water data, or comparisons between cloud liquid water samples at different levels, are felt to be justified. There is no way to guarantee that large spatial and temporal variations in cloud water chemistry did not exist. However, small-scale variability should have been filtered out of the data because of the large horizontal distances (10 km) required for an in-cloud sample. The precipitation collected at the surface in 30 min increments also represents an average cloud fallout over the same horizontal scale. In addition, the radar photographs of the precipitating cloud line on 5 March indicate little temporal variation in cloud dimensions or intensity during the sampling interval. Thus, the averaging inherent in data collection should have removed any small-scale spatial or temporal variation. In addition, the sampled portion of the clouds was felt to be representative of the cloud region contributing precipitation to the surface collector.

The high concentrations of pollutants observed in the cloud-base liquid water during the snow shower on 5 March are intriguing. At first glance, the lowered concentrations in the cloud top sample of liquid water appears to result from dilution as a consequence of ascent and condensation. However, there is little meteorological or chemical evidence to support the notion that air is ascending from cloud base to the 1500 m level. Indeed, the cloud liquid water chemistry observations imply different source regions for the materials observed at 670 and 1525 m. The chemical components observed at the lowest level of the cloud were most likely drawn into the cloud through the cloud base, while those materials detected at cloud top likely entered the cloud through the sides at altitudes slightly less than 1525 m.

If the sulfate was incorporated into the cloud water during nucleation of drops, it is evident from the observations at cloud base that only about 55% of the available, subcloud sulfate mass was activated. If this nucleation mechanism was responsible for the cloud liquid-water sulfate concentrations, then the concentration of sulfate at the surface should have depended primarily on the number of "dirty" cloud droplets

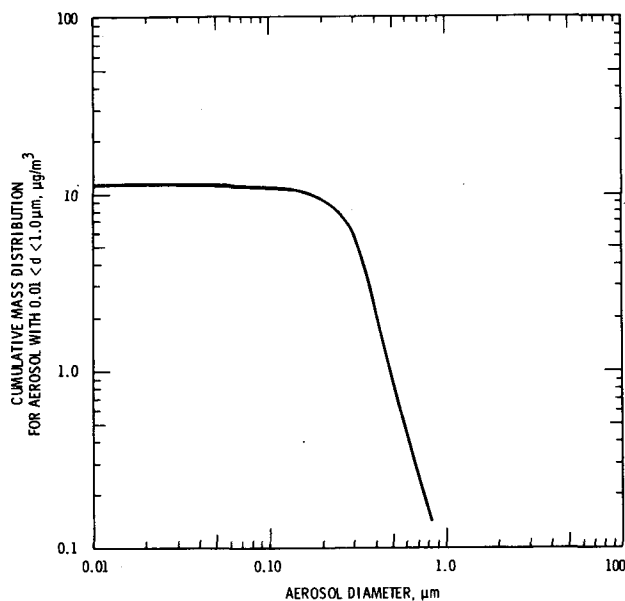


FIG. 5. Mass distribution on 5 March 1977 for aerosol with dimensions between 0.01 and 1.0 μm . A bulk density of 2000 kg m^{-3} is assumed.

accreted by relatively pure snowflakes as they fell through the cloud.

A portion of the sulfate detected in the cloud and precipitation water may also have resulted from oxidation of absorbed SO_2 . The aqueous phase oxidation possibility cannot be disproved. However it is difficult to imagine how the available sulfate at cloud base could *not* have accounted for all of the sulfate observed in the cloud water. For example, assume a bulk density of 2000 kg m^{-3} for the total aerosol (Laktionov, 1972), and assume 90% of the measured sulfate mass was distributed over particle sizes $< 1.0 \mu\text{m}$. Also consider natural time and spatial variabilities of the observed mass concentrations of sulfate, total aerosol and liquid water to be on the order of 10%. Then, the observed submicron sulfate aerosol would represent 38 to 57% of the total submicron aerosol mass if it was composed primarily of H_2SO_4 or 52 to 78% of the total submicron aerosol mass if it was primarily $(\text{NH}_4)_2\text{SO}_4$. Since the natural, submicron sulfate was most likely composed of soluble H_2SO_4 or its neutralization products (Charlson, *et al.*, 1974), the mean solubility (ratio of soluble to insoluble mass) of the 5 March submicron aerosol was at least between 0.38 and 0.78, and probably higher.

Given the observed cumulative mass distribution for total, submicron aerosol shown in Fig. 5, and assuming that the solubility of the submicron particulate matter is independent of particle size, one can show that for any distribution of soluble, sulfate aerosol (e.g., 20% of the particles are 90% soluble, 10% are 40% soluble, etc.) such that the average solubility ϵ of the submicron distribution is $0.38 < \epsilon < 0.78$, a cloud supersaturation of 0.1% or less would have been sufficient to account

for the entire observed concentration of sulfate in the cloud water. As noted in the Introduction, such supersaturations are frequently exceeded for the cloud types observed on 5 March.

To illustrate the above statement with a simple example, we presume that the average solubility of the submicron aerosol spectrum was 0.4, and assume that the solubility was a consequence of soluble sulfate. We then let 60% of the particles contain 5% of the soluble mass while the remaining 40% of the particles are 92.5% soluble (to give a mean solubility of 0.4). If the soluble sulfate was $(\text{NH}_4)_2\text{SO}_4$, then at a cloud supersaturation of 0.1%, all of the 5% soluble particles with diameters $> 0.65 \mu\text{m}$ would have formed cloud droplets, while all of the 92.5% soluble particles with diameters $> 0.14 \mu\text{m}$ would have activated. The critical diameter-solubility-supersaturation relationships used here come from Fitzgerald (1973). Thus, all particles with dimensions $> 0.65 \mu\text{m}$ would have become cloud droplets. From the cumulative mass diagram for 5 March in Fig. 5, those aerosol $> 0.65 \mu\text{m}$ accounted for $0.34 \mu\text{g m}^{-3}$ of the total submicron mass. Since, for this example, these particles are assumed 40% soluble, $0.14 \mu\text{g m}^{-3}$ of sulfate mass is contained in particles $\geq 0.65 \mu\text{m}$.

Similarly, in the size interval between 0.14 and $0.65 \mu\text{m}$, $10.1 \mu\text{g m}^{-3}$ of total mass is available. Since only the 92.5% soluble particles are activated in this interval and because the highly soluble particles represent only 40% of the total aerosol concentration, $3.7 \mu\text{g m}^{-3}$ of sulfate is activated from this second size interval.

Summing to get the total sulfate contribution for this hypothetical example gives $3.8 \mu\text{g m}^{-3}$ of sulfate incorporated into cloud water. In order to provide the observed concentration of sulfate (33 mg l^{-1}) in the measured 0.1 g m^{-3} of cloud water, $3.3 \mu\text{g m}^{-3}$ of $(\text{NH}_4)_2\text{SO}_4$ needed to be activated. Thus, the supersaturation of 0.1% yields more than enough sulfate in the cloud water.

Similar examples using more complex distributions of soluble aerosol [both H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$] yield the same conclusions. If the average solubility exceeds 0.38 and the cloud supersaturation was near 0.1%, then nucleation of preexisting sulfate could account for all of the sulfate encountered in the cloud liquid water at cloud base on 5 March.

There are no data to substantiate the assumption of solubility being independent of particulate size, as was assumed above. However, the computed, cumulative mass distribution for 5 March places restrictions on major deviations from this assumption. For example, if the larger aerosol (e.g., those particles $> 0.4 \mu\text{m}$) did not contain sulfate and were completely insoluble, then the remaining smaller aerosol would have been required to be nearly pure sulfate to account for the sulfate measured with the hi-volume samplers. Cloud supersaturations of 0.1% would still activate particles $> 0.1 \mu\text{m}$, and the above speculation about preexisting

TABLE 4. Surface observations on 17 March.

Sample	Time (EST)	Muskegon temperature (°C)	pH	SO ₄ (mg l ⁻¹)	NO ₃ (mg l ⁻¹)	Cl (mg l ⁻¹)	NH ₄ (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	Comments
B1	1915-1953	4	6.8	1.2	2.5	0.4	0.6	0.4	6.3	1.7	0.5	band passage
B2	1940-2016		6.7	0.8	1.3	0.3	0.3	0.1	—	0.9	0.2	
B3	2000-2037	2	6.3	0.6	1.2	0.2	0.3	0.1	0.1	0.6	0.2	
B4	2025-2100		6.3	1.6	1.9	0.3	0.5	0.4	0.5	1.0	0.3	band arrives at 2045
B5	2045-2116	1	5.8	4.3	2.9	0.5	0.5	1.0	0.1	1.8	0.6	band arrives at 2045

sulfate accounting for the cloud water sulfate would be unaltered.

Similarly, if only the larger aerosol were soluble, or if more than 10% of the sulfate was in particles >1.0 μm, then cloud supersaturations even lower than 0.1% would be sufficient to place the appropriate amount of sulfate in the cloud liquid water.

b. 17 March

Table 4 presents all of the surface precipitation chemistry data taken from sequential samples at a single site during the storm of 17 March. The snowfall commenced at 1915 EST and continued beyond the final sampling interval. Approximately 0.3 mm of (melted) precipitation fell during the sampling period.

In contrast to 5 March the surface precipitation of 17 March was considerably less acidic and contained about 1/10 the sulfate concentration. The high pH values (~6.4) may have resulted from contamination by the Muskegon urban plume. Surface sampling locations were intended to be remote from distinguishable urban plumes but aircraft intercepts at 670 m established that the surface sampling location was just to the north of the plume. Upward diffusion and interaction with the southerly winds at higher levels may have carried flakey, basic, ash particles over the surface sampling location.

Several mechanisms may have contributed significant fractions to the sulfate concentrations observed at the ground on 17 March. Although the sulfate concentration in the air below cloud base was quite low (2.4 μg m⁻³), inertial impaction may have been an important contributor to surface sulfate concentrations. Snowflake dimensions on 17 March were observed to be between 1 and 2 mm. According to Locatelli and Hobbs (1974), a 2 mm flake typically has a mass of 2 × 10⁻⁷ kg. Then, if 10% of the total observed subcloud sulfate mass is assumed to be contained in particles with an average diameter of 2.0 μm, the number of sulfate particles collected by a 2 mm snowflake after a 15 min fall from cloud base to the ground would equal about 30. Thus, the sulfate concentration in surface precipitation would have been ~1 mg l⁻¹. Table 4 displays the observed concentrations of sulfate which ranged between 0.6 and 4.3 mg l⁻¹. Therefore, inertial impaction could have been responsible for some, but not all of the wet sulfate deposition on 17 March.

If a large fraction of the total atmospheric ammonia observed on 17 March was available as ammonia gas, then the gas-phase concentrations of NH₃, SO₂ and O₃, and the observed pH suggest the potential for aqueous phase production of sulfate by the Scott-Hobbs (1967) or the Penkett (1972) mechanisms. Sufficient liquid water appears to have been available in the falling snowflakes. Indeed, extensive melting and evaporation into the dry layer beneath cloud base enabled the snow to reach the surface despite the initially warm (4°C) surface temperatures on 17 March. Estimates of the available liquid water concentration can be obtained by presuming a flake concentration of 1 l⁻¹, and a flake mass of 2 × 10⁻⁷ kg 10% of which is liquid water. Then the total liquid water content of the snowflakes would have been near 0.025 g m⁻³.

Fig. 6 is based on this liquid water content of 0.025 g m⁻³ and presents predictions of aqueous phase sulfate production from the Scott-Hobbs and the Penkett models. As shown in the figure, up to 30 mg of sulfate per liter of liquid water could have been produced in 12 min. Dilution by the remaining 90% ice mass could have then reduced the sulfate concentrations to observed surface values.

The mathematical formulations needed to apply the Scott-Hobbs or the Penkett oxidation models have been presented in detail in numerous publications (see, e.g., Easter and Hobbs, 1974; Penkett *et al.*, 1977; Yue *et al.*, 1975) and are not presented here. Observed concentrations of SO₂ and O₃ were used for initial model conditions, while the NH₃ concentrations were varied between 0.5 and 1.7 ppb to account for their uncertainty as a result of measuring only total ammonia concentrations. The curves of Fig. 6 also include depletion of ambient gas vapor pressures because of adsorption and conversion.

To obtain the curves of Fig. 6, the rate constant *k* of O₂ oxidation was taken as $k = 7.8 \times 10^{-4} + 3.54 H^{0.5}$, where *k* has units of s⁻¹ and H is in mol per liter (Yue *et al.*, 1975). The rate constant for O₃ oxidation was taken as $k = [4.4 \times 10^4 H^{0.1} [M^{-0.9} s^{-1}]]$ from Larson *et al.* (1977). Both rate constants were applied at a temperature of 270 K.

The first three sulfate observations in Table 4 are consistent with an expected decrease in sulfate concentrations as less melting occurs when the evaporating, melting snowflakes cool their environment. However,

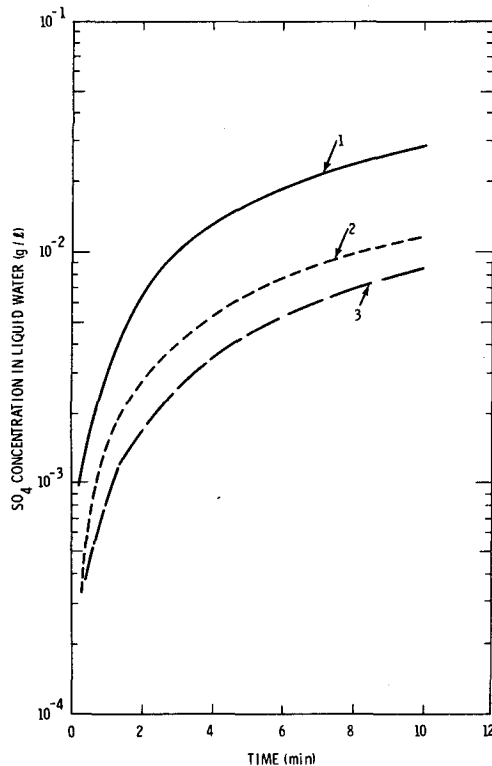


FIG. 6. Sulfate production in 0.025 g m^{-3} of liquid water as a function of time. Curves 1 and 2 are for SO_2 oxidation by O_2 ; curve 3 is for SO_2 oxidation by O_3 . Concentrations of ambient SO_2 and NH_3 are initially 4.7 and 1.7 ppb, respectively, for curve 1, and 4.7 and 0.5 ppb, respectively, for curves 2 and 3. Ozone and CO_2 concentrations are 65 and 2.83 ppm, respectively.

this melting-transformation mechanism cannot account for the increased sulfate concentrations after 2000 EST when both the temperature and the pH continued to decrease.

The observed concentrations of the other chemical constituents in the precipitation all behave in manners similar to sulfate; i.e., decreasing concentrations with time followed by increasing concentrations. Thus, during the period when the snowflakes were the wettest and when the pH was highest, there is little indication of any behavior unique to sulfate—such as aqueous phase production.

By far the most striking relationship in Table 4 is the correspondence between enhanced wet removal and the passage of bands of precipitation (see “comments” in Table 4). The greater radar returns from these bands suggest more intense precipitation and a strong likelihood of significant cloud liquid water concentration. The simultaneous increase in the concentration of all the materials in Table 4 during the band passages suggests enhanced below-cloud removal associated with larger collector particles and greater precipitation rates. However, with the exception of sodium, sulfate appears to be removed somewhat more efficiently than the other materials during the band passages. Thus, it is possible

that the nucleation-riming mechanism evident on 5 March was also playing an important role in the sulfate removal on 17 March.

6. Summary

The data presented in this paper are limited, and therefore cannot be considered typical of what is normally encountered in cloud or precipitation water. The data are, however, consistent with certain ideas about how sulfate is incorporated into cloud water and transported to the surface by precipitation. In the 5 March case study, the cloud water sulfate concentration could be accounted for by postulating the activation of preexisting, soluble sulfate aerosol at the cloud edges. The sulfate wet-removal mechanisms for this particular storm appeared to rely on the accretion, by snowflakes, of the cloud water which contained high concentrations of sulfate. Examination of data from the 17 March storm event also produced some evidence to support the contention that a nucleation-accretion mechanism was responsible for the bulk of sulfate removal by precipitation. The surface concentration of sulfate for both of these storms appeared to be related to the mass of the relatively clean collector snowflakes and to the number of “dirty” cloud droplets captured during the snowflakes’ passage through the cloud.

Much of the interpretation of the preceding sections was speculative because of the uncertainties in the actual size distribution of the sulfate aerosol and its relationship to the total aerosol size distribution. A complete specification of atmospheric sulfur transformation and removal by aqueous phase processes requires a knowledge of the size distribution and nucleating capabilities of the existing sulfate aerosols. Vertical profiles of these aerosol characteristics must also be obtained to define source regions of sulfates within the clouds. In addition, to study the possible transformation of SO_2 to SO_4 within the cloud and the falling precipitation, vertical profiles of NH_3 , O_3 and H_2O_2 should be obtained.

The need for such extensive measurements illustrates a current weakness in sampling capability. Cloud systems, in contrast to clear-air systems, represent discontinuities in the atmosphere and can rarely be considered homogeneous over time intervals of several hours. In order to characterize the cloud inflow environment, samples must be taken rapidly. One rarely has the opportunity to leisurely obtain a 40 min high-volume filter sample at several altitudes or at several locations relative to the precipitating system. The need clearly exists for rapid response techniques to provide mass and size distributions of sulfur and related gases and aerosol.

Acknowledgments. The authors gratefully acknowledge the assistance provided by the aircraft pilots R. F. Edwards and R. L. McIlvain, by the aircraft

crew R. N. Lee and K. M. Busness, and by J. M. Thorp who simultaneously coordinated the aircraft and surface observations and operated the weather radar. The assistance and cooperation provided by the NWS personnel at Muskegon is also appreciated. Surface data were collected by J. R. Geyer, T. J. Whitten and M. Lebeis. Their efforts are greatly appreciated. Many hours of data reduction were accumulated by J. E. Rothert, M. T. Dana and D. R. Drewes. Their efforts are recognized with gratitude. This research was supported by the U.S. Energy Research and Development Administration under Contract EY-76-C-06-1830.

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