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STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

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Authors:

Richard G. Semonin
Janyce D. Bartlett
Van C. Bowersox
Donald F. Gatz
Daniel Q. Naiman
Mark E. Peden
Randall K. Stahlhut
Gary J. Stensland

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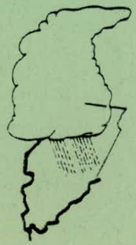

Richard G. Semonin
Principal Investigator

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STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

ABSTRACT

The analysis of aerosol samples obtained in rural east-central Illinois reveals a seasonal maximum in SO_4 during May-July and a similar pattern for NH_4. The annual median SO_4 is about 1-1.5 $\mu g/m^3$. In contrast to these ions, NO_3 displays highest values in the cold season. Soil-related species (Ca, K) seem to maximize in relation to farm tillage and harvesting practices.

The NO_3 in recent precipitation samples over the northeast U.S. increased between 1 and 2 times the values observed in the mid-1950's. The areal distribution is very similar for 1955 and 1979. Over the same time frame, the NO_x emissions have more than doubled. A one year sample of aerosol NO_3 levels at the rural Illinois site show the same seasonal trend as the precipitation concentrations.

A case study from SCORE-78 suggests that all ion concentrations analyzed from sequentially collected samples decreased from the onset of rain to a minimum corresponding to the heaviest rain rates. The concentrations varied by a factor of 10 during the shower. The site of the sequential sample collection was in a region of little horizontal gradient in the concentrations as determined from a spatial network. This feature of chemical wet deposition is important to the development of descriptive and numerical models of scavenging.

Four groups of elements in 10 event rain samples were identified using factor analysis. The groups include soluble and insoluble crustal elements, soluble pollutant metals and sulfate, and insoluble pollutant metals. The interpretive analysis is incomplete at this time, but the goal is to partition the total chemistry into various source terms. Utilizing the factor analysis approach, the St. Louis METROMEX precipitation chemistry data showed that the SO_4 deposition patterns group consistently with those of other soluble pollutants. Further, interpretation of both aerosol and rainwater SO_4 concentrations suggest that there is no need to consider SO_2 scavenging to explain the high concentrations downwind of the city. Additional factor analysis efforts on the St. Louis rainwater data set revealed that soluble and insoluble concentrations of a given element have different deposition patterns suggesting that scavenging and/or precipitation formation processes dictate the patterns (assumming the same source). The St. Louis rain sampling network data were studied to determine the density of stations required to estimate areal mean deposition values. The conclusions show that the density is dependent on the element of interest, but all elements show less spatial correlation than the rainfall.

An approach to managing the vast data base of rain chemistry used in the above studies is described. The software also examines the data for certain aspects of quality assurance. Finally, the procedures used to analyze ambient air filter samples is discussed. These procedures are now standardized in the laboratory insuring data entering the archive to be of uniform quality.

CHAPTER 1

AMBIENT AEROSOL MEASUREMENTS AT CHAMPAIGN, ILLINOIS

Gary J. Stensland and Janyce D. Bartlett

INTRODUCTION

The Illinois State Water Survey (ISWS) has been involved in a major research program to investigate the precipitation scavenging of trace constituents in the atmosphere. One part of this study, the routine collection and analysis of event precipitation samples, was begun in May, 1979 at the Willard Airport, 10 kilometers south of Champaign, Illinois. Previous research had shown the usefulness of simultaneously measuring the chemical concentrations in both air and precipitation. Therefore a routine ambient air sampling program was included with the rain collection project. The field methods and laboratory procedures for the ambient aerosol sampling were chosen to be consistent with the goals and procedures for the precipitation chemistry sampling.

A chapter in the Seventeenth Progress Report presented a description and a rather thorough evaluation of our sampling procedure (Stensland and Bartlett, 1979). A major emphasis of the report was to describe differences when various filter media and filter set-ups were used for determining ambient aerosol levels of the following soluble ions: NO_3, NH_4, SO_4, and Ca. This present chapter will discuss our soluble extractions procedure versus the new extraction procedure which will be used for our future ambient aerosol filter extractions.

This chapter will first briefly describe the sampling and extraction procedures for all the filter samples to be discussed. Then three types of data will be presented. First a comparison of Whatman versus Nuclepore filters for about 70 samples will be presented. Other features of this same data set were discussed in the previous progress report (Stensland and Bartlett, 1979). Second, a comparison of Nuclepore versus Fluoropore filters for six samples is presented. The final section will present the results for one year of daily aerosol sampling at the Willard Airport site.

EXPERIMENTAL PROCEDURE

The field site (CMI) was located at Willard Airport ten kilometers south of Champaign-Urbana in east-central Illinois. The surrounding area is predominately rural farmland although a golf course is located due east of CMI. The low-volume aerosol samplers were mounted on a seven meter tower with two samplers at a six meter height and a third at four meters. The sampling apparatus consisted of a Gast piston-type vacuum pump and an inverted polyethylene funnel (30 cm dia.). The funnel, serving as a weather shield, housed the filter unit. The unit was mounted face down with the filter surface 2 cm from the funnel's rim.

After the collection period, the filters were stored in sterilized petri dishes at room temperature. Storage time was usually 2 months but ranged from several days to 5 months. Recent work by Smith et al. (1978) indicates that an aerosol filter's chemical stability is dependent on storage technique and duration. In particular, they reported losses of nitrate (25%) and ammonium (40%) from high-vol, glass-fiber filters that had been stored without a container at room temperature for 3 months. However, their work did not consider contained filters at room temperature so no direct application of their results can be made.

The filters were extracted in 25 ml of deionized water by vigorous agitation (wrist-action shaker) for 20 minutes at room temperature. The solutions were filtered with Millipore HA filters to remove insoluble particles. This technique has been shown to be essential in order to maintain ionic stability in aqueous solutions of this nature (Peden and Skowron, 1978).

The analytical methods for the $SO_4^{=}$, NO_3^-, and NH_4^+ were methylthymol blue, cadium reduction diazotiation, and the Barthelow reaction, respectively, all automated on the Technicon Autoanalyzer II. Calcium magnesium, sodium, and potassium ions were determined by flame atomic absorption using an Instrumentation Laboratories AAES 353. Total suspended particulate (TSP) was determined gravimetrically for the Nuclepore^{tm} filters (37 mm dia., .8 μm pore size).

WHATMAN VERSUS NUCLEPORE COMPARISON

Figures 1-7 present the raw data for the 73 paired samples collected from June through September, 1977. In Figure 1 it is clear that the Nuclepore filters collected only a small fraction of the amount of NO_3 that the Whatman filters collected. It can also be seen that the two data sets are correlated to only a small degree. Figure 2 indicates that the correlation is better for NH_4. The Nuclepore filters are again clearly collecting less NH_4 than the Whatman filters. For SO_4 in Figure 3 the correlation is obviously quite good, and in Figure 4 the Ca correlation appears to be even better. In Figure 4 the only real extreme descrepancy arises on Julian days 195 and 196. Figures 5-7 present the other soil related ions. The correlations can be seen to be quite reasonable although the Mg and Na correlations do not appear to be as good as for Ca or K.

The data in Figures 1-7 can of course be scrutinized with a variety of statistical procedures. However, it is often comforting to examine the raw data, and in this manner a better intuitive feeling for the data set is sometimes attained. Some very basic statistics for the data in Figures 1-7 are presented in Table 1. These data confirm what was qualitatively apparent from the figures.

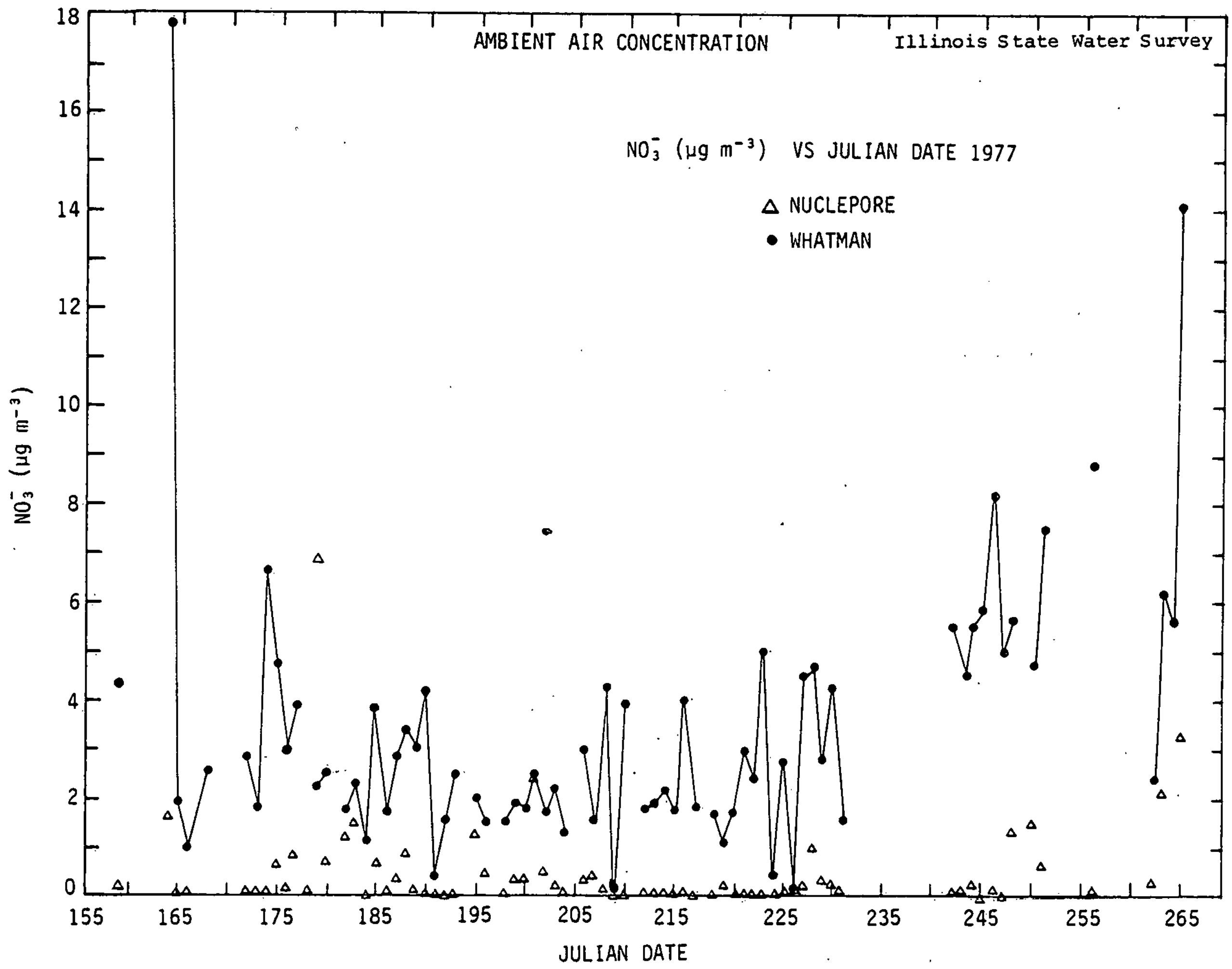

Figure 1. Daily data for ambient aerosol nitrate collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

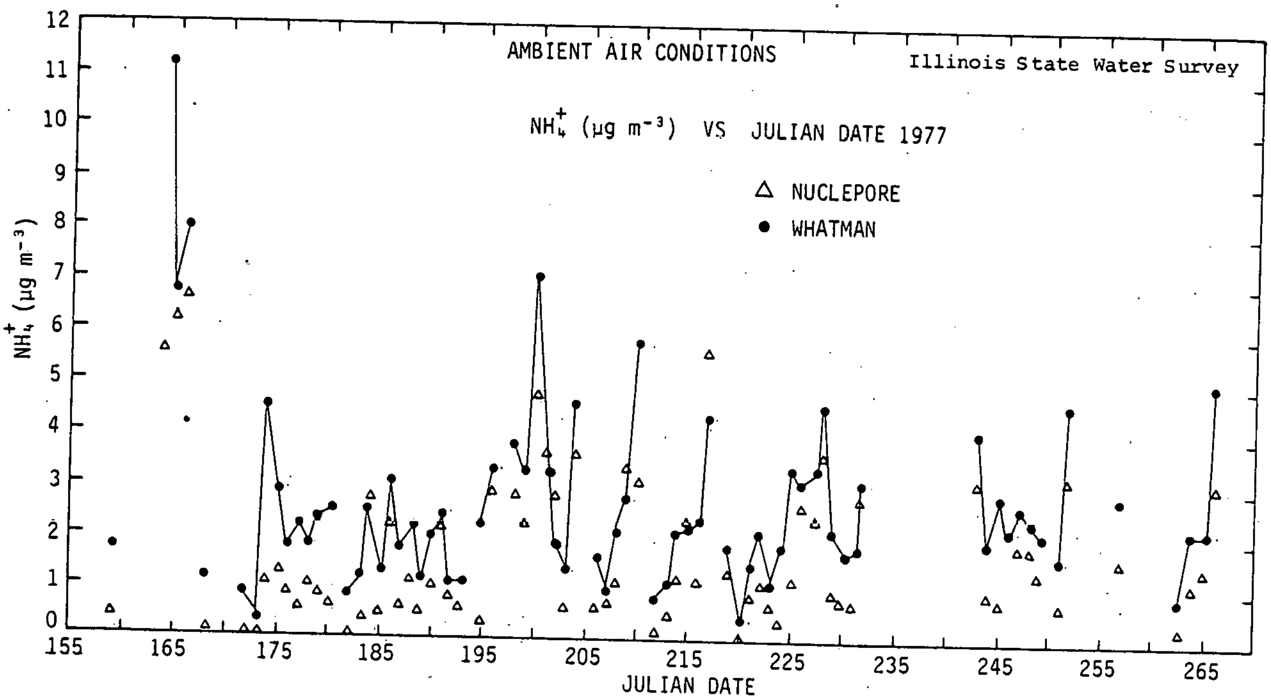

Figure 2. Daily data for ambient aerosol ammonium collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

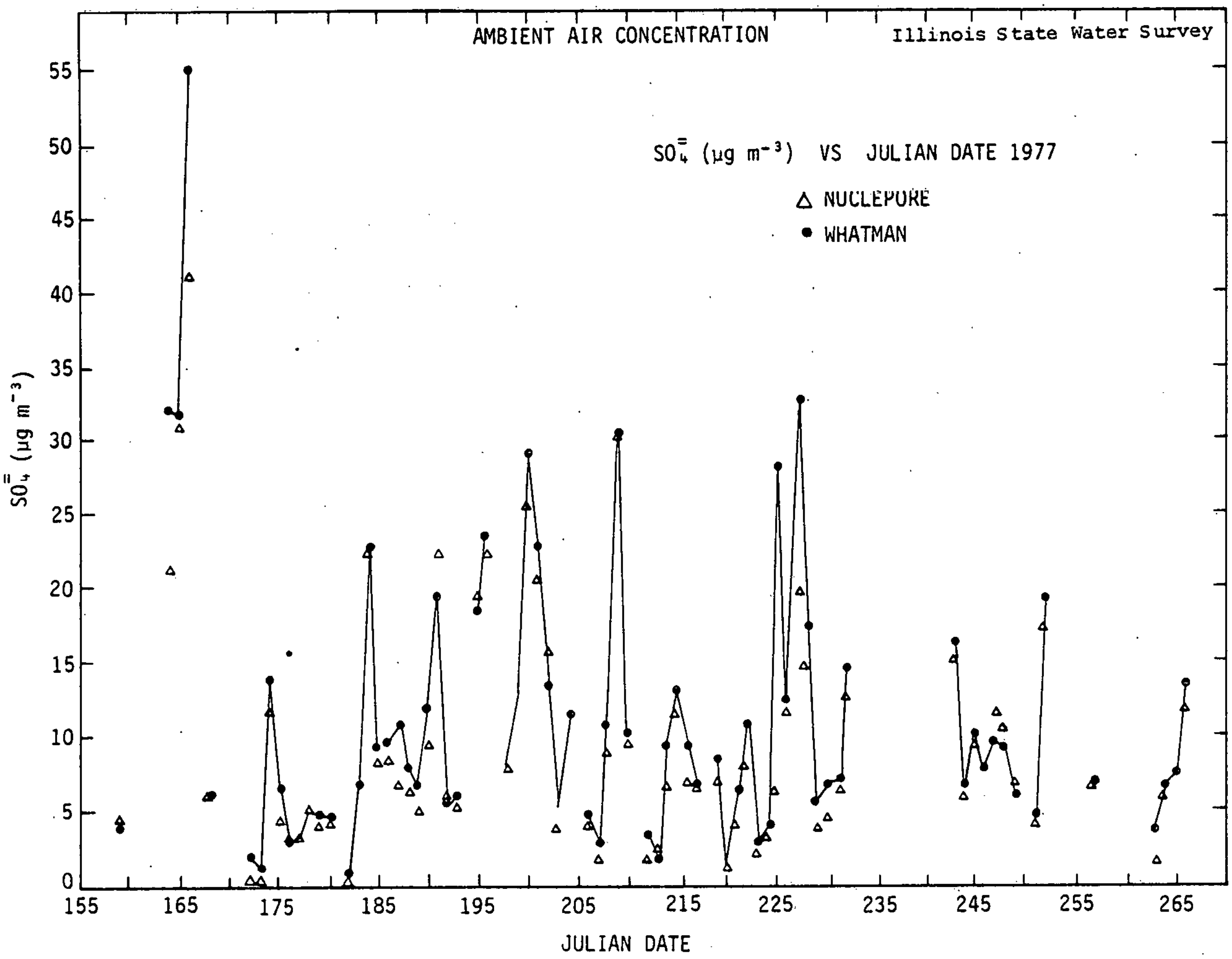

Figure 3. Daily data for ambient aerosol sulfate collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

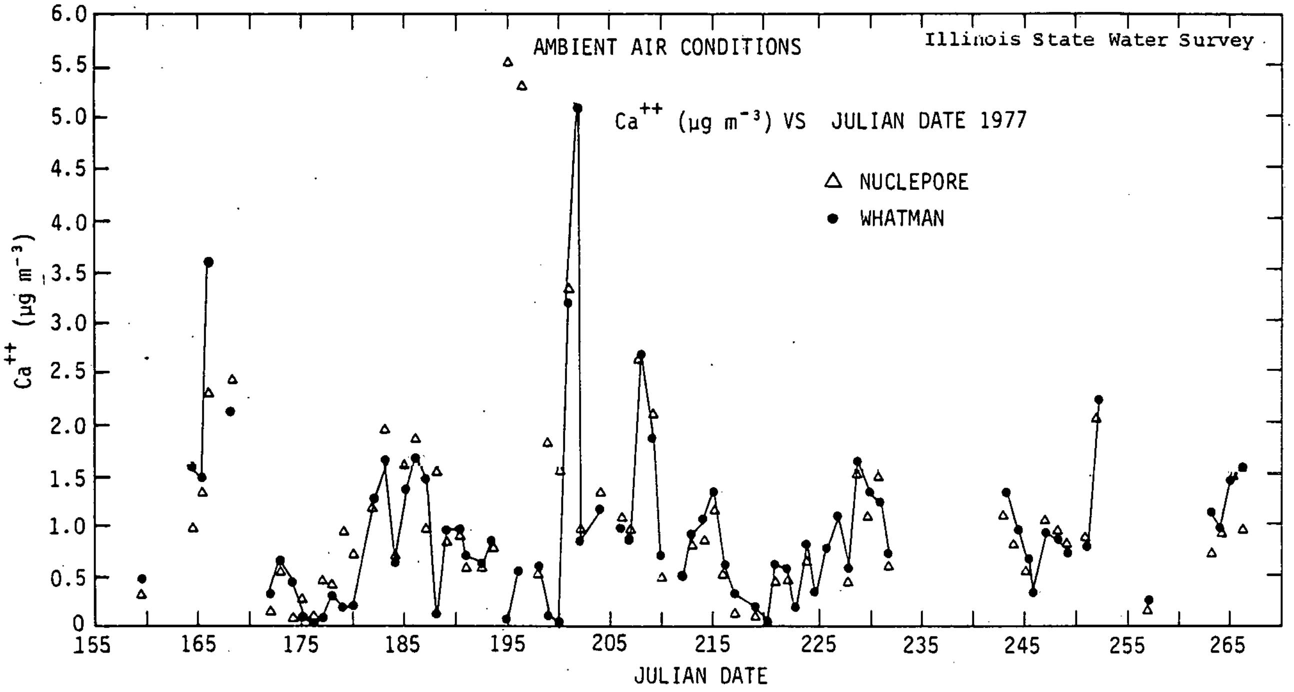

Figure 4. Daily data for ambient aerosol calcium collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

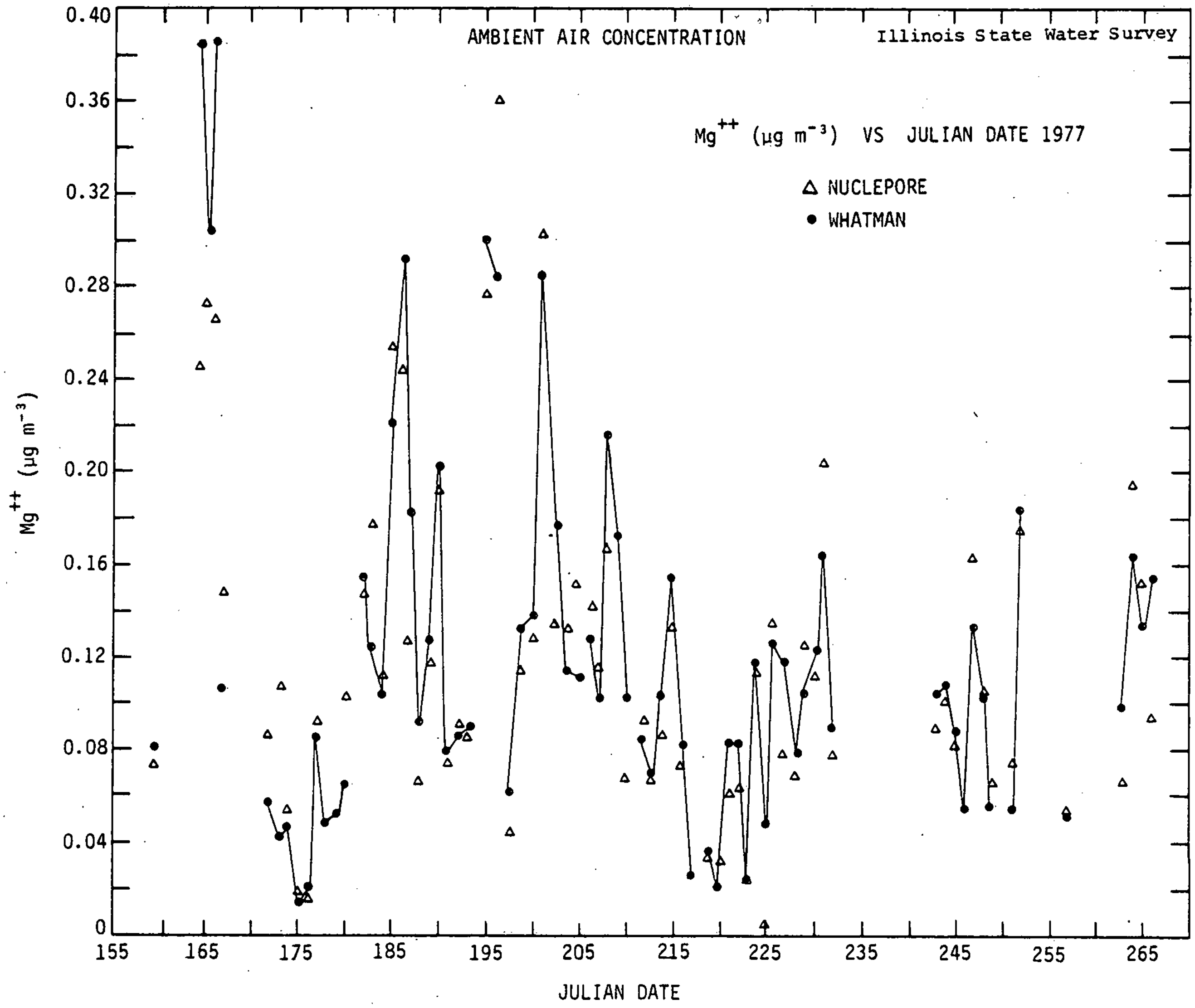

Figure 5. Daily data for ambient aerosol magnesium collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

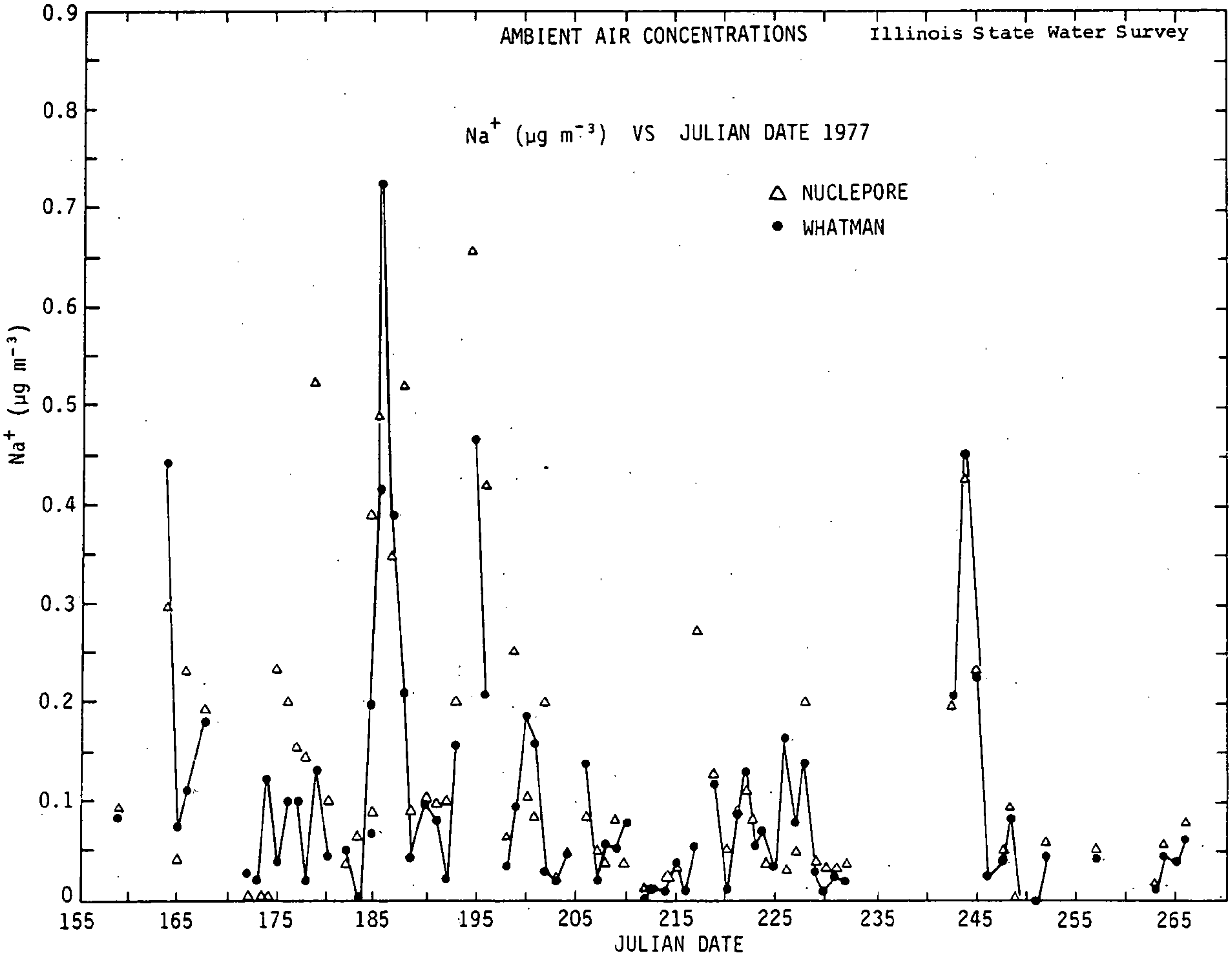

Figure 6. Daily data for ambient aerosol sodium collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

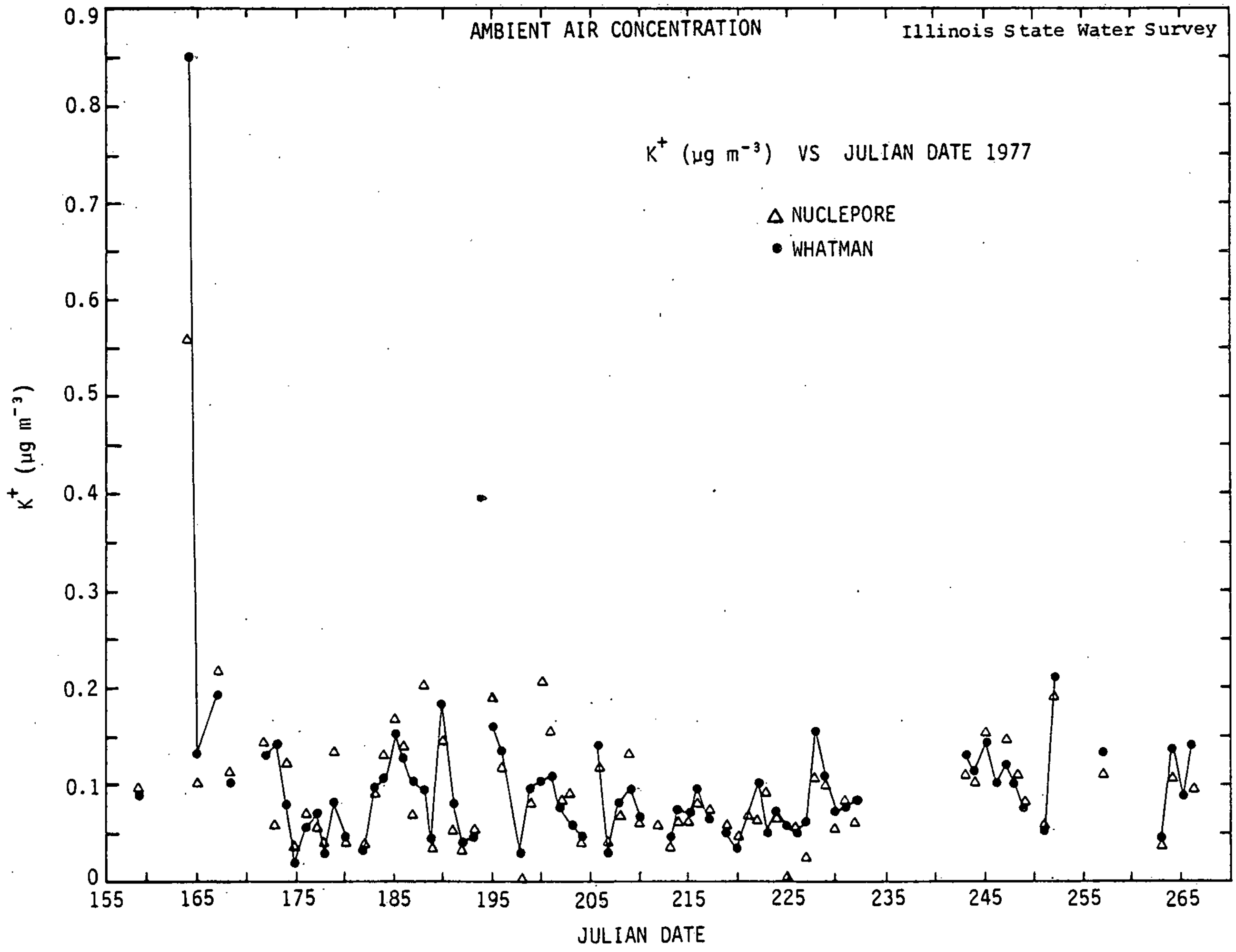

Figure 7. Daily data for ambient aerosol potassium collected simultaneously with two different filter media at Willard Airport, Champaign, Illinois.

Table 1. Medians and linear correlation coefficients for the Nuclepore versus Whatman filter data which was displayed in Figures 1-7.

	NO_3	NH_4	SO_4	Ca	Mg	Na	K
Median (Nuclepore)	.12	1.26	6.47	.87	.10	.09	.08
Median (Whatman)	2.53	2.32	8.15	.80	.10	.07	.08
Ratio: Whatman/Nuclepore	21.1	1.84	1.26	.92	1.00	.78	1.00

FLUOROPORE VERSUS NUCLEPORE COMPARISON EXPERIMENT

The purpose of this comparison was to examine the potential differences in collection efficiencies of two types of membrane filters; a Nuclepore (mfg) polycarbonate membrane (Nuclepore, 37 mm dia., .8 μm pore size) and a Millipore (mfg) polytetrafluoroethylene membrane with a polyethylene net backing (Fluoropore^{tm}, 37 mm dia., 0.5 μm pore size). The chemical constituents of interest includes SO_4, NO_3, NH_4, Ca, Mg, Na, and K.

For a six day period in September 1978 (at Bondville, Illinois, 5 km west of CMI) simultaneous collection of ambient air samples was performed using Fluoropore (37 mm, .5 μm) and Nuclepore (37 mm, .8 μm) filters. Sampling was done for 1/2 hour per hour during the 24 hour collection period. Face velocities of the Fluoropore averaged 89 cm/sec (±5 cm/sec) while the Nuclepore mean averaged 81 cm/sec (±4 cm/sec). TSP was not done for Fluoropore due to its hygroscopic nature. The total air volume sampled ranged from 15 to 21 m^3. The extraction procedure involved shaking the filter in 25 ml of deionized water for 20 minutes followed by filtration to remove insoluble particles.

a) Blank Comparison

Blank levels of any new filters are a primary consideration when sampling low level constituents. Table 2 summarizes the Fluoropore data for 4 extraction blanks and compares them with existing Nuclepore extraction blank levels (blank filters are extracted via the procedure described above).

Table 2 suggests that Fluoropore blank levels were about the same as Nuclepore for SO_4 and NH_4 ions. The blank levels of the remaining ions were much greater for the Fluoropore filters. This is only a problem if extraction solution values of the aerosol samples approach these blank concentrations.

Table 2. Blank comparison.

	Median Values (mg/L)						
	SO_4	NO_3	NH_4	Ca	Mg	Na	K
Fluoropore (Lab. Blk)	.10	.40	.02	.08	.017	.117	.013
Nuclepore (Field Blk)	.20	.13	.03	.03	.004	.022	.004

Table 3. Extraction solution levels of the six Fluoropore aerosol samples.

	(ppm) = (mg/l)						
	SO_4	NO_3	NH_4	Ca	Mg	Na	K
Mean	3.8	3.2	1.3	1.0	.152	.263	.177
Median	4.1	3.1	1.4	1.2	.155	.250	.139
Minimum	1.7	1.9	.51	.29	.067	.228	.099

For all the ions except Na, the minimum solution concentration measured was at least 4 times greater than the blank levels for the Fluoropore filters. The minimum value of Na was within 2 times the blank levels. Furthermore, the mean and median for this one were not much greater than the minimum. Thus, for Na collection the Fluoropore data were unreliable. Since the Fluoropore filters were preloaded by the manufacturer we cannot clarify whether the cause of the high Na blank levels was from the filters or a result of improper handling techniques. If the contamination resulted from the latter cause, it is conceivable to improve the reliability of the Na data.

In summary, though higher blank levels were found on the Fluoropore, they were small in relation to the ion concentration of the extraction solution with the exception of Na ion.

b) Ambient Air Concentration ($\mu g/m^3$) Comparison

The ambient air values for both filters were plotted vs. time as shown in Figures 8 and 9 for SO_4, NO_3, NH_4, Ca, Mg, Na, and K.

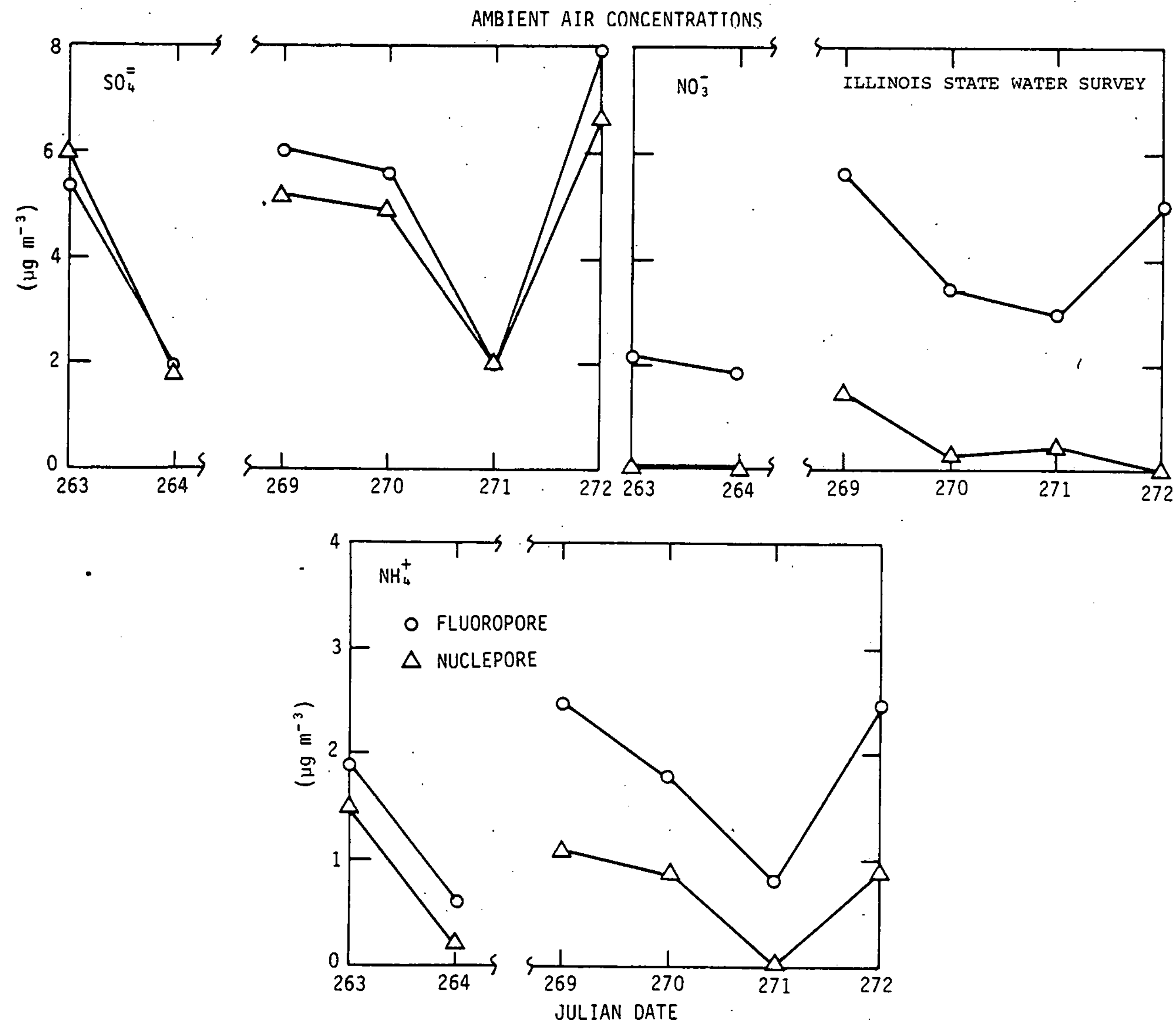

Figure 8. Ambient aerosol data for two filter media on six days for three soluble ions at the Bondville, Illinois, field site.

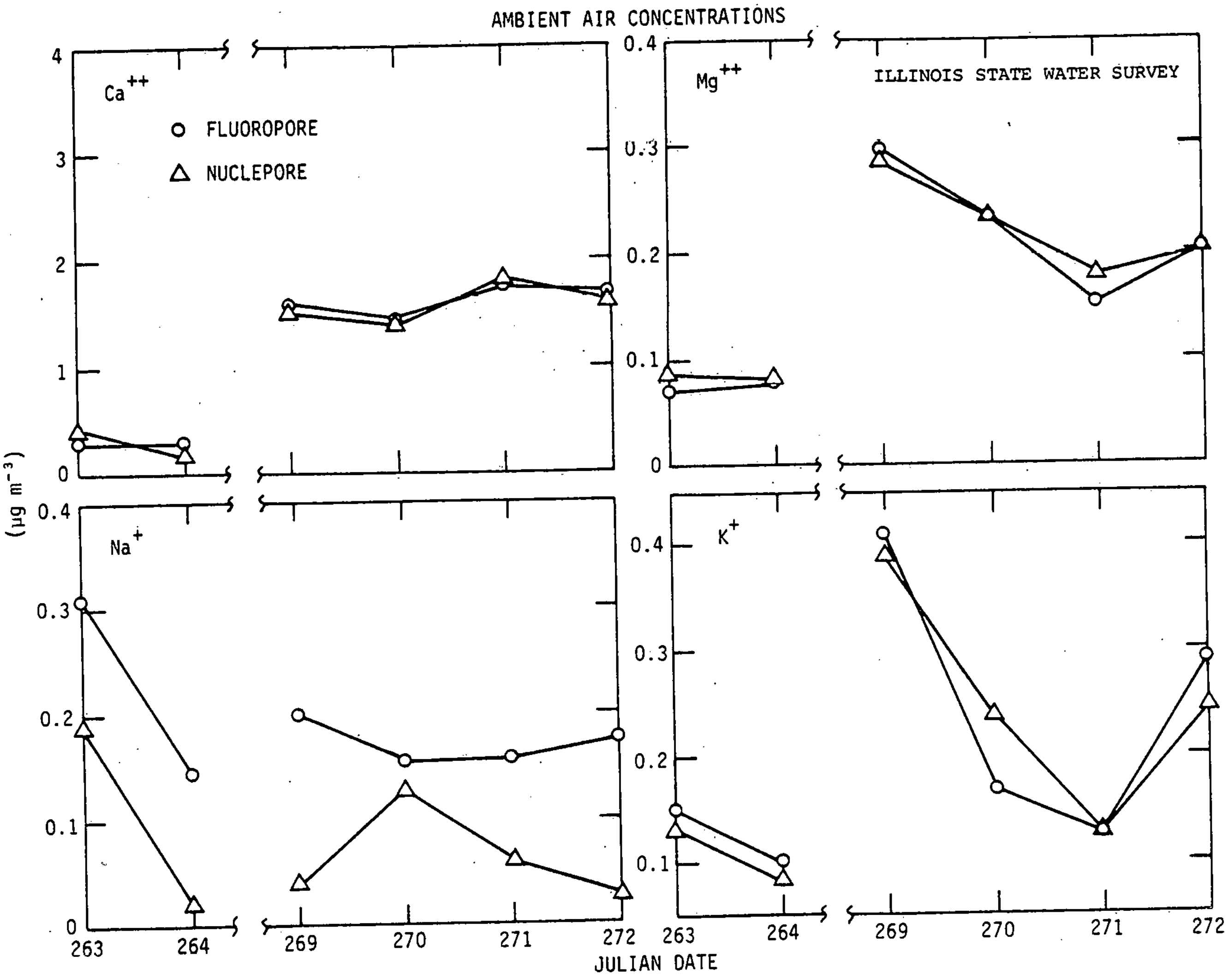

Figure 9. Ambient aerosol data for two filter media on six days for four soluble ions at the Bondville, Illinois, field site.

The results for Fluoropore and Nuclepore were in good agreement for Ca, Mg, K, and SO_4. However, dissimilar results were found for NO_3, NH_4 and Na. In all cases, the Fluoropore produced far greater ambient air concentrations. There was little similarity in trend for NO_3 and Na. However, for NH_4 the two filters had the same trend but the differences were too great to be explained by sampling technique error. Table 4 summarizes the percent increase on the Fluoropore filters defined by the formula:

$$\frac{[\text{Fluor}] - [\text{Nucl}]}{[\text{Nucl}]} = \times 100 = \%.$$

Table 4. Percent increase of ion concentration on Fluoropore in relation to Nuclepore.

Sample Number	SO_4	NO_3	NH_4	Ca	Mg	Na	K
263	-8.5%	9700*%	23.4%	-18.%	-19.5%	62%	18%
264	14.5	8595*	202	42	1.3	564	27
269	16.1	275	117	5.2	4.9	393	5.1
270	16.3	1169	87	1.6	2.6	23	-28.4
271	1.0	585	3248*	-6.2	-11.8	156	-.8
272	19.6	22117*	184	6.2	2.9	565	19.1

*Net extraction value within 2 x detection limit.

Once again it can be observed that for SO_4, Ca, Mg, and K the percent increases were with the sampling error and thus no significant difference was apparent. However, the percent increase values for NO_3, NH_4, and Na reinforce the results qualitatively observed in the figures. The greatest discrepancies were found with the NO_3 values followed by Na and then NH_4.

Laboratory research (Appel, 1978) has not found evidence of artifact nitrate production on Fluoropore filters. The Fluoropore did have a smaller pore size. However, if the NO_3 particles are larger than SO_4 particles as noted by Appel (1974) one can also disregard pore size as a solution to the discrepancies.

The polytetrafluoroethylene (Fluoropore composition) might have a better adsorption capacity than the polycarbonate (Nuclepore composition). The Fluoropore filter also has the polyethylene net backing. Polyethylene is noted for adsorption of water and this possibly produces the hygroscopic effect noted with the Fluoropore filters. The presence of water could also explain the higher collection efficiency of the Fluoropore for NO_3 since HNO_3 and NH_3 could be attracted to the water present on the Fluoropore filter. Nevertheless, these results add to the overall puzzle in regards to what filter medium produces the "true value" for NO_3 and NH_4 aerosols in ambient sampling.

In summary, Fluoropore concentrations were comparable to Nuclepore for SO_4, Ca, Mg, and K but were drastically higher for NO_3, NH_4, and Na. No definite conclusion on the reason for these discrepancies can be drawn from this limited data set.

MONTHLY AMBIENT AEROSOL COMPOSITON
AT WILLARD AIRPORT, CHAMPAIGN, ILLINOIS

From May, 1979 to September, 1979 the ambient aerosol was sampled from noon to midnight of each day on Nuclepore filters. For the remainder of the year the vacuum pumps were cycled to sample one-half hour out of each hour and thus these daily Nuclepore filters represent averages over the 24 hour periods. Table 5 indicates that most of the daily filters produced ion concentrations in the extraction solution which were more than twice the blank values. This criteria represents an attempt to determine how much good data were obtained. All the percentages in Table 5 are greater than 94% except for Na where the value was 82%.

Figures 10-13 present the results for the first year of our ambient aerosol sampling program. We prefer to examine the maximum and the median curves to identify the interesting patterns. The monthly mean curve can be strongly influenced by a few large values during the month.

Table 5. Percentage of the daily Nuclepore aerosol samples with an extraction solution concentration greater than twice the blank concentration for the seven ions.

	NO_3	NH_4	SO_4	Ca	Mg	Na	K
Number of samples	306	307	305	307	307	306	306
Percent > 2X Blank	82%	96%	98%	96%	99%	94%	99%

In Figure 10 we see that SO_4 does indeed have some very high values in the months of May-July. The median SO_4 curve indicates that the winter days typically have lower SO_4 levels than for the months with warmer temperatures. The patterns for NH_4 in Figure 11 are quite similar to those for SO_4 in Figure 10. From the figures, it appears that the annual median SO_4 was about 1-1.5 $\mu g/m^3$. This is about the mass ratio expected if the particles were usually $NH_4(HSO_4)$. However, if the true NH_4 value is 1.8 times greater as suggested by the Whatman filter data presented in Table 1, then the mass ratios would be more like that for $(NH_4)_2SO_4$. The NO_3 curves in Figure 10 are distinctly different than for SO_4 and NH_4, with the highest

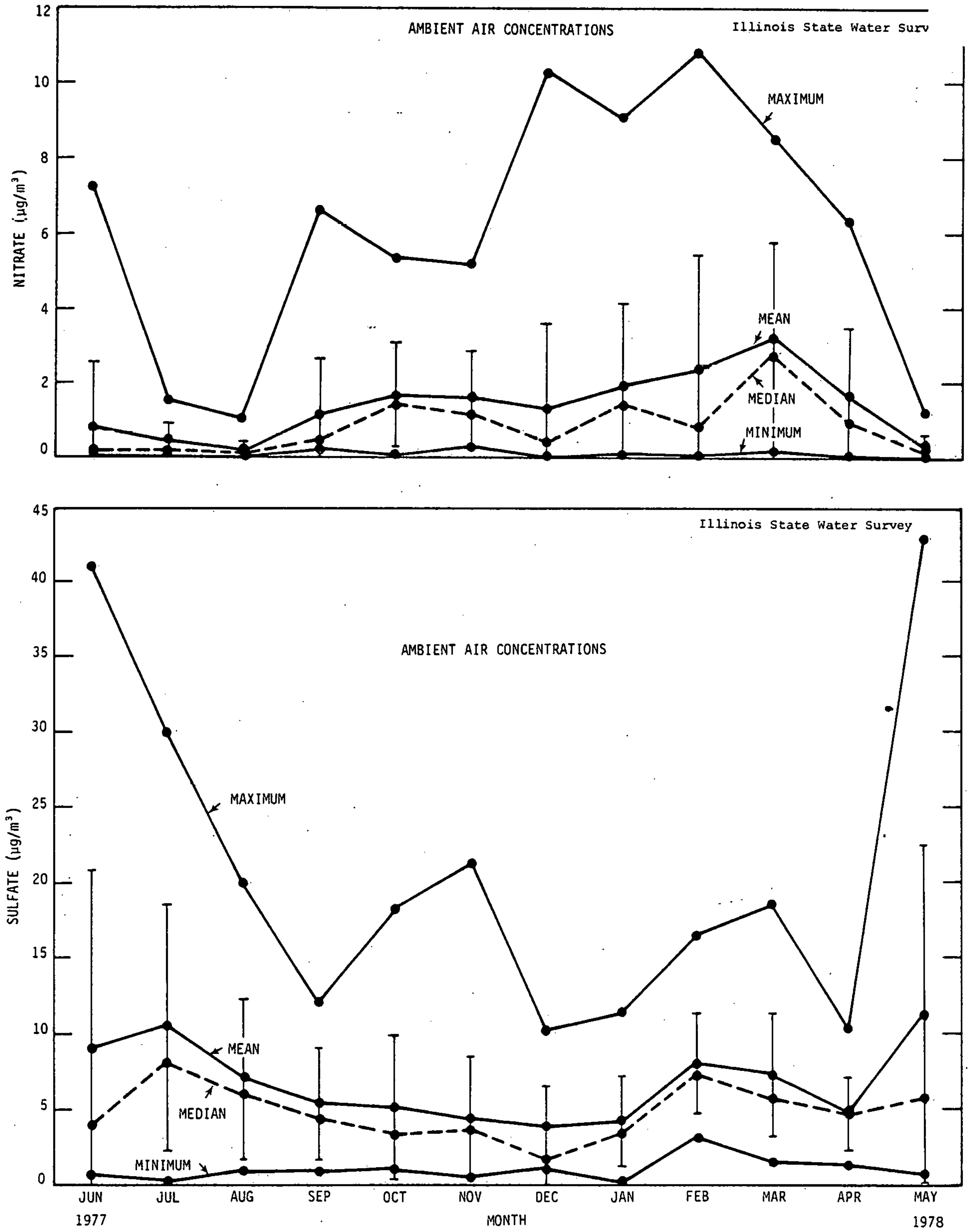

Figure 10. Monthly data for ambient aerosol nitrate and sulfate for daily samples collected at Willard Airport, Champaign, Illinois.

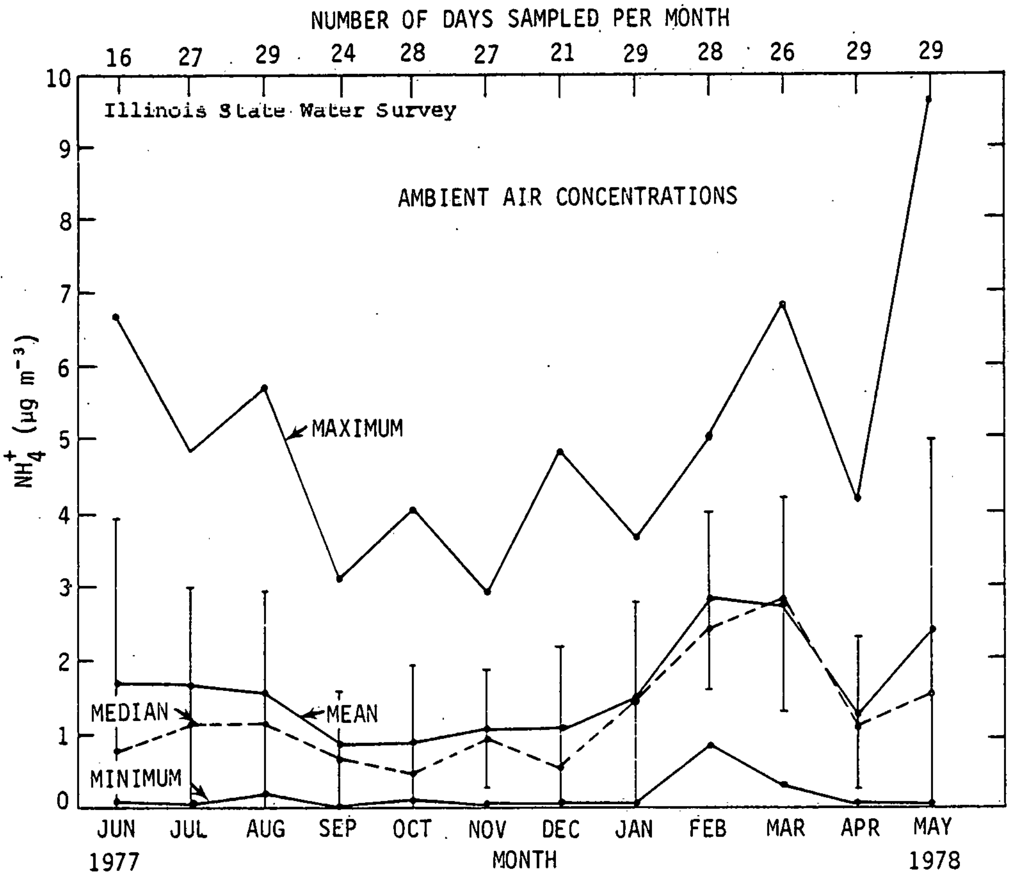

Figure 11. Monthly data for ambient aerosol ammonium for daily samples collected at Willard Airport, Champaign, Illinois.

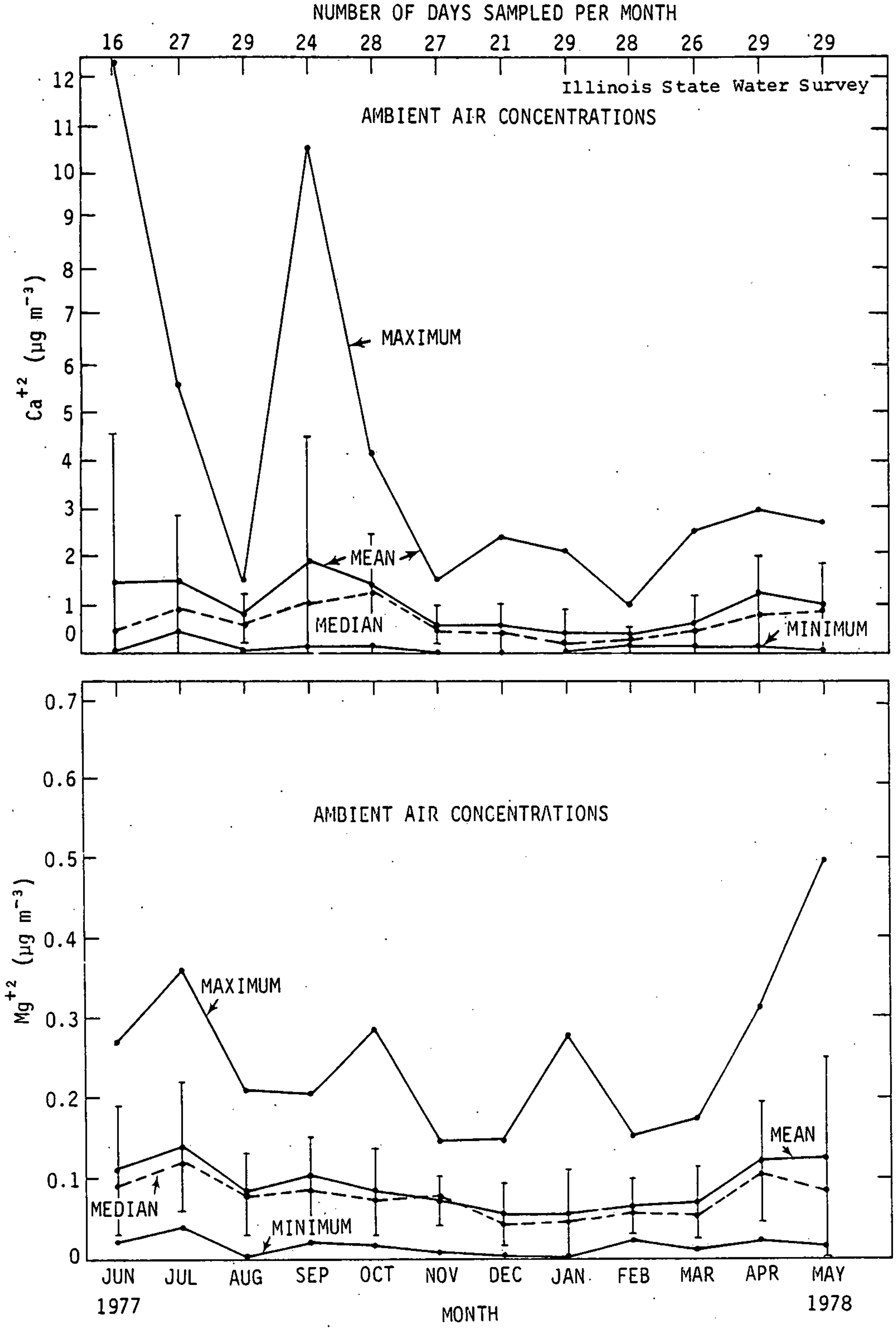

Figure 12. Monthly data for ambient aerosol calcium and magnesium for daily samples collected at Willard Airport, Champaign, Illinois.

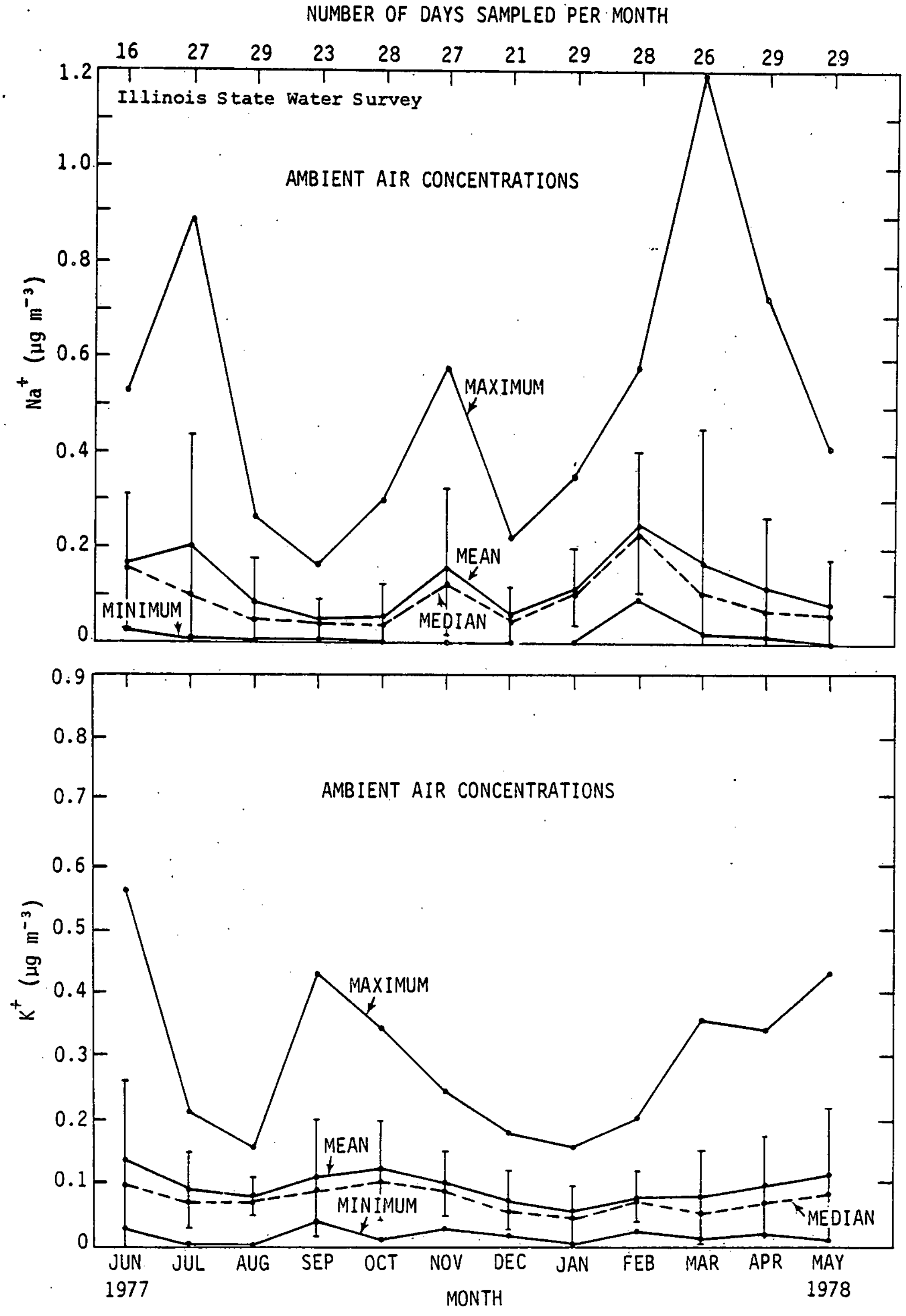

Figure 13. Monthly data for ambient aerosol sodium and potassium for daily samples collected at Willard Airport, Champaign, Illinois.

values being in the cold months. One possible explanation of the NO_3 pattern is increased retention on the filter in the cold months due to a decrease in the volitization effects which may result in a loss of the NO_3 from the filters in warm months. Hopefully, research currently underway at other laboratories will provide the information needed to decide if the NO_3 pattern in Figure 1 is a physical reality or just a sampling problem.

Figure 12 and 13 present the data for the assumed soil related constituents. The maximum curves for Ca and K are seen to be very similar and the median curves generally have the same patterns as the maximum curves. The increase in the levels of Ca and K in April and May and the peak in June is most certainly related to the farmland tillage activities. The increased values in the median curves of Ca and K in September and October is probably also due to farming activity, in this case harvesting instead of planting of the corn and soybeans.

During the warm summer days of July and August, the tar oozes to the surface of the asphalt covered secondary roads. A rock coating is then applied to these numerous wet tar spots. This rock coating often seems to be crushed limestone and dolomite. Therefore, the visually distinct dust clouds from cars passing over these crushed rock covered roads would be expected to produce a peak for the daily filters for Ca and Mg. In fact, no strong peak is present for August 1977, though Mg does have a small peak in July. In general Mg seems to have maximum values quite unlike the other ions on Figures 12 and 13. This is surprising since Ca and Mg patterns have been found to be very similar in the rain chemistry data for our area.

Previously we have suggested that in the winter months, with the plowed ground surfaces (thus free of vegetation), the dust levels indicated by Ca and Mg in the rain and on the aerosol filters would be high (Stensland, 1978). This pattern is not apparent in the aerosol data of Figures 12 and 13 for 1977-1978. This may turn out to be quite generally true since the plowed fields seem to be typically damp or snow covered in our area in the winter months and thus protected from wind erosion.

Finally, the Na pattern on Figure 13 is different than that for the other ions, especially for the maximum curve. We suggest that the November and March peaks in the maximum curve are due to the airborne transport of road deicing materials to the aerosol sampling site. This explanation is of course useless in explaining the peak in July.

FUTURE RESEARCH

Currently we are in the process of extracting the daily aerosol filters for the two years following the data displayed in Figures 10-13. The samples were collected at the Bondville field site, located about 10 kilometers southwest of Champaign and about 8 kilometers northwest of the Willard Airport site used for the first year of data collection. It will be interesting to see if the patterns of the various ions in Figures 10-13 are found in the next two years of data.

Event precipitation samples have been collected at the field sites and in the next year these data will be compared to the aerosol data.

During SCORE-78 and SCORE-79 additional filter types and other aerosol sampling instruments were used and these data will be compared in the next year.

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CHAPTER 2

NITRATE MEASUREMENTS IN PRECIPITATION FOR THE STUDY OF TRENDS AND PATTERNS

Gary J. Stensland

INTRODUCTION

One of the major ions in precipitation samples is nitrate. Nitrate is an important constituent to study if the acid precipitation phenomenon is to be understood (Likens, 1976). Nitrate patterns and trends in precipitation are examined in this chapter with five different data sets.

The spatial patterns and the time trends of nitrate in precipitation will be examined. The data are from studies carried out in the United States in the mid 1950's and the late 1970's. For the temporal trends, data from the northeastern United States will be emphasized. An annual cycle of the nitrate concentrations in precipitation for Champaign, Illinois will be compared to ambient aerosol data for the same location. Some of the data in this chapter are reproduced from the Seventeenth Progress Report since this allows for a more complete description of the situation.

PRECIPITATION QUALITY PATTERNS AND TRENDS

With respect to assessing the effect of air pollution emissions on air quality and human health, a large national ambient air monitoring network has been in continuous operation for about 20 years. In contrast, there has been a shortage of precipitation quality data for the United States. It is only recently that the adverse effects of altered precipitation quality have aroused national and international concern. As a result, a national precipitation chemistry network for the United States, utilizing standardized collection and analysis methods, recently began operation. This program, the National Atmospheric Deposition Program (NADP), which has both monitoring and research objectives, officially began operation in October 1, 1978 and currently includes about 60 collection sites distributed across the United States.

The spatial distribution pattern of nitrate in precipitation in the eastern United States in 1955-1956 (Figure 1) is generally similar to that for 1978-1979 (Figure 2). In particular, the relatively large region of elevated nitrate values in the northeast is present in both data sets. From this area of high concentrations the values clearly decrease toward the southeastern United States and there are lower values in the New England states. At this time the sparcity of NADP sites in the West does not allow any detailed comparison with the Junge data. Furthermore, the NADP data presented in

Figure 2 should be considered preliminary due to the short sampling time span. For Figure 2 most of the sites had data for five months, from October 1978 through February 1979. The remaining sites had data for time intervals varying from 1 month to 8 months.

The data in Figures 1 and 2 for the *northeast* suggest that the present concentrations of nitrate are higher than those for 1955-1956, by about a factor of two. This general time trend is also followed for the sites from North Carolina to Florida. The time trend can be questioned for at least three reasons: 1) weighted averages are plotted on Figure 1 and medians are plotted on Figure 3, 2) a year or less of data are shown in each figure, and 3) the NADP data in Figure 2 are generally for only the winter months. These three difficiencies are at least partially overcome with additional time trend data presented in Table 1, which is reproduced from Stensland (1979b). The primary sites in Table 1 (connected by dashed lines) include CM (Champaign, IL), IT (Ithaca, NY), SC (State College, PA), WM (Williamsport, PA), CH (Charlottesville, VA), and RO (Roanoke, VA). The 1954 data in Table 1, from the Larson and Hettick (1956) study, provide a data point one year prior to the 1955/56 Junge data. Likewise, the MAP3S data (Dana *et al.*, 1978), denoted as 1978 in Table 1, are actually for the one year period from September 1977 to August 1978 and thus do not coincide in time with the NADP data shown in Figure 2.

The upper portion of Table 1 displays the nitrate data for the midwestern site and the lower portion presents the data for the eastern sites. The dotted lines connect those sites for which it is considered most appropriate to calculate ratios between the recent and the older concentrations. The right hand column provides additional data for comparison to the middle column. The basic feature to note in Table 1 is that the nitrate ratios for each site are greater than one but less than two. Thus, the increase in time is not as great as indicated by the comparison between Figures 1 and 2.

Table 1. Nitrate concentrations in precipitation (mg/ℓ as NO_3^-) and ratios of recent values to historical values.

1977	Ratio	1954	1955/56
CM: 1.85	(1.5)	CM: 1.25	CO: .58

1978	Ratio	1955/56	1955/56
IT: 1.71	(1.3)	WM: 1.31	BU: 1.12
SC: 1.67	(1.3)	WM: 1.31	AL: .77
CH: 1.54	(1.8)	RO: .84	WA: .54

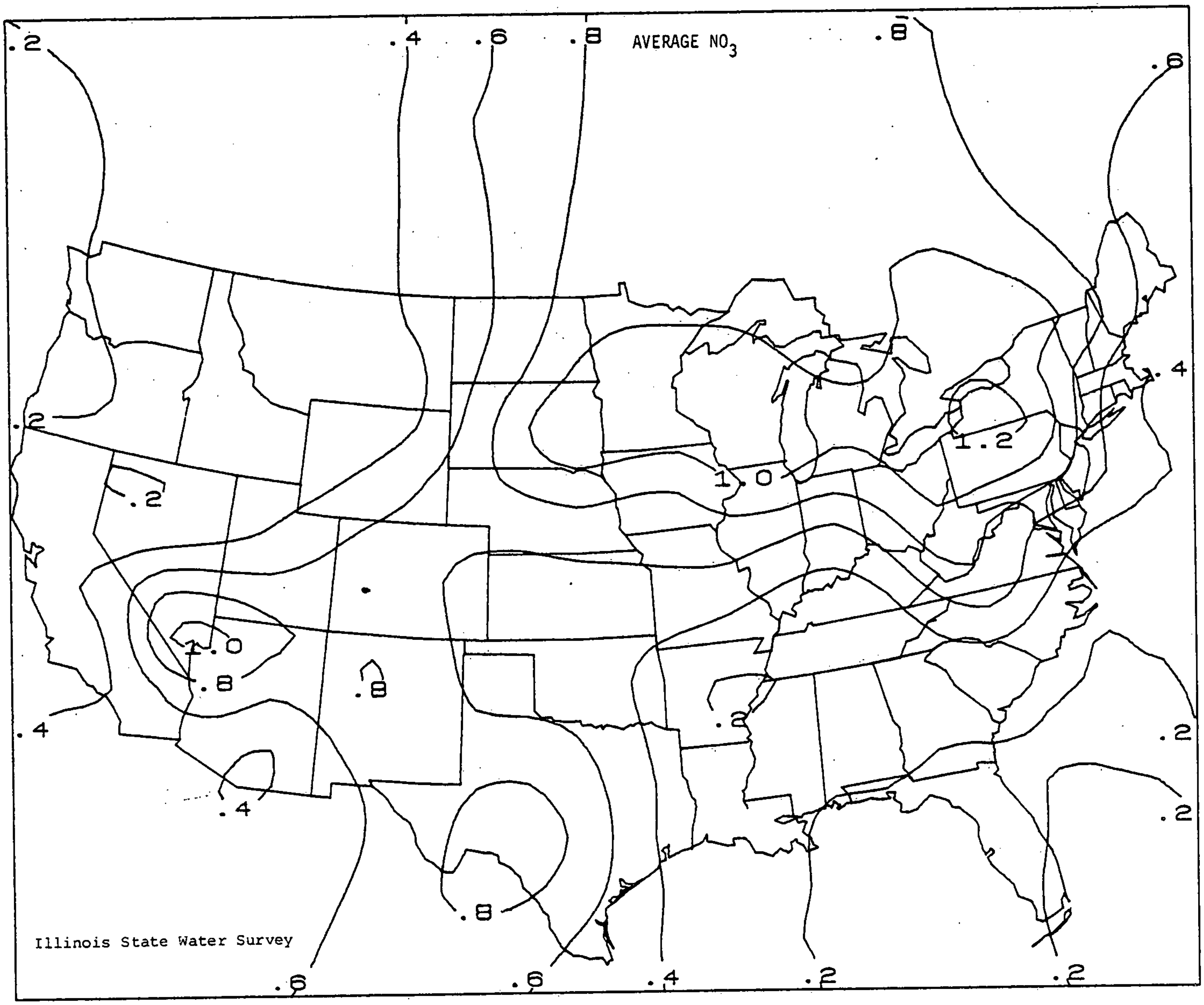

Figure 1. Contours of the sample volume - weighted concentrations of nitrate for the Junge network, in operation from July 1955 to June 1956 (cf. Junge, 1958, and Stensland, 1979a).

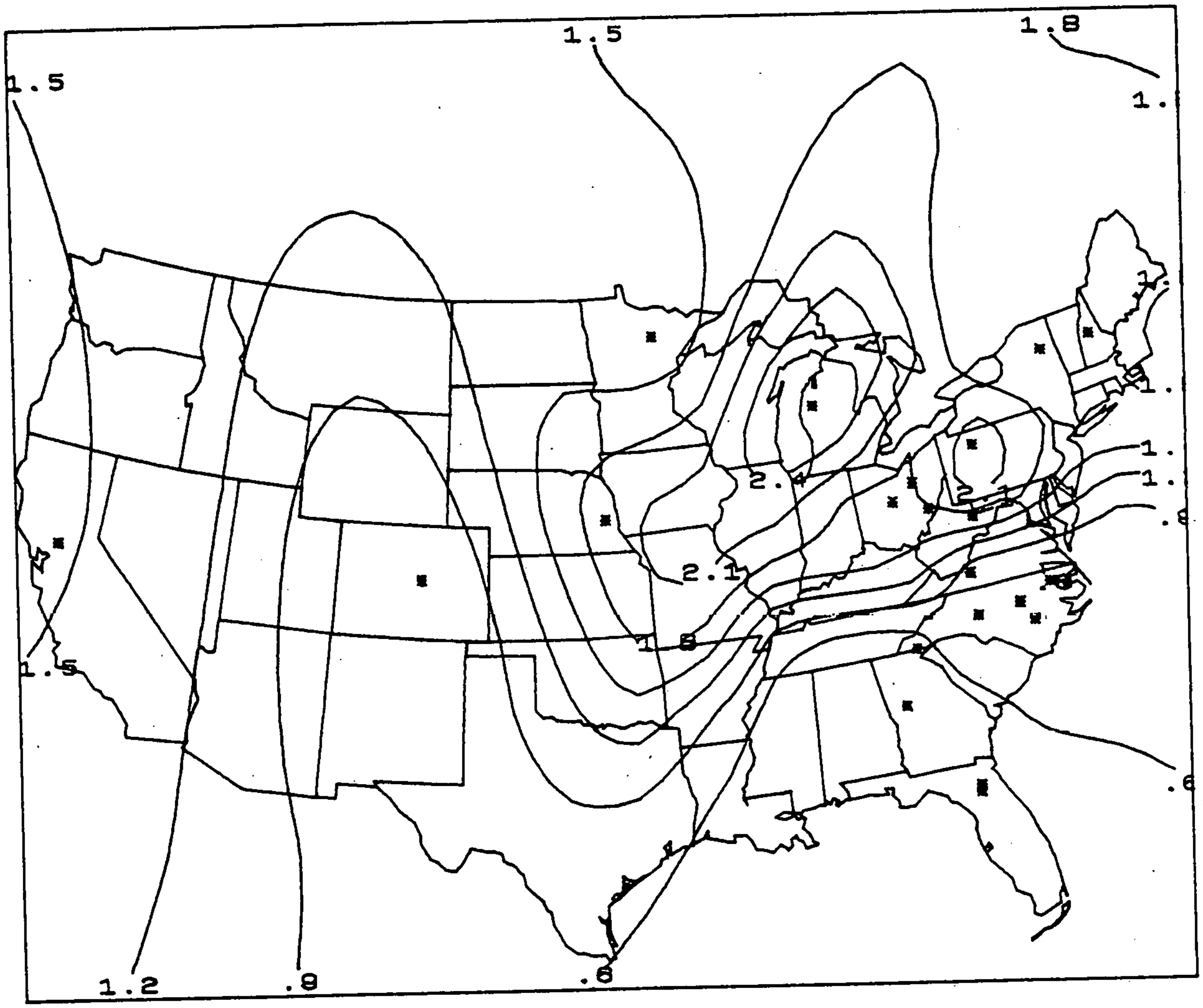

Figure 2. Contours of the median nitrate concentrations from the initial results from the National Atmospheric Deposition Program (NADP, 1979).

For comparison to the nitrate trend in precipitation, the nitrogen oxide emissions for the United States are shown in Figure 3, along with the sulfur oxide emissions. The data for this plot was tabulated from several government reports (summarized in Stensland, 1979b). The emissions data are values for the entire United States. It is assumed that the trends for these emissions data are representative of the sources contributing to the air and precipitation quality at sites in the eastern United States. A study of the geographical distribution of the 1972 emissions data does show that the EPA Air Quality Regions I-V (basically the United States east of the Mississippi) contributed 70% of the total nitrogen oxide emissions (National Research Council, 1973). The same study showed that six states, New York, Pennsylvania, Ohio, Michigan, Indiana, and Illinois, contributed 45% of the total.

From Figure 3 it is seen that from mid-1950 to 1976 the nitrogen oxides increased from about 11 to 23 million metric tons per year, or by a factor of 2.1. At the same time the sulfur oxides increased from about 20 to 27 million metric tons per year, or by a factor of 1.3. The NO_2 (representing NO_x) thus increased by 12 units while the SO_2 (representing SO_x) increased by 7 units. On an elemental basis, N increased by 3.6 units while S increased by 3.5 units. Since the acids in preciptation, HNO_3 and H_2SO_4, each have a single N and S atom, the NO_x and SO_x emission changes indicated on Figure 3 would have had about the same potential to produce increased acidity in precipitation. However, the rate of increase of NO_x has been greater than for SO_x in the past twenty years and if this pattern continues, future changes in precipitation acidity would be expected to be due more to NO_x emissions than SO_x emissions, if SO_x and NO_x both get converted in equal percentages to acid species in precipitation.

Finally, it is useful to do to a rough mass balance calculation to evaluate Figures 1-3 for consistency. Minnesota and the states east of the Mississippi make up USEPA Regions I, II, III, IV and V. As stated previously, the 1975 report by the National Research Council (1973) indicated that these five regions emitted 70% of the U.S. NO_x emissions. Therefore we will assume that $[(0.7) \cdot (3.6 \times 10^{12} g) = 2.52 \times 10^{12}\ g = 2.52\ Tg]$ more N was emitted in these states in the late 1970's compared to the mid 1950's. These 2.52 Tg of N are equal to about 11.2 Tg as NO_3. Now for the NO_3 deposited in precipitation an examination of Figures 2 and 3 for the states in regions I-V suggests that the 1955 average NO_3 was about 0.6 mg/L and 1979 average NO_3 was about 1.4 mg/L. The area of these states is $250 \times 10^{10}\ m^2$. The normal annual total precipitation for these states is about 114 cm (45 inches). From these estimates it follows that the annual water deposition is 285×10^{13} L. Thus the increase in NO_3 deposition in precipitation is $(1.4-0.6)\ (285 \times 10^{13}) = 228 \times 10^{13}\ mg = 2.28\ Tg$. Thus only $(2.28 \div 11.2) \times 100 = 20\%$ of the increased NO_x emissions are needed to explain the increased deposition in precipitation. Since only a fraction of the emitted material is returned to the earths surface as wet deposition, this rough mass balance establishes the consistency of Figures 1-3, without searching for other emission sources for NO_x.

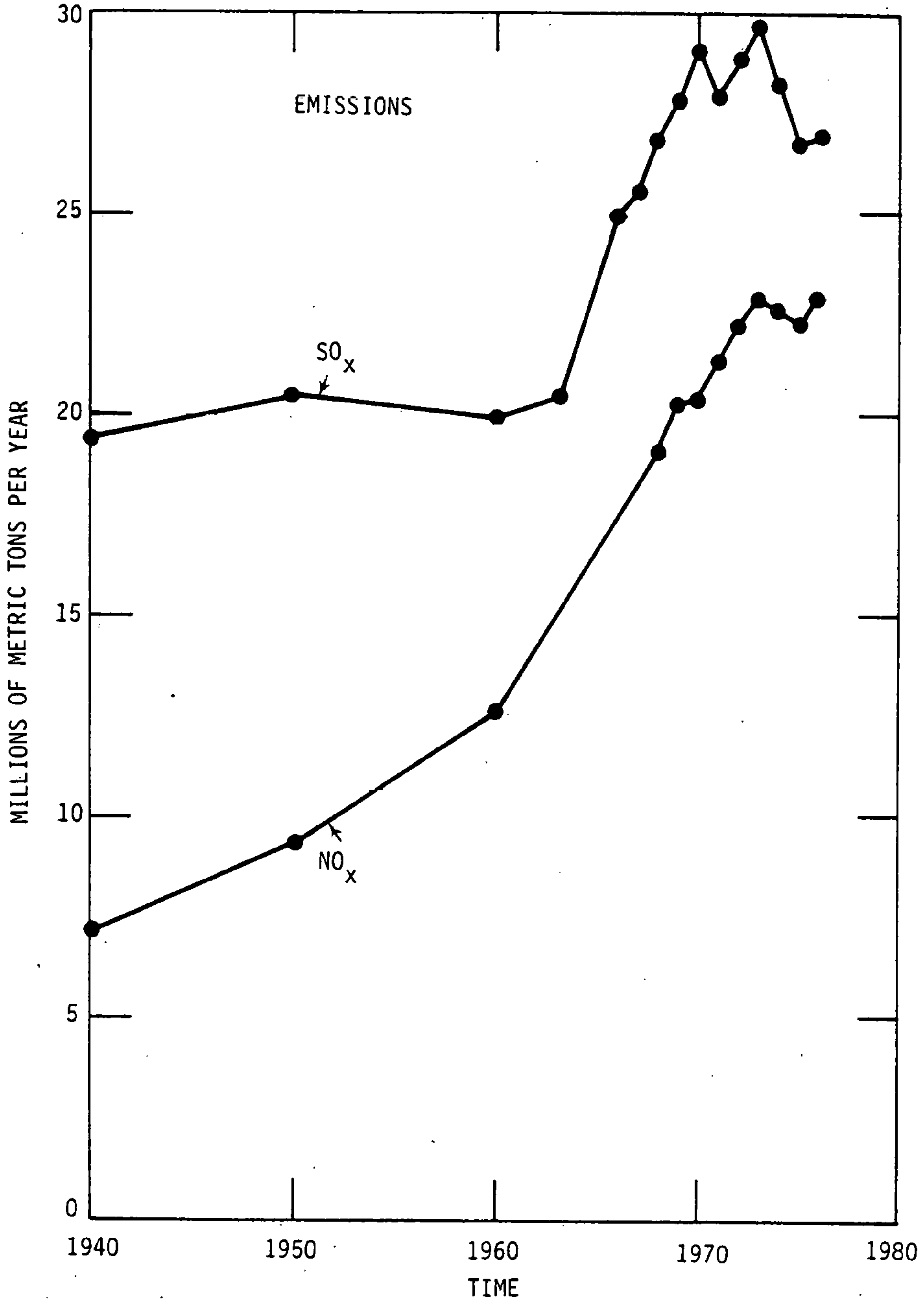

Figure 3. Emission trends for NO_x and SO_x from the data in various government reports, as tabulated by Stensland (1979b).

DAILY PRECIPITATION AND AEROSOL DATA FOR ILLINOIS

Particles in the ambient air are incorporated into raindrops and snowflakes. Therefore interesting and useful data should result if the same chemicals are monitored in both air and precipitation at a site. A reasonably short sampling interval, such as daily sampling, is desirable. Also due to the complexity of the scavenging processes, it is necessary to obtain a large number of samples in order to identify persistent features. This type of sampling was carried out at the Willard Airport site ten kilometers south of Champaign, Illinois, from June 1977 to May 1978.

In Figure 4 are plotted the nitrate concentrations for the daily precipitation samples, collected with an ISWS wet/dry sampler. Since the nitrate is always high with a small amount of precipitation, it is best to exclude such cases when comparing to air concentrations. For Figure 4, the cases with daily precipitation < 1 mm have not been included and this explains why no data point is shown for about one third of the samples collected at the field site.

The ambient air data from Nuclepore filter samples collected at the same site are shown in Figure 5. From 21 to 29 daily samples were available to calculate the statistics for each month except for June 1977 when only 16 were available. The lines on Figure 5 connect the maximum, minimum, mean, and median values for each month. Figure 6 presents the concurrent data for sulfate. The sampling procedure consisted of drawing air through filters at about 30 lpm for either 30 or 45 minutes out of each hour for the 24 hour sampling interval, so that about 20 cubic meters of air were sampled. However, in June, July and part of August, the procedure was modified to sample continuously for 12 hours, usually from noon to midnight. The aerosol collection media were Nuclepore filters, 37 mm in diameter, and with 0.8 µm pore diameters. The filters were extracted by placing them in 25 ml of deionized water and shaking for 20 minutes with a wrist-action shaker. The anions were then determined by standard colorimetric procedures with a Technicon II Auto Analyzer.

The nitrate in Figure 5 has a peak in the mean and median curves in March while the four largest maximum values extend from December through March. Sulfate in Figure 6 has peaks in the median curve in February and in July. The dramatic feature in the sulfate data is the very large maximum monthly values in May and June.

In Table 2 are presented the median precipitation and aerosol values for nitrate and sulfate for two periods of five months duration, selected to coincide with the aerosol nitrate peak and valley trends in Figure 5. The May-September interval is basically a summer interval while the December-April interval is basically a winter interval. The median data in Table 2 suggest that sulfate is not significantly different in the summer versus the winter period for either the aerosols or the precipitation. However, for nitrate the median precipitation concentrations are a factor of 1.8 higher in the winter than the summer but a factor of 11 higher in the ambient air. It does

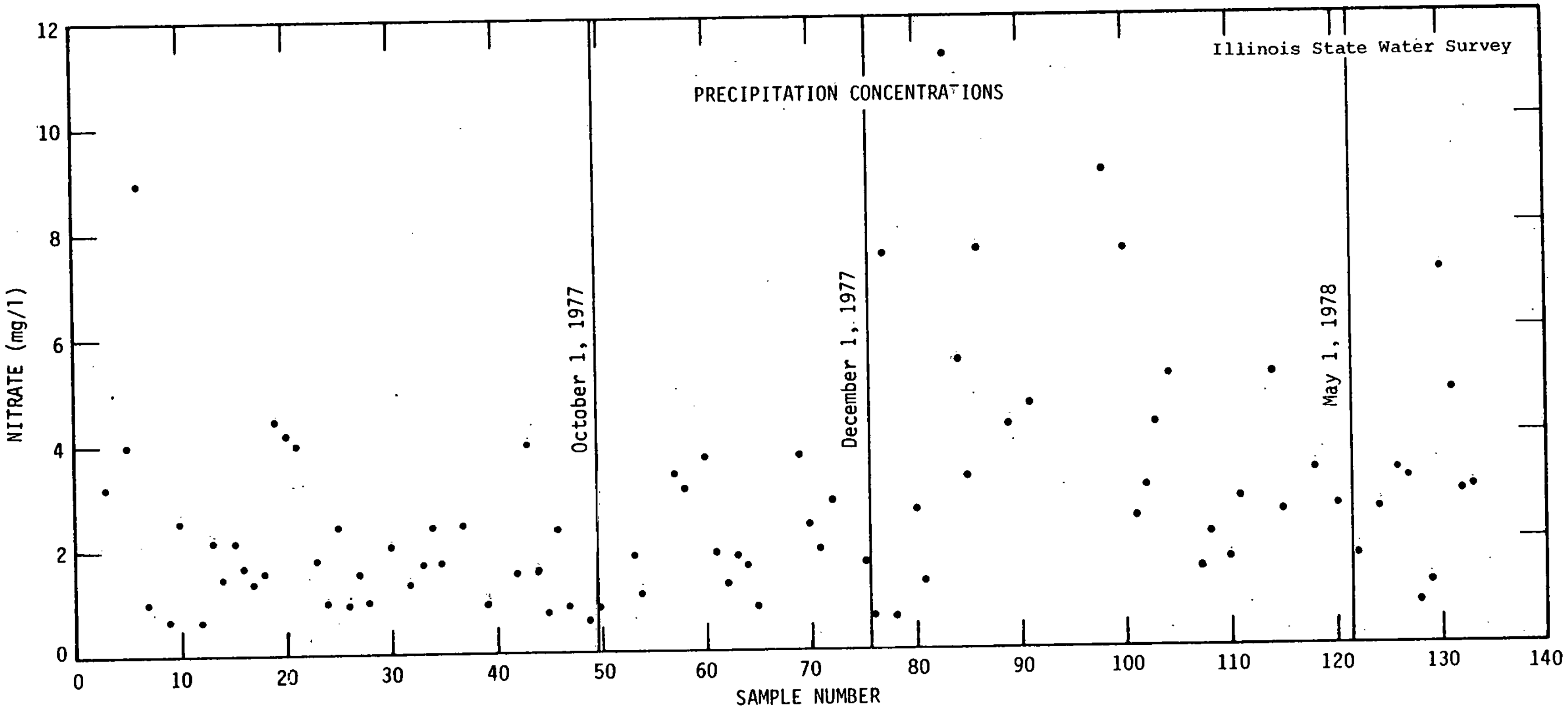

Figure 4. Nitrate concentrations in daily precipitation samples, collected at Willard Airport, Champaign, IL from June 1977 to May 1978.

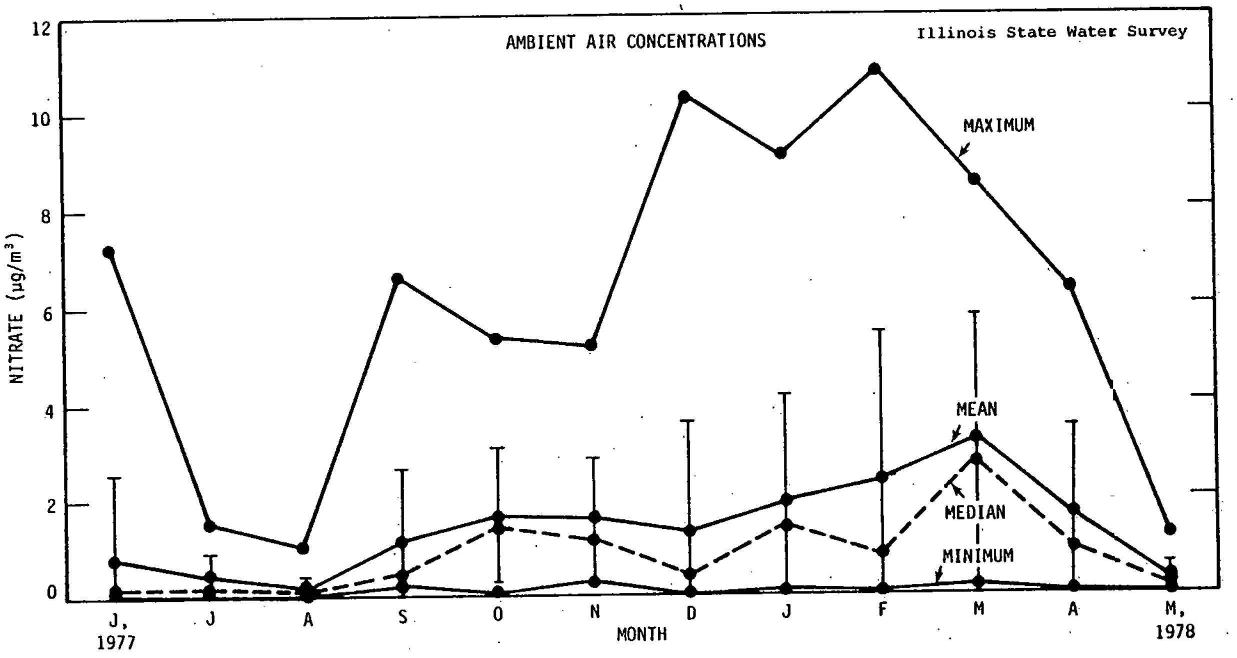

Figure 5. Monthly averages for ambient aerosol nitrate concentrations for daily samples collected at Willard Airport, Champaign, IL.

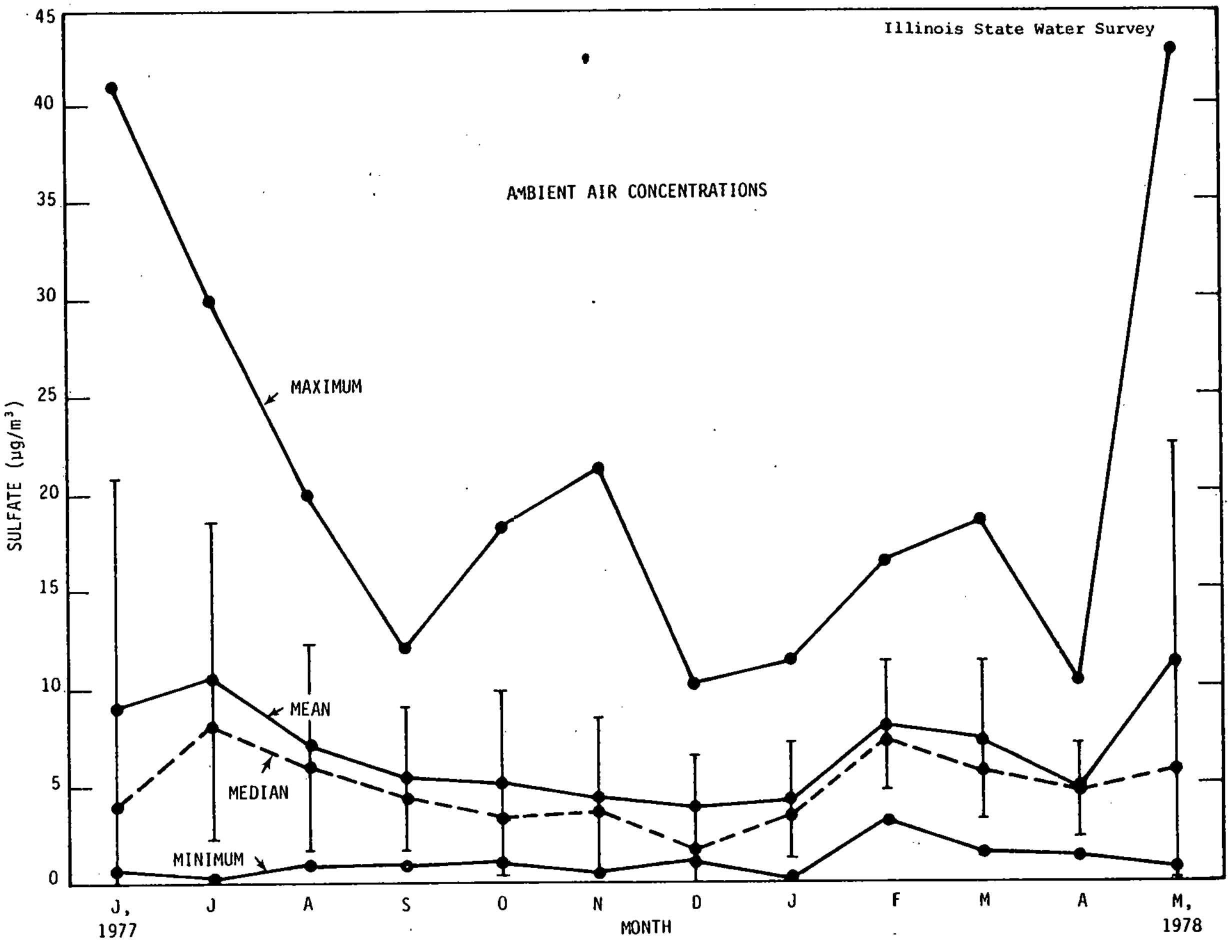

Figure 6. Monthly averages for ambient aerosol sulfate concentrations for daily samples collected at Willard Airport, Champaign, IL.

therefore seem that, in a general sense, the trends for nitrate in aerosols and precipitation are consistent. Hence, the suggestion that the higher nitrate in winter precipitation might be due to more efficient scavenging by the ice phase, does not have to be invoked. However, it is strange that nitrate aerosol concentrations should have the strong seasonal trend shown in Table 2 while sulfate does not. The transportation source emissions, which are very important for NO_x but not for SO_x, should not have such a seasonal trend. Two of the possible explanations for the differences in the aerosol and precipitation nitrate trends are:

a) that the nitrate in precipitation results from scavenging of both gaseous and particulate species and that the gaseous species have a seasonal trend opposite that of aerosol nitrate, or

b) that the Nuclepore filters were not providing accurate aerosol nitrate values and that perhaps the measurement error had a seasonal trend.

Table 2. Median nitrate and sulfate concentrations in ambient aerosols ($\mu g/m^3$) and in precipitation (Mg/ℓ) for one year at Champaign.

	Ambient Aerosol	Precipitation
(NO_3^-), May-Sept	0.1	1.8
(NO_3^-), Dec-Apr	1.1	3.3
($SO_4^=$), May-Sept	5.9	3.8
($SO_4^=$), Dec-Apr	5.0	4.1

From the data in Table 2, it should also be noted that the sulfate/nitrate ratios in precipitation are much different than for the aerosols. This could again be due to the two possible explanations just discussed.

Bowersox (1980) has interpreted the event precipitation data at a central Pennsylvania site for a two year period. A seasonal pattern was identified for sulfate, but not nitrate, which is opposite the data trend reported in Table 2. Additional data will be studied for the Illinois site to see if this pattern persists.

CONCLUSIONS

1. With respect to the spatial pattern of nitrate concentrations in precipitation, the limited data available show that the current distribution in the eastern United States is similar to that observed in 1955/56. The highest values have occurred north of the Ohio River, from Wisconsin to New York. The values are generally higher in the northeast than in the southeast. The current data for the western United States are too limited to compare to the 1955/56 data.

2. With respect to the temporal trend of nitrate in precipitation, all the data show increased concentrations in the late 1970's compared to the mid-1950's. The amount of increase is variable, depending on which sites and which years are compared but ranged from about a factor of 1.3 increase up to a factor of 3. This is in general agreement with the rise in NO_x emissions for United States, which increased by about a factor of 2.1 from 1955 to 1976.

3. For one year of data at Champaign, IL, the ambient aerosol nitrate levels had the same seasonal trend as for the nitrate in precipitation, namely higher levels in the winter months than in the summer months. This is different than the trend observed at the MAP3S in central Pennsylvania site and needs further investigation.

Conclusions regarding temporal and spatial patterns of nitrate concentrations in precipitation can not be more specific at this time due to the lack of an adequate data base.

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CHAPTER 3

SCORE-78 CASE STUDY FOR JULY 2, 1978

Gary J. Stensland

DESCRIPTION OF THE EXPERIMENT

The Summer Chemistry Of Rain Experiment for 1978 (SCORE-78) began on 1 June 1978. The objectives of the study were to assess the variability of convective rainfall chemistry on very small time and space scales, and to relate this variability to meteorological parameters, air quality parameters, and the chemical sources. To accomplish these objectives, precipitation chemistry sampler sites, which were separated by about 1.5 kilometers and serviced after individual rain showers, were in operation until the end of July 1978. The rapid servicing of the sites protected against ion concentration increases due to evaporation and dry deposition. The rain samples were usually filtered or refrigerated within 6-24 hours of collection, in order to minimize sample changes due to such things as the slow dissolution of particulate matter.

The 23 sites in the SCORE-78 network are shown in Figure 1. Basically there were two sampling lines, oriented north-south, with a site separation of about 1.5 kilometers. At the airport site (AT) and at sites 1-12 were located weighing type of recording raingages, with 6-hour rotation of the chart allowing excellent time resolution of rain accumulation rate. Similar raingages were located at sites 13-21 except that 24-hour chart rotation gears were used. A hailpad was co-located at all sites. Bulk rain chemistry samplers were located at sites 4, 9, and 13-21. Wet/dry samplers of the HASL type were located at sites 1-9, BT, and AT. BT refers to the sampling platform 35 meters above the ground, on the top of a wooden tower.

During the eight weeks of the experiment, rain occurred somewhere on the network on 18 days, with individual chemistry samplers being serviced up to 4 times on some days. Two of the SCORE-78 rain events have been discussed in previous progress reports (Stensland, 1978 and Stensland, 1979).

RAINWATER CHEMISTRY FOR SHOWER ON JULY 2, 1978

This rain shower occurred at 1530 CDT on July 2. The buckets at all the sites were changed in the morning of July 2, following rains during the night. Rains also had occurred in the afternoon hours of June 30 and July 1. The total rain amounts at all the sites were substantial and thus there is no chance that blowing dust could have settled into the bulk buckets before this July 2 rain shower. Evaporation from the bulk buckets was also negligible since they were removed within 90 minutes of the end of the rain shower.

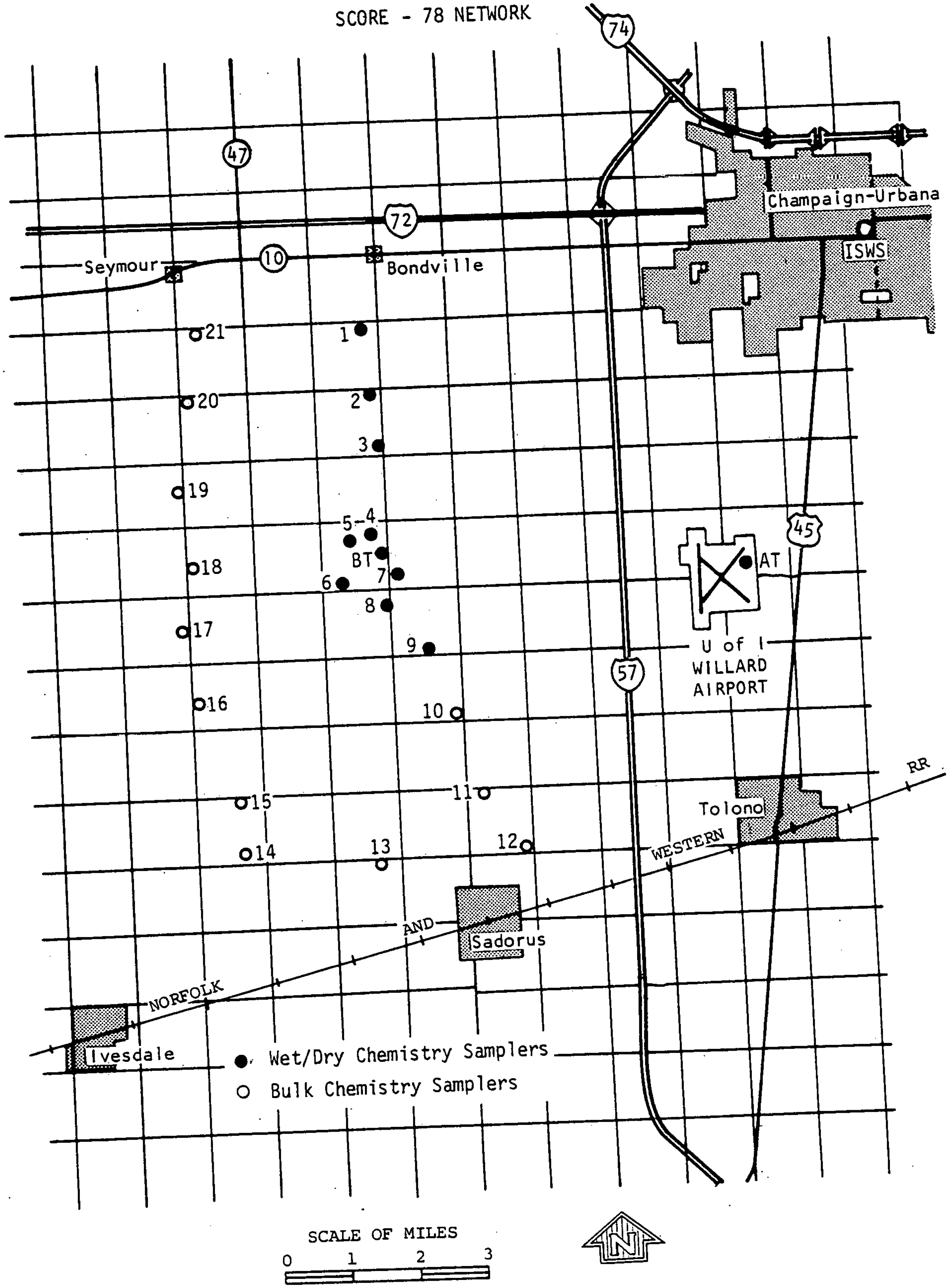


Figure 1. The SCORE-78 network.

Figures 2-4 display the contours for the various ion concentrations, pH, conductivity, and sample volume. The asterisks indicate the sites for which data were available to generate the contours. In particular, event chemistry data is missing for sites 4, 6, and 8 and site BT was not used for this analysis (cf. Figure 1). In Figure 2 the volume contours range from 38 ml to 380 ml. The minimum volume of 15.7 ml was collected at site 14, in the southwest corner. The rainfall amounts were probably zero to the south of the network, and thus the chemistry contours which extend into this region are of course fictitious. More generally the contours are, of course, reliable estimates of the actual patterns only near the area where the sites are located. Thus, the area between the two north-south sites should be quite well represented. The objective analysis program used in creating the coutour patterns was allowed to produce some round off of extreme values.

The rain rate curves (to be discussed later) show that the shower lasted about 30 minutes at each site. There was no other rain on the network for several hours before or after this shower so it would seem to be a rather ideal case of a single shower on the network. Since 0.01 inch of rainfall produces about 8 ml of water in the buckets, the sample volume pattern indicates that the rainfall varied from about 0.02 inch in the south to 0.47 inch in the north.

The SO_4 in Figure 2 has a general inverse correlation to the sample volume, with higher SO_4 values in the south and lower values in the north. There are analomies, such as at site 13, the south central site, where many of the ions are low and the sample volume was also very low. Also the lower sample volumes in the northern part of the network are not associated with corresponding high values of SO_4, NO_3, or NH_4.

The SO_4, NO_3 and NH_4 patterns in Figure 2 are very similar to each other. Likewise, the Ca and Mg patterns in Figure 3 are very similar to each other and to SO_4, NO_3, and NH_4 in Figure 2. The SO_4 and NO_3 values in Figure 2 vary across the shower by a factor of 2-3 while the Ca and Mg in Figure 3 vary by a factor of 5-6. This latter feature seems to be quite generally true for the SCORE-78 cases studied so far. Table 1 summaries the results for 6 cases, where the July 2 shower is identified as case 183 (which is the Julian day for the case). Notice that the median Ca and Mg variation is greater than for SO_4 and NO_3 but less than that for sample volume.

The patterns for Na and K on Figure 3 are similar to each other but somewhat different than for Ca and Mg. Cl on Figure 4 is different from any other ion pattern but is most similar to Na and K. The values for Na, K, and Cl were frequently near the blank levels for our procedures and this may explain why these ions are usually somewhat different than those for the other ions.

Finally, the pH for the July 2 case is shown on Figure 4, and ranged from about 4.2 to 4.5. From the raw data it was noted that the lowest pH occurred with the highest SO_4 value and the highest pH with the lowest SO_4 value.

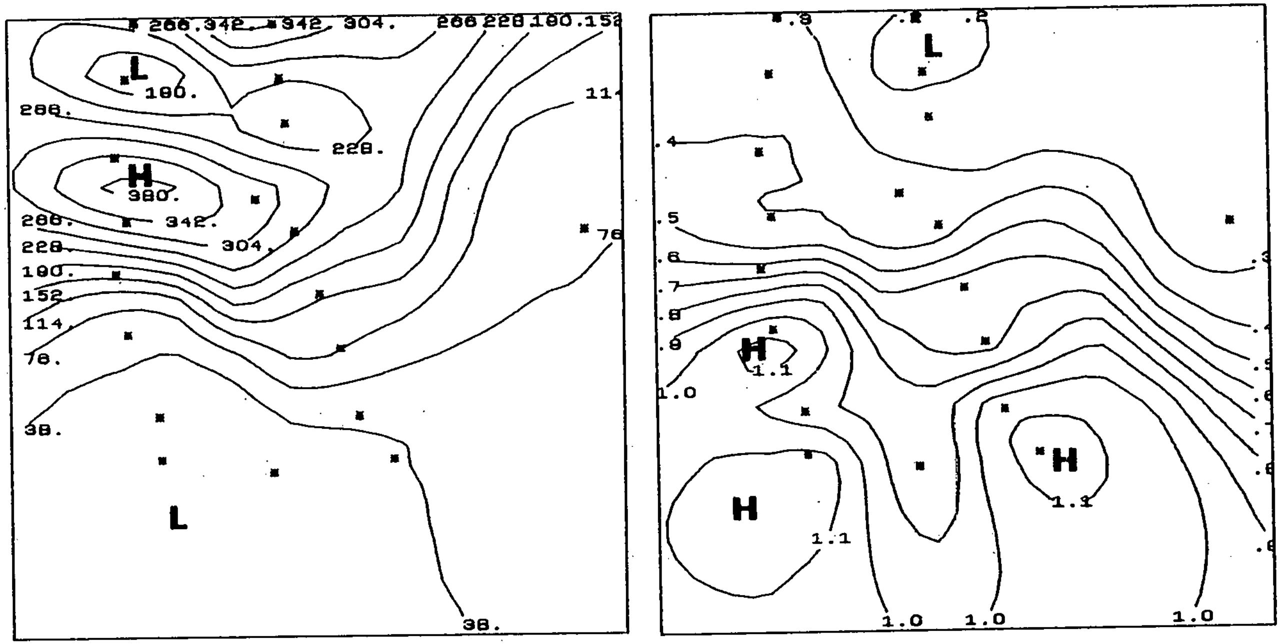
Table 1. Ratios of the second highest to the second lowest ion concentration for samples from single rain shower cases in SCORE-78.

		Ratios For:				
Case	Number of Samples	NO_3^-	$SO_4^=$	Ca^{++}	Mg^{++}	Volume
171	14	1.6	1.8	3.0	2.5	1.9
181	18	2.0	1.8	2.5	3.7	5.2
182	8	1.6	1.6	1.8	1.9	3.5
183	20	3.4	2.1	6.3	7.0	20.2
193	20	2.0	2.5	3.0	3.4	2.3
194	23	1.8	1.6	2.4	2.5	5.2
Median		1.9	1.8	2.8	3.0	4.4

The sample volume pattern in Figure 2 indicates that intense portions of the shower affected the northwest portion of the network. Furthermore, the elongations of the patterns in the north might suggest that the cells were moving south-southeast, with two main cells in evidence. Figures 5 and 6 display the actual rain rate curves for some of the sites. The highest sample volume on Figure 2 is located near gage 19, which is displayed in Figure 5. The rain rate pattern at gage 19 is complex, with 4 strong bursts of rain combining to produce the simple closed high on the Figure 2 contour pattern. At site 20, about 1.5 miles north of site 19, the rain rate pattern is very different. On the east line, at sites 3 and 9, the rain rate curves are quite different from each other and from those on the west line.

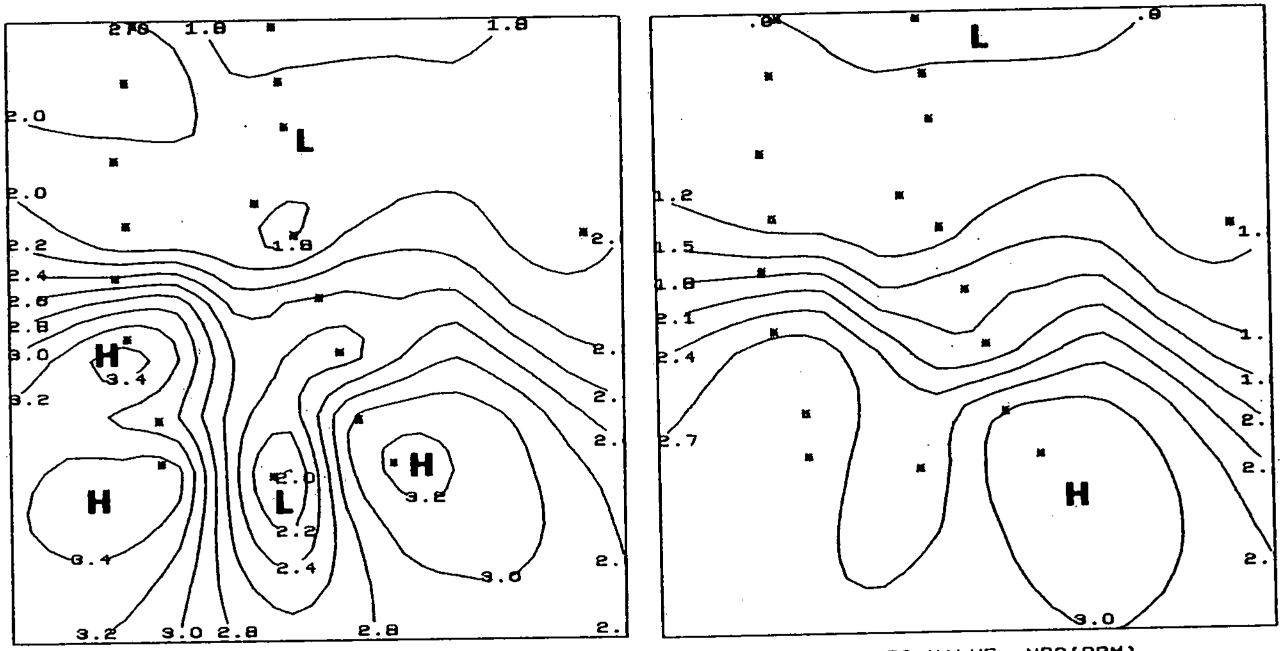
Figure 6 displays the rain rate curves for 3 sites which are within a mile of each other, and which are in between the 4 sites, displayed in Figure 5. It is only on this finer space scale that the rain rate patterns are quite similar. At site 7 we see that the rain shower was composed of 3 peaks or bursts of rain, each being several minutes duration. Site 6 only shows two of the peaks. At site 4 both the second and third peaks are somewhat stronger than at site 7. Figures 5 and 6 demonstrate that the rain shower was much more complex than could be anticipated by looking at the sample volume contours in Figure 2.

A Survey-designed sequential rainwater collector was operational at site 4 for some of the SCORE-78 events. Sequential data for the July 2 case is shown in Figure 7. The site 4 rain rate curve is reproduced at the top of Figure 7 with dots indicating the end times for the collection of the sequential samples. The individual sample volumes and collection times for the sequential samples were used to derive a best estimate of the proper position for the dots on the rain rate curve.



SCORE - GROUP 183 VALUE: SAMP. VOL.

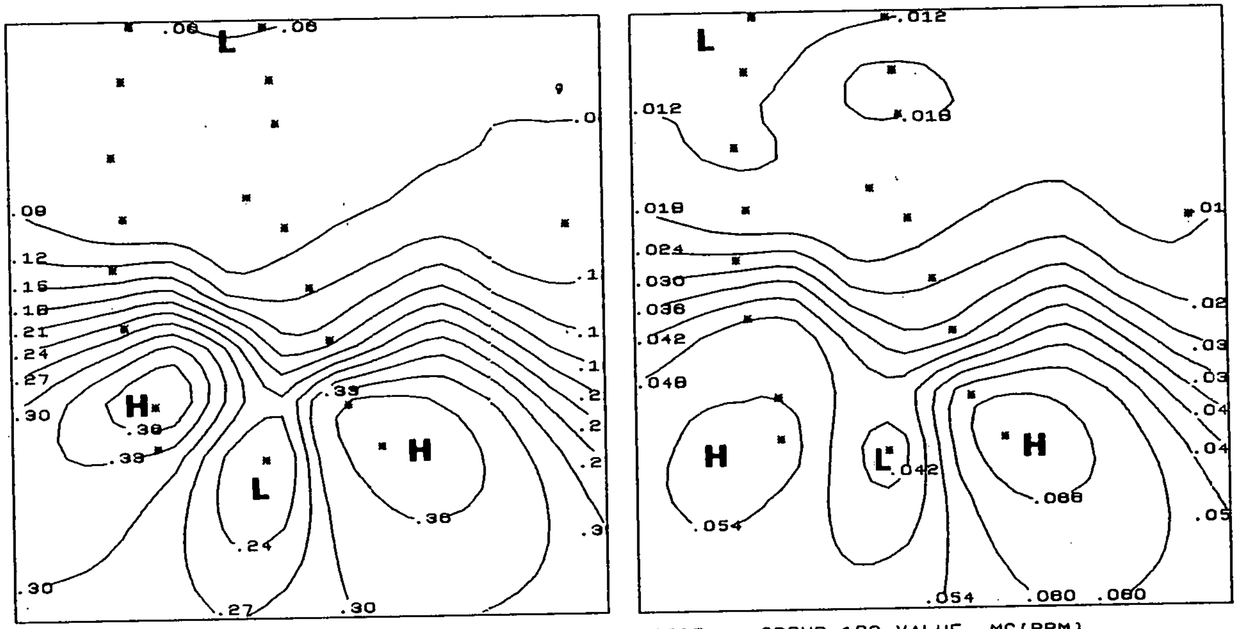
SCORE - GROUP 183 VALUE: NH4(PPM)



SCORE - GROUP 183 VALUE: SO4(PPM)

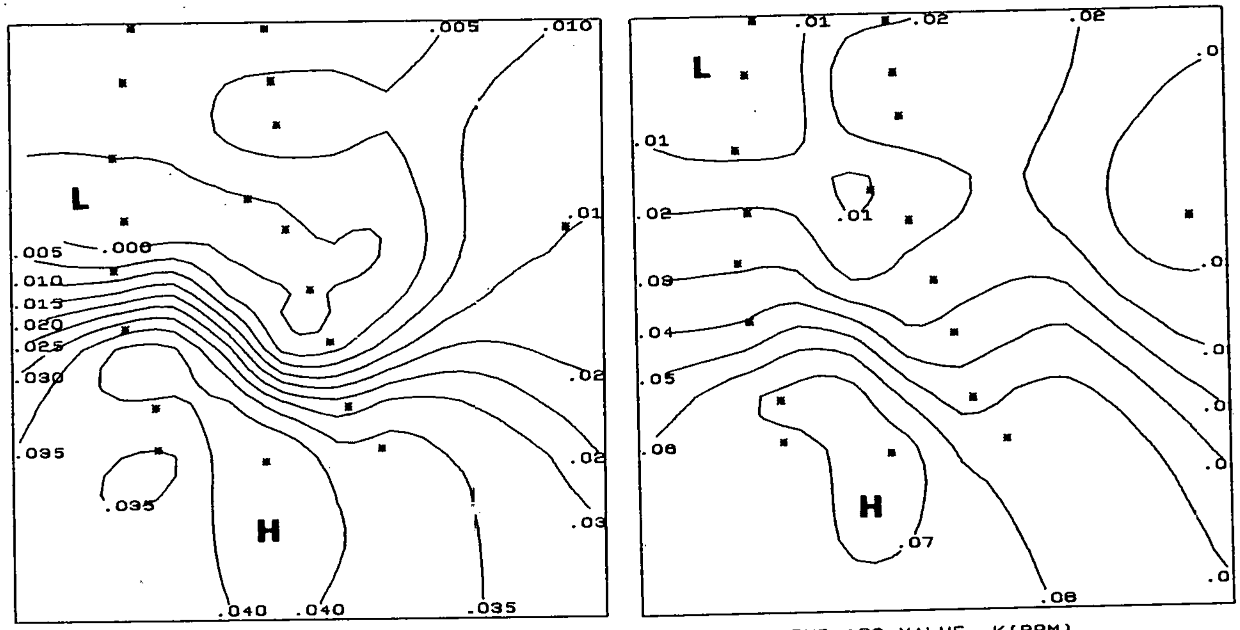
SCORE - GROUP 183 VALUE: NO3(PPM)

Figure 2. The spatial pattern of sample volume and of the concentration ammonium, sulfate, and nitrate ions for the shower of July 2 , 1978.



SCORE - GROUP 183 VALUE: CA(PPM)

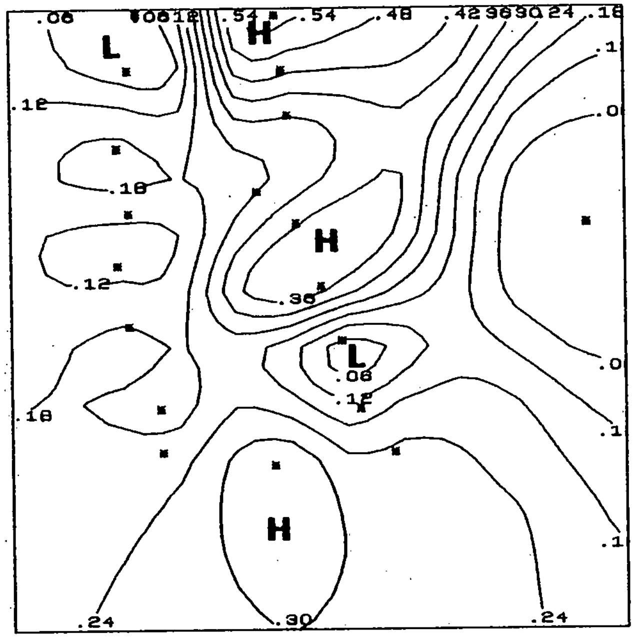
SCORE - GROUP 183 VALUE: MG(PPM)



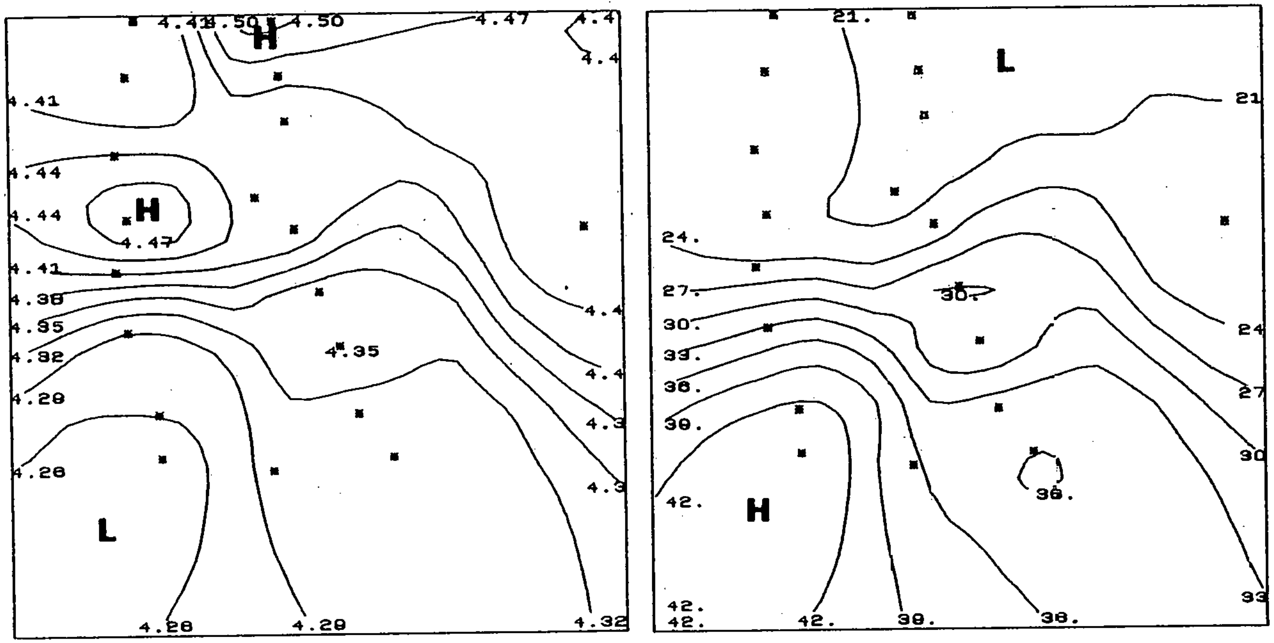
SCORE - GROUP 183 VALUE: NA(PPM)

SCORE - GROUP 183 VALUE: K(PPM)

Figure 3. The spatial pattern of ionic concentration of calcium, magnesium, sodium, and potassium from the shower of July 2, 1978.



SCORE - GROUP 183 VALUE: CL(PPM)



SCORE - GROUP 183 VALUE: PH(MEAS)

SCORE - GROUP 183 VALUE: COND(MEAS)

Figure 4. The spatial pattern of chloride ion, measured pH, and conductivity (μS/cm) for the shower of July 2, 1978.

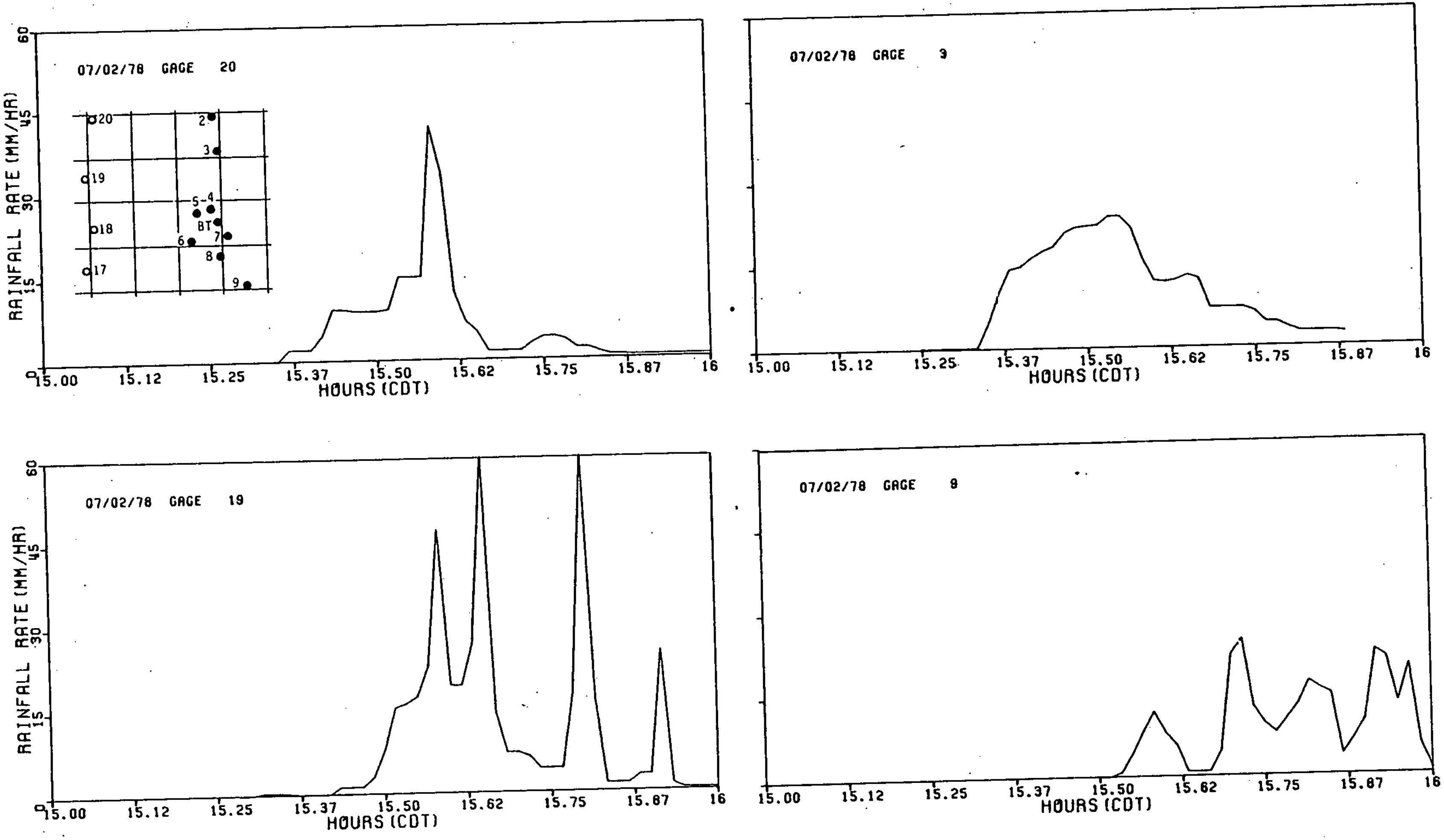


Figure 5. Rainfall rate plots at four SCORE-78 sites for July 2, 1978.

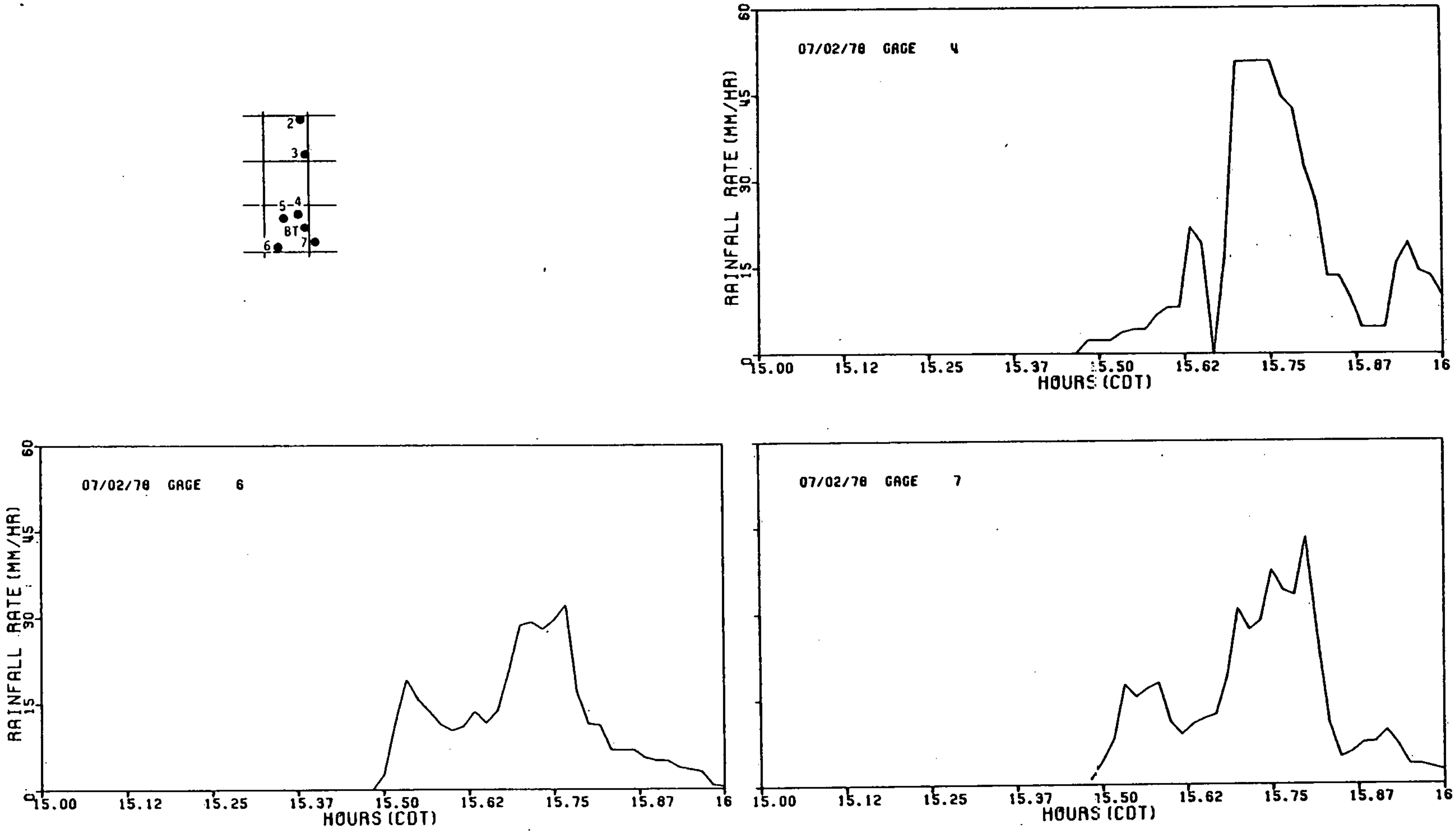


Figure 6. Rainfall rate plots at three SCORE-78 sites for July 2, 1978.

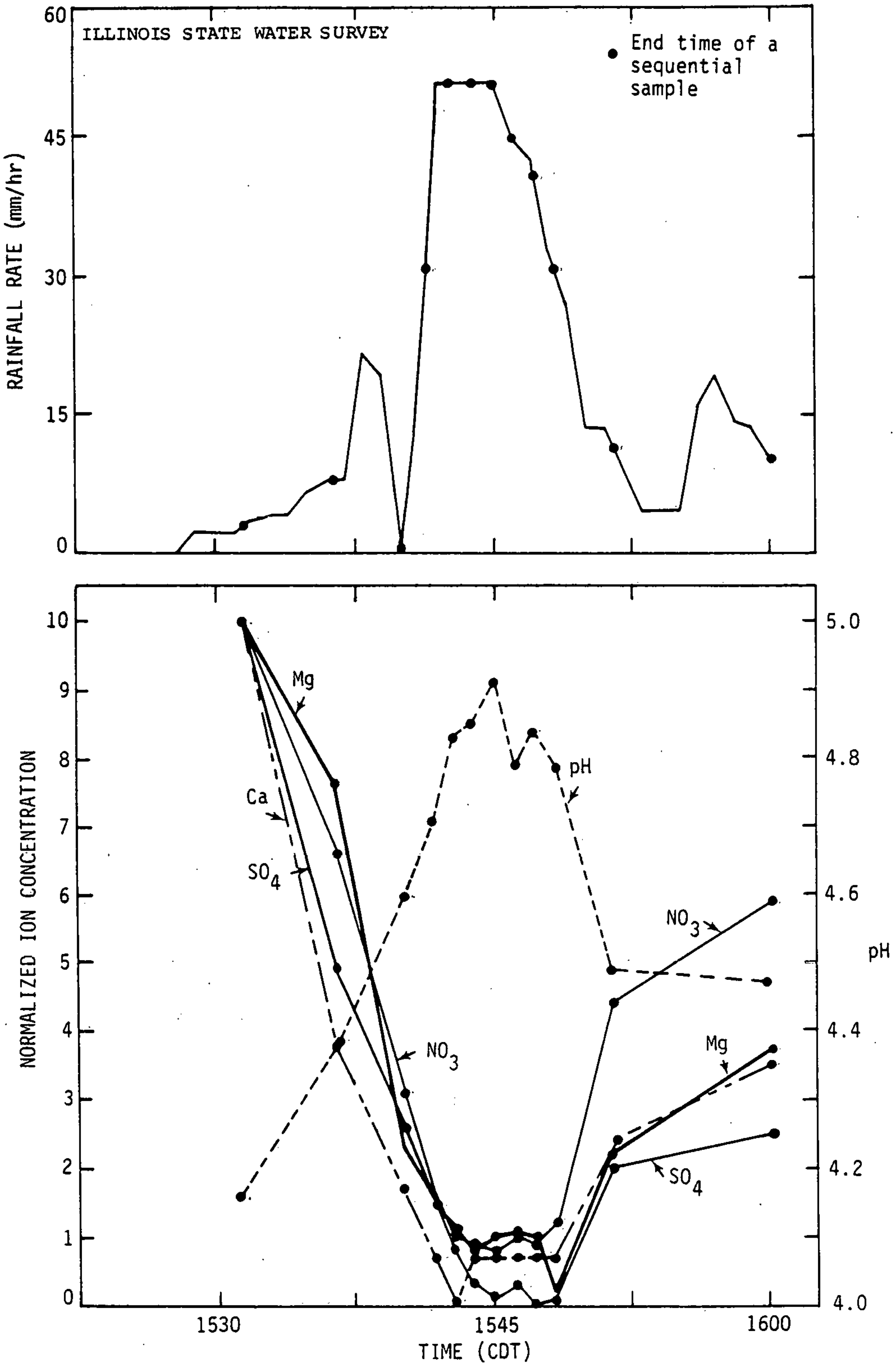


Figure 7. Rainfall rate plot, pH plot, and calcium, magnesium, nitrate and sulfate concentrations sequential samples for site 4 on July 2, 1978.

The different ions all exhibited the same pattern for the sequential samples. Therefore only four are shown in the bottom half of Figure 7. For this figure the concentrations were all normalized with the values for the first sequential sample. The ion concentrations are high at the beginning of the rain shower, decrease in the middle when the rain rate is highest, and increase at the end but do not rise as high as the initial values. The ion concentrations change by more than a factor of 10 during the shower. This variation is greater than that observed in Figures 2 and 3. It is interesting that this large variation in sequential concentrations occurs at a site where the spatial pattern, such as for Ca in Figure 3, was very smooth, i.e., lacking in strong gradients.

The pH in Figure 7 rises from about 4.1 to 4.9 and then ends up about 4.5. This is in agreement with the event pH of 4.4-4.5 for the region of site 4 on Figure 3. The sequential pH changes in response to the changes in all the other ions. However, for these acid samples, HNO_3 and SO_4 are the major ions so it is to be expected that as SO_4 and NO_3 decrease, H will decrease in order that a charge balance is maintained. Thus, this explains the pH time trend in Figure 7.

SUMMARY

Future work on the SCORE-78 data set will include an attempt to relate the daily ambient aerosol values collected at site 4 to the rain chemistry data. Figures 2-4 indicate that the large spatial variability will probably make it a necessity to consider ratios of ions instead of their absolute magnitude.

Figures 2-4 indicate that a single sampling site does not represent well the chemistry of convective rain events. Thus, sample compositing (i.e., weekly sampling) and data compositing (i.e., monthly or seasonal averages) will be most useful in establihsing regional spatial patterns or long term time trends. These results are being formulated in a quantitative manner in the continuing research on this contract.

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CHAPTER 4

MULTIELEMENT ANALYSES OF SELECTED SAMPLES FROM SCORE-1979

Donald F. Gatz and Gary Stensland

Examination of 10 METROMEX events (Gatz, 1980) by factor analysis of rainwater impurity deposition data showed that certain elements consistently grouped together on separate factors. The four groups identified were:

1) soluble crustal elements;
2) insoluble crustal elements;
3) soluble pollutant metals and sulfate, and
4) insoluble pollutant metals.

This indicates that each element in a group had a similar deposition pattern to the other elements in the same group, but that the different groups had different (acutally, orthogonal) deposition patterns. A given deposition pattern (e.g., that of soluble pollutants) was not the same geographically from storm to storm, but certain features, such as deposition maxima near sources, were highly consistent.

The METROMEX results suggested that a similar effort, with additional elements analyzed, would be fruitful in SCORE-79, where the presence of a dense surface wind measuring network and extensive aircraft sampling data could perhaps provide a more complete explanation of the observed deposition fields than was obtained in METROMEX.

Thus, both soluble and insoluble fractions from 102 rain samples were selected for analysis. The samples included wet-only, bulk, and sequential samples collected on three different days, as follows:

<u>13-14 July 1980</u>

4 wet-only samples from event 4 (single cell)

12 wet-only samples from event 5 (single cell)

13 wet-only samples combining events 3, 4, and 5

30 bulk samples combining events 3, 4, and 5

<u>24 July 1980</u>

17 wet-only samples from event 10 (single cell)

26 sequential samples from event 10

The samples were analyzed for many elements and ions using both conventional flame atomic absorption (FAA) and inductively-coupled argon plasma (ICAP) spectroscopy, and the Technicon Autoanalyzer II (AAII), as shown in Table 1.

Sample analyses are nearly completed, and the data will soon be ready for keypunching.

The overall rainfall pattern for the rain of 13-14 July 1979 and the locations of the various types of samples collected are shown in Figure 1.

Analyzed results will be converted to depositions and analyzed in terms of both single cell and multiple cell depositions. Factor analysis will be used where feasible to analyze the deposition patterns.

Table 1. Multiple ions and elements measured in specially-selected samples from SCORE-79, by analysis method and solubility fraction.

	Soluble fraction			Insoluble fraction
	AAII	FAA	ICAP	ICAP
$SO_4^=$	X			
NO_3^-	X			
Cl^-	X			
NH_4^+	X			
Na		X		
Mg		X		
K		X		
Ca		X		
B			X	X
Ba			X	X
Co			X	X
Cr			X	X
Cu			X	X
Fe			X	X
Mn			X	X
Ni			X	X
Pb			X	X
Si			X	X
Zn			X	X

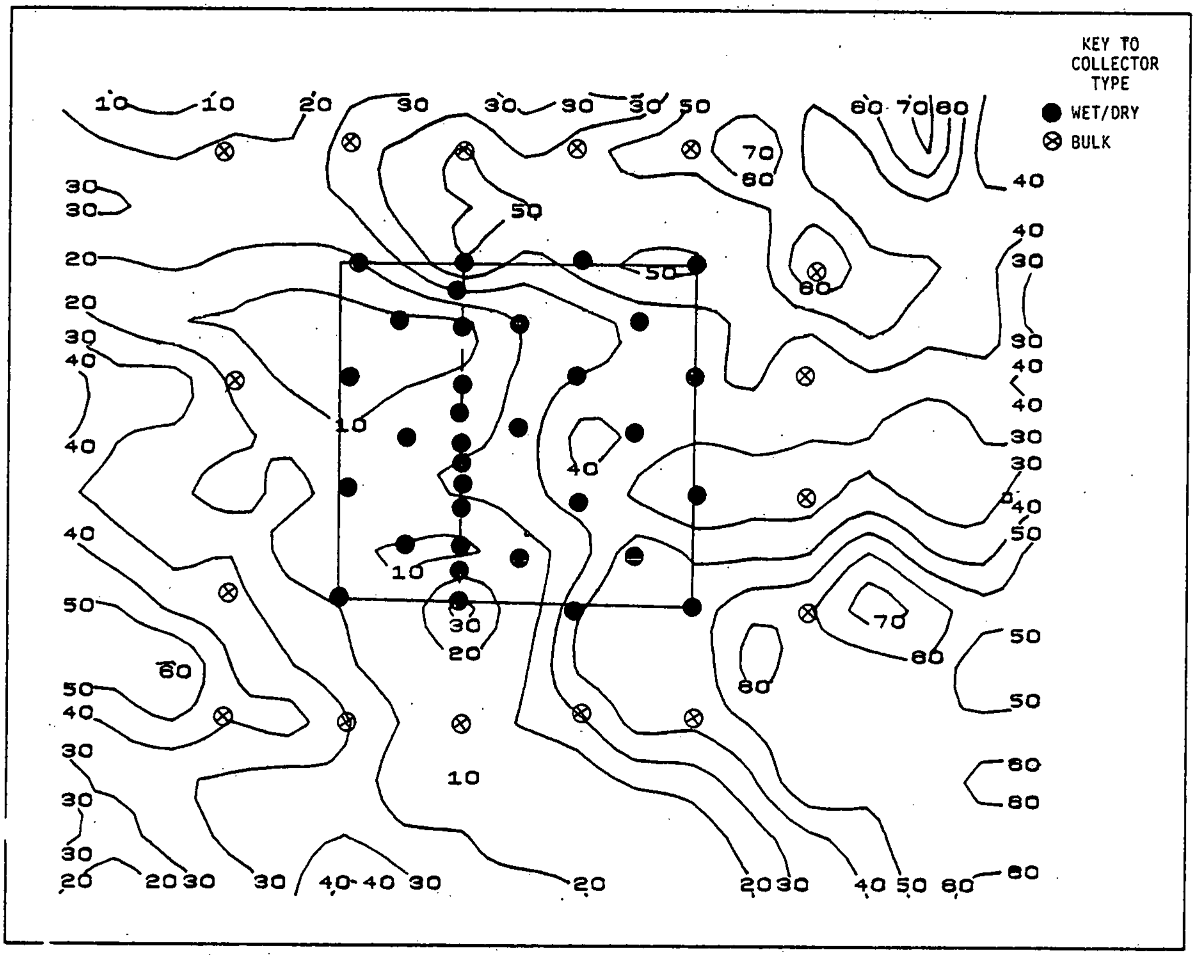

Figure 1. The overall rainfall pattern for 13-14 July 1979 and the locations of the various types of samples collected.

CHAPTER 5

AN URBAN INFLUENCE ON DEPOSITION OF SULFATE AND SOLUBLE METALS IN SUMMER RAINS*

Donald F. Gatz

EXTENDED ABSTRACT

As part of METROMEX the Illinois State Water Survey measured the areal deposition of both soluble and insoluble fractions of a number of elements or ions in rain during the summers of 1972 to 1975. The measurements included Li, Na, Mg, K, Ca, Fe, Zn, Pb, and Cd. These elements represent both natural and man-made sources. Soluble sulfate deposition was measured in four of the events sampled in 1974 and 1975. Further, the data set includes measurements of sulfate and metal concentrations in ground level air, which allows the testing of a key feature in the reasoning of Hales and Dana (1979) that led to their conclusion that sulfur dioxide scavenging was significant in summer rains at St. Louis.

These data were analyzed to show the urban effect on sulfate deposition and its variability. In addition, the data are analyzed to test whether they are consistent with the conclusions of Hales and Dana (1979) regarding the importance of local sources and sulfur dioxide scavenging.

The methods used to analyze both precipitation and aerosol samples have been given in detail previously (Gatz *et al.*, 1978; Gatz, 1978) and are omitted here.

Factor analysis was used in a previous paper (Gatz, 1979; also see Chapter 6 of this Progress Report) to determine which rainwater constituents had similar deposition patterns in individual storm events. In each of four rain events in which soluble sulfate deposition was measured, factor analysis showed that its deposition pattern was most similar to that of soluble pollutant metals (Pb, Zn, and Cd) and to the rainfall pattern. In contrast, soluble soil elements, insoluble soil elements, and insoluble pollutants were found to have separate patterns of deposition in individual events.

The general agreement between sulfate deposition and soluble Zn deposition for the four events mentioned above suggests that the long-term average deposition pattern (i.e., over many events) for soluble Zn is similar to that of sulfate, which was measured in only four events. The average Zn deposition (ng/cm/event) pattern has maximum soluble Zn deposition very close to the suspected sources. Since sulfate deposition was similar to soluble Zn deposition in three of the four individual events mentioned earlier, we might expect a similar, but not identical urban influence for sulfate deposition.

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Since deposition of materials in rain is influenced by their concentrations in air, it is of interest to examine the spatial distribution of airborne sulfate in the St. Louis area. Examination of median concentrations at 12 sites where aerosol samples were collected during the summer of 1972-1975 showed maximum values in urban areas and minimum values in rural areas. The ratio of the highest to the lowest medians at many sites was 2.3 for sulfate. This is similar to previously reported urban/rural sulfate ratios in the eastern U.S. Importantly, examination of airborne sulfate patterns in the St. Louis area on individual summer days confirmed that similar distributions also occurred on individual days. This is important because it contradicts the perceived "highly uniform" atmospheric sulfate concentrations in the St. Louis area, which led Hales and Dana to conclude that SO_2 scavenging was necessary to produce the high concentrations in rain that they observed just downwind of the city.

The present data show that patterns of both airborne and rainborne sulfate are similar, which may obviate the need to infer SO_2 scavenging.

Our results do, however, agree with those of Hales and Dana in implying that local sources caused the observed local enhancement of sulfate in rain.

Factor analyses showed that sulfate deposition patterns group consistently with those of other soluble pollutants and rainfall. The loading values from the factor analyses suggested, and a comparison of actual deposition patterns showed, that soluble pollutants and rainfall depositions were generally similar in their major features, but differed in some details.

It appears very significant that sulfate deposition patterns are similar to soluble pollutant metals and rainfall, but not to insoluble metals or soluble soil elements. These relationships should be determined by the distribution of sources and by the processes of scavenging and/or precipitation formation. Source distribution can probably explain why pollutant distributions are different from those of soil elements, but the reason why soluble and insoluble materials have different deposition patterns would appear related to scavenging and/or precipitation formation processes.

Any further statements at this time are speculative. One could speculate that the association between the deposition patterns of sulfate and soluble metals implies that the sulfur is scavenged in the same way as the metals, namely by particulate (sulfate) scavenging. Other explanations, however, involving sulfur dioxide scavenging by cloud droplets with high catalyst concentrations, can also be envisioned. Whatever mechanisms are eventually proposed, however, they must now be consistent with the observations reported here.

In summary, observations reported here and others in the literature agree that rainfall deposits at least some locally-emitted sulfur at short distances downwind of the sources. This causes enhanced deposition and variability in the affected areas. Airborne sulfate concentrations near St. Louis vary by a factor of 2-3 from urban to rural locations on individual days. This variation is roughly the same as that observed in either concentration or deposition of sulfate in rain. Thus, there is no need to invoke in-cloud scavenging of sulfur dioxide to explain enhanced sulfur in rain near the city, since there is ample aerosol sulfate and an available scavenging mechanism (nucleation) to account for it. The observation of consistently similar deposition patterns for sulfate and soluble pollutant metals places some interesting constraints on possible scavenging mechanisms and suggests that more detailed study of this group of materials would be fruitful for understanding the processes involved.

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CHAPTER 6

ASSOCIATIONS AND MESOSCALE SPATIAL RELATIONSHIPS AMONG RAINWATER CONSTITUENTS*

Donald F. Gatz

During Project METROMEX, between 1972 and 1975, approximately 90 sets of daily precipitation samples were collected from mesoscale sampling networks of 80- 85 collectors near St. Louis. For a number of these sample sets, soluble and insoluble fractions of up to 10 elements or ions, representing both natural and man-made sources and a range of particle sizes, were measured. The elements measured included Li, Na, Mg, K, Ca, Fe, Zn, Cd, and Pb; $SO_4^=$ ion was determined as well.

In a search for information about how these rainwater constituents were scavenged from the atmosphere, or how they participated in the formation of precipitation, it is of interest to examine their patterns of deposition on the earth's surface (mass cm^{-2}). Concentrations in rain (mass cm^{-3}) could also have been chosen, but this paper treats only depositions. Deposition has an advantage over concentration in that it is not affected by evaporative loss of water from the collectors.

Specifically, it is of interest to ask whether the deposition patterns of the various constituents were all the same, or all different, or whether there were several major groups, and also how the constituent deposition patterns related to each other, to the location of emission sources, and to the rainfall pattern.

These questions were examined in 10 rain events sampled during the summers of 1972, 1974, and 1975. Factor analysis was used to identify groups of constituents having similar deposition patterns.

The analytical results for 10 storms are summarized in Table 1, which gives mean deposition values for the valid samples from each event. Soluble and insoluble fractions of the various elements or ions are listed separately. Mean rainfall for each event is also shown. Mean deposition patterns for the soluble fraction of a number of the elements have been discussed by Gatz et al. (1978).

The factor analysis results consist primarily of loadings tables and factor scores tables. The loadings tables may be presented directly, to show the groupings of variables according to similar deposition patterns. Loadings

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*Paper accepted for publication in the Journal of Geophysical Research, April, 1980.

Table 1. Summary of network mean deposition of rainfall and rain water constituents in 10 storms, for valid samples only.

	Units	11 Aug 1972	2 Aug 1974	9 Aug 1974	13 Jul 1975	18 Jul 1975	19 Jul 1975	31 Jul 1975	1 Aug 1975	13 Aug 1975	14 Aug 1975
No. of Valid Samples		24	58	56	78	74	66	61	78	71	65
Soluble Fraction											
Li	pg cm^{-2}	419	197	95.1	83.1	209	175	61.6	165	114	77.6
Na	ng cm^{-2}	753	320	383	--	--	--	--	--	--	--
Mg	ng cm^{-2}	279	173	114	204	115	51.7	34.7	41.7	61.7	66.1
K	ng cm^{-2}	1380	505	162	176	521	411	196	428	316	190
Ca	ng cm^{-2}	9230	3430	1910	2150	4210	2220	1870	1900	2580	1760
Fe	ng cm^{-2}	--	--	--	--	--	--	--	--	--	27.9
Zn	ng cm^{-2}	20.0	15.6	32.4	14.6	13.1	5.38	5.68	4.10	4.78	16.1
Cd	pg cm^{-2}	1200	--	--	145	--	--	--	114	--	336
In	pg cm^{-2}	163	--	--	--	--	--	--	--	--	--
Pb	ng cm^{-2}	25.8	--	--	--	--	7.68	--	--	--	23.6
SO_4	ng cm^{-2}	--	6530	--	4670	--	1960	--	4430	--	--
Insoluble Fraction											
Li	pg cm^{-2}	340	--	272	76.4	42.1	46.4	31.4	10.5	22.4	56.4
Na	ng cm^{-2}	771	--	244	--	--	--	--	--	--	--
Mg	ng cm^{-2}	67.3	--	28.3	--	--	27.5	--	--	--	30.6
K	ng cm^{-2}	147	--	105	32.3	56.4	38.1	19.8	10.9	3.67	34.6
Ca	ng cm^{-2}	120	--	31.0	--	--	129	--	--	--	137
Fe	ng cm^{-2}	--	--	176	76.6	83.1	48.4	28.8	41.4	30.8	96.0
Zn	ng cm^{-2}	5.20	--	2.79	5.40	3.15	3.83	0.57	2.31	1.53	5.9
Pb	ng cm^{-2}	--	--	--	--	--	8.90	--	--	--	6.33
Rainfall	mm	21.3	11.3	11.3	10.3	7.56	1.98	3.96	7.26	5.74	10.4

tables are presented here only for the event of 13 August 1975, to illustrate the results. For deposition data from a network of samplers, the information in the factor scores tables is best conveyed by plotting and analyzing the values on a network map. Examples of factor scores patterns are presented for the storm of 13 August 1975 in Figures 1 and 2. The factor scores are plotted along with actual depositions for the variables with the highest loadings on the respective factors.

The loadings table from factor analysis of deposition data from 13 August 1975 is presented in Table 2. The loadings are equivalent to correlation coefficients between variables and factors. Thus, they show which variables are involved with each factor, and the degree of involvement. Loadings < 0.50 contribute < 25% of the variance between variable and factor and are ordinarily shown (in parentheses) only if no values > 0.50 occurred. This makes the table more readable, while preserving its major features.

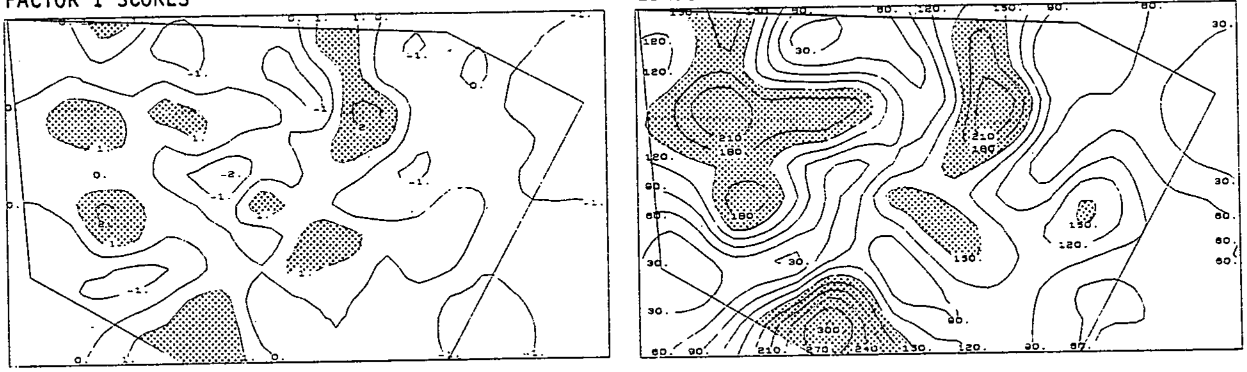
Table 2 shows that only 3 factors explain 63% of all the variance of the 10 variables. The soluble soil elements Li, Ca, K, and Mg have high loadings on Factor 1, indicating that these elements had deposition patterns that were similar to each other, but different from those of the other variables. This is illustrated in Figure 1, which compared the actual deposition patterns of soluble Li, Ca, K, and Mg, with that of the scores for Factor 1. Scores for each factor have mean 0, standard deviation 1, and are weighted sums of the original normalized data. The weights reflect the degree of involvement of the variable with the factor. Note that Li, Ca, and Mg, which have loadings of 0.88 or more (Table 2), had deposition patterns which were very similar to each other and that of the factor scores, while Mg, with a loading of only 0.69, a had somewhat less similar pattern.

Table 2. Loadings table from factor analysis on deposition data from Storm of 13 August 1975.

	Factor		
	1	2	3
Soluble Li	0.93		
Soluble Ca	0.92		
Soluble K	0.88		
Soluble Mg	0.69		
Insoluble K		0.78	
Insoluble Fe		0.74	
Insoluble Li		0.67	
Soluble Zn			0.82
Rainfall			0.60
Insoluble Zn			(0.49)
Variance explained, %	35	15	13
Cumulative variance, %	35	50	63

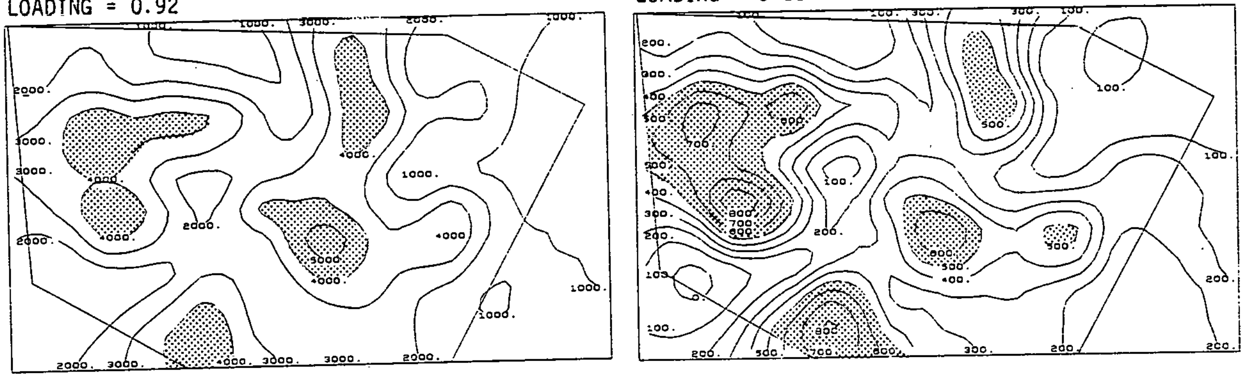
FACTOR 1 SCORES

SOLUBLE Li DEPOSITION, pg cm^{-2}
LOADING = 0.93



SOLUBLE Ca DEPOSITION, ng cm^{-2}
LOADING = 0.92

SOLUBLE K DEPOSITION, ng cm^{-2}
LOADING = 0.88



SOLUBLE Mg DEPOSITION, ng cm^{-2}
LOADING = 0.69

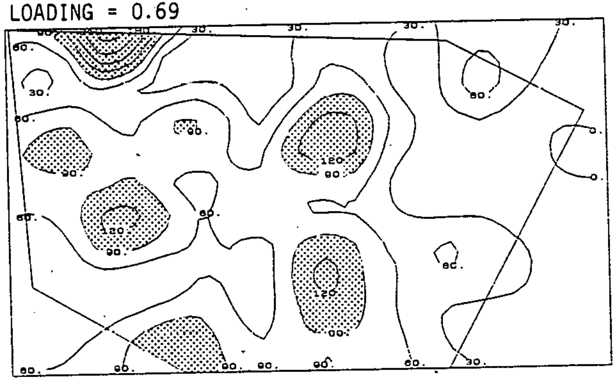


Figure 1. Comparison of scores pattern for Factor 1 with actual deposition patterns of the heaviest-loaded variables, for the rain of 13 August 1975.

Returning to Table 2, Factor 2 shows highest loadings for three insoluble soil elements, while Factor 3 had high loadings for soluble Zn and rainfall. Insoluble Zn is also shown here, although its loading of 0.49 indicates that its deposition pattern was not greatly similar to the factor score pattern. This is also shown in Figure 2, which compares actual deposition patterns and the factor scores pattern for Factor 3.

The groupings of variables on factors was examined for all ten events. The most important characteristic of these results to point out is the consistent occurrence of four main groups of variables.

(1) soluble soil elements: Li, Na, Mg, K, Ca;

(2) insoluble soil elements: Li, Na, K, Ca, and sometimes Fe;

(3) soluble pollutants: Zn, Cd, Pb, $SO_4^{=}$;

(4) insoluble pollutants: Zn, Pb, and sometimes Fe.

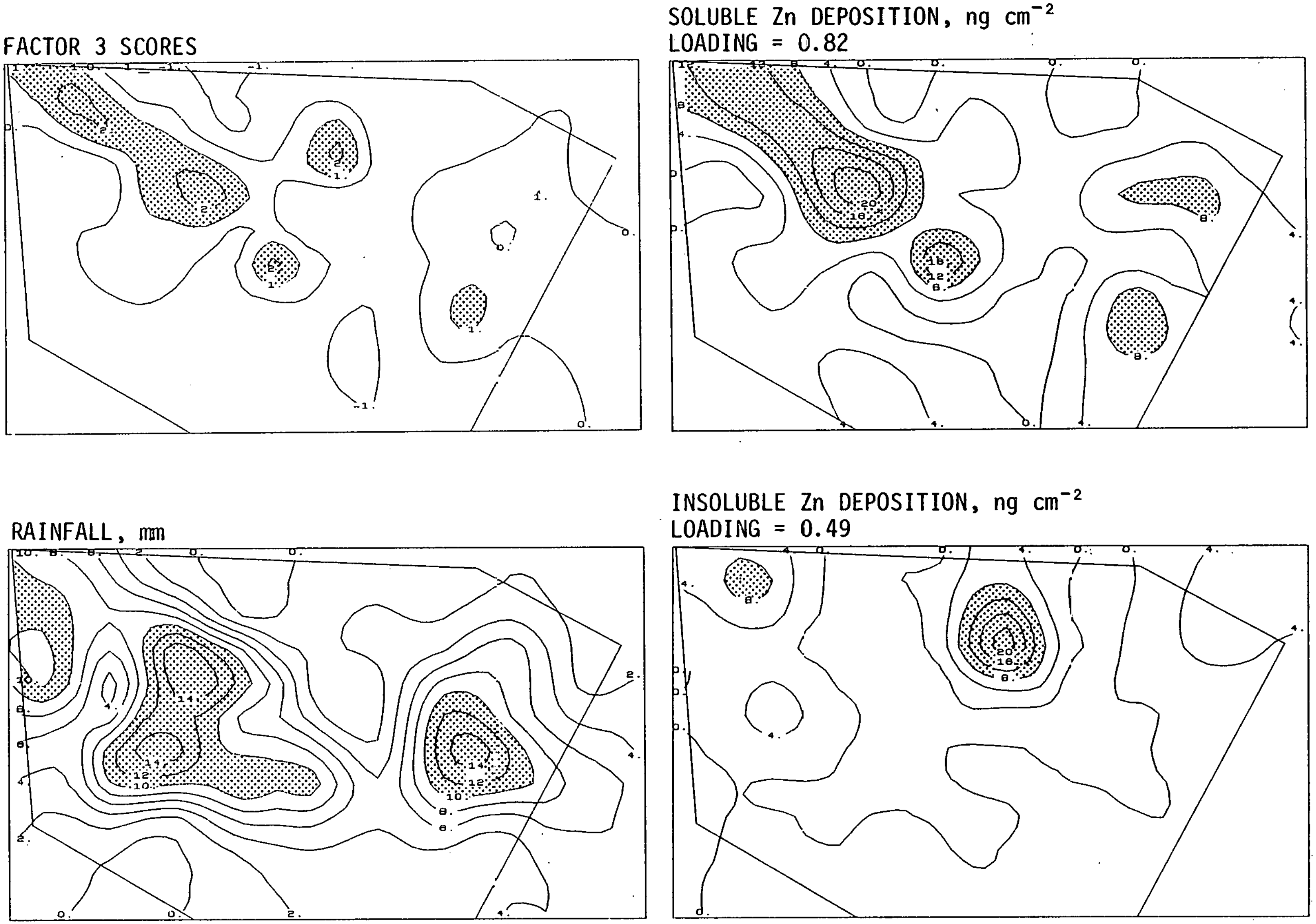
These four groups with minor variations, can be identified in each of the 10 events.

The results presented so far have centered on the grouping of variables according to similar deposition patterns. We consider next the actual patterns of these depositions, and how they relate to each other, to source locations, and to rainfall distribution.

These relationships are summarized briefly in Table 3. Both soluble and insoluble portions of the soil elements had little or no tendency for their deposition maxima to occur near pollutant sources (cities and industrial areas), but both tended to deposit heavily in areas of sharp rainfall gradient. Both soluble and insoluble portions of the pollutant elements had strong tendencies for their deposition maxima to occur near sources. The soluble pollutants tended to have maximum deposition in the heaviest rain, but there was no relationship between deposition maxima and heavy rain for the insoluble portions.

Table 3. Summary of the relationship of deposition patterns to urban areas and heavy rains.

Deposition type	Tendency for deposition maxima to occur near cities or industrial areas	Location of deposition maxima relative to heavy rain
Soluble soil elements	none	in sharp gradients
Insoluble soil elements	slight	in sharp gradients
Soluble pollutants	strong	coincident
Insoluble pollutants	strong	no relationship



FACTOR 3 SCORES

SOLUBLE Zn DEPOSITION, ng cm^{-2}
LOADING = 0.82

RAINFALL, mm

INSOLUBLE Zn DEPOSITION, ng cm^{-2}
LOADING = 0.49

Figure 2. Comparison of scores pattern for Factor 3 with actual deposition patterns of the heaviest-loaded variables, for the rain of 13 August 1975.

In summary, factor analysis, of multielement deposition of both soluble and insoluble materials in single storms over networks of approximately 2000 km^2 near St. Louis have revealed that four main groupings of deposition patterns occur.

1) Soluble soil-derived elements,
2) Insoluble soil-derived elements,
3) Soluble pollutants, and
4) Insoluble pollutants.

Soil elements and pollutants would be expected to have different deposition patterns in rain because their sources are distributed differently. However, the findings that soluble and insoluble portions of the same element also have different patterns suggests that scavenging and/or precipitation formation processes are responsible.

These findings also suggest that these processes might be studied by multielement analyses of rain samples collected from single cells by mesoscale networks of collectors.

CHAPTER 7

SPATIAL VARIABILITY OF RAIN WATER IMPURITIES IN MESOSCALE EVENTS

Daniel Q. Naiman and Donald F. Gatz

This brief report is a summary of an investigation of the spatial variability of precipitation impurities in the METROMEX network of precipitation samplers. A full report of this work is now in preparation, and will appear as Research Report No. 5 on this contract. We concentrate in this summary on the reasons why precpitation impurity variations are important and on some typical results. The extensive statistical-mathematical development and the detailed results will appear in the Research Report.

INTRODUCTION

Information on total rain volume over an area is of interest to a variety of scientists and engineers. The specific time period of the rain accumulation that is of interest varies with the application of the information. For example, engineers responsible for urban storm water runoff are concerned with time periods measured in hours, while those interested in crop yields may need weekly or monthly values.

Similarly, users of information on total deposition of the impurities in rain will vary in their requirements for the time period of the deposition measurements. Atmospheric scientists measuring the deposition of tracer materials released into a thunderstorm or charting deposition patterns of different impurities to learn more about precipitation scavenging processes need measurements on the time scale of individual storm duration. However, those concerned with long-term trends in deposition, or with nutrient budgets in a watershed, may be satisfied to know seasonal or annual inputs.

If rainfall were uniform over some area for a given time period, one could obtain the area mean rainfall or total rain volume from one measurement of rainfall anywhere in the area. However, completely uniform rainfall rarely occurs over areas involved in most situations of practical importance. Multiple measurements are then recommended to improve the accuracy of estimating the area mean or the total volume of rain over an area.

Similarly, if rainfall varied, but rainfall constituent concentrations were uniform over an area, we could estimate the deposition of constituents from a single rain water collector (to provide a sample for analysis) and multiple raingages. However, again, concentrations vary spatially within rains, so multiple collectors are required to estimate the mean or total deposition in an area.

We feel intuitively that the greater the variability of rainfall, or rain impurity deposition, over an area, the more raingages or collectors will be required to reach a given accuracy in estimating the area mean. Thus, several earlier studies have been directed toward measuring variability of rainfall or deposition over areas of varying size and over time periods of varying length. Some of these have emphasized the sampling requirements for various purposes, while others have been concerned with evaluating the accuracy achievable for a given network size and instrument spacing.

The purpose of this paper is to show how taking account of spatial correlation improves the accuracy of estimating summer rainfall and deposition from single events using open collectors (corrected for dry deposition contributions) over 2000 km^2 in the St. Louis area. Arranged in a square grid network with 5 km collector spacing.

A DESCRIPTION OF THE MODEL DEVELOPMENT

Our first step was to develop estimates of the mean rainfall, or of the mean impurity deposition or concentration, over some area, using observed values at a number of discrete points within the area. The usual estimator for this value is simply the sum of the observed values divided by the number of observations.

We next derived an alternative expression, called the best linear unbiased estimator (BLUE), for the area mean, based on the assumption that for a single event the process is weakly stationary and circularly symmetric. This means, 1) that the expected value of the process (i.e., rainfall, deposition, or concentration) at any point in the network is the area mean, and 2) that for each pair of points in the area, the covariance depends only on the distance between them.

The variance of any linear unbiased estimator (including the sample mean), which is a measure of its uncertainty, is the product of the point variance (i.e., the usual variance of the network observations) and the variance reduction factor (VRF), which depends only on the correlation function (i.e., the variation of the correlatin coefficient with distance between samplers), and the geometry of the network (i.e., sampler density, number of samplers, and the shape and size of the network).

The VRF that might be chosen by a naive analyst who does not take account of the correlation between observations, would be the reciprocal of the number of observations. For our network of 80 collectors, the naive VRF is 1/80, or 0.0125.

In the case where correlation is present between sampling points, we adopted a model of the correlation function that was a smooth non-negative function which decays montonically to zero in any direction from the origin. This expresses our belief that the correlation beween samplers should be near one when they are very close, and decrease to zero as the distance between the collectors increases.

For the 1972-1974 METROMEX precipitation chemistry network, we computed VRF's for the simple exponential correlation function

$$\rho(r) = e^{-kr} \qquad (1)$$

where r is the distance between collectors. Results are shown in Figure 1 for the VRF of the sample.

We defer the details of these developments to the forthcoming Research Report No. 5, and go on to present results.

RESULTS

Our data base consisted of 14 events from 1972-1974 having measurements of soluble Li, Na, Mg, K, Ca, and Zn. Figure 2 shows the variation of correlation with sampler separation distance for rainfall, where the individual points are mean values for all combinations of samplers over a given distance interval and over all 14 events. Standard error estimates of the correlations are also shown as a function of sampler separation at the bottom of Figure 2. The solid curve is the maximum likelihood fit to the data points, using the exponential function shown in (1) above.

Similar results are given for the deposition and concentration of Ca in Figures 3 and 4, respectively. No fitted curve was computed for concentrations since, as Figure 4 shows, the correlations decayed very rapidly to zero. For rainfall and deposition (Figures 2 and 3) the estimated values were usually negative for separations beyond about 20 km, so the family of functions used for fitting was not ideal. However, this probably had a minor effect on the degree of variance reduction achieved since the short distance correlations tend to be much larger than the more distant correlations in terms of absolute value.

A summary of results for rainfall and the soluble portions of six elements is given in Table 1. The results are summarized in terms of the parameter k in the exponential correlation function, the corresponding separation distance, $r_{0.5}$, at which the correlation becomes 0.5, the VRF, and the relative confidence interval on the network mean deposition when spatial correlation is accounted for.

The results show that the dropoff in correlation was most rapid for Li, which reached a correlation of 0.5 at a separation of only 0.87 km, and least rapid for rainfall, for which $r_{0.5} = 3.0$ km. Soluble Zn had the second most rapid decrease in correlation, while the remaining elements were clustered at $r_{0.5}$ values only slightly smaller than that of the rainfall. The corresponding relative confidence intervals on the areal mean deposition, taking account of spatial correlation, ranged from 0.54 to 0.81 of those that would be obtained otherwise.

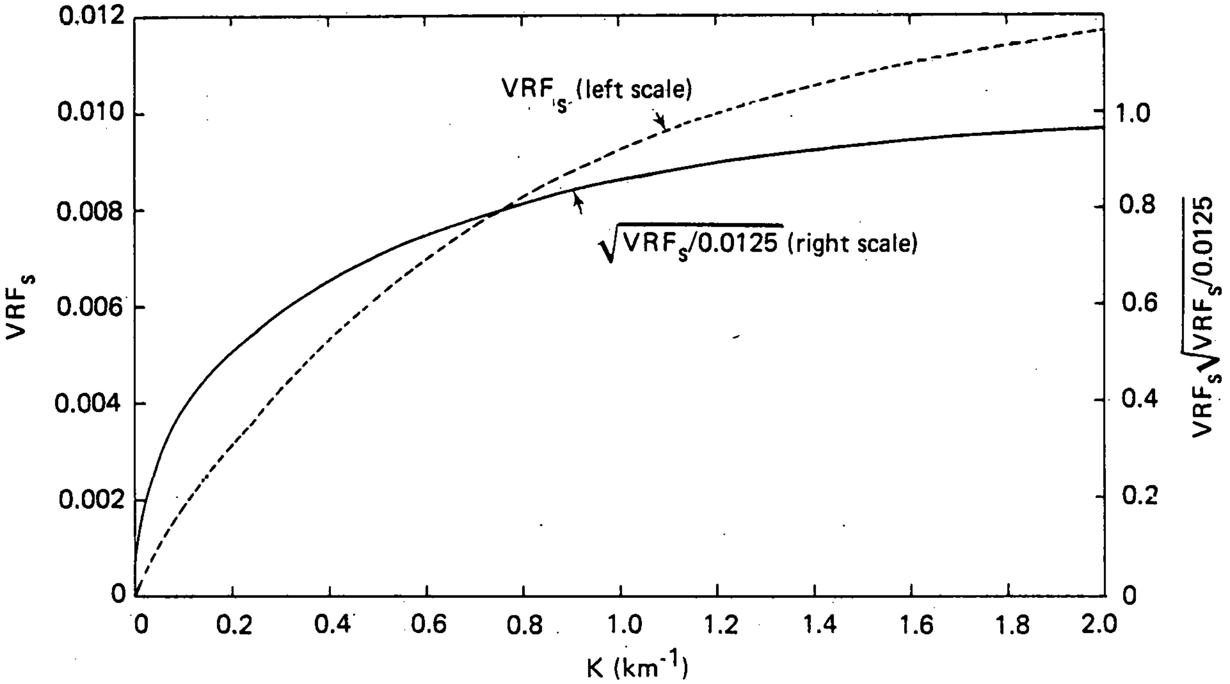


Figure 1. Variation of VRF_s and $\sqrt{VRF/0.0125}$ with sampler separation distance, for 14 events in the 1972-1974 METROMEX precipitation chemistry network.

Table 1. Summary of results for rainfall and soluble elemental deposition for 14 events in 1972-1974 METROMEX precipitation chemistry network.

	k, km^{-1}	$r_{0.5}$, km	VRF	$\sqrt{VRF/0.0125}$
Rainfall	0.234	3.0	0.0036	0.54
Li	0.795	0.87	0.0082	0.81
Na	0.244	2.8	0.0037	0.54
Mg	0.291	2.4	0.0042	0.58
K	0.250	2.8	0.0038	0.55
Ca	0.247	2.8	0.0037	0.54
Zn	0.451	1.5	0.0058	0.68

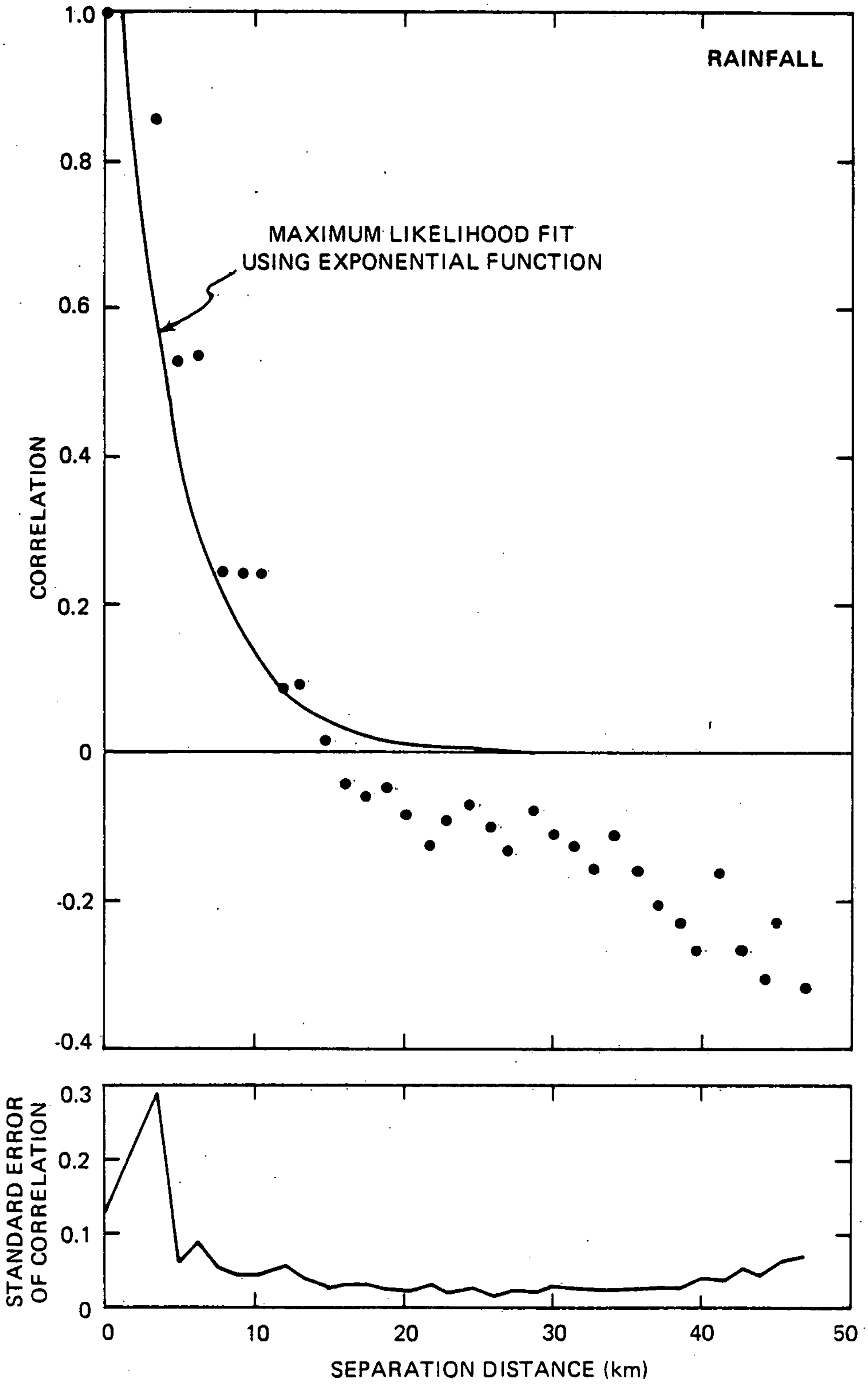


Figure 2. Observed spatial correlations for rainfall.

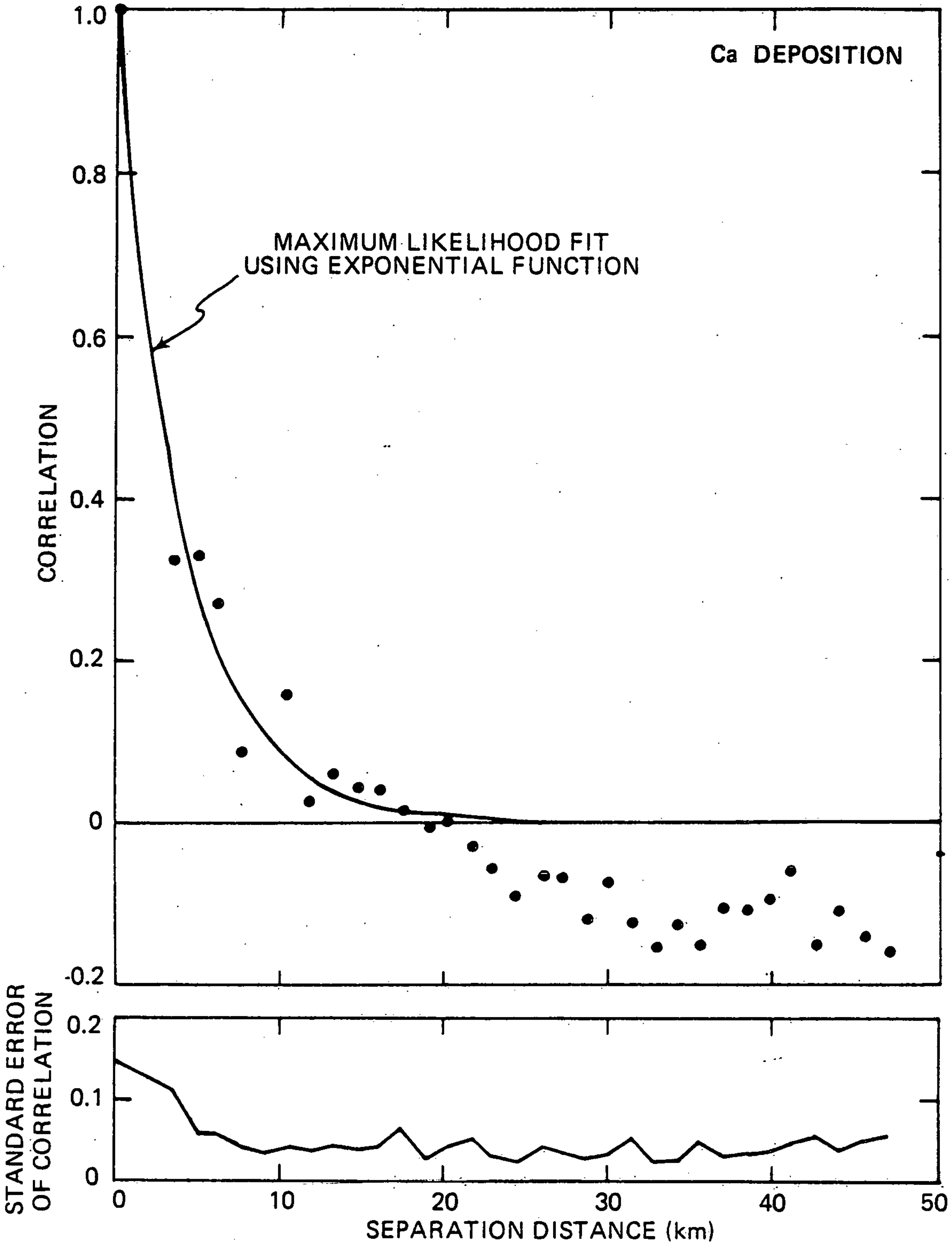


Figure 3. Observed spatial correlations for Ca deposition.

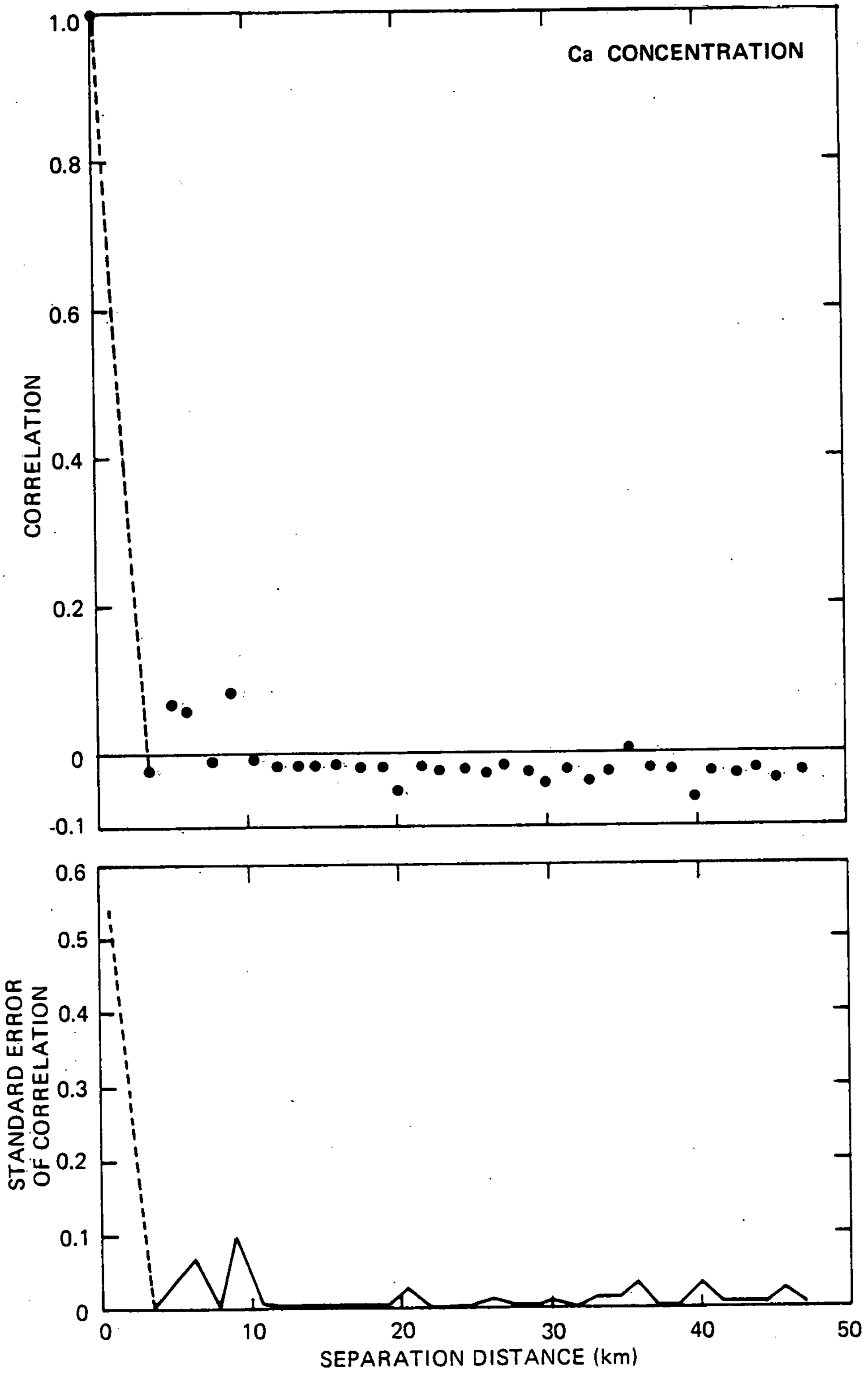


Figure 4. Observed spatial correlations for Ca concentrations.

DISCUSSION AND CONCLUSIONS

This is a unique set of data on precipitation impurity variability, since it was collected in single events, and over a relatively limited area (2000 km^2) near a large urban center. It shows a much more rapid dropoff in the spatial correlation function than has been observed in monthly samples, for example. In 14 summer events from 1972 to 1974, the mean correlation function for rainfall dropped to 0.5 in 3.0 km, and dropped even more rapidly for deposition of soluble impurities. Zn, which is known to have a number of point sources in the area, reached a correlation of 0.5 in only 1.5 km. The dropoff for Li was even more rapid, but the reasons for this behavior are not clear. Perhaps, as we have suspected for some time, it too has point sources in the area. It is also possible that the behavior of Li may also be related to its use as a tracer in a number of the events analyzed.

This rapid decrease of the correlation function with distance for events stands in contrast to previous results for monthly samples. Karol and Myatch (1972) observed that correlations of several elements or ions reached 0.5 at distances ranging from 90 to 450 km in the USSR, and Granat (1976) obtained very similar results in Sweden.

For rainfall and the soil derived elements, which have rather uniformly distributed sources, taking account of the spatial correlation of deposition gives confidence intervals on the network mean that are about half of those that would otherwise be obtained. For elements such as Zn, which have more localized sources, there is still improvement, but not as much; the improvement is about 30%.

It should be noted that these results were obtained from sampling during summer seasons, when convective rainfall is prevalent. Convective rainfall is known to be more variable than that falling from layered clouds. In addition, the influence imposed by the city on both pollutant source distributions and downwind rainfall may also contribute to increased variability in this data set.

At this point in the research, it appears that between rainfall itself, deposition of impurities, and concentration of impurities, rainfall has the most spatial correlation. Deposition of elements having relatively uniform sources, such as Mg, Ca, K, and Na from the earth's crust, has slightly less spatial correlation on an event basis. Impurity concentrations have very little spatial correlation.

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CHAPTER 8

A PRECIPITATION CHEMISTRY DATA MANAGEMENT SYSTEM - SUMMARY

Randall K. Stahlhut and Van C. Bowersox

Over the past several years the large amount of precipitation chemistry data collected by the Illinois State Water Survey (ISWS) has made it necessary to develop an automated data management system. This system has two principle features: (1) a computerized data base to store the information in an easily and selectively accessible form, and (2) a library of computer programs to process and check the data for consistency and errors and to organize and report the data in formats amenable to the data user and to the data analyst. Together these features combine to provide a simple and efficient means of managing large precipitation chemistry data sets.

THE COMPUTERIZED DATA BASE

The precipitation chemistry data base was implemented using the Scientific Information Retrieval (SIR) system (Robinson et al., 1979) available at the University of Illinois. This system is structured hierarchically (Figure 1), in that a single identifier, a CASE, may "own" many other data records. In this application a CASE is a unique seven character identifier assigned to each precipitation sample by laboratory personnel. Each sample (or CASE) must "own" both a COMMON record and an INITIAL ANALYSIS record, while it may "own" a REANALYSIS record or both REANALYSIS and CORRECTED ANALYSIS records. This design is particularly appropriate for managing data for the Central Analytical Laboratory (at the ISWS) of the National Atmospheric Deposition Program (NADP), the St. Louis METROMEX, and the SCORE projects.

Every sample is associated with a COMMON record, comprised of certain non-chemical data and field measurements. Identifying information such as where (e.g., the site name), when, under what conditions the sample was collected (e.g., wet-only, bulk, etc.), and under what conditions it was received for analysis are included in this record. Any measurements made at the time or place of the sample recovery are stored in this block, as well. The utility of the COMMON record within the data base system is that information stored therein can be selectively cued, so that certain categories of samples can be retrieved. For example, a listing of all wet-deposition-only samples from a given collection site can easily be generated using the retrieval methods available in conjunction with these COMMON records.

The other "mandatory" record is the INITIAL ANAYLSIS record, which simply contains the results of the ion concentration determinations made in the laboratory along with the date of the pH and solution conductance measurements, if appropriate.

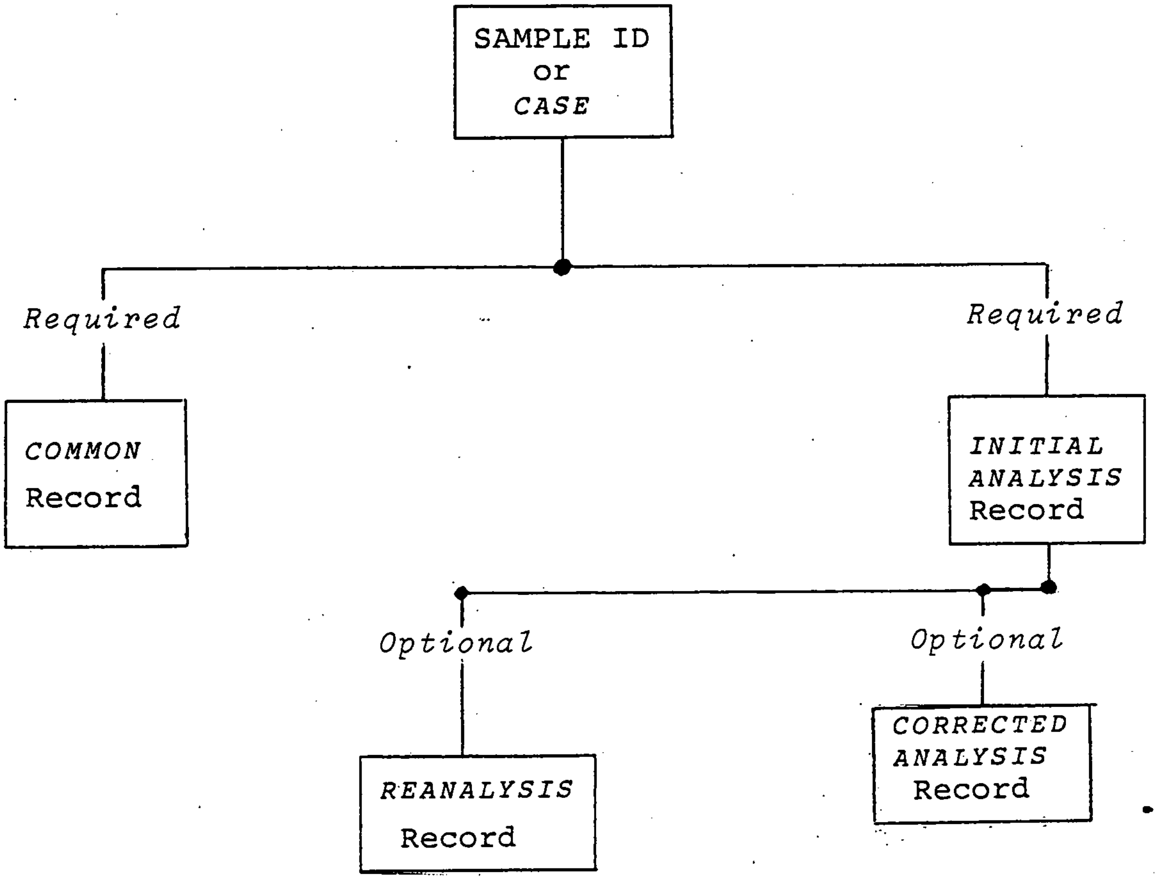

Figure 1. Structure of precipitation chemistry data base.

Two optional data records may also exist for any one sample: 1) a REANALYSIS record and 2) a CORRECTED ANALYSIS record. Both of these records store the same types of information present in INITIAL ANALYSIS records, with an added field to indicate the conditions under which samples were stored between initial analysis and reanalysis (e.g., room temperature or refrigerated). No CORRECTED ANALYSIS record can exist in the absence of a REANALYSIS record, but the existence of a REANALYSIS record does not imply the existence of a CORRECTED ANALYSIS. Simply put, if and only if the results of a reanalysis show that there was an error in the initial analysis will a CORRECTED ANALYSIS be created. This CORRECTED ANALYSIS record will contain measured values from the initial chemical and analysis except where those (erroneous) values were replaced by the (correct) results from the reanalysis.

All of the records within the data base system have read (or input) and write (or output) security restrictions that limit the accessibility to perform these functions to authorized users. This limited accessibility is designed, of course, to prevent any inadvertent modifications or misuse of the data. The COMMON and INITIAL ANALYSIS data are entered into the data base system from computer files created from hard copy (e.g., hand written or printed data sheets). All such data transcriptions between hard copy and computer file are entered and re-entered, with the requirement that there be complete agreement or "verification" between the two entries. The REANALYSIS and CORRECTED ANALYSIS data are entered into the data base directly from laboratory data sheets using a computer interactive procedure written for that purpose. These data are also "verified" upon entry.

In order to retrieve stored data, SIR has a simple-to-use facility for extracting desired subsets of the entire data set in a form suitable for use by an external program or suitable for use by one of the available internal statistical programs. Selective retrievals of this sort are based on classes or categories of COMMON records. For example, SELECT IF (PRECIP LT .5) will access all samples (CASES) where the measured wetfall at the sampling site was less than one half of an inch. Once accessed, a retrieval might be performed which would list for all such samples the COMMON data or the INITIAL ANALYSIS data or the data from some other record. This is a frequently used routine for generating simple data summaries. A second type of retrieval allows more than one data record to be listed. That is, a listing of the INITIAL ANALYSIS and the REANALYSIS for a pre-selected group of samples can be generated. This is especially useful in performing ion stability studies. These two types of retrievals are the most often used, but the variations on these basic types are enumerable, owing to the versatility of the data base system. Perhaps the biggest advantage in using this system, however, is that all of these retrievals can be performed interactively.

THE DATA PROCESSING LIBRARY

In addition to having a facility for easy and efficient data storage and retrieval, such as the data base, it is also necessary to be able to manipulate and perform certain calculations on these data. This data processing function must be capable of generating reports, tables, plots, etc., which summarize the data in an easily interpretable format. Summaries of this sort are invaluable for checking the consistency and correctness of the analytical values and for performing research and interpretive studies, as well. A library of computer programs has been developed to perform this function. All of these programs are user interactive and so all are adapted for use on a remote computer terminal.

This data processing library consists of (a) a set of subroutines with a driver program, and (b) several larger programs which perform specialized tasks. Each subroutine focuses on an individual task, such as the performance of an input function, a print function, or some other functions. These various subroutines are invoked by a driver program. The driver program interrogates the user through a series of prompts to determine what the assigned job shall be and what data shall be used as input. It then coordinates the flow of information and the processing of tasks among the subroutines to accomplish that job. Other specialized programs were created to accomplish such specific tasks as objectively contouring a grid network of data (Achtemeier, 1977) or calculating parameters that describe the statistical distribution of a data set. These programs are independent of the driver/subroutine set, but are part of the overall data processing library. The driver/subroutine program is particularly appropriate for processing the routine kinds of jobs necessary to support the flow of information to the researcher.

Much of the routine report and data processing must be routed through a key subroutine called IONBAL. For this reason, data that have gone through IONBAL can be stored in a computer file for use in subsequent jobs performed on the same data. This eliminates the need for repeated execution of subroutine IONBAL, saving computer time (and money). Part of the output from this subroutine can even serve as the input for several of the special programs mentioned above. Input for IONBAL comes from either of two sources, the precipitation chemistry data base or a specially created file. In either case the input needs to be tailored to the research project of choice, since each project involves (perhaps) analyses of different ions and the investigation of different parameters. Various project-specific subroutines prepare or tailor the input upon call from the driver program. It is evident that the IONBAL subroutine is sufficiently versatile to process data from any of the ongoing precipitation chemistry efforts at the ISWS.

IONBAL is a general purpose routine which has as its foremost task to assess the results of the chemical analyses of precipitation samples by determining the degree to which the positive and negative ions in solution are in balance. Fourteen soluble ions can be considered in this computation. All samples with an excessive charge imbalance resulting from this calculation are flagged for reanalysis.

Various other quality assurance checks are also performed including checks that: (1) all input is properly sequenced, (2) all input is legally defined, (3) all essential information is present, etc. Any of these latter checks that prove negative will prompt a pointed error message and will often cause failure of the routine to complete its operation. Results of the ion balance determinations are statistically summarized and are presented in various tabular and graphical displays. Data that can be fully processed by the IONBAL routine are sufficiently free of errors to run in any of the other subroutine programs.

Another oft used subroutine, the site summary program, prepares a listing of data and information for precipitation samples collected at a given site or sampling location. Included in this summary are results of the laboratory chemical analyses, field pH and field conductivity, sample volume and calculated mass depositions, and information to identify the sampling periods. The content of this summary makes it convenient for use as a quick, preliminary look at the data for preliminary interpretation. It can also be readily scanned for inconsistencies and errors of omission that are not searched for in IONBAL. The remaining programs in the subroutine library execute input/output roles in the scheme of data flow directed by the driver program.

The computerized data base system and the library of processing programs have been operationally integrated into an effective scheme for precipitation chemistry data management. These systems continue to evolve as needs arise to manipulate and report the data in new and more effective presentations and as new and different data sets stress an increased generality of the data storage and data process features. Ultimately, the motivation for continued improvement in the data management system stems from the desire to best serve the needs of the data user and the data interpreter.

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CHAPTER 9

ANALYTICAL CHEMISTRY LABORATORY

Mark E. Peden

The Atmospheric Chemistry Laboratory facility which originated under this contract has undergone further expansion during the past fiscal year. One additional laboratory bay has been added which is devoted to sample processing and preliminary chemical measurements. The Dionex Model 12 automated ion chromatograph was received in December, 1979 and methods development has been ongoing since installation in January, 1980. In an effort to most effectively utilize the capabilities of the ion chromatographic technique, modifications in both hardware and software components have been made to achieve the lowest possible detection limits. The flexibility of the ion chromatograph provides an excellent means for identifying any organic acid constituents in precipitation and aerosol samples. Additionally, anions such as flouride and bromide, which are not normally encountered at detectable limits in atmospheric samples but can influence the ionic balance at higher levels, can now be routinely determined. The relationship between sulfate and sulfite species in precipitation can also be delineated by use of ion chromatographic separations. This information is vital in assessing both conversion rates of sulphur compounds in aqueous solutions and also the relative importance of gaseous versus particulate contributions to rainfall acidity.

The Fourth-Environmental Protection Agency (EPA) Precipitation Reference Sample Interlaboratory Comparison was initiated in February, 1980 through the Environmental Monitoring and Support Laboratory (EMSL) in Research Triangle Park, North Carolina. Ampules of synthetic precipitation concentrates were sent to over 30 laboratories, including international facilities participating in the World Meteorological Organization (WMO) Precipitation Chemistry Network. As in the three previous exercises, the atmospheric chemistry laboratory at the Water Survey is participating in the round robin performance testing. Sixteen inorganic parameters including trace metals, are determined in these solutions. Results will be forwarded to the EMSL in June, 1980 for tabulation with the rest of the cooperating laboratories. Past results from performance audits of this type have documented the expertise of the atmospheric chemistry laboratory in accurately determining the trace levels of ions normally encountered in precipitation samples.

The six-week field experiment conducted during July-August 1979 (SCORE-79) incorporated 60 precipitation chemistry samples. Thirty wet-only collection devices were utilized in conjunction with 30 bulk precipitation collectors of similar aerodynamic design. A total of 850 samples were processed in a two-month period which included 400 wet-only samples, 200 bulk, 100 dry deposition, and 150 sequential samples. Chemical analyses are completed for all but the dry deposition samples. Approximately 50% of the chemical data have been machine processed and are ready for interpretation utilizing the vast array of raingage (260) and wind measurement sites (88). One-hundred samples, which encompassed wet, bulk, and sequential collection modes, were analyzed by inductively-coupled argon plasma emission spectrometry for an expanded list of elements which included trace metals. These data will be used in conjunction with aerosol measurements to elucidate the relationship between air and precipitation concentrations of chemical constituents. Refined factor analysis techniques will be utilized to numerically characterize these relationships.

CHAPTER 10

AMBIENT AIR FILTER EXTRACTION PROCEDURES

Janyce Bartlett and Gary J. Stensland

The collection and analysis of precipitation events and aerosol samples is part of an attempt to study the scavenging effects of precipitation. The parameter of major concern is the resultant pH of the precipitation produced from the interaction of these two media. The pH is affected by those constituents that are scavenged and dissolved by the precipitation from the aerosol present in the atmosphere. The major constituents involved in determining this parameter include the following ions: SO_4, NO_3, Cl, NH_4, Ca, Mg, Na, and K. Analysis of these ions in both the precipitation and air samples will allow for a better understanding of the relationship between the two chemical reservoirs with respect to the precipitation pH. This chapter will describe considerations in selecting an extraction procedure for the ambient aerosol filters. The rationale for using both the original technique and a new method will be discussed. The new procedure will be used for future analysis of the Bondville field station aerosol samples.

A major problem in determining the ions of an ambient aerosol sample is developing an analytical method that will best simulate the dissolution of the particles by precipitation. Our initial approach was to develop a method that would extract the "soluble" ions from the aerosol filters. We defined "soluble" as being "those ions that would dissolve in deionized water at room temperature." Based on this definition, we developed an extraction method described in a previous report (Stensland, 1979). It involved agitating the filter in 25 ml of deionized water at room temperature for twenty minutes. This method was used on the June 1977 to August 1978 ambient air filters, collected daily at Willard Airport, 10 kilometers south of Champaign. These data are presented in the previous chapter. From this data set, a group of 57 filters was extracted twice to see if any significant amounts of the above mentioned ions were remaining on the filters after the first extraction. The results produced detection limit levels in the second extraction solution for all the ions except Ca and Mg. It is generally known that the compounds containing these two ions are not as readily soluble as those consisting of SO_4, NO_3, NH_4, Na and K. However, the concentrations in the second extraction for these two ions never amounted to more than ten percent of the total concentration. This amount was considered insignificant and therefore no attempt was made to account for the increase by either adjusting the data or modifying the extraction procedure.

As our work with ambient aerosols continued, we became increasingly interested in the soil particle component of these aerosols. Research on another project indicated that the Ca and Mg levels obtained from extracting bulk soil samples was drastically influenced by the pH of the solutions used to extract the ions (Stensland, 1979). Stensland's results showed a four fold increase in Ca and Mg when extraction solutions were changed from deionized water (pH $\sim$ 5.8) to a nitric acid solution with a pH = 3. It was assumed that the soil "cation exchange capacity" (CEC) was the parameter responsible for the increase in Ca and Mg at lower pH extraction solutions. CEC is defined as the ability of organic and mineral soil particles to adsorb cations onto their surfaces. The cations that play a major role in this process include Ca, Mg, Na, K, and H. The amount of "exchangable" ions available in a soil varies from one soil type to another. Typically, the soils in the area of this field study have high CEC values with Ca usually accounting for one- to two-thirds of this quantity. If a considerable amount of the aerosol sample was made up of soil particles this CEC parameter could be of major importance on precipitation pH. The hydronium ions could be removed from the solution by the exchange process, thus increasing the pH value and the concentration of ions such as Ca, Mg, Na, and K.

The above results suggested that the original extraction method for the ambient air filters was not accounting for the possible influence of the soil particle CEC since the extraction solution was deionized water. It was proposed to develop a new extraction technique to account for the "exchangable" ions as well as the soluble ions. A simple calculation was done to estimate the quantity of hydronium ion needed to exchange with all the Ca from an aerosol sample. The following hypothetical extreme case was considered:

I. Assumptions

   A. Filter aerosol mass = 2 mg (This would be a very heavy loading on our 37 mm diameter Nuclepore filters).

   B. All aerosol mass is soil particles.

   C. Soil "exchangable Ca" = 200µeq/100g (soil).

   D. All the Ca on the soil particles goes into the extraction solution and is being replaced by hydronium ions.

II. Calculations

   A. Amount (µeq) of exchangable Ca in 2 mg of soil and on the aerosol filter is:

      20meq/100g = 0.2µeq/mg = .4µeq/2mg

   B. Amount (µeq) of exchangable Ca in 25 ml of extraction solution:

      .4µeq/25 ml = 16µeq/l

   C. List of pH values and corresponding amount (µeq/ℓ) of hydronium ion:

pH	µeq/ℓ
4.8	16µeq/ℓ
4.0	100
4.5	316
3.0	1000

From the above calculations one can see that a solution with pH=4 would have an ample supply of hydronium ions to exchange on the soil particles. However, there is another factor to consider. The term "exchange" implies a reversible reaction. The equilibrium of the exchange process may be quite different at a pH=4 versus pH=3. By utilizing Le Chatelier principle the reaction in eq. 1 can be driven to the right as to be considered complete and "irreversible" (Skoog and West, 1963). This is done by having an unlimited reservoir of hydronium ions available for the exchange process.

$$\underset{\text{(adsorb on soil)}}{Ca^{+2}} + \underset{\text{(excess in extraction solution)}}{H^{+}} \rightleftarrows \underset{\text{Soil}}{H^{+}} + \underset{\text{(extraction solution)}}{Ca^{+2}} \qquad (1)$$

To account for this factor it was concluded that an extraction solution of pH=3 should remove all of the ions, "exchangable" and "soluble" that could effect the precipitation pH. At this point it is important to note that "soluble" has been redefined. It now means "those ions that would dissolve in a pH=3 solution at room temperature." For most of the ions considered here this should have little effect since their compounds completely dissociate in deionized water at room temperature. However, this is not the case for Ca^{+2} and Mg^{+2}. Their compounds are at equilibrium with the dissociated ions. This equilibrium can be effected by the pH of the solution. Thus, lowering the pH would increase the concentrations of these two ions. It is hypothesized that a pH=3 extraction solution will better simulate the interaction of precipitation and the aerosol with respect to obtaining the "soluble" ions scavenged from the aerosol by precipitation. This rationale is based on the fact that even precipitation pH values have been as low as 3 (Stensland, 1979) and weekly samples have reached 3.5 (NADP, 1978).

An experiment was performed to see if any observable change in the ion concentrations occurred when ambient aerosol filters were extracted in pH=3 solutions instead of deionized water. The extraction method included agitating the aerosol filters in 25 ml of deionized water for two days, filtering, then reextracting the remaining particulates in a pH=3 HCl solution for two days and filtering again. The results are shown in Table 1 giving the percent increase in ion concentration (ppm) due to the pH=3 solution, and the aerosol mass for that particular filter. Only Ca and Mg were the ions considered. The ambient aerosols were collected at our Bondville field site. Only two samples showed a significant increase in Ca, with none in Mg. But these two samples had the highest aerosol mass from the group of filters extracted. Furthermore, the field log records indicate farming activity on both of those sampling days.

Similar work in a different project (Miller, 1979) analyzed a set of 30 filters collected during the fall of 1978 harvest season. Forty percent of their aerosol filters showed a significant increase for both Ca and Mg in the second extraction of pH=3 solution. (Based upon the above calculations and test experiment.)

It was concluded that the extraction method (for our future aerosol samples) be changed from DI to pH=3. The time of agitation was increased from

Table 1. Percent increase in Ca and Mg concentrations due to second extraction in pH=3 solution.

Filter Sample Number	Percent Increase Ca%	Mg%	Aerosol Mass (mg)
235	1.5	5.8	1.03
248	0	.2	.50
250	5.0	1.4	.63
284	0	0	.44
325	0	.5	.26
338	0	1.4	.11
018	0	1.1	.91
045	0	0	.71
069	4.0	1.0	.15
106	4.0	3.0	.34
139	25.0	5.6	2.13
163	11.0	4.0	1.15
177	3.5	2.0	.81
190	0	0	.59
217	5.7	0	.54

20 minutes to two days to more accurately simulate the rain sample exposure to the particles since the samples usually are not filtered before 24 to 48 hours after the rain event.

When the ambient aerosol filters are extracted, the resulting solution concentrations are occasionally low for some ions, and become uncomfortably close to the system blank values. Therefore, as the new extraction procedure was being formulated, checks were necessary to be sure that the system blank values were not going to become higher than those associated with the previous extraction procedure.

The blank levels for filtration blanks (25 ml of extraction solution filtered across the Millipore HA filter) and Nuclepore filter extracted in deionized water (DI) and pH=3 solution are shown in Table 2.

Table 2. Comparison of DI extraction solution versus pH=3 extraction solution for filtration blanks and Nuclepore filter blanks.

		Median Ion Concentration (ppm)				
Blank	Extraction Solution	Ca	Mg	Na	K	Number of Samples
Filtration	DI	.04	.010	.027	.009	21
Blank	pH=3	.02	.003	.030	.009	6
Nuclepore*	DI	.02	.005	.036	.011	21
Filter Blank	pH=3	.02	.003	.046	.009	6

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*Nuclepore polycarbonate membrane filter; diameter .37 mm pore size = .8µm.

It was found that there was no increase in the four ion concentrations for the filtration blanks when pH=3 solution was used instead of DI. Furthermore, the Nuclepore filter blanks did not increase when extracted in pH=3 solution versus DI. Thus, a single extraction with a pH=3 solution using a Millipore HA filter in the filtration process would cause no data loss due to contamination.

In summary, the ambient aerosol filter extraction method has been modified in order to account for the possible effect that "exchangable" ions from soil particles could have on precipitation pH and to better simulate the "soluble" ions scavenged by precipitation.

The previous method only allowed for the extraction of readily "soluble" ions (those dissolving in deionized water); thus excluding the soil component of the aerosol common in agricultural areas and potential ions available to acidic precipitation.

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