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STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

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by

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## STUDY OF ATMOSPHERIC POLLUTION SCAVENGING

## ABSTRACT

The continued study of historical precipitation chemistry, air quality, and emissions data shows that the nitrate concentrations in precipitation have increased over the past 20 years with little change in sulfate concentrations. An analysis of aerosol concentrations at MAP3S precipitation collection sites show consistently higher elemental concentrations at urban Champaign, Illinois than sites at Whiteface Mountain, New York and rural Champaign. Scavenging ratios at Whiteface exceeded those obtained previously at St. Louis, Missouri possibly due to mid-tropospheric long-range transport and differing synoptic situations. Factor analysis of 6 storms during METROMEX show that different deposition patterns were found for the soluble and insoluble concentrations of the same element. This suggests different scavenging processes may be active for these fractions. Using METROMEX data, no correlation was found between pollutant source strength and the urban-related precipitation anomaly. Four different Nuclepore air filter setups were used to compare air concentrations of sulfate, nitrate and ammonium. The sulfate comparison was good, but the large variability for nitrate and ammonium raise serious questions on the credibility of measurements using Nuclepore as the collection medium.

The details of a case study of wet deposition from SCORE-78 are presented and show the pollutant concentrations are more variable than the rainfall. A brief description of the progress on the SCORE-79 project is presented. The progress on acid rainfall studies show that the high pH values in the Midwest in the mid-1950's was due in part to elevated concentrations of calcium and magnesium. A variety of model calculations are presented to show the effects of adjusting past data to currently observed values. A recent expansion of the analytical laboratory facilities is described and recent results of continuing research on ionic stability of precipitation samples are given.

## CHAPTER 1

### A COMPARISON OF SULFATE AND NITRATE IN PRECIPITATION IN 1955 AND 1977 TO EMISSIONS AND AIR QUALITY TRENDS

Gary J. Stensland

#### INTRODUCTION

The atmospheric cycles of sulfur and nitrogen include the following components: (a) emission of the compounds from the earth's surface into the atmosphere; (b) transport and transformation of these compounds in the atmosphere; and (c) wet and dry removal of the compounds from the atmosphere. This paper will examine time trends for data from each of these three components but will emphasize the analysis of precipitation chemistry data.

Polluted air, resulting from source emissions should, on the average, produce polluted precipitation. Furthermore, temporal changes in the emissions of sulfur and nitrogen compounds should produce corresponding changes in the concentrations in the air and in the precipitation. The relationship between emissions levels and air and precipitation quality is a physical fact if the time and space boundaries are defined appropriately. For example, if the global emissions of sulfur increase, the average air quality for sulfur for the globe will decrease. This paper will examine annual average values for the northeastern United States for the mid-1950's versus the late 1970's. The appropriateness of this choice of time and space scales will be commented on at various places in this paper.

#### DISCUSSION OF DATA

The major thrust of this paper is to present and discuss the sulfur and nitrogen data for precipitation. These results are then compared to information in the literature on air pollution emissions and air quality.

##### Precipitation Quality Data

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 and still is 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, has recently begun operation (NADP, 1979). This program, the National Atmospheric Deposition Project (NADP), which has both monitoring and research objectives, officially began operation on October 1, 1978 and currently includes 25 collection sites distributed across the United States. Many state and federal organizations are making contributions towards developing the NADP, but the primary contribution currently comes from forest and agricultural experiment stations which maintain sites and pay for the chemical analysis of the samples.

Past precipitation quality networks in the United States have often been characterized by limitations of their spatial or temporal scale or by limitations in their collection and analysis procedures. Some of the networks were research projects which probably met their objectives even though they were characterized by some of the limitations just enumerated.

The analysis presented here was undertaken because precipitation chemistry data have recently become available for the 1977-78 period and therefore can be compared with existing data from the 1950's. The various data sets are summarized in Figure 1 and Table 1. The MAP3S network (Battelle Pacific Northwest Laboratories, 1977), is still in operation and now consists of eight sites in the Northeast. Beginning in September 1977, the samples from this project were analyzed for all the major cations and anions as described by Dana *et al.* (1978). From Table 1 it is noted that there was about one year of data for each of the three MAP3S sites used for this analysis (IT, SC, and CH). The Illinois State Water Survey (ISWS) began a precipitation chemistry collection program near Champaign, Illinois in May 1977, and this site (CM) provided data for this paper (Stensland, 1979). In addition, an ISWS study by Larson and Hettick (1956) at the same site from October 1953, to August 1954, provided historical data for this analysis. The Junge network was in operation from July 1955 to June 1956, and provided the remainder of the historical data (Junge and Gustafson, 1956; Junge, 1963). The Junge network consisted of 62 sites distributed across the continental United States. Data from eight of the sites will be used in this paper. The dashed lines in Figure 1 enclose those sites considered most important for the present analysis while the solid lines indicate the additional sites which provide comparative data.

The type of precipitation chemistry data needed for this study were ion concentrations for wet-only samples. That is, evaporation losses and dry deposition effects had to be absent. There are data available from some networks where automatic wet-only collectors were used but where the protective cover did not make a tight seal with the sample container. Evaporation and contamination during non-rain periods probably occurred and therefore such data were not used.

For the MAP3S sites, an automatic wet-only sampler is used to collect event samples, where event refers basically to a daily sample. The collecting funnel is thoroughly rinsed after each sample is removed. The MAP3S sites are all located at least several kilometers away from the nearest urban areas. The 1977 ISWS samples were collected in a manner very similar to the MAP3S samples, with a HASL collector being used. The 1954 ISWS samples consisted of manual collections of precipitation events using, a 1.2 meter diameter stainless steel funnel which was uncovered and well rinsed at the beginning of the events. Finally, the

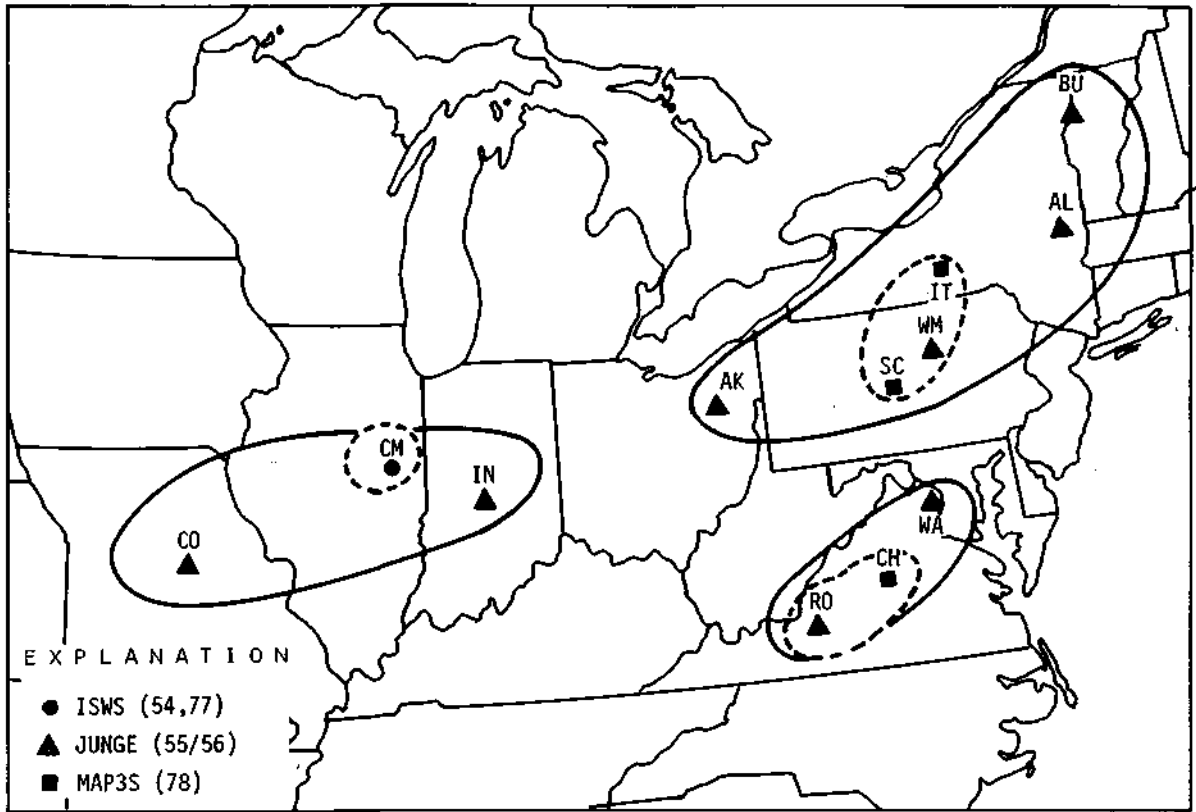


Figure 1. Regional groupings of precipitation sampling sites used to compare sulfate and nitrate in precipitation.

Table 1. A listing of the collection sites, the population of the nearby urban areas, and data period being used.

<u>Abbreviation</u>	<u>Site</u>	<u>1970 Population</u>	<u>Data Period</u>
AK	Akron, OH	298,000	7/55-6/56
AL	Albany, NY	127,000	7/55-6/56
BU	Burlington, VT	36,300	7/55-6/56
CH	Charlottesville, VA	36,000	9/18/77-7/31/78
CM	Champaign-Urbana, IL	83,000	10/53-8/54, 5/77-2/78
CO	Columbia, MO	44,000	7/55-6/56
IN	Indianapolis, IN	530,000	7/55-6/56
IT	Ithaca, NY	31,000	9/21/77-9/ 4/78
RO	Roanoke, VA	100,500	7/55-6/56
SC	State College, PA	27,800	9/24/77-9/15/78
WA	Washington, DC	810,000	7/55-6/56
WM	Williamsport, PA	41,000	7/55-6/56



1955-56 Junge samples were collected with a plexiglas funnel and polyethylene bottle which were exposed only during precipitation events. The event samples were sent to the analytical laboratory and composited to provide one sample per site per month. The samplers were located at Weather Bureau facilities so that personnel would be available to expose the collecting funnels during the precipitation events. Some of the Junge sites were closer to cities and industrial areas than desirable, but the consistent data patterns produced by the study indicated that most of the sites produced data representative of their region.

It is well known that the ion concentrations in rain and snow events are strongly related to the precipitation amounts; when the amount is less than about 5 mm, the concentrations are usually very high. To compensate for this effect many researchers use the sample volume-weighted averages for data interpretation. Another approach, to remove the effects of extreme values, is to report median values. Table 2 displays both the median and the sample volume-weighted averages for the MAP3S sites. The median values are consistently higher for each of the ions.

The sulfate and nitrate concentration data from the projects shown in Figure 1 are presented in Tables 3 and 4. Accurate sample volumes were not available for the 1954 ISWS data. Therefore for all the ISWS data in Tables 3 and 4 (site CM) the median concentrations are given. For the Junge data the monthly compositing procedure produced sample volume-weighted concentrations. The available Junge data for sulfate consisted of an annual weighted average which had been calculated from the monthly values. The Junge nitrate data were available only as quarterly weighted averages. Therefore the Weather Bureau precipitation data for the Junge sites were used to calculate the annual weighted average nitrate data given in Table 4. Since the Junge data and the MAP3S data are to be compared, the MAP3S sample volume-weighted averages are listed in Tables 3 and 4 instead of the median values.

The upper portion of Table 3 gives the sulfate 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 same format is used in Table 4. The basic feature to note in the tables is that the sulfate ratios are near one, while those for nitrate are greater than one. These trends will now be compared to emissions and air quality trends.

#### Emissions Data for Sulfur and Nitrogen Oxides

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 sites in selected portions of the northeastern United States. A study of the geographical distribution of the 1972 emissions data shows that the EPA air quality regions I-VI (basically the eastern United States) contributed 80% of the total nitrogen oxide emissions (NRC, 1973). The same study showed that six states, New York, Pennsylvania, Ohio, Michigan, Indiana, and Illinois, contributed 45% of the total. For sulfur oxides the study indicated that the northeast sector of the United States accounted for about half of the total sulfur oxide emissions.

Table 2. Median concentrations and sample volume weighted average concentrations for the MAP3S samples (mg/ ).

	Sulfate			Nitrate		
	Number of Samples	Median	Weighted Average	Number of Samples	Median	Weighted Average
IT	54	2.88	2.66	55	2.17	1.71
SC	86	2.88	2.54	86	2.26	1.67
VA	51	2.79	2.46	51	1.74	1.54

Table 3. Sulfate concentrations in precipitation (mg/£ as  $\text{SO}_4^-$ ) and ratios of recent values to historical values.

MIDWEST			
1977/78	Ratio	1954	1955/56
CM: 3.79	(1.2)	CM: 3.10	CO: 3.10 IN: 2.67
EAST			
1977/78	Ratio	1955/56	1955/56
IT: 2.66	(0.8)	WM: 3.48	BU: 2.89 AL: 2.29
SC: 2.54	(0.7)	WM: 3.48	AK: 3.26
CH: 2.45	(0.9)	RO: 2.67	WA: 2.67

Table 4. Nitrate concentrations in precipitation (mg/ as  $\text{NO}_3^-$ ) and ratios of recent values to historical values.

MIDWEST			
1977/78	Ratio	1954	1955/56
CM: 1.85	(1.5)	CM: 1.25	CO: .58 IN: .53
EAST			
1977/78	Ratio	1955/56	1955/56
IT: 1.71	(1.3)	WM: 1.31	BU: 1.12 AL: .77
SC: 1.67	(1.3)	WM: 1.31	AK: 1.05
CH: 1.54	(1.8)	RO: .84	WA: .54

It is generally accepted that anthropogenic sources dominate over natural sources for industrialized areas such as the Northeast. Of the various source categories, Cavender *et al.* (1973) state that fossil fuel combustion at stationary sources dominates for the sulfur oxides. In 1970 about 78% of the sulfur oxides were emitted from these sources. Steam electric power plants were the major stationary sources contributing 57% of the sulfur oxide emissions. In total, coal combustion accounted for about 65% of all the sulfur oxide emissions. Cavender *et al.* (1973) reported that gasoline combustion in motor vehicles accounted for 34% of the nitrogen oxides emissions in 1970 while coal, fuel oil, and natural gas combustion in stationary sources accounted for 44% of the total.

The time trend of the estimated emissions is summarized with Table 5. The EPA report (USEPA, 1977) providing the data for the lower half of Table 5 warned that the earlier estimates (upper half of Table 5) had not been calculated in the same way and thus would not be exactly comparable. This explains why, for instance, the two 1970 estimates for sulfur oxides do not agree. The data in these tables are expressed as SO<sub>2</sub> and NO<sub>2</sub>. In Table 6 the data from Table 5 were normalized by making the two 1970 values agree. This normalization procedure is a reasonable and practical approach that allows the 1940 to 1976 time period to be examined. Table 6 shows that the nitrogen oxide emissions increased much more than the sulfur oxide emissions. 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 a factor of 1.3. The relatively small increase in the sulfur oxide emissions is explained by Cook (1971) as due to the fact that natural gas and low sulfur oil and coal have become more heavily used since the mid-1950's. The larger growth rate in the nitrogen oxide emissions is due to the large increase in energy consumption for electric power and transportation. From 1955 to 1970 Cook (1971) showed that the former increased by a factor of 2.6 and the latter by a factor of 1.6.

Some additional emissions data for the 1960's are displayed in Tables 7 and 8. The Table 7 data were obtained from five separate reports. The most recent emissions report includes the best data base and the most accurate calculational procedures and thus produces the most accurate estimates for a given year. To intercompare the various estimates the data were normalized by comparing the most recent year on a given line of Table 7 with the same year on the lowest line where data were available (i.e., the most recent emissions estimate). This produced a scaling factor that was applied to each year on that particular line of Table 7 to produce the normalized values for that line in Table 8.

### Air Quality Trends

Sulfate data were collected in the National Air Surveillance Network on glass fiber filters using high volume air samplers. Altshuller (1976, 1977) has presented a detailed analysis of the sulfate and sulfur dioxide data from 1963 thru 1974. Altshuller's east coast region included sites in the New England States and then southward along the coastline to Washington, D. C. while the Midwest region, east of the Mississippi, extended westward from central Pennsylvania to St. Louis. Therefore the precipitation sites from Ithaca to Roanoke (cf. Fig. 1) fall on the boundary of Altshuller's two regions.

Table 5. Estimated nitrogen oxide and sulfur oxide emissions for the Continental United States (millions of metric tons per year)

	<u>1940</u>	<u>1950</u>	<u>1960</u>	<u>1970</u>			
Nitrogen Oxides <sup>a</sup>	7.2	9.4	12.7	20.6			
Sulfur Oxides <sup>a</sup>	19.5	21.6	21.1	30.8			
	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>
Nitrogen Oxides <sup>b</sup>	20.4	21.3	22.2	22.9	22.6	22.2	23.0
Sulfur Oxides <sup>b</sup>	29.1	27.9	28.8	29.7	28.2	25.7	26.9

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<sup>a</sup>Source: Cavender *et al.* (1973) (p. 4, Table 1)

<sup>b</sup>Source: USEPA (1977) (p. 5-1, Table 5-1)

Table 6. Normalized emissions estimates as calculated from Table 5 (millions of metric tons per year).

	1940	1950	1960	1970
Nitrogen Oxides	7.1	9.3	12.6	20.4
Sulfur Oxides	18.4	20.4	19.9	29.1

	1970	1971	1972	1973	1974	1975	1976
Nitrogen Oxides	20.4	21.3	22.2	22.9	22.6	22.2	23.0
Sulfur Oxides	29.1	27.9	28.8	29.7	28.2	25.7	26.9

Table 7. Estimated sulfur and nitrogen oxide emissions (millions of metric tons per year).

	1940	1950	1960	1963	1966	1967	1968	1969	1970
SO <sub>x</sub> <sup>a</sup>				21.2	25.9				
SO <sub>x</sub> <sup>b</sup>					28.0	28.8	30.1		
SO <sub>x</sub> <sup>c</sup>							28.7	30.3	
SO <sub>x</sub> <sup>d</sup>	19.5	21.6	21.1				28.4	29.4	30.8
SO <sub>x</sub> <sup>e</sup>									29.1
-----									
NO <sub>x</sub> <sup>b</sup>							15.2	17.8	18.7
NO <sub>x</sub> <sup>c</sup>							20.6	21.6	
NO <sub>x</sub> <sup>d</sup>	7.2	9.4	12.7				19.3	20.4	20.6
NO <sub>x</sub> <sup>e</sup>									20.4

<sup>a</sup>Source: US DHEW (1969) (p. 20, Table 2-1, of this 1969 report)

<sup>b</sup>Source: US DHEW (1970) (p. 5, Table 2, of this 1970 report)

<sup>c</sup>Source: CEQ (1971) (p. 212, Table 1, of this 1971 report)

<sup>d</sup>Source: Cavender *et al.* (1973)(p. 4, Table 1, of this 1973 report)

<sup>e</sup>Source: US EPA (1977) (p. 5-1, Table 5-1, of this 1977 report)



For the urban sites Altshuller observed that the sulfur dioxide levels decreased considerably, but that the sulfate decreased by a much smaller amount for the east coast sites and remained level or increased slightly for the Midwest sites, east of the Mississippi.

For the non-urban sites the sulfur dioxide levels were very low and thus no trends were determined. The sulfate concentrations from 1965 to 1972 decreased somewhat for the east coast sites (8.1 to about  $7.7 \mu\text{g}/\text{m}^3$ ), but increased at the midwestern sites, east of the Mississippi, ( $7.3$  to  $10.4 \mu\text{g}/\text{m}^3$ ). Although the sulfate in precipitation was not examined for the same time interval it is interesting to note that the eastern precipitation sites in Tables 3 and 4 showed decreases in time and the midwestern site (CM) showed an increase.

The data in Table 6 and Table 8 suggest that rapid changes in sulfur emissions occurred between 1963 and 1970. Due to the data gap of 1964-1965, however, it is not possible to say if the 1965-1974 air quality data encompass the entire region of rapid sulfur emissions change or just a portion of it.

#### SUMMARY AND CONCLUSIONS

To simplify the discussion, some of the results from the last section are summarized in Table 9. No confidence limits are available for the data in the table so caution should be used in interpreting the results. With respect to precipitation, the sampling periods of about one year are probably too short to provide stable values. However, that is all that is available from the sites for the mid 50's.

For precipitation it does seem clear that the nitrate concentrations have changed more since the mid 1950's than the sulfate concentrations and perhaps the sulfate concentrations have even decreased. These trends are in general agreement with the sulfur oxide and nitrogen oxide emissions data in the second line of Table 9. However, it appears that the trends of concentration in precipitation are not as steep, especially for the nitrogen. If accurate, this analysis indicates that a smaller fraction of the emissions are removed by wet processes in the late 1970's in contrast to the mid 1950's. Previous reports by Likens (1976) and the NRC (1977), using other precipitation data for the eastern United States, have also noted that nitrate concentrations have increased more rapidly than sulfate concentrations.

With respect to air quality, the data in Table 9 are not extremely useful for comparison purposes since the time interval is different from that for the precipitation data. However, the fact that the trends at the east coast sites are different than for the midwestern sites does emphasize that similar spatial scale variations need to be examined for precipitation chemistry, when the data become available. In the same manner, the detailed geographical pattern of the emission sources needs to be considered.

Finally, using data in Tables 3, 4, and 6, it is of interest to note that the S/N ratios for precipitation and for the emissions estimates are about the same. For example, for the SC site in 1977/78 the S/N ratio is 2.2 and for 1976



Table 9. Sulfur and nitrogen ratios (levels for the recent time divided by those for the earlier time).

	<u>Sulfur</u>	<u>Nitrogen</u>
Precipitation Quality	0.8 to 1.2 (1977÷1954)	1.3-1.8 C1977÷1954)
Total Emissions	1.3 (1976÷1955)	2.1 (1976÷1955)
Air Quality	0.9 for east coast sites (1972÷1965) 1.4 for Midwest sites, east of the Mississippi (1972÷1965)	No Data

the S/N emissions ratio is 2.0. This is in marked contrast to S/N ratios measured for ambient aerosol samples. For 73 daily ambient aerosol samples in summer 1977 from the CM site, the S/N ratio was about 5 when Nuclepore filters were used and about 80 when Whatman 41 filters were used (Stensland and Bartlett, 1979). These diverse ambient aerosol ratios mainly stress that sampling problems still exist.

The nitrogen and sulfur emissions are almost entirely gaseous while the precipitation scavenges both gaseous constituents and the secondary products which are gaseous and aerosol. Thus, there is not a straight forward explanation for the fact that the S/N ratios agree quite well for emissions and precipitation.

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## CHAPTER 2

### WEEKLY AEROSOL FILTER MEASUREMENTS AT THREE MAP3S PRECIPITATION CHEMISTRY SITES

Donald F. Gatz

#### INTRODUCTION

Weekly aerosol samples were collected on 0.8  $\mu\text{m}$  pore diameter Nuclepore filters at the Whiteface Mountain, New York, and Charlottesville, Virginia, MAP3S sites between May 1977 and May 1978. A similar set of filters was collected at two different sites in and near Champaign, Illinois, between June 1975 and May 1978.

Weekly aerosol sampling at all sites was halted in May, 1978, to permit evaluation of possible deficiencies in the sampling method. Preliminary evaluations suggest that the data already collected are useful for most purposes, but that total concentrations of atmospheric elements (including those on very large particles) would be better measured (especially in windy conditions) by a more nearly isokinetic sampler.

This report presents and compares trace element concentrations, abundances, and enrichments at the Whiteface and Champaign sites. In addition, scavenging ratios for  $\text{SO}_4^-$ , K, and Ca are given for the Whiteface site. Various sampling difficulties and the loss of samples in a fire limited the Charlottesville data set to only 7 samples, not enough for a valid comparison.

#### METHODS

Pre-weighed 37 mm Nuclepore filters with 0.8  $\mu\text{m}$  diameter pores were exposed in plastic holders face down under 25 cm diameter polyethylene rain shields, about 1 m above grass or a flat roof. At the Charlottesville (C) and Whiteface (WF) sites, the collections were made over grass. The Champaign collections between June 1975 and June 1977 were made in a ventilated instrument shelter on the roof of the Water Survey Headquarters in Champaign. This is the Champaign urban site (CU). From June 1977 to May 1978 the Champaign samples were collected over grass at the University of Illinois Willard Airport, which we designate the Champaign rural site (CR), about 8 km south of Champaign.

Elemental analysis of the filters was performed at Crocker Nuclear Laboratory, University of California - Davis, using ion-excited X-ray fluorescence (Flocchini *et al.*, 1972; 1976). Further details of the sampling and analysis procedures were given by Gatz (1978).

Beside being expressed in units of concentration in air, the elemental measurements are given in terms of their abundance and enrichment. Abundance refers to the mass of an element per unit mass of airborne particulate matter (expressed in percent). The enrichment factor, EF, of an element x relative to soil composition is given (Rahn, 1971; Zoller et al., 1974) by

$$EF = (C_x/C_{Si})_{\text{aerosol}} / (C_x/C_{Si})_{\text{soil}}$$

where the C's are concentrations of element x and Si in aerosol material and in soils. The soil compositions used were those of Vinogradov (1959). Enrichment values near 1.0 indicate soil sources, while values of 10 or more signal clear non-soil sources.

Results are also given for scavenging ratios, W, (Gatz, 1976), which are defined by

$$W = \frac{k\rho}{X}$$

where k is the concentration in rain ( $\mu\text{g/g}$ ), X is concentration in air ( $\mu\text{g/m}^3$ ), and  $\rho$  is the density of air, taken as  $1200 \text{ g/m}^3$ .

## RESULTS

Mean concentrations, abundances, and enrichment factors are given in Tables 1 to 3. Results for Charlottesville are given for completeness, but are not discussed, because of the small number of samples. Separate results are given for the two Champaign sampling locations, because they represent two different environments, urban and rural.

Results of the scavenging ratio calculations for the Whiteface Mountain site are given in Table 4. The aerosol data were broken into 2 separate periods, fall 1977 and spring 1978, by the loss of the winter filters in a fire at the Crocker Nuclear Laboratory, University of California - Davis. Thus, results are summarized for each period and for both combined. Results are given for  $\text{SO}_4^-$  ion, Ca, and K, the only common species in the precipitation and aerosol analyses.

## DISCUSSION

### Aerosol Composition Measurements

Let us consider one element at a time, comparing mean concentrations, abundances, and enrichments among the WF, CU, and CR sites. This analysis should characterize the occurrence of the elements, and their general kinds of sources, at the several sampling locations.

Table 1. Mean elemental concentrations (ng m<sup>-3</sup>) measured in weekly samples.

	Location			
	Whiteface Mountain	Champaign urban	Champaign rural	Charlottesville
No. of samples	30	78	28	7
Al	306	760	598	1180
Si	592	3710	2740	2140
S	1500	3900	2620	4100
K	84	491	254	229
Ca	152	3880	1670	348
Ti	22	171	56	104
Mn	23	87	46	29
Fe	121	994	501	430
Zn	15	112	49	23
Br	20	207	63	28
Pb	77	1120	336	241
TSP*	13600	47100	31200	39100

\*Total suspended particulate matter.

Table 2. Mean elemental abundances (percent) measured in weekly aerosol samples.

	Location			
	Whiteface Mountain	Champaign urban	Champaign rural	Charlottesville
No. of Samples	30	78	28	7
Al	2.29	1.71	1.84	3.09
Si	5.00	7.80	9.56	5.50
S	11.87	8.40	8.75	10.50
K	0.72	1.05	0.88	0.61
Ca	1.25	8.20	5.61	0.90
Ti	0.19	0.39	0.18	0.26
Mn	0.24	0.19	0.16	0.077
Fe	1.02	2.15	1.70	1.09
Zn	0.14	0.26	0.17	0.060
Br	0.19	0.47	0.22	0.072
Pb	0.81	2.55	1.05	0.64

Table 3. Mean enrichment factors, relative to soil composition given by Vinogradov (1959), from weekly aerosol samples.

	Location			
	Whiteface Mountain	Champaign urban	Champaign rural	Charlottesville
No. of Samples	30	78	28	7
Al	2.1	0.94	1.0	2.7
Si	(1.0)	(1.0)	(1.0)	(1.0)
S	1160	530	430	880
K	3.9	3.6	2.5	2.9
Ca	7.1	28.1	15.9	4.0
Ti	3.1	3.9	1.6	3.6
Mn	22.6	10.3	7.4	5.6
Fe	2.0	2.7	1.8	1.8
Zn	250	270	150	75
Br	3000	4700	1800	970
Pb	6300	13000	4900	4500



Table 4. Scavenging ratios for the Whiteface Mountain site, using weekly aerosol samples and daily precipitation samples composited to weekly.

	August-October, 1977			March-May, 1978			Both periods combined				
	n*	Arithmetic mean	Volume weighted mean	n*	Arithmetic mean	Volume weighted mean	n*	Arithmetic mean	Volume weighted mean		
SO <sub>4</sub> <sup>=</sup>	8	1990	2110	SO <sub>4</sub> <sup>=</sup>	8	1210	1250	SO <sub>4</sub> <sup>=</sup>	16	1600	1760
Ca	7	910	690	Ca	8	1990	2054	Ca	15	1480	1300
K	8	1210	560	K	8	1250	1320	K	16	1230	870

\*n = number of weekly sampling periods

The mean concentration of Al (Table 1) was greatest at CU, even though concentrations were less than the detection limit in 42% of the samples. The concentration was lowest at WF, about 41% of the CU value. However, the Al fraction of the total aerosol (Table 2) was greatest, 2.29%, at WF. The Al enrichments were all near 1.0, indicating a predominantly soil or crustal source. The larger concentration at the CU site, relative to CR, suggests that urban activities such as construction and transportation cause the suspension of soil materials from urban surfaces. A similar enhancement of soil element concentration in urban areas was found at St. Louis (Gatz, 1977a).

Si concentrations were also greatest at CU. They were least at WF, where the mean value was only 15% of that at CU. Both Champaign sites, but especially CR, had larger Si abundances than the WF value. The CR site, with an abundance of 9.56%, exceeded the WF value of 5.00% by a factor of nearly 2. This difference may reflect some runway construction activities at the airport during the sampling there, or it could be caused by a variation in abundance with particle size. Both Champaign sites would be expected to sample a greater fraction of large particles from nearby sources than the remote forested WF site.

Concentrations of S were also highest at CU and lowest at WF. Table 2 shows that S is either the largest or second largest fraction of the total mass of those elements measured at the three sites. Nearly all of the S is expected to be in the form of  $\text{SO}_4^-$  ion, the abundance of which is three times the S abundance. Thus, from Table 2 we see that  $\text{SO}_4^-$  ion accounts for 25% to 35% of the mean total mass at the three sites. The WF site, although remote, had the highest S abundance, at 11.87%, a value which corresponds to a  $\text{SO}_4^-$  abundance of about 35% of the total aerosol mass. This is a clear illustration of the effect of long distance transport on aerosol composition in the northeastern United States. The enrichment values between 400 and 1200 (Table 3) show that the S source is very definitely not the soil.

The CU site also had the highest mean K concentration,  $491 \text{ ng m}^{-3}$ , which was twice that of CR, and almost six times that at WF. K accounted for about 1% of the total aerosol mass at all three sites, but the highest value occurred at CU. The enrichments ranged from 2.5 to 3.9 (Table 3), a hint of a possible non-soil contribution.

Mean Ca concentrations (Table 1) were once again highest at CU, at  $3880 \text{ ug m}^{-3}$ , some 25 times the WF value and more than double the CR value. The three sites rank in the same order when comparing abundances (Table 2), although the differences are less. Ca was the second largest contribution, at 8.20%, to the total mass at CU. The enrichment figures show non-soil Ca at all three sites. The two highest values occurred at CU and CR. The CR enrichment may result from a combination of limestone gravel road dust and  $\text{CaCO}_3$  from agricultural field liming. The even higher value at CU may reflect these rural sources in addition to urban limestone dust and abraded cement road materials.

For Ti, concentrations were highest, again, at CU and lowest at WF. The Ti abundance was also highest at CU, with CR and WF about equal. The Ti enrichment was greatest at CU, which is consistent with an earlier finding (Gatz, 1977b) that some of the CU samples were contaminated by

Ti and Zn from the white paint on the weather shelter in which the samples were collected. The Ti enrichment at WF is also high enough to suggest a possible pollutant component.

Mn concentrations were also greatest at CU; abundances were rather uniform, however, at about 0.2%. Enrichments suggest pollutant contributions at all three sites; the largest enrichment occurred at WF, which is consistent with other results suggesting a long range pollutant transport effect.

Fe concentrations were again highest at CU and lowest at WF, with the high/low ratio about 8. Abundances ranged from about 1% to about 2%, with Cu again highest, WF lowest. Enrichments suggest that Fe is primarily soil derived, with a possible pollutant contribution in the urban area.

Zn concentrations maintained the familiar pattern with CU highest, WF lowest. Abundances ranged narrowly from 0.14 to 0.26, and enrichments show major non-soil contributions. A portion of the CU Zn is contamination from paint, however.

Br and Pb may be discussed together, since they have the same major source, namely auto exhaust. Both had their highest concentrations at CU and lowest at WF. The same is true for abundances, with Br values ranging from about 0.2-0.5% and Pb values from 0.8-2.6%. Enrichments show major non-soil sources at all three sites, but highest values at CU, with the heaviest local traffic. The high enrichments at WF are again consistent with a considerable contribution to local aerosol from long distance transport.

#### Scavenging Ratio (W) Measurements

The results for  $\text{SO}_4^-$  are based on the assumption that S in airborne particulate matter is entirely  $\text{SO}_4^-$  ion. Implicit in the scavenging ratio calculation is the further assumption that  $\text{SO}_4^-$  in precipitation was collected only by scavenging of sulfate aerosol, with no contribution from  $\text{SO}_2$  gas. Since the dominant mode of scavenging leading to  $\text{SO}_4^-$  in precipitation has not been clearly established, these scavenging ratios should be viewed as provisional.

The W results for the fall and spring seasons, while showing some striking differences, cannot be given great weight because of the small number of samples. However, the results given in Table 4 show maximum W values for  $\text{SO}_4^-$  in the fall, and for Ca and K in the spring. The arithmetic and volume-weighted means are in good agreement in the spring, but discrepancies appear for Ca and K in the fall. Because of the small sample size, no particular importance is attached to this finding.

The combined data sets show that  $\text{SO}_4^-$  had the highest W values, followed by Ca and K. The rank was the same for both the arithmetic and the volume-weighted means.

Volume-weighted mean W values for Ca and K at St. Louis were 350 and 550, respectively (Gatz, 1977c); the WF values are higher by factors of 3.7 and 1.6,

respectively. If the particle size distributions for these elements yield smaller mass median diameters (MMD), as would be expected in a remote forested site, these results are counter to the relationship between W and MMD observed at St. Louis. Those results showed W increasing with MMD. The W values found for  $\text{SO}_4$  at WF are much higher than would have been predicted from the St. Louis results, since  $\text{SO}_4$  is generally acknowledged to reside primarily on submicrometer particles.

Possible causes for this discrepancy are 1) a potential difference in the vertical distribution of the airborne materials, and 2) probable differences in the type of precipitation, at the two locations. At St. Louis the measurements were made in summer, with predominantly convective precipitation. Under such conditions, the vertical distribution of aerosols is generally quite uniform, even though strong sources at or near the surface may be present. At WF, where long-distance transport is important, the maximum aerosol concentrations probably occur aloft, especially since surface sources are absent or weak. Furthermore, fall and spring precipitation can generally be expected to be non-convective, which also lessens the chance of strong vertical mixing. These concepts are consistent with the finding that cloud water collected on the WF summit frequently contains very high concentrations of  $\text{SO}_4$  and other pollutants, while surface elemental concentrations, as shown in Table 1, are extremely low.

#### CONCLUSIONS

Elemental concentrations in air were consistently higher at the Champaign urban site than at the Champaign rural site or at Whiteface Mountain. Champaign urban to rural ratios of mean concentrations ranged from 1.3 to about 3, while Champaign urban to Whiteface ratios ranged from 2.5 to 25.

Enrichments relative to soil at the three sites generally agreed that S, Zn, Br, and Pb have almost exclusively non-soil sources. Mn and Ca also have significant non-soil sources. K and Ti may have some non-soil sources.

Differences between Champaign urban and rural concentrations of soil elements may be caused by suspension of urban soils by urban activities.

The Whiteface measurements confirm that pollutants can reach remote areas of the northeastern United States by atmospheric transport from distant sources.

Scavenging ratios at Whiteface exceeded similar ratios measured at St. Louis. Differences in vertical distribution of aerosols, brought about by long range transport aloft and differing meteorological situations at St. Louis and Whiteface are possible causes.

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## CHAPTER 3

### FACTOR ANALYSIS OF WET DEPOSITION DATA FROM SINGLE STORMS IN THE METROMEX CHEMISTRY NETWORK

Donald F. Gatz

#### INTRODUCTION

During summers between 1972 and 1975, approximately 90 sets of daily precipitation samples were collected from networks of 80-85 collectors near St. Louis. In 13 of these daily data sets, depositions of both soluble and insoluble portions of 7-10 elements or ions were measured. The species measured include Li, Na, Mg, K, Ca, Fe, Zn, Cd, In, Pb, and  $\text{SO}_4^-$  ion. Not all species were measured in any given data set, nor were both soluble and insoluble portions of the same element always measured.

The major sources of the materials measured in the rain include both natural ones (soil aerosols) and anthropogenic ones (industrial emissions). These sources include some widely distributed ones (soil, auto exhaust), some point sources (incinerators, steel plants), and some that may be a combination of local and distant sources (power plants, industry).

An analysis of the spatial distribution of the various soluble and insoluble components and a comparison between components and rainfall should yield insights into the processes by which these various materials are deposited by rain.

The purpose of this report is to show that factor analysis is a convenient analytical tool for such comparisons.

#### PROCEDURE

The methods used to collect samples, analyze them, and process the data have been given in detail earlier (Gatz *et al.*, 1978) and are outlined here only briefly. The methods used in factor analysis have also been published (Gatz, 1978) and only the main points are covered here.

Rain samples were collected in two different sampling networks in METROMEX. Both are shown in Fig. 1. The lower rectangular network of 80 sites was used between 1972 and 1974, and the upper network of 85 sites was operated in 1975. Rain was collected in pre-cleaned open wide-mouth bottles mounted on top of metal fence posts. Samples were ordinarily changed at daily intervals.

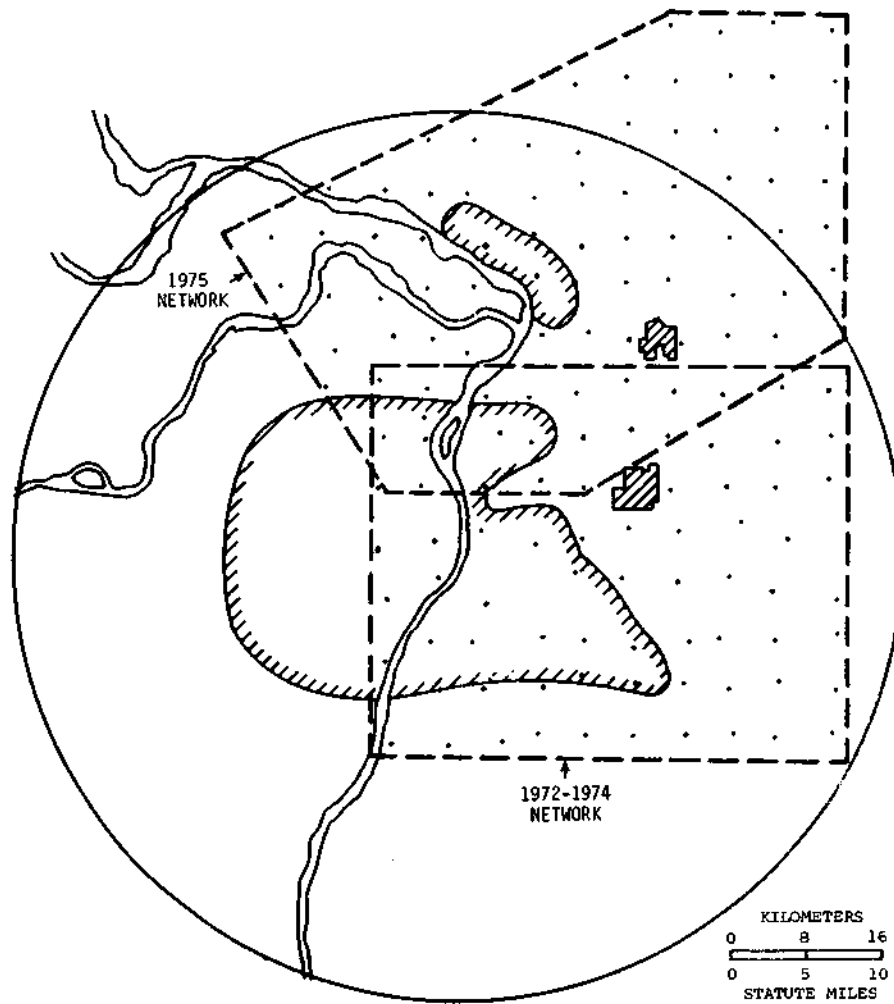


Figure 1. Precipitation chemistry sampling networks, METROMEX, 1972-1975.

In the laboratory, sample bottles were weighed with and without the water sample to determine sample mass and volume. The samples were measured for pH and conductivity, and then filtered through leached 0.45  $\mu\text{m}$  pore diameter Millipore type HA filters to remove insoluble particulate matter. The filtrate was acidified to pH 2 and stored in polyethylene bottles. Filters were dried, folded, and stored in plastic vials.

Filtrate samples were analyzed directly using standard flame or flameless atomic absorption spectrophotometry. Filters were dissolved in strong acids, and analyzed using the same methods.

The raw analytical data were computer-corrected for blanks, dilutions, and dry deposition, and the data were edited to remove obvious outliers caused by contamination. Analytical measurements were made in concentration units ( $\text{mass cm}^{-3}$ ) but concentrations were multiplied by sample volume and divided by collector area to obtain deposition units ( $\text{mass cm}^{-2}$ ), which were used in subsequent factor analyses.

Factor analysis is a multivariate statistical technique useful in showing relationships among multiple variables measured in a series of samples. It may be applied to any data set in the form of a matrix where each column is a measured variable and each row a separate object being measured. Other matrix arrangements are also permissible.

Factor analysis has been discussed in detail by Harman (1967) and Rummel (1970). It has recently been applied to environmental problems by Hopke et al. (1976), Gatz (1978), and others.

The data analyzed here were arranged with elemental or ion depositions as columns and sampling sites as rows. Each data set was collected from a single daily storm event. With this arrangement of the data, relationships between variables (elements or ions) appear in the loadings table, which shows how the variables group into factors. The first factor is that linear combination of original variables that explains more of the variance than any other possible combination. The second factor explains more of the remaining variance than any other possible combination, and is independent of the first; that is, the correlation coefficient between factors is zero. The total number of factors computed is equal to the number of variables, but ordinarily the first few explain most of the variance and only these are kept for rotation to a final solution.

The factor scores table is the other important result of a factor analysis. The factor scores appear in a table with factors as columns and sampling sites as rows. For each factor the scores have mean 0, standard deviation 1. For these data, they show the spatial distribution of the factors. For example, the factor scores for a given factor plotted on a network map reproduce very closely the deposition pattern of any element with a high loading on that factor. Examples of both loadings and factor scores for a number of individual storm data sets are given in the next section.



## RESULTS AND DISCUSSION

### Comparison of Factors and Element Depositions

For multielement deposition data from a single day's rain samples from a network of collectors, factor analysis is a convenient way of discovering a) which elements have similar deposition patterns (from the loadings table), and b) what those patterns are (from the factor scores table). Some of this information could be obtained by plotting and analyzing the deposition pattern of each element, and then visually comparing them. Factor analysis does the same job more quickly, because it eliminates the need to plot and analyze each deposition pattern. Furthermore, it gives a quantitative value (loading) that expresses how well each variable matches the factor pattern. Loadings are correlation coefficients between variables and factors. In addition, factor analysis allows one to see the main deposition patterns by plotting the factor scores for each one only once.

These points are illustrated in Table 1 and in Figs. 2-4, which compare the results of a factor analysis and the original deposition data for samples collected from a rainstorm on 13 August 1975. The loadings are given in Table 1, in which values less than 0.50 have generally been omitted for clarity. The table shows that three factors accounted for 62.6% of the total variance of the data. Factor one alone accounted for 35.0% of the variance explained, and had high loadings for the soluble portions of Li, Ca, K, and Mg. Of these, Li had the best fit to factor 1, with a correlation coefficient (loading) of 0.93. Soluble Ca, K, and Mg had successively less correlation with the factor.

The highest loadings on factor 2 were for the insoluble portions of three elements, K, Fe, and Li. As a group, these three variables are not as well correlated with factor 2 as were the four on factor 1, since the loadings are generally smaller.

The three variables with the highest loadings on factor 3 were soluble and insoluble Zn, and rainfall. The 0.49 loading for insoluble Zn, although less than 0.50, was included (in parentheses) because it was the highest loading for insoluble Zn on any of the three factors.

Figures 2, 3, and 4 compare the factor scores patterns of factors 1, 2, and 3, respectively with the deposition patterns of variables having the highest loadings on each. It is quite clear that variables with loadings of 0.80 or more match the factor patterns very well, but the match is not as good as the loadings decrease to near 0.50. Overall, however, comparing factors with the original deposition data gives the impression that there were three basic deposition patterns, consisting of 1) soluble soil materials, 2) insoluble soil materials, and 3) pollutant Zn and rainfall. Insoluble Zn could quite conceivably rate a pattern of its own, as indicated by its low loading on factor 3.

### Factor Analysis Results for Other Days

Preliminary results for five more storms are given in Tables 2-6. The results are preliminary in the sense that selection of the final data set,

Table 1. 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, %	35.0	14.8	12.8

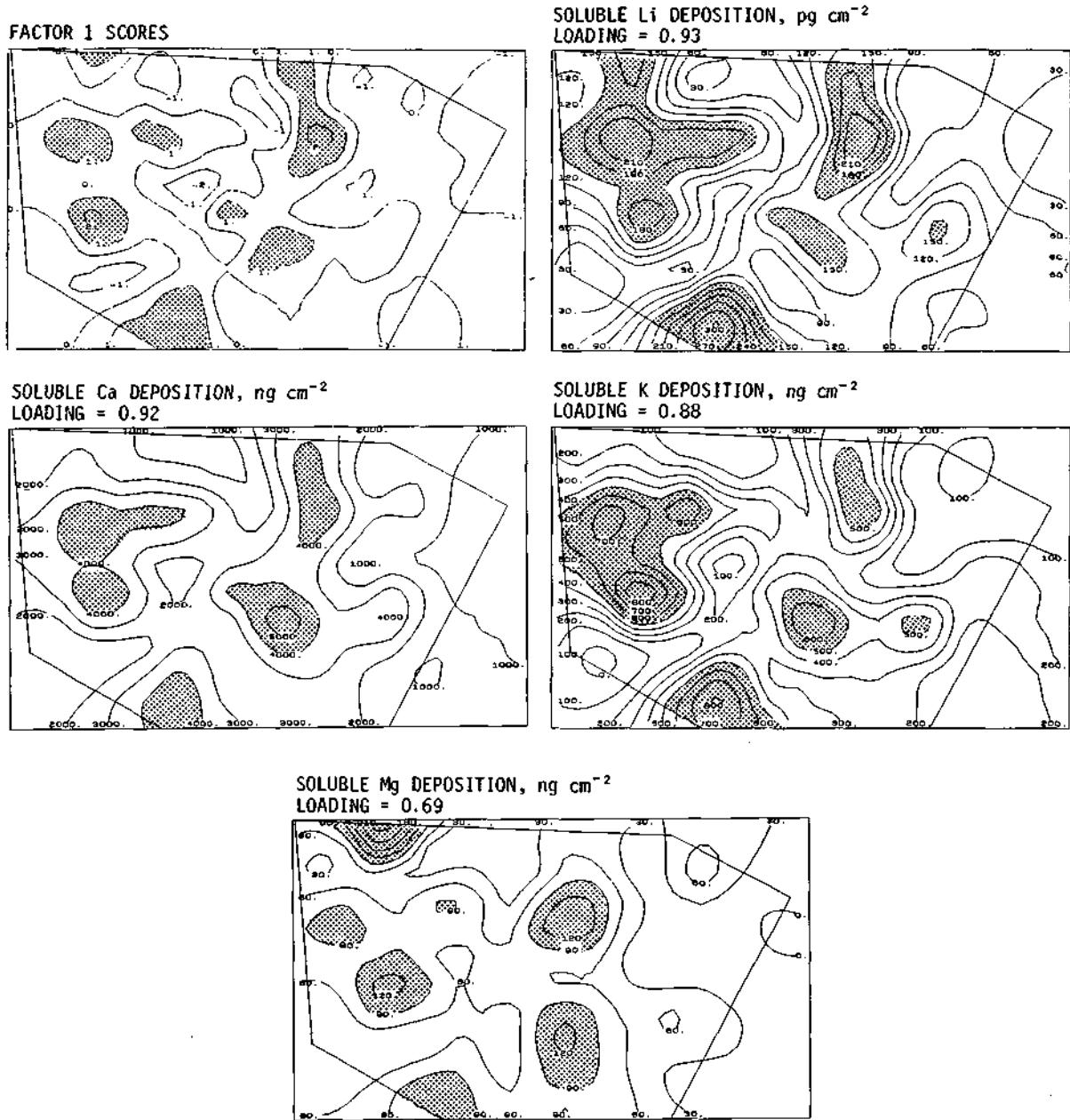


Figure 2. Factor 1 scores and deposition patterns of associated chemical constituents, 13 August 1975.

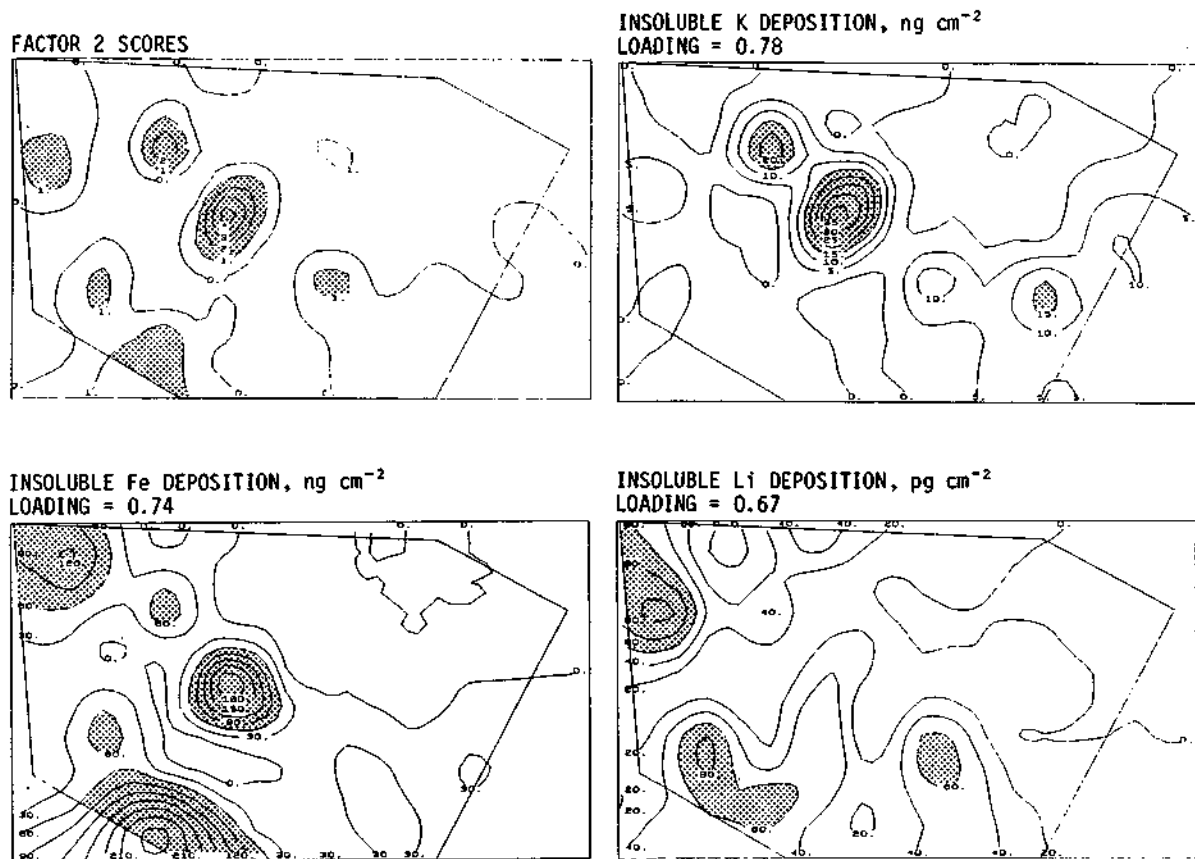


Figure 3. Factor 2 scores and deposition patterns of associated chemical constituents, 13 August 1975.

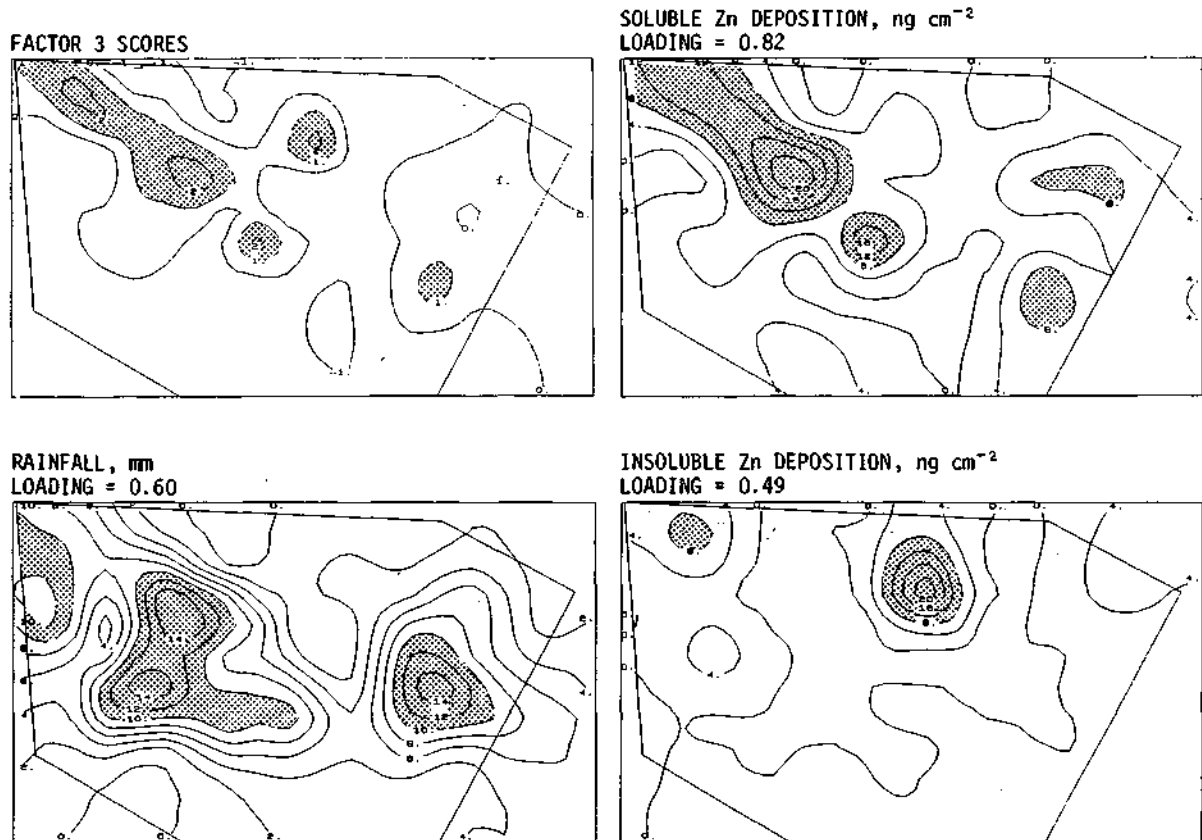


Figure 4. Factor 3 scores and deposition patterns of associated chemical constituents, 13 August 1975.

based on outliers identified in preliminary analyses, has not been made. However, experience with the data has shown that removal of outliers mostly affects the factor scores; loadings generally change very little.

Results in Tables 2-6 show that the variables group rather consistently into four major factors: 1) soluble soil elements (Li, Na, Mg, K, and Ca), 2) insoluble soil elements (Li, Na, Mg, K, Ca, and Fe), 3) soluble pollutants (Zn, Cd, Pb,  $\text{SO}_4^-$ ), and 4) insoluble pollutants (Zn). In addition, materials released as tracers into precipitation systems (Li, In), occasionally appear as separate factors, giving evidence that the tracer materials were detected in the rain.

Rainfall was also used as a variable. It was not consistent in the factor with which it associated, but frequently it was with a soluble pollutant factor.

The preliminary results of the groupings of variables on factors appear to show two major features: 1) soluble and insoluble portions of the same element appear on different factors, i.e., they have different deposition patterns, and 2) soil and pollutant elements have different deposition patterns. The spatial distributions of pollutant sources and soil sources are different, and could thus be expected to produce different deposition patterns. However, the finding that soluble and insoluble materials appear on different factors may reflect differences in physico-chemical processes of precipitation formation and scavenging. This is important because it suggests a new tool, namely chemical analysis of meso-scale network precipitation collections, for elucidating precipitation formation processes. If valid, this method could be especially useful in explaining fundamental precipitation processes and their role in scavenging of atmospheric pollutants.

Some of the best clues to the processes involved should come from analyzing the spatial deposition patterns. Both the relationships between variable groups, such as the patterns of soluble and insoluble soil materials, and the relationships between these patterns and the rainfall pattern should be useful.

Deposition patterns from single convective cells should be most useful, since the cell is the basic unit of convective rainfall. Unfortunately, the METROMEX precipitation chemistry data set, because of the 5-km collector spacing and the daily sample collection period, is made up almost exclusively of multicellular storms.

On the other hand, one objective of the SCORE-1978 and 1979 experiments in central Illinois was to obtain samples from single convective cells. These data appear to be ideally suited to factor analysis for the purpose of determining differences in deposition patterns of rain constituents, and their meanings. The 1979 experiment offers the best hope of definitive data because of the extensive radar data and three-dimensional wind data that will be available to show the three-dimensional structure and circulation of the precipitation systems.

Table 2. Loadings table from factor analysis on deposition data from storm of 11 August 1972.

	Factor				
	1	2	3	4	5
Soluble Li	0.96				
Soluble K	0.94				
Soluble Ca	0.92				
Soluble Na	0.91				
Soluble Mg	0.85				
Rainfall	0.75	0.52			
Insoluble Li	0.59				
Soluble Pb		0.76			
Soluble Zn		0.73			
Soluble Cd		0.68			
Insoluble Mg			0.73		
Insoluble Ca			0.62		
Insoluble K			0.56		
Insoluble Zn				0.92	
Soluble In					0.87
Insoluble Na					0.65
Variance explained, %	37.6	17.2	10.4	8.5	6.2

Table 3. Loadings table from factor analysis on deposition data from storm of 13 July 1975 (preliminary).

	Factor			
	1	2	3	4
Insoluble Fe	0.91			
Insoluble K	0.86			
Insoluble Li	0.64			
Soluble S <sub>04</sub> =		0.77		
Soluble Zn		0.72		
Soluble Cd		0.62		
Rainfall		0.55		
Soluble Ca			0.92	
Soluble K			0.88	
Soluble Mg			0.61	
Soluble Li				0.76
Insoluble Zn				-0.65
Variance explained, %	32.5	14.6	13.0	9.2



Table 4. Loadings table from factor analysis on deposition data from storm of 18 July 1975 (preliminary).

	Factor			
	1	2	3	4
Soluble Ca	0.90			
Soluble K	0.84			
Soluble Li	0.83			
Soluble Mg	0.82			
Insoluble Li		0.94		
Insoluble K		0.93		
Insoluble Fe		0.91		
Rainfall			0.83	
Insoluble Zn			-0.67	
Soluble Zn				0.98
<b>Variance</b>				
explained, %	30.6	27.8	11.1	10.0

Table 5. Loadings table from factor analysis on deposition data from storm of 1 August 1975 (preliminary).

	Factor			
	1	2	3	4
Insoluble Fe	0.96			
Insoluble Li	0.96			
Insoluble K	0.96			
Insoluble Zn	0.50	(0.49)		
Soluble K		0.92		
Soluble Mg		0.84		
Soluble Ca		0.59		
Soluble $\text{SO}_4^-$			0.78	
Soluble Cd			0.73	
Rainfall			0.73	
Soluble Zn				0.80
Soluble Li				0.77
Variance explained, %	32.8	16.6	14.9	10.0

Table 6. Loadings table from factor analysis on deposition data from storm of 5 August 1975 (preliminary).

	Factor		
	1	2	3
Soluble Li	0.90		
Soluble Ca	0.89		
Soluble K	0.88		
Insoluble K		0.87	
Insoluble Li		0.80	
Insoluble Fe		0.64	
Rainfall			0.84
Soluble Zn			0.60
Soluble Mg			0.54
Insoluble Zn			
Variance			
explained, %	28.5	18.0	13.0

## SUMMARY AND CONCLUSIONS

Preliminary analyses have been carried out on six storms in which the deposition of both soluble and insoluble constituents was measured over 80-85 collector networks near St. Louis.

Factor analysis is a convenient way of analyzing the data to show which deposition patterns are similar and how the major deposition patterns differ from each other.

Four main deposition patterns were detected: 1) soluble portions of soil elements, 2) insoluble portions of soil elements, 3) soluble portions of pollutants, and 4) insoluble portions of pollutants. The fact that different deposition patterns were found for soluble and insoluble portions of the same element suggests that different precipitation and/or scavenging processes may be involved for the respective materials. Careful analyses of the various deposition patterns and case studies of the structure of the associated rain system, especially single convective cells, should provide clues to the nature of these processes, and their scavenging efficiencies.

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## CHAPTER 4

### AN INVESTIGATION OF POLLUTANT SOURCE STRENGTH-RAINFALL RELATIONSHIPS AT ST. LOUIS

Donald F. Gatz

#### INTRODUCTION

The rapid increase in annual precipitation at La Porte, Indiana, during the 1940's was accompanied by a similar jump in the number of smoke and haze days at Chicago. This caused speculation that airborne pollutants might be involved in some way in increasing the precipitation at La Porte. Since then a number of papers have examined relations between aerosols and rainfall. Both increases and decreases in rainfall have been attributed to increased concentrations of the aerosol or some component of the aerosol, such as condensation nuclei.

If pollutants cause urban-related increases in rainfall, then the indices of pollutant source strength downwind of the sources should be highly correlated with rainfall at locations determined by the surface winds and storm motion. Of course, if significant correlations were found, causation would not be proven; other reasons might be responsible. However, to gain insight into the relationships between pollutants and rainfall that may possibly exist in the St. Louis area, it seemed useful to perform a correlation analysis.

This paper reports the results of a correlation analysis between 1) daily factor scores (indices of source strength), and 2) storm rainfall in 21 selected areas near St. Louis to test the null hypothesis that there is no correlation between pollutant source strengths and summer rainfall near St. Louis.

#### METHODS

Rainfall was measured in the 250-gage METROMEX network of recording raingages. Average rainfall for each storm was calculated for the 16 areas shown in Fig. 1, plus the four quadrants and the whole area east of the Mississippi River.

The factor scores used in the correlation analysis with rainfall data were calculated as part of the factor analyses performed for an earlier paper (Gatz, 1978). For details, see Gatz (1978) or a more complete version of the present paper, to be published in the Journal of Applied Meteorology.

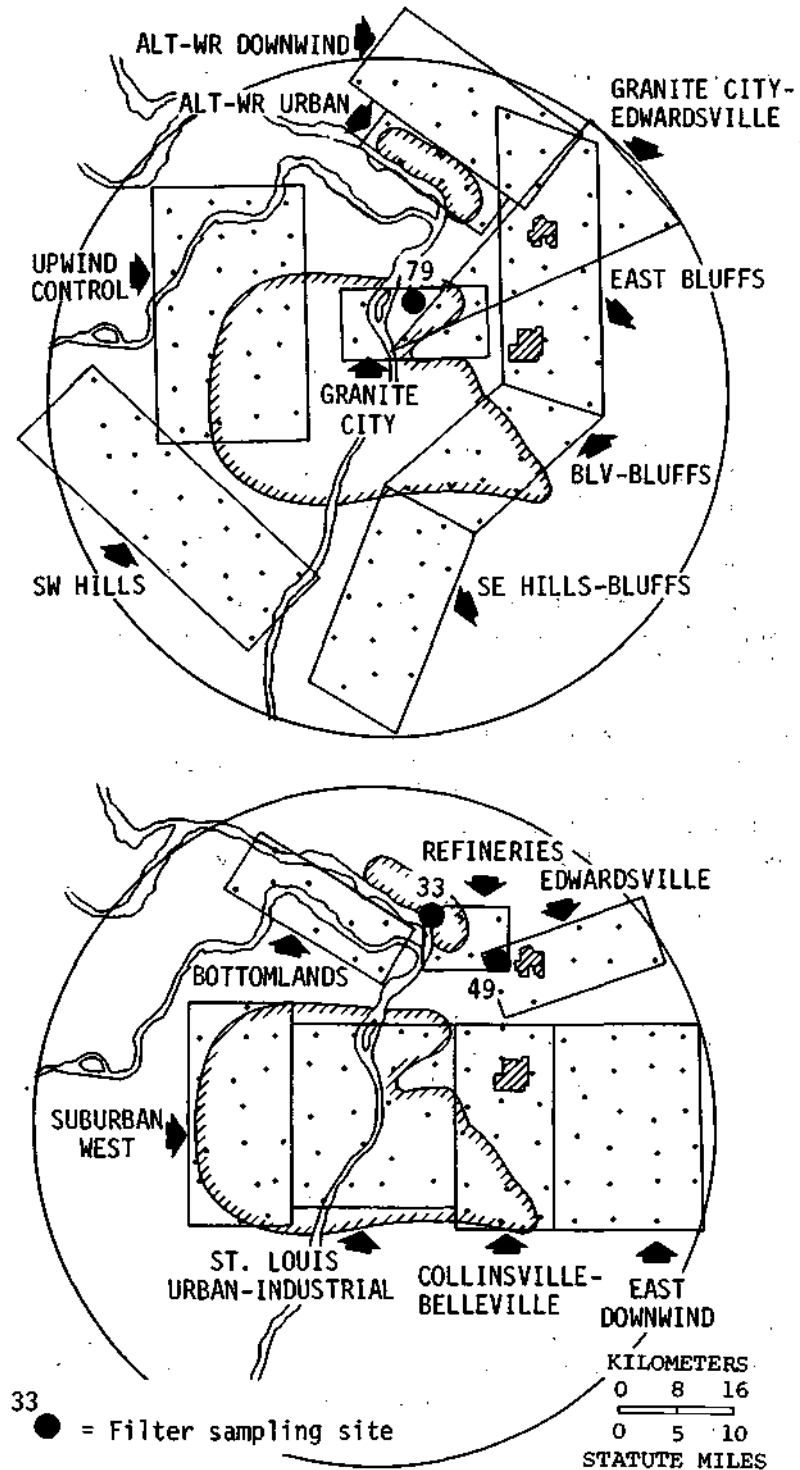


Figure 1. The subdivisions of the METROMEX 250 raingage network used from which rainfall data were compared with factor scores.

The task of testing the hypothesis that all correlation coefficients,  $r$ , between factor scores and rainfall in subareas, equal zero is one of simultaneous inference.

This simultaneous test was performed using the Bonferroni inequality. The Bonferroni relationship says that the probability that all statements (i.e., hypotheses regarding the significance of individual values of  $r$ ) are correct (i.e.,  $r$  not significantly different from zero) is at least as great as 1 minus the sum of the probabilities that each statement (individually) is incorrect.

The choice of the number of hypotheses to test simultaneously varies with the degree of statistical conservatism one wishes to maintain. In this work, significance tests were performed for two different degrees of conservatism, and the results are presented and compared.

## RESULTS

Correlation coefficients between mean storm rainfall and aerosol source factor scores were calculated for every combination of 21 rainfall areas and 48 separate source strength indices identified at 12 filter sampling sites in the St. Louis area. The results are given in Table 1, which shows only  $r$ -values significant at  $\alpha = 1\%$  or  $\alpha = 5\%$ , for two different simultaneous testing procedures.

Table 1 shows that no correlation coefficients were found to be significant, even at  $\alpha = 10\%$ , when all 1008 correlations were tested simultaneously. The table also shows that 2 correlations were significant at  $\alpha = 1\%$ , when testing under the less conservative condition.

We shall thus consider in more detail the four correlations significant at the 1% or 5% levels in Table 1, part B. There are several general things to notice about the results in Table 1. The three factors having the highest correlations with rainfall occurred at three different filter sampling locations. The three factors were all different in the sense that a different set of elements was associated with each. All three of the factors could be classified as "pollutants," and all had positive correlations, indicating that rainfall had increased with enhanced element concentrations.

Figure 1 shows that the rain area of high correlation with factor 3 at site 33 is immediately adjacent to the filter sampling site. This is an auto exhaust factor, with high loadings on Br and Pb. The same rain area was also highly correlated with factor 2 at filter site 49, immediately adjacent to the southeast. This is an industrial metals factor, and strongly associated with southwest winds. Enhanced rainfall could conceivably have fallen in the refineries area after cells moving from the southwest had ingested the pollutants near their sources.

Figure 1 shows the two rain areas having identical high correlations (Table 1) with factor 5 at site 79. This again is an industrial metals factor, whose source is almost certainly the large steel mill in Granite City.

Table 1. Correlation matrix, showing values significant at 1% and 5% levels for two testing procedures.

	Filter site no./factor no. (no. of data pairs)				
	33/3*	49/2**	79/5***	113/3	303/2
Rain subarea	(52)	(31)	(25)	(49)	(32)
A. Testing all correlations simultaneously: no correlations significant at a - 10%, $\kappa = 1008$ .					
B. Testing sets of 21 rain subareas simultaneously: $\kappa = 21$ .					
Collinsville- Belleville			0.62(1%)		
Belleville bluffs			0.62(1%)		
Refineries	0.39 (5%)	0.52 (5%)			
* Associated elements (loadings): Br(0.92), Pg(0.76).					
** Associated elements (loadings): Zn(0.81), Pb(0.76), Ti(0.57), Fe(0.52), SW winds(0.87).					
*** Associated elements (loadings): Mn(0.84), Fe(0.76).					



## DISCUSSION

It is prudent to examine a few of the most significant correlations between rainfall and pollutant source factors, to see whether they suggest any mechanisms for pollutant enhancement of urban summer rainfall that are physically reasonable.

The rain areas of high correlation are all relatively close to the respective filter sites. Is it physically reasonable that storms that ingested polluted air observed at these sites would have produced enhanced rainfall in the various areas found most highly correlated? Are these observations consistent with previous results that suggest rain enhancement after cells ingest the "urban plume"?

The rainfall distributions found by Vogel and Huff (1978) for SE surface winds and SW storm motion feature a broad rainfall maximum across the northern part of the research circle, which includes the refineries area where rainfall was found to be highly correlated with two different pollutant factors. The pattern for SE surface winds and NW storm motion includes rainfall peaks in the areas where the rain was highly correlated with factor 5, site 79.

For SW surface winds and NW storm motion an area of maximum rainfall near Alton-Wood River again includes the refineries area. For SW storm motion, however, the patterns do not coincide at any point.

These comparisons show that all rain areas of significant correlation are *included* in areas of high mean rainfall under certain combinations of surface winds and storm motion. However, the converse is not true; many places with high rainfall do not correlate significantly with any source strength indices. Furthermore, in each case where there is agreement between patterns for certain combinations of wind direction and storm motion, there is disagreement for other combinations.

In addition, the fact that the three pollutant factors found to be significantly correlated with rainfall all represent *different* pollutant sources appears to be a crucial observation. One of these factors (auto exhaust) was identified at all 12 sampling sites (Gatz, 1978), but only at site 33 was it correlated with rainfall in any of the rain areas.

Thus, a physically reasonable explanation for the few high correlations is not apparent, and we appear to be justified in accepting the verdict of the simultaneous test of all 1008 correlations; none of the correlations is significantly different from zero.

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## CHAPTER 5

### MEASUREMENTS OF ATMOSPHERIC NITRATE, SULFATE, AMMONIUM, AND CALCIUM USING VARIOUS FILTER SETUPS

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 at a rural site near Champaign, Illinois in May 1977. Gatz (1976) has 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. Both types of samples were analyzed for the same water soluble constituents, namely  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ . This paper will report on a series of short duration field experiments conducted to evaluate some aspects of the aerosol sampling program. In particular, experiments will be discussed that compared Whatman 41 filters with various Nuclepore filter setups. Data for water soluble sulfate, nitrate, ammonium, and calcium will be presented.

Coultant (1977) has shown that artifact sulfate forms on certain types of filters, which are generally characterized by the property that they produce a basic solution when placed in deionized water. Spicer and Schumacher (1977) have shown that different filters produce extremely variable nitrate results. With respect to the nitrate measurement problem, the results reported in this paper will actually produce more questions than answers. This is of course unfortunate since the nitrate and sulfate are of primary importance in acid precipitation samples to which ambient aerosol data are being compared.

#### EXPERIMENTAL PROCEDURE

This section will present the general methodology and then describe the experimental configurations for the four filter comparison studies.

## General Methodology

The site for these aerosol sampling experiments was located at Willard Airport (CMI), seven 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. It is the author's belief that the aviation facility had a negligible effect on the ambient aerosol levels for the constituents included in this study, with the exception of calcium which was probably effected by nearby gravel covered parking lots.

Most of the low volume aerosol sampling at CMI was carried out on a seven meter tower. Two filter samplers were at a six meter height with a third at four meters. On occasion a fourth filter sample was collected at a ground site 30 meters away from the tower. Throughout this paper it should be assumed that the samples were taken on the tower since ground level samples will be explicitly identified.

Gast piston-type vacuum pumps were used for the sampling. Initial and final pressure drops and flow rate values were manually recorded from the pressure gauge and rotameter of the pumps. The pumps were calibrated using a dry gas meter. Flow readings were corrected to standard pressure; no correction was made for temperature.

The mean of the corrected initial and final flow values was used to calculate the air volume sampled. Samples where the final flow was less than about 75% of the initial flow were discarded due to the consequential inaccuracy of the air volume determination.

To protect the samples from rain the filter holders were mounted face down under inverted polyethylene funnels. The funnels were 30 centimeters in diameter and the filter holder was positioned such that the filter surface was about 2 centimeters above the bottom edge of the funnel.

Five types of filter samplers were utilized in the experiments. Table 1 provides a list of the materials, their physical parameters and abbreviations that will be used in this paper to describe the five samplers.

After the sampling period and before the extraction step, the filters were stored in sterilized petri dishes at room temperature. Storage time was usually no longer than one to two months with a maximum of 5 months for some filters. Smith *et al.* (1978) have recently reported considerable losses of nitrate and ammonium on high-vol, glass-fiber filters which had been stored without a container at room temperature. For nitrate they reported a 25% loss at 3 months storage and for ammonium a 40% loss.

To determine total suspended particulate concentrations the Nucl (37, 0.8) filters were weighed prior to and after the sampling period. The filters were stored in a 47% relative humidity chamber for at least 24 hours before the final weight was measured.

In the extraction procedure, each filter was placed in a pre-washed 50 ml Nalgene linear polyethylene (LPE) bottle with 25 ml of deionized water and agitated for 20 minutes on a wrist action shaker at room temperature. This

Table 1. Summary of the Five Filter Samplers used for the Field Sampling.

<u>Filter Samplers</u>	<u>Filter Diameter (mm)</u>	<u>Filter Pore Diameter (um)</u>	<u>Filter Holders</u>	<u>Abbreviation</u>
Nuclepore	37	0.8	Millipore Field Monitor	Nucl(37,.8)
Whatman 41	25		Gelman (Delrin)	What 41
Dual Nuclepore	47	0.8,0.8	Nuclepore Multiple Filter Holder	Dual(47,.8,.8)
Dual Nuclepore	47	12,0.2	Nuclepore Multiple Filter Holder	Dual(47,12,.2)
Nuclepore	47	.4	Nuclepore Single Filter Holder	Nucl(47,.4)

solution was then filtered through a Millipore HA 0.45  $\mu\text{m}$  filter and collected in another 50 ml Nalgene LPE bottle.

The extraction solutions were stored at room temperature for a maximum of one month before the ion concentrations were measured. A study on rain samples by Peden and Skowron (1978) has shown that the filtered samples maintained steady ion concentrations over a 6 week period for sulfate, nitrate, ammonia, calcium, and other constituents. Since the filter extraction solutions in this study are comparable to the rain samples in ion levels and handling procedures, it can be concluded that the ions are stable for a one month storage period.

The analytical methods for the sulfate, nitrate, and ammonium ions were methylthymol blue, cadmium reduction diazotization, and the Barthelow reaction, respectively, all automated on the Technicon Autoanalyzer II. Calcium ion concentrations were determined by flame atomic absorption using an Instrumentation Laboratory Atomic Absorption Emission Spectrophotometer 353. Analysis of  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  were also done but will not be considered in this paper. The analyses were performed in the ISWS Atmospheric Chemistry Laboratories which have been involved with routine analyses of these ions in precipitation samples for a number of years. The facility is presently serving as the Central Analytical Laboratory for the National Atmospheric Deposition Project (NC-141 Project).

To check for contamination of the air filters during field and laboratory procedures, deionized water blanks (DIBK), laboratory filter blanks (for Nucl (37, .8), Dual (47, .8, .8), and What 41) and field filter blanks (for Nucl 37, .8) were included with each extraction set. Table 2 presents the concentration levels for these blanks as well as the detection limits of the analytical procedures and the typical concentrations of the extraction solutions.

Field filter blanks were transported to and from the field site, and also went through the weighing procedures used to determine TSP, whereas laboratory blank filters did not.

For  $\text{SO}_4^{--}$ , all the blanks in Table 2, with the exception of Dual (47, .8, .8), were at the level of detection. The Dual (47, .8, .8) laboratory blanks were higher than the levels for the other filter blanks, but all five of the Duals were done in the same extraction set. Therefore, the sulfate value is probably not very representative of the true blank value for the Dual (47, .8, .8) filter. Nitrate levels in Table 2 are close to the detection limit for all filters except the field filter blanks. Since the constant humidity chamber used in the TSP procedure utilized a saturated lithium nitrate solution, this could possibly be the contamination source for  $\text{NO}_3^-$  in the field filter blanks.

For  $\text{NH}_4^+$  only the What 41 filters in Table 2 show a high blank level with other values being close to the detection limit. For  $\text{Ca}^{++}$ , all the blank values were low.

In summary, all the quality control filter blank values in Table 2 are small when compared to the typical sample values which are listed in the last column of the table. Field filter blank values were subtracted from the extraction solution concentrations for the Nucl (37, .8) filters. The laboratory blank values were used for all the other filters.

Table 2. Analytical Detection Limits, Median Ion Concentration (mg/l) for Blanks and Typical Samples.

	Detection Limits	Laboratory Blanks			What 41	Field Filter	Typical
		DIBK	Nucl (37,.8)	Dual (47,.8, .8)		Blank, Nucl(37, .8)	Sample Concentrations <sup>a</sup>
SO <sub>4</sub> <sup>=</sup>	.20	.20	.20	.60	.20	.20	4.40
NO <sub>3</sub> <sup>-</sup>	.03	.03	.03	.05	.06	.13	.70
NH <sub>4</sub> <sup>+</sup>	.03	.03	.05	.03	.10	.03	1.00
Ca <sup>++</sup>	.02	.02	.02	.02	.02	.03	.60
Number of Blanks		30					

The typical sample concentrations are the median ion values determined from all the filter data presented in this paper.

A series of triplicate Nucl (37, .8) samples were collected for a 20 day period to determine the precision of the sampling methods. Figure 1 shows the variation in the daily ion concentrations measured with these filters. The Nucl (37, .8) UP was on the "upper pump" (at the six meter height); Nucl (37, .8) MP was on the "middle pump" (at the six meter height) and Nucl (37, .8) LP was on the "lower pump" (at the four meter height). From these data, a relative standard deviation was calculated for each of the ions. The statistical procedure included pooling the variances determined for each of 20 triplicate sets and then dividing the square root of the pooled variance by the average of the triplicate means (Ostle and Mensing, 1975). The results are summarized in Table 3.

Two values are given for  $SO_4$  since there was a much greater variance in the measurements at concentrations above  $10 \mu\text{g}/\text{m}^3$ . This phenomenon was not as apparent in the other ion measurements, therefore no division in these data were made.

The errors in analytical procedures, determination of the air volume sampled and the determination of the filter blank values were also evaluated. They were found to be negligible in comparison to the error produced by the sampling method.

In summary, these relative standard deviations will not affect the conclusions of this paper since the ion concentration discrepancies reported in the next section are considerably greater.

#### Experimental Configuration of the Four Filter Comparison Studies

Experiment I extended from June 1977 to September 1977. Ambient air samples were collected using What 41 and Nucl (37, .8) setups. Sampling occurred continuously for a 12 hour period on each day. A total of 73 pairs of samples were obtained. Face velocities were about 180 cm/sec for the What 41 and 30 cm/sec for the Nucl (37, .8) setups.

In Experiment II, daily aerosol samples were taken by four different filter samplers: Nucl (37, .8), Dual (47, .8, .8), What 41, and Nucl (47, .4) (this last filter sampler was operated at ground level). The experiment took place for an eight day period in April 1978. Ambient air was drawn through the filter samplers for 45 minutes out of each hour during the 24 hour sampling periods. The Nucl (37, .8) and Dual (47, .8, .8) flow rates were set at 30 lpm and 50 lpm, respectively, to produce a face velocity of about 40 cm/sec for both filters.

The third experiment extended for 8 days in May 1978. Two Nucl (37, .8) filter samplers and a Dual (47, .8, .8) sampler collected aerosol samples for 45 minutes out of each hour during the 24 hour sampling periods. Face velocities of all three filters were about 40 cm/sec. One of the Nucl (37, .8) filters was weighed prior to and after the sampling period in order to determine TSP.

The fourth experiment took place during an 11 day period in April 1978. Aerosol samples were taken with Nucl (37, .8) and Dual (47, 12, .2) setups. Again, the aerosol samples were collected for 45 minutes out of each hour during the 24 hour sampling periods. A critical orifice giving a flow of 3 lpm was used with the Dual (47, 12, .2).

For all the filter setups, except the Dual (47, 12, .2), the air volume sampled was approximately  $20 \text{ m}^3$ .



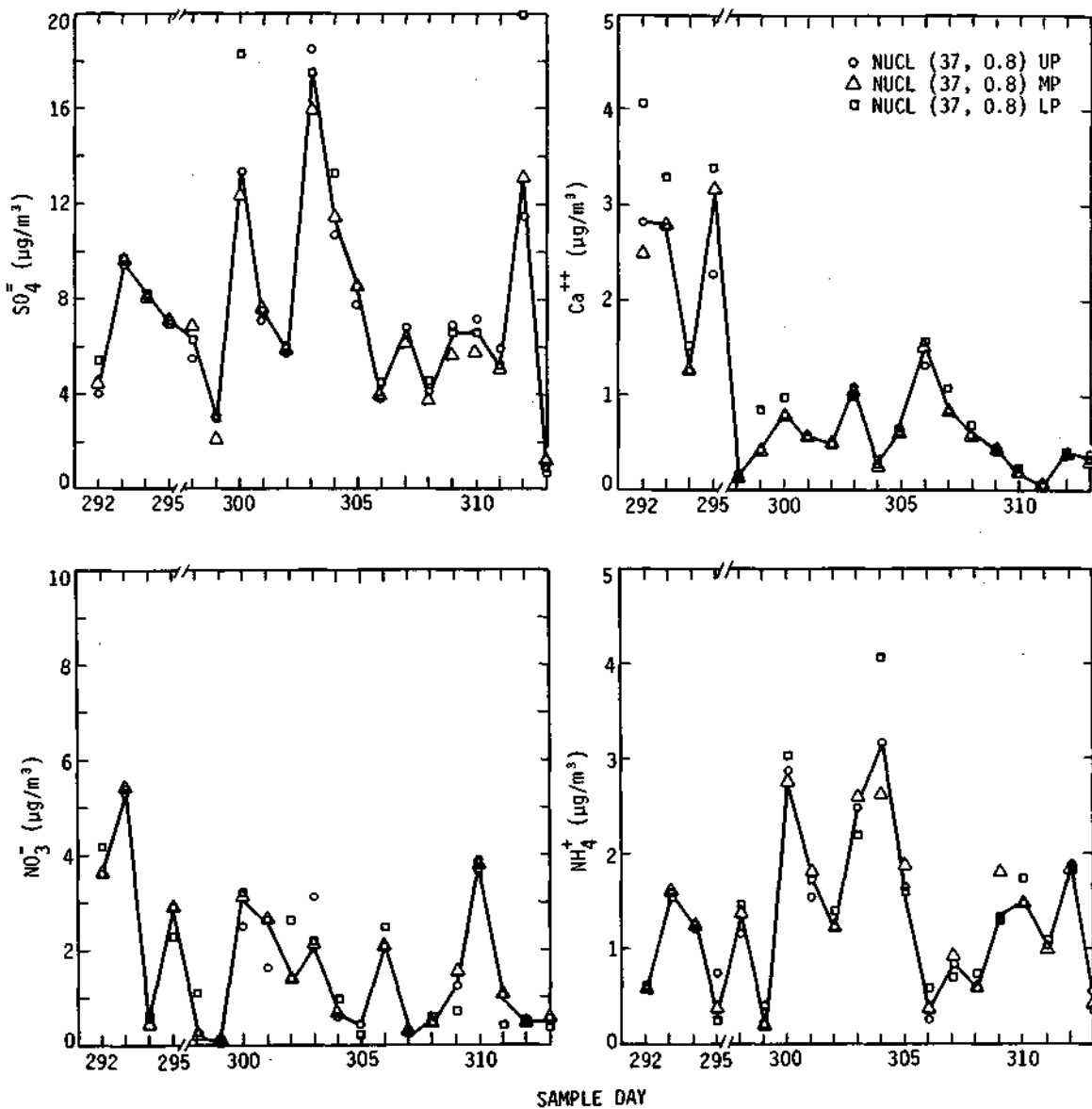


Figure 1. Daily aerosol concentrations of water soluble sulfate, calcium, nitrate and ammonium for triplicate Nuclepore filters.

Table 3. Statistical Results of Triplicate Filter Data.

	(Pooled Variance) <sup>½</sup> (µg/m <sup>3</sup> )	Average of Triplicate Means (µg/m <sup>3</sup> )	Relative Standard Deviation (%)	Number of Triplicate Sets
<b>SO<sub>4</sub><sup>-</sup></b> , >10 µg/m <sup>3</sup>	3.11	15.1	±21	4
<b>SO<sub>4</sub><sup>-</sup></b> , <10 µg/m <sup>3</sup>	.43	5.85	± 7.4	16
<b>NO<sub>3</sub><sup>-</sup></b>	.27	1.66	±16	20
<b>NH<sub>4</sub><sup>+</sup></b>	.17	1.36	±13	20
Ca <sup>++</sup>	.21	.98	±21	20

## RESULTS AND DISCUSSION

Results for the 73 paired samples of Experiment I are summarized in Table 4. The paired t-test indicated that the  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  mean values were all significantly larger for the What 41 compared to the Nucl (37, .8). The  $\text{NO}_3^-$  means had the greatest difference with the What 41 mean being 6 times that of the Nucl (37, .8).  $\text{NH}_4^+$  followed with a 1.5 fold increase in the What 41 mean. The  $\text{SO}_4^{2-}$  mean had the smallest increase of only 1.2 times that of the Nucl (37, .8).

There are some possible explanations for the higher What 41 values. The most obvious is the interaction of gaseous  $\text{NO}_x$  and  $\text{SO}_x$  molecules with the What 41 filter media to produce artifact  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$ . Coulant (1977) has shown that artifact  $\text{SO}_4^{2-}$  formation is greater on high pH filters. Tests in our laboratory have shown that What 41 filters produce pH values of about 7.0 when placed in 25 ml of deionized water, much higher than for Nuclepore filters.

The second explanation is the occurrence of chemical reactions which reduce the ion concentrations on Nucl (37, .8), but not on What 41. Harker et al. (1977) suggested that sulfuric acid might be reacting with the  $\text{NO}_3^-$  particles and thereby releasing  $\text{HNO}_3$  (gas). The present study did not determine what fraction of the ambient sulfate aerosol was acidic and thus no correlations with  $\text{NO}_3^-$  losses could be attempted.

The third possibility is the loss of a significant fraction of the particles thru the 0.8  $\mu\text{m}$  pore openings, thus producing low values on the Nucl (37, .8). The laboratory results of Liu and Lee (1976) indicate that the Nucl (37, .8) setups would have been only about 50-60% efficient for 0.2  $\mu\text{m}$  diameter particles. Some researchers have characterized ambient  $\text{SO}_4^{2-}$  particles as having diameter sizes within the 0.2  $\mu\text{m}$  to 0.6  $\mu\text{m}$ -range (e.g., Tanner et al., 1979 and Hering et al., 1978). Thus filter efficiency problems could be suspected as causing the  $\text{SO}_4^{2-}$  discrepancies. This point will be discussed later in conjunction with Table 6. Orel and Seinfeld (1977) have presented data and modeling results which show that for Los Angeles the  $\text{NO}_3^-$  particles were larger than the  $\text{SO}_4^{2-}$  particles. Therefore if particles were being lost thru the filter pore openings, then the discrepancy between What 41 and Nucl (37, .8) should have been greater for the smaller particles (i.e.,  $\text{SO}_4^{2-}$ ). In fact the data in Table 4 show that the reverse effect was observed, that is, a larger discrepancy for  $\text{NO}_3^-$  than for  $\text{SO}_4^{2-}$ .

Experiment II included dual Nuclepore filters with 0.8  $\mu\text{m}$  pore diameter to look for filter efficiency problems. In addition, a 0.4  $\mu\text{m}$  pore size Nuclepore filter was included which would collect the small particles more efficiently than the 0.8  $\mu\text{m}$  filters. The results for Experiment II are presented in Figure 2 (the abscissa is the Julian date). The What 41 and Nucl (37, .8) did produce the same differences in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  as those observed in Experiment I. However, Figure 2 displays large differences for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  between each of the three Nuclepore setups. This result was very surprising and disturbing.

While the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  agreement was poor the three Nuclepores did agree very well for  $\text{SO}_4^{2-}$ . With respect to  $\text{Ca}^{++}$  the four filter setups agreed reasonably well except on day 102. Vehicular traffic south of the ground site where Nucl (47, .4) was located may have produced airborne dust and thus the large  $\text{Ca}^{++}$  value compared to the other three samplers on the tower.

Table 4. Summary of Data for Nucl (37, .8) and What 41 in Experiment I.

Ion Species	Ion Concentration ( $\mu\text{g}/\text{m}^3$ )						Statistical Results	
	Nucl (37, .8)			What 41			Paired t Value	P (t) One-tailed
	Median	Mean	Std. Dev.	Median	Mean	Std. Dev.		
$\text{SO}_4^-$	6.5	9.4	.9	8.2	11.1	1.1	4.10	.0001
$\text{Ca}^{++}$	0.9	1.15	1.13	.8	.98	.89	-1.48	.0716
$\text{NO}_3^-$	0.12	.6	1.1	2.5	3.7	2.8	8.67	.0001
$\text{NH}_4^+$	1.3	1.7	1.5	2.3	2.7	1.8	8.91	.0001

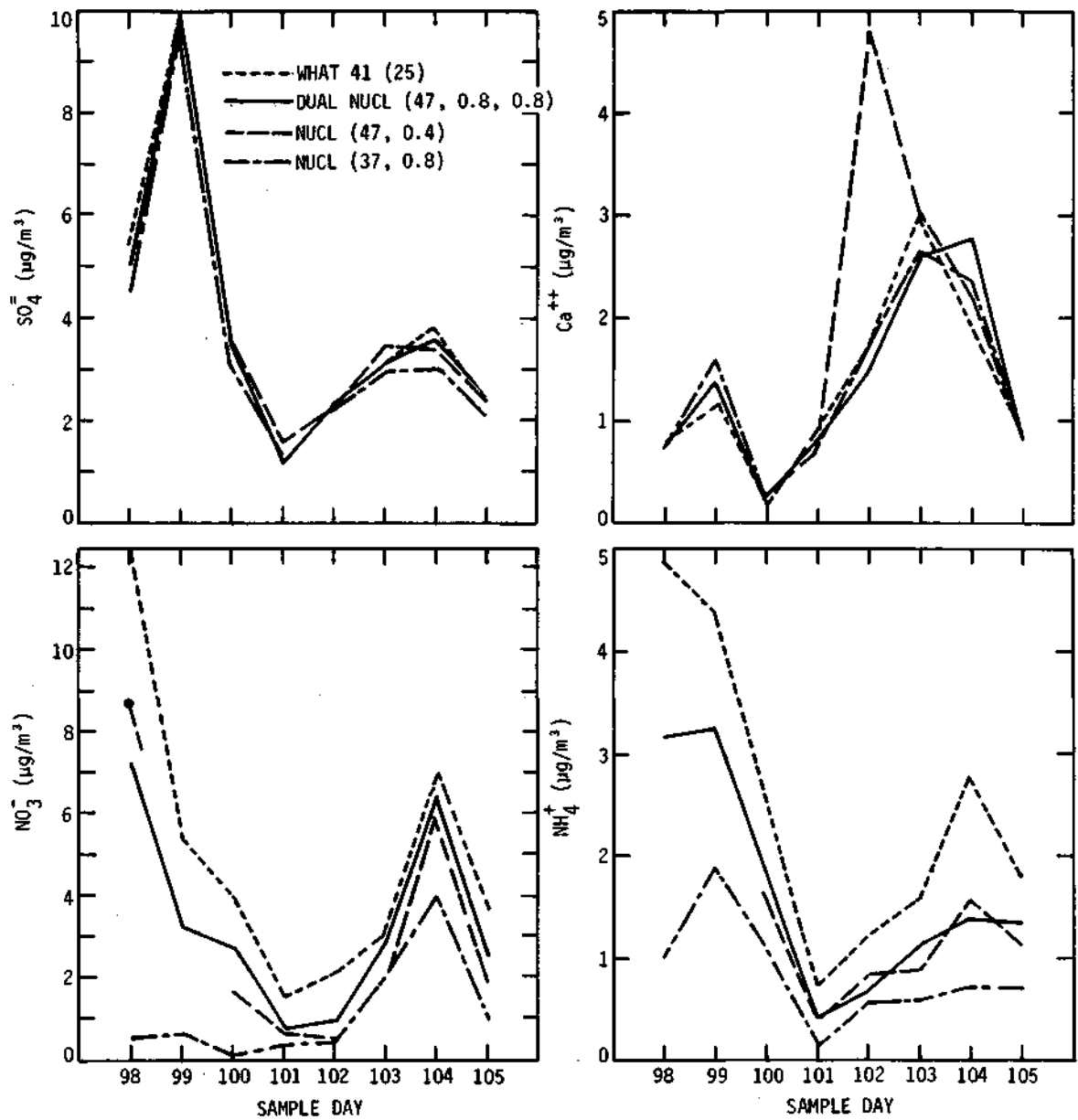


Figure 2. Daily aerosol concentrations of water soluble sulfate, calcium, nitrate and ammonium for Experiment II.

Experiment III focused attention on Dual (47, .8, .8) and Nucl (37, .8) to see if the results in Experiment II could be duplicated. Furthermore, the possible effects on nitrate levels by the constant humidity chamber, containing lithium nitrate, were tested. One Nucl (37, .8) was kept unweighed while the second Nucl (37, .8) was weighed via the usual procedure. Figure 3 shows the daily levels of the three filters for Experiment III. There is no significant difference in the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  levels for the two Nucl (37, .8) setups and therefore the weighing procedure is not to be considered as a valid explanation for the low levels of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  on the Nucl (37, .8) setups. Once again the Dual (47, .8, .8) and Nucl (37, .8) produced comparable  $\text{SO}_4^{2-}$  and  $\text{Ca}^{++}$  levels but the Dual gave higher levels of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .

Table 5 summarizes the results for the 16 paired samples from Experiments II and III. Each ion's mean value, standard deviation and median value are given for both samplers. Results of the paired t-test for equality of means are also presented. The paired t-test indicates that the  $\text{SO}_4^{2-}$  means for the Dual (47, .8, .8) and Nucl (37, .8) are not statistically different, although the Dual (47, .8, .8) showed higher levels for 14 samples. The paired-t test confirms that the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  means were different for the Dual (47, .8, .8) versus the Nucl (37, .8). The Dual shows a 3.4 fold increase in the mean  $\text{NO}_3^-$  and a 1.6 fold increase for  $\text{NH}_4^+$ . The difference in the  $\text{Ca}^{++}$  means was significant at the 5% level but not the 1% level.

As stated earlier, the face velocities for the Nucl (37, .8) and Dual (47, .8, .8) were approximately equal. This should have produced similar aerosol depositions on each filter type. However, there still exists the sampling problem of pulling the aerosol particles from a horizontal air stream upward to the filters mounted under the plastic funnels. Gatz (1979) and Hardy *et al.* (1976) have shown that the  $\text{Ca}^{++}$  particles are relatively large, several micrometers in diameter or larger, and thus more susceptible to these sampling problems as compared to  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  particles. McFarland *et al.* (1977) have addressed the problem of collecting 5, 15, and 30  $\mu\text{m}$  diameter particles with an Andersen sampler mounted such that the particle laden horizontal airstream had to be drawn downward, into the vertically oriented sampler. They found that the collection varied considerably for different wind speeds. May *et al.* (1976) have demonstrated that particles with diameters of 20-50  $\mu\text{m}$  diameter will be sampled accurately only with collecting surfaces directed into the wind.

Finally, even though the  $\text{Ca}^{++}$  data in this paper are probably somewhat inaccurate due to the sampling geometry used, it is important to observe that the various sampling setups did produce relatively similar results. Since the  $\text{Ca}^{++}$  particles are most likely larger than the  $\text{NO}_3^-$  particles, the big discrepancies in the  $\text{NO}_3^-$  data can not be explained by sampling geometry problems.

Table 6 summarizes data for the first and second filters in the Dual (47, .8, .8) setups of Experiments II and III. If significant quantities of the smaller aerosol particles were passing through the Nucl (37, .8) then the levels on the second filter of the Dual (47, .8, .8) setup would probably be substantial. The last column of this table indicates that the second filter contained only 5-8% as much material as the first filter. Therefore it is again suggested that the Nucl (37, .8) did not have low levels of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  due to a filter efficiency problem. Furthermore Figure 2, where the Nucl (37, .8) and the Nucl (47, .4) were compared, showed that the  $\text{SO}_4^{2-}$  levels were about the same on the 0.4  $\mu\text{m}$  and the 0.8  $\mu\text{m}$  filters. Also, Dams *et al.* (1972) indicate that the What 41 filters should be very efficient with the high face velocities used in this study

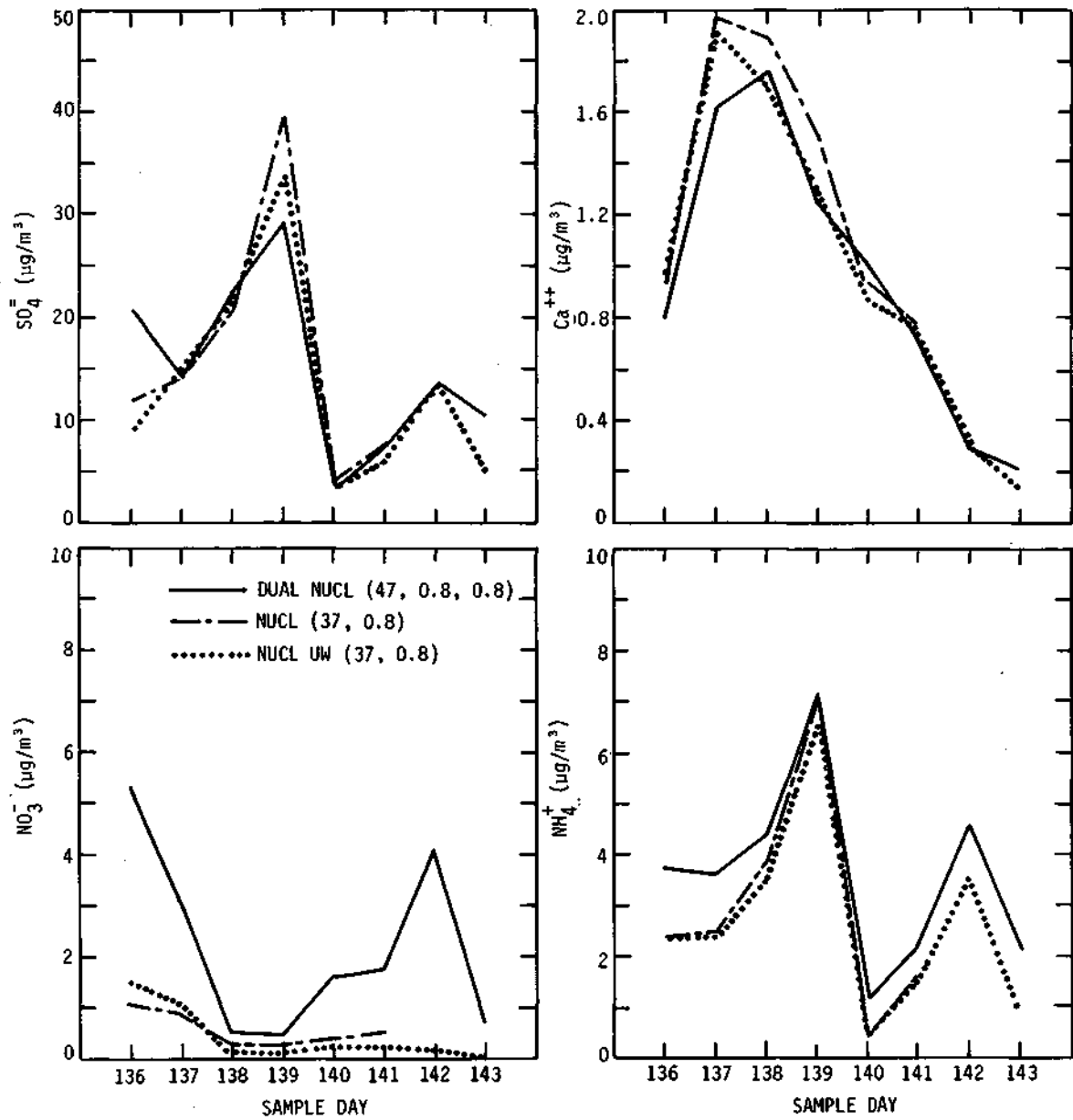


Figure 3. Daily aerosol concentration of water soluble sulfate, calcium, nitrate and ammonium for Experiment II.

Table 5. Summary of Data for Nucl (37, .8) and Dual (47, .8, .8) in Experiments II and III.

Ion Species	Ion Concentration ( $\mu\text{g}/\text{m}^3$ )						Statistical Results	
	Nucl (37, .8)			Dual (47, .8, .8)			Paired t Value	P (t) One-tailed
	Median	Mean	Std. Dev.	Median	Mean	Std. Dev.		
$\text{SO}_4^-$	5.7	8.8	9.3	5.0	9.5	8.4	-0.72	.2412
$\text{Ca}^{++}$	.9	1.2	.69	.8	1.1	.7	1.74	.0210
$\text{NO}_3^-$	.4	.8	1.0	2.7	2.7	2.1	-4.50	.0003
$\text{NH}_4^+$	1.5	1.7	1.6	2.2	2.7	1.7	-6.9	.0001

Table 6. Ion Levels on the First and Second Filters of the Dual (47, .8, .8).

	First Filter			Second Filter			$\frac{\text{Mean of Second}}{\text{Mean of First}}$
	Median	Mean	Std. Dev.	Median	Mean	Std. Dev.	
$\text{SO}_4^-$	7.77	8.97	8.07	.268	.464	.78	.05
$\text{NO}_3^-$	2.05	2.58	2.03	.106	.154	.12	.06
$\text{NH}_4^+$	2.0	2.45	1.68	.16	.206	.14	.08



(about 180 cm/ sec). Thus, since Table 4 shows that the  $\text{SO}_4$  levels on What 41 were only about 20% greater than on Nucl (37, .8), and some artifact  $\text{SO}_4^-$  on What 41 was to be expected, the Nucl (37, .8) could not have been missing a significant amount of  $\text{SO}_4^-$  due to collection efficiency problems.

The last phase of this study, Experiment IV, was once again a comparison between a single filter and a dual filter unit, the Nucl (37, .8) versus the Dual (47, 12, .2). A major problem encountered in Experiment IV was that the low flow of 3 lpm for the dual setup, resulted in very low ion levels in the extraction solutions. Therefore the laboratory blank values applied to the dual nuclepore extractions were often close in magnitude to the actual extraction values. Both were uncomfortably close to the analytical limit of detection. As a result the  $\text{SO}_4^-$  values from the Nucl (37, .8) were larger than Dual (47, 12, .2). But this result was very sensitive to the laboratory blank value chosen. If the assigned blank value of .6 mg/l for  $\text{SO}_4^-$  was reduced by 50%, which was a reasonable assumption, then the  $\text{SO}_4^-$  values for the two setups were identical. Similar problems arose for  $\text{Ca}^{++}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . However, any reasonable assignment of the laboratory blank values for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  produced the feature wherein the Nucl (37, .8) had lower values for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  than the Dual (47, 12, .2). Thus, even though the data in Experiment IV were not very accurate, the same trends were evident as observed in Experiment II and III.

#### CONCLUSIONS

The general result of most importance was that four different filter samplers, all using Nuclepore filters, collected very different amounts of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  while simultaneously the  $\text{SO}_4^-$  agreement was good. The data show that this feature could not be attributed to a filter efficiency error. No other explanation is known or proposed and thus the credibility of stating that Nuclepore samplers can accurately measure ambient  $\text{NO}_3^-$  and  $\text{NH}_4^+$  levels is open to serious question.

Specific results will now be given for What 41, Nucl (37, .8), and Nucl (47, .8, .8) samplers. The Nucl (47,\* .4) and Nucl (47, 12, .2) sampler results will not be explicitly listed due to the relatively small number of samples.

- (1) On What 41, the median  $\text{NO}_3^-$  value was 20.8 times as large as for Nucl (37, .8). For  $\text{NH}_4^+$ , the median was 1.8 times larger. For  $\text{SO}_4^-$ , the median was 1.3 times larger. The means and paired-t statistics are summarized in Table 3.
- (2) On Dual (47, .8, .8), the median  $\text{NO}_3^-$  value was 6.0 times as large as for Nucl (37, .8). For  $\text{NH}_4^+$ , the median was 1.5 times larger. For  $\text{SO}_4^-$ , the median was 0.9 times as large. The summarized data in Table 4 show that the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  means were significantly different but this was not true for  $\text{SO}_4^-$ .
- (3) The mean  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  levels on the second filter of 16 Dual (47, .8, .8) samples was only 5 to 8% of the levels found on the first filters. These data, and a comparison with What 41 and Nucl (47, .4) data, suggest that the 0.8  $\mu\text{m}$  pore size Nuclepore filters

sampled the ambient aerosol quite adequately. In consideration of the reported small size of ambient  $\text{SO}_4^{\pm}$  particles and laboratory filter efficiency data, this result is somewhat surprising.

The work reported in this paper is being continued. Field data for one teflon filter experiment and for an additional Dual (47, .8, .8) sampler experiment are now being analyzed.

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CHAPTER 6

SCORE-78 CASE STUDY FOR JULY 1, 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 Fig. 1. Basically there were two sampling lines, oriented north-south, with a site separation of about 1.5 kilometer. At the airport site (AT) and at sites 1-12 were located the 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. After reviewing all the raingage charts, there appear to be 12 cases where sampling of the rainfall from a single raincell was accomplished. Eight of these cases have been studied in some detail while the data from the remaining 4 cases have not yet undergone any interpretation.

RAINWATER CHEMISTRY FOR SHOWER ON 1 JULY 1978

On 30 June 1978, a hailstorm moved across the network between 1503 and 1550 CDT, and additional showers followed during the night. The total rainfall across the network varied from 0.28 inch to 1.20 inch. On the

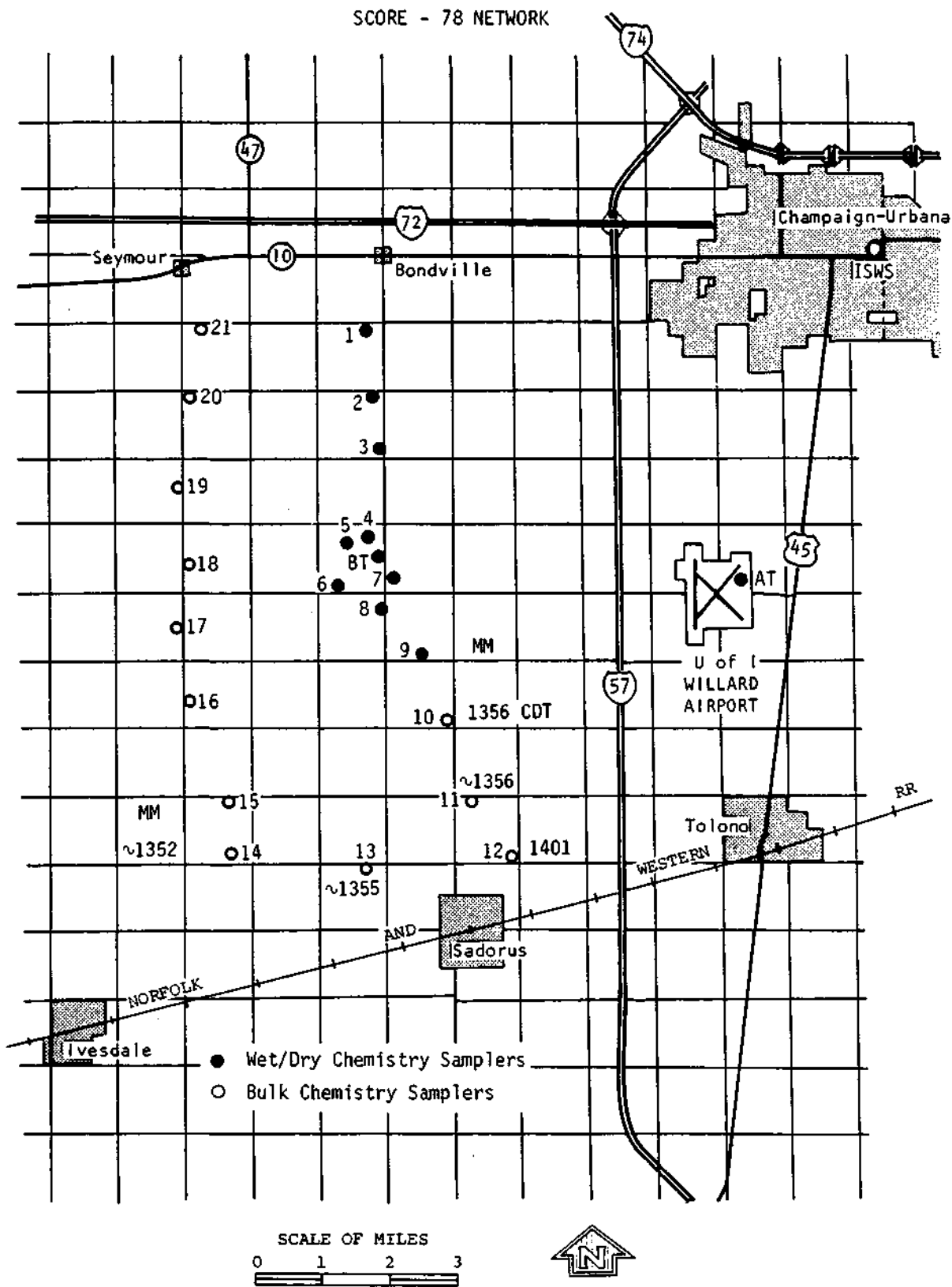


Figure 1. The SCORE-78 network showing the time of beginning of rainfall on 1 July 1978.

following day, a small shower formed in the southeastern portion of the network, giving rainwater samples at sites 9-15. From the rainfall start and end times shown on Figs. 1 and 2, it appears that the shower, which lasted only 5-10 minutes at any one site, formed on the network and then moved southeastward off the network. Figure 3 presents the sample volume and pH contours for the shower, with the asterisks denoting the locations of sites 9-15. The isopleths on the Figs. 3-5 were produced by a computer program. The program used an objective map analysis technique based on a successive corrections scheme developed by Barnes (1964, 1973) and modified by Achtemeier (1978). The sample volume pattern shows that the strongest portion of the raincell affected site 13 and the fact that site 11 had a greater sample volume than site 12 suggests that this small raincell was already dissipating as it moved southeastward off the network. The 1345 CDT surface weather observations for Willard Airport were  $T = 88^{\circ}\text{F}$ ,  $T_D = 74^{\circ}\text{F}$ ; wind was 10 knots from  $240^{\circ}$ ; there was 7/10 sky cover, 3/10 opaque; and haze reduced the visibility to 4 miles.

Table 1 contains the actual parameter values for the rainshower. Since 0.01 inch of rainfall was equivalent to a sample volume of about 8 ml, the sample volume values in Table 1 indicate that the rainfall for the shower varied from 0.04 inch to 0.17 inch. The on and off times refer to when the bulk precipitation chemistry samplers were installed and removed at each site. The fact that the exposure time was indeed short and that it had rained substantial amounts in the previous 24 hours imply that evaporation should have been negligible and that dry deposition effects would have been small. By comparing the sample volumes in Table 1 for gage 9W (the wet/dry at site 9) with gage 9 (the bulk collector at site 9) it is seen that about 3 ml might have been lost due to evaporation, and such a 10% correction could bring the ion concentrations for 9W into better agreement with those for 9. However, somewhat different collection efficiencies for the two rainwater chemistry samplers could also account for both the different sample volumes and the different ion concentrations in 9W versus 9. For Figs. 3-5, the data for gage 9 was used since gages 10-15 were also bulk collectors.

It is important to determine which ions produce similar spatial patterns for the single rainshowers. A useful tool to qualitatively examine the patterns are the computer produced contours in Figs. 4 and 5. There are, of course, no real ion concentrations in many portions of the figure, since rain did not fall over the entire network. However, the contours in the non-rain areas are the mathematical impressions resulting from the spatial variation among the seven discrete data points.

In Fig. 4, the spatial patterns for  $\text{SO}_4$  and  $\text{NO}_3$  are observed to be almost identical. Likewise, the spatial patterns for Ca and Mg are essentially identical but somewhat different than for  $\text{SO}_4$  and  $\text{NO}_3$ . This might be a reflection of the scavenging of Ca/Mg particles versus sulfur and nitrogen which have both particulate and gaseous components in the ambient air. Although particulate nitrate levels in the atmosphere are somewhat uncertain at this time due to measurement problems, the data do seem to be suggesting that the particulate nitrate is a small component compared to the gaseous forms (Spicer and Schumacher, 1977; Stensland and Bartlett, 1979). The implication is thus that much of the rainwater nitrate probably results from the scavenging of the gases  $\text{HNO}_3$  and  $\text{NO}_2$ . The fact that the  $\text{SO}_4$  and  $\text{NO}_3$  patterns in Fig. 4 are so similar suggest that gaseous scavenging of sulfur species was possibly very significant in this event.

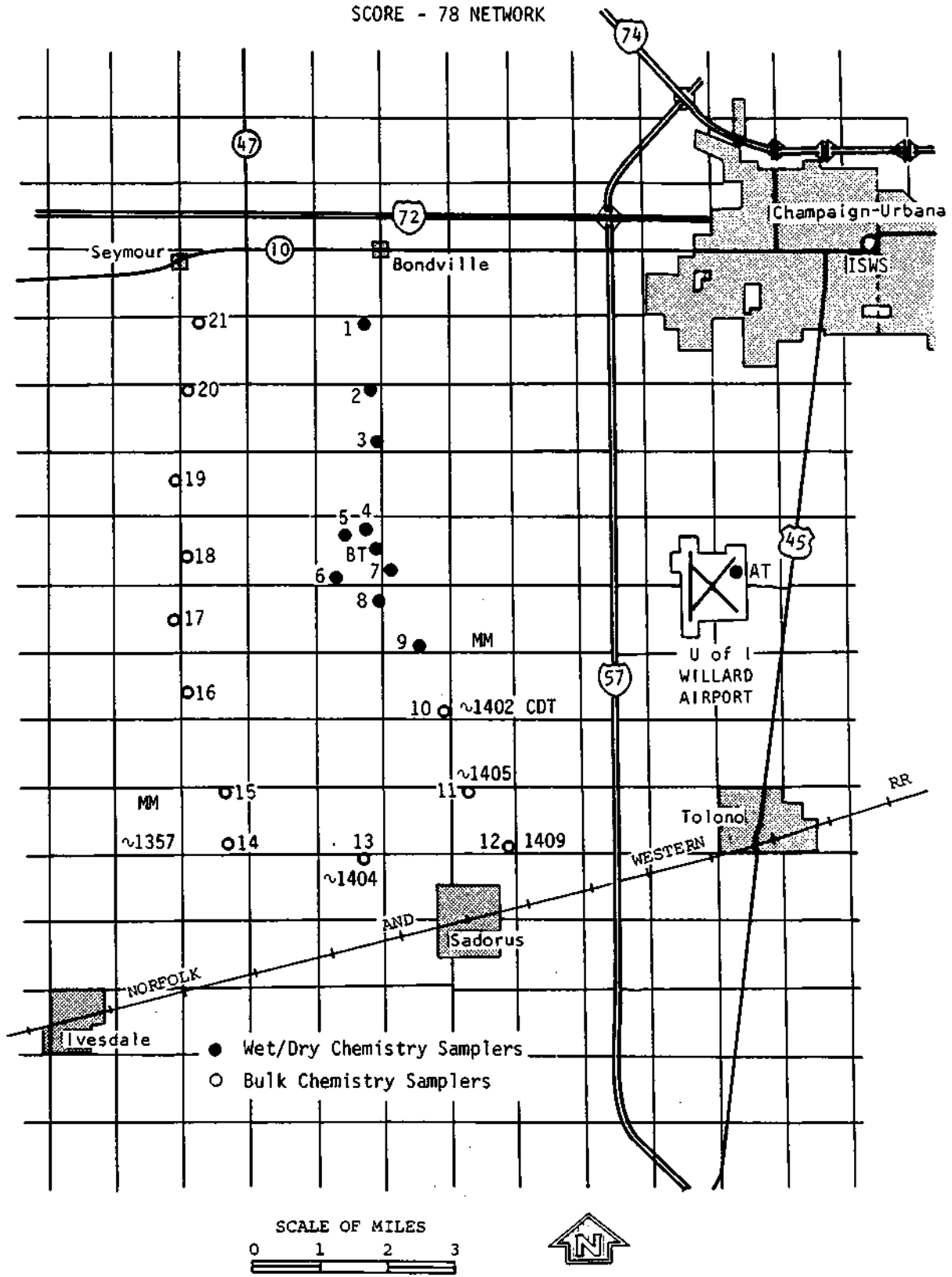


Figure 2. The time of ending of the rainfall for the 1 July 1978 single shower.

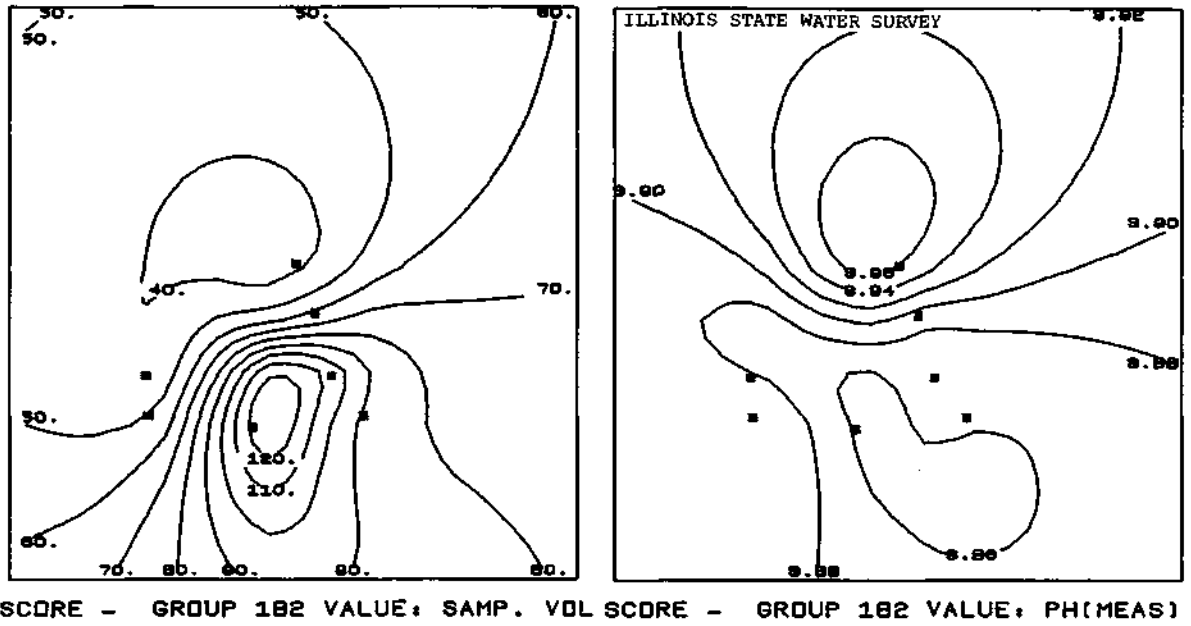


Figure 3. The spatial variation of sample volume (mL) and pH for the rainshower of 1 July 1978.



Table 1. Numerical data for the 1 July 1978 event in SCORE-78. Ion concentrations are expressed in microequivalents per liter.

Gage	Date On	Time On (CDT)	Date Off	Time Off (CDT)	Sample Volume (mL)	Measured pH	Measured Conductivity ( $\mu\text{mhos/cm}$ )	Calculated pH
9W	1 July	1216	1 July	1534	36.6	4.01	53.4	4.01
9	1 July	1217	1 July	1532	33.7	4.02	52.5	4.05
10	1 July	1210	1 July	1418	50.9	3.83	77.8	3.83
11	1 July	1205	1 July	1427	136.9	3.90	70.8	3.88
12	1 July	1158	1 July	1444	58.5	3.85	78.9	3.81
13	1 July	1151	1 July	1501	124.9	3.85	76.6	3.84
14	1 July	1145	1 July	1509	54.5	3.94	65.0	3.96
15	1 July	1139	1 July	1516	35.8	3.84	86.9	3.68

Gage	( $\text{SO}_4^-$ )	( $\text{NO}_3^-$ )	( $\text{Cl}^-$ )	( $\text{Ca}^{++}$ )	( $\text{Mg}^{++}$ )	( $\text{K}^+$ )	( $\text{Na}^+$ )	( $\text{NH}_4^+$ )	<u>anions</u> cations
9W	114.5	39.4	2.54	23.4	4.6	0.77	1.78	28.8	1.00
9	124.3	37.9	3.38	30.4	6.3	1.02	2.57	36.0	1.04
10	168.0	61.1	5.36	30.4	5.2	1.59	6.92	43.8	1.00
11	146.8	47.9	3.10	23.0	4.8	.74	2.13	36.0	.97
12	192.6	60.8	4.51	40.9	8.6	1.07	3.04	48.2	.94
13	161.4	51.1	2.54	19.5	3.1	.46	2.44	43.8	.98
14	141.6	45.5	2.54	36.4	4.4	1.05	2.35	-36.0	1.03
15	218.0	71.6	9.03	55.9	14.6	2.71	4.74	13.3	.79

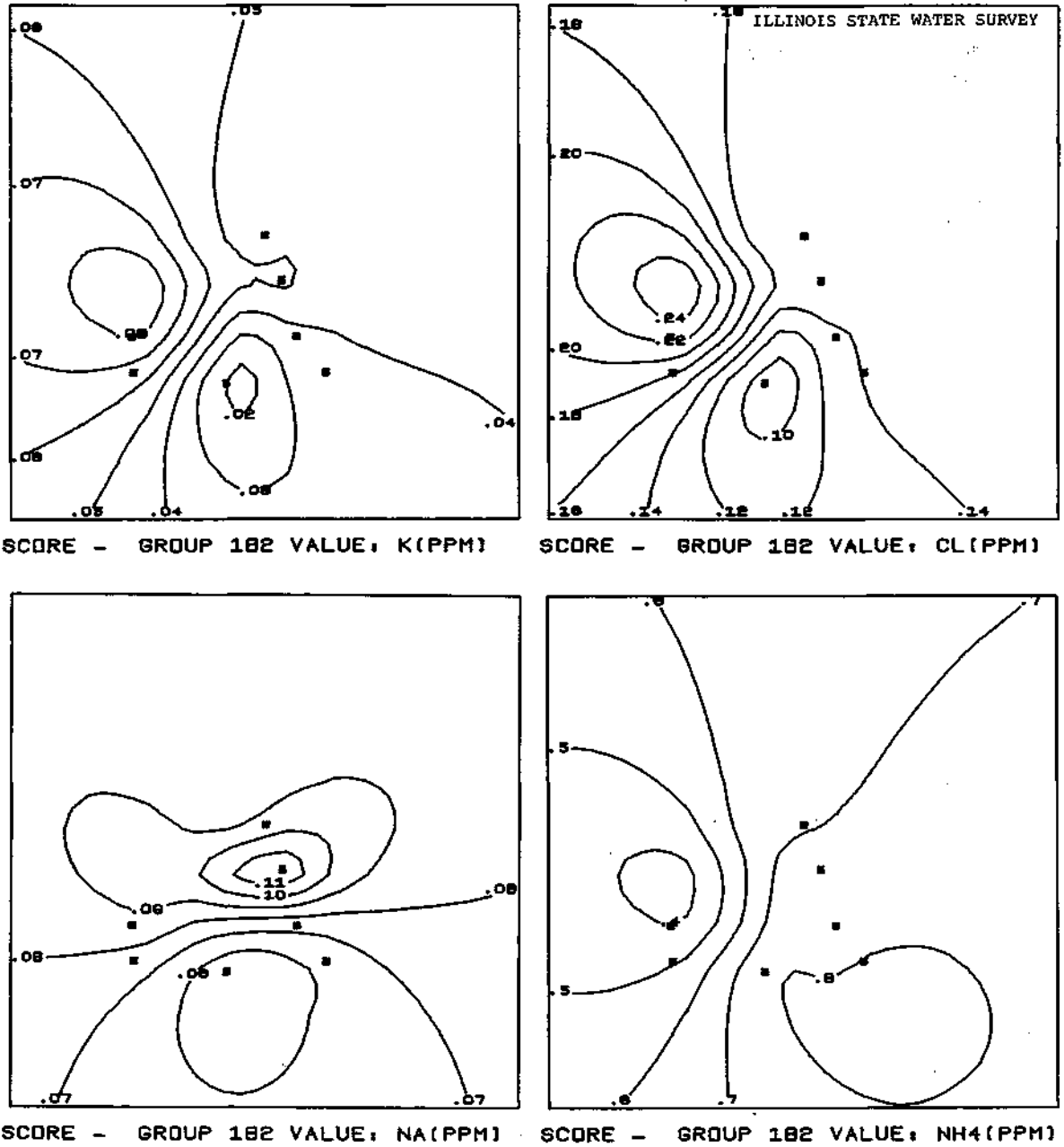


Figure 4. The spatial variation of ionic concentration of sulfate, nitrate, calcium, and magnesium in the rainwater from the shower of 1 July 1978.

It is also important to note the magnitude of the spatial variations. The SO<sub>4</sub> and NO<sub>3</sub> concentrations vary less across the raincell than do Ca, Mg, and sample volume, for either the contour values or the actual values in Table 1. This may result from Ca/Mg particles being scavenged as CCN particles and then being diluted the most in the strongest part of the raincell, where the sample volume at the ground is greatest. On the contrary, as this dilution of Ca/Mg is taking place in the cloud, a more continuous removal of the gaseous sulfur and nitrogen species would produce a smaller dilution effect for SO<sub>4</sub> and NO<sub>3</sub>.

Data for 4 more ions are presented in Fig. 5. The patterns for K and Cl are very similar, and are somewhat different than those for Ca and Mg in Fig. 4. The patterns for Na and NH<sub>4</sub> are both very different from any of the other ions. If part of the scavenged sulfate was ammonium sulfate particles, then the NH<sub>4</sub> pattern might be expected to have features of a particulate species. But this is not observed since the NH<sub>4</sub> pattern is much different than those for Ca, Mg, K, or Na. However, if the rainwater NH<sub>4</sub> is tending toward equilibrium with a constant ambient air level of NH<sub>3</sub>, then the highest rainwater NH<sub>4</sub> values would be found with the lowest pH (or highest H<sup>+</sup>) levels. In fact, the pH and NH<sub>4</sub> patterns in Figs. 4 and 5, or the data in Table 1, do indicate that this trend exists. Somewhat of an exception in Table 1 is gage 15, but the poor anion/cation ratio does suggest that some ion was probably measured or recorded incorrectly for this particular sample.

#### SUMMARY

In summary, the conclusions for the 1 July event are:

- (a) Some ions had very similar spatial concentration patterns and others had patterns unlike those for any measured ion.
- (b) As a corollary to (a), it follows that there cannot be a perfect inverse relationship between sample volume and ion concentrations, although the relationship should be best for particulate species such as Ca and Mg.
- (c) The spatial patterns for SO<sub>4</sub> and NO<sub>3</sub> compared to Ca and Mg suggested that gaseous scavenging of sulfur was significant.
- (d) A comparison of the NH<sub>4</sub> and pH patterns suggested, though not strongly, that the NH<sub>4</sub> pattern was at least partly a result of a trend towards chemical equilibrium with the ambient air ammonia concentration.

The generality of these conclusions will be evaluated with the other single raincell events from SCORE-78.

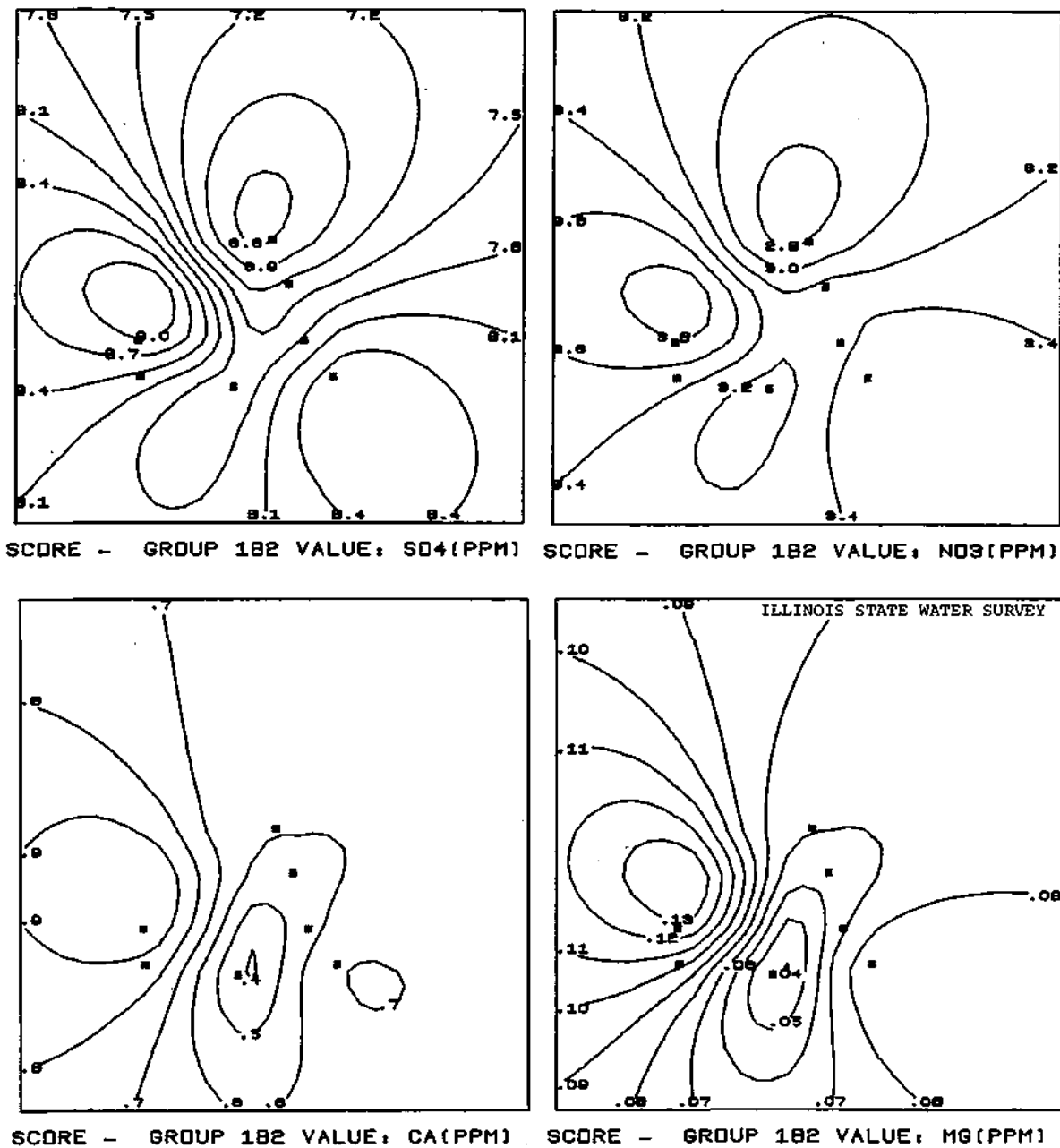


Figure 5. The spatial variation of ionic concentration of potassium, chloride, sodium, and ammonium in the rainwater from the shower of 1 July 1978.

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CHAPTER 7

SCORE-79

Gary J. Stensland

BRIEF SUMMARY

The field measurements for the Summer Chemistry Of Rain Experiment for 1979 (SCORE-79) will begin on 2 July. The major objective of SCORE-79 is to assess the surface rainfall chemistry variability. A second objective is to relate this variability to cloud parameters, air quality measurements on the ground and from airplanes, chemical source characteristics, and other meteorological measurements.

Two other large field measurement programs will be occurring at overlapping times and locations with SCORE-79. The University of Virginia, Illinois State Water Survey, and National Oceanic and Atmospheric Administration experiment (VIN) will investigate the relationship between surface weather and the development and growth of convective clouds and surface rainfall. The field measurements in VIN will be carried out between 1 July and 30 August in the area shown in Fig. 1. The scope of the measurements included in VIN and SCORE-79 are summarized in Table 1. As part of the MAP3S program, the measurements for the Central Illinois Rainfall Chemistry Experiment (CIRCE) will also be carried out in the area shown in Fig. 1. CIRCE measurements will, for the most part, be carried out between 9 July and 22 July with the facilities listed in Table 2.

The location of the summer 1979 precipitation chemistry samplers is shown in Fig. 2, with the PNL samplers being operated only during the CIRCE experiments. The large square box in Fig. 2 encompasses the raingages shown in Fig. 1. In Fig. 2, the dense north-south line of wet/dry samplers will hopefully provide additional small time and space scale cases such as were sampled in SCORE-78. The rest of the precipitation chemistry sites in Fig. 2 are designed to provide data on a larger scale, of several kilometers and a few hours, at the minimum.

In summary, SCORE-79 contains the sampling scale of SCORE-78 as well as a larger scale. This is possible due to the more than doubling of the number of chemistry collectors, including the older wet/drys used in 1978 plus 20 new units being built for SCORE-79. However, the major difference between the successive year SCORE experiments is that the extensive data base being collected for VIN and CIRCE will be available for the data interpretation phases of SCORE-79.

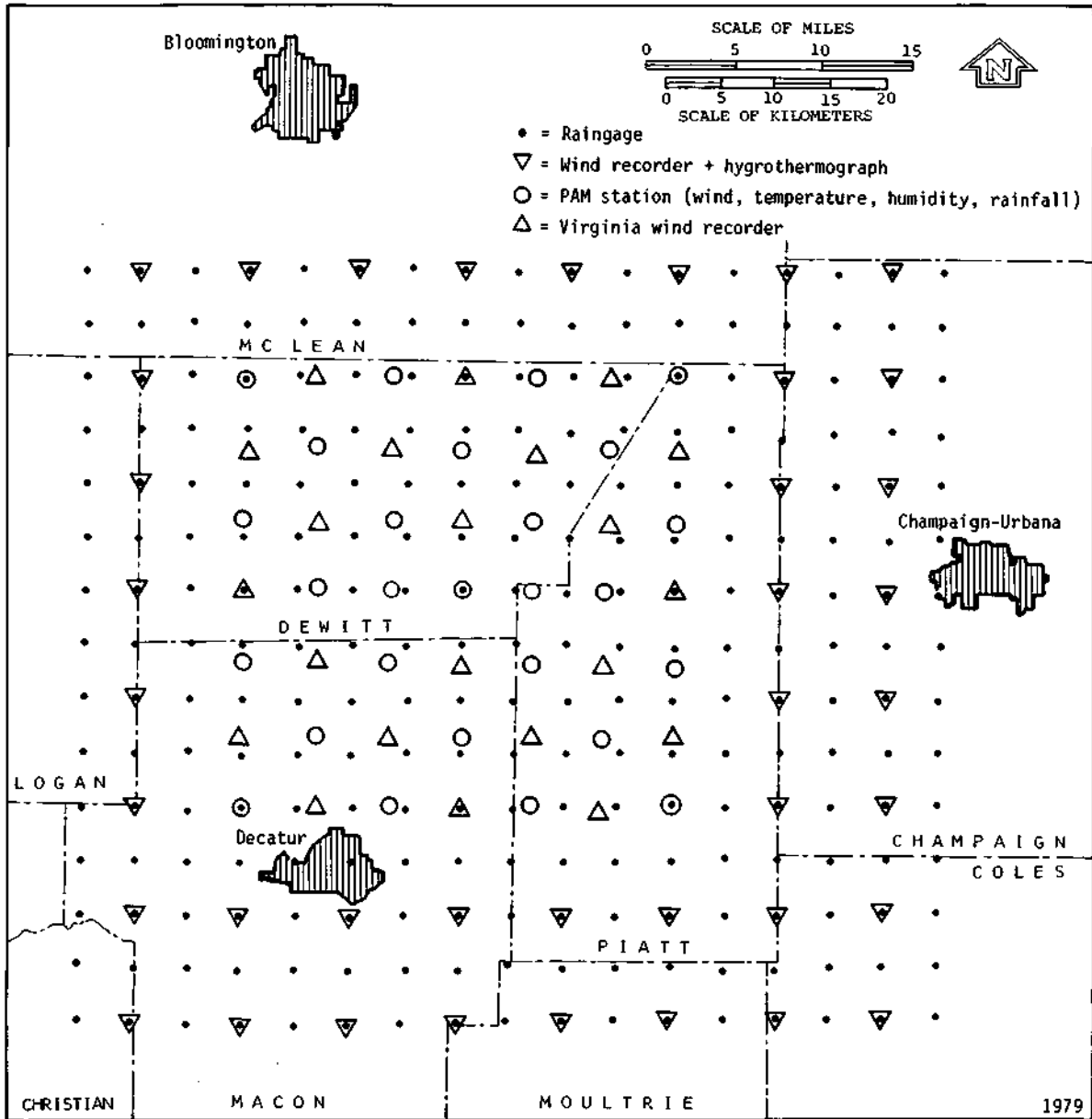


Figure 1. The network of raingages, surface wind, and hygrothermographs for the SCORE-79/VIN/CIRCE field experiment.

Table 1. List of facilities for the SCORE-79 and VIN experiments.

Equipment Item	Description
ISWS Raingage Network	Array of 260 recording raingages spaced at about 5 km intervals.
NCAR PAM (Portable Automated Mesomet) System	System of 27 remote weather stations, with 10-13 km spacing with a high-density network. Measurements at each station include surface winds, rainfall, temperature, pressure, and humidity. Telemetry to central recording and data-processing station occurs on a real-time basis.
Wind Network	About 22 additional wind sensors will be placed in the high density network to complement PAM. Between 20-30 additional wind sensors will be placed in a low density array around the HDN.
Pilot Balloon Facilities	Balloon soundings from three stations surrounding high density wind network. 30-minute sounding frequency anticipated for intensive study periods.
Radiosonde Facilities	Special NWS soundings from Peoria and/or Salem stations. Additional soundings from radar site at CMI airport.
CHILL Doppler Radar	Dual wavelength Doppler radar system for reflectivity and velocity measurements as well as for precipitation analysis.
Precipitation Chemistry Network	Array of 30 wet-dry precipitation chemistry collectors (HASL) distributed throughout network.
Trace gas and Aerosol Sampling Stations	Two ground stations on the network, including streakers, 24-hour low-vols, and a dichotomous sampler.



Table 2. Facilities for the CIRCE experiment.

#### ANL Facilities

A captive balloon (kytoon) PBL profiling system will be operated routinely, primarily through the early morning to early afternoon period, but extended as required by the VIN/SCORE/CIRCE cooperation. Profiles obtained by use of the kytoon packages will be supplemented with data derived from the WHAT (for Wind, Height, and Temperature) double-theodolite and radiosonde system. Acoustic probing of the lower atmosphere to determine mixed layer heights and temperature turbulence intensities will proceed at all times.

The University of Wisconsin LIDAR system will be operated in close collaboration with the ANL PBL studies.

A basic set micrometeorological data (especially fluxes of heat, moisture and momentum) will be measured.

#### BNL Facilities

The Britten Norman Islander is equipped for detailed investigation of air chemistry, at relatively low speed. It will be used for sub-cloud monitoring and for profiling throughout the daylight hours.

#### PNL Facilities

30 bulk precipitation chemistry samplers will be deployed in collaboration with ISWS. Chemical analysis of the collected rainfall will be conducted at ISWS.

The DC-3 aircraft is equipped for air- and cloud-sampling applications. It will be used in both roles during CIRCE, with emphasis on those occasions conducive to the generation of deep convective circulations.

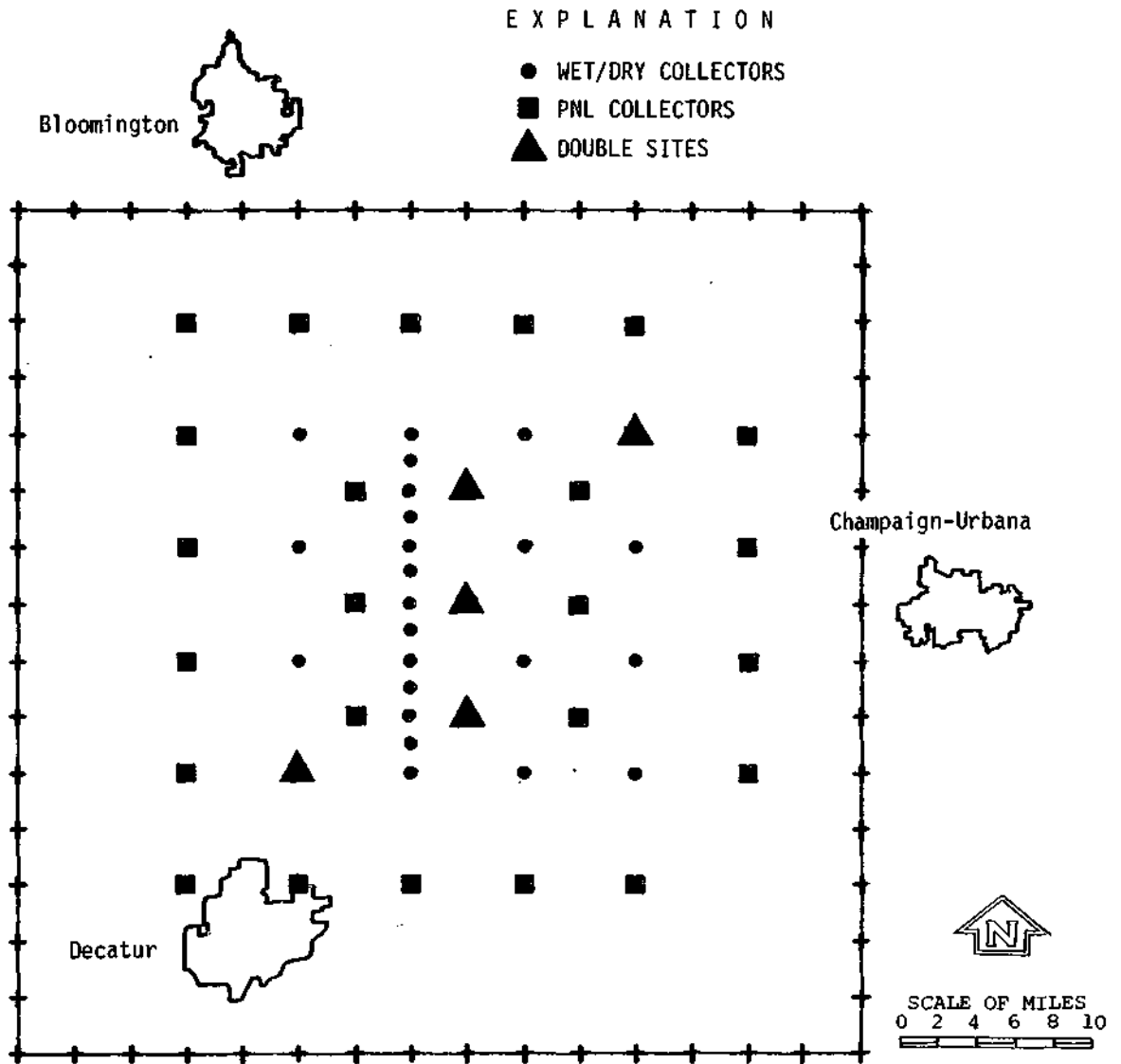


Figure 2. The network arrangement of wet/dry and bulk precipitation collectors for the SCORE-79 experiment.

CHAPTER 8

CALCULATING PRECIPITATION pH, WITH APPLICATION TO THE JUNGE DATA

Gary J. Stensland

INTRODUCTION

Three important reasons to have a good method to calculate the pH of precipitation are:

- (1) To be able to calculate the pH for those older data sets for which this parameter was not reported.
- (2) To be able to interpret the pH trend data for various precipitation chemistry data sets.
- (3) To provide a good quality control check on the chemical analyses for precipitation samples, by comparing the calculated pH with the measured pH. This is equivalent to checking the ion charge balance for the samples.

This Chapter will expand upon results presented in the two previous Progress Reports (Stensland, 1977; Stensland, 1978).

GENERAL METHOD

In a rain or melted snow solution, a charge balance is maintained. If a term called Net Ions is defined as

$$\begin{aligned} (\text{Net Ions}) = & (\text{SO}_4^{--}) + (\text{NO}_3^-) + (\text{Cl}^-) - (\text{Ca}^{++}) - (\text{Mg}^{++}) - (\text{NH}_4^+) \\ & - (\text{Na}^+) - (\text{K}^+), \end{aligned} \quad (1)$$

then the charge balance equation, consisting of the major ions, is

$$(\text{H}^+) - (\text{HCO}_3^-) = (\text{Net Ions}), \quad (2)$$

with each concentration in units of microequivalents per liter (ueq/L). Although Eq. 2 is not exactly correct, since some ions have not been included in (1), the relation has been found to work reasonably well for rain and snow samples. With the appropriate chemical equilibrium constants, it can be shown that  $(\text{HCO}_3^-) \approx 490 (\text{OH}^-)$  and for samples with  $\text{pH} < 8$ ,  $(\text{CO}_3^{--}) \ll (\text{HCO}_3^-)$ . Thus, the two ions OH and  $\text{CO}_3^{--}$  need not be considered in the charge balance equation.

Assuming that falling raindrops are in equilibrium with atmospheric carbon dioxide ( $P_{CO_2} = 320 \times 10^{-6}$  atm), then the chemical equilibria relationships can be used to give

$$(\text{HCO}_3^-) - K_H K_1 P_{CO_2} / (\text{H}^+) \quad (3)$$

where  $K_H$  is the constant in Henry's Law and  $K_1$  is the first dissociation constant of  $\text{CO}_2$  in water (for  $25^\circ\text{C}$ ,  $K_H = 0.034 \times 10^{-6}$   $\mu\text{eq/L/atm}$  and  $K_1 = 4.5 \times 10^{-1}$   $\mu\text{eq/L}$ ). Substituting Eq. 3 into Eq. 2 and solving the quadratic equation for  $(\text{H}^+)$  gives

$$(\text{H}^+) = \{ (\text{Net Ions}) \pm [ (\text{Net Ions})^2 + (4K_H K_1 P_{CO_2}) ]^{0.5} \} / 2. \quad (4)$$

In Eq. 4, only the plus sign in front of the bracketed term gives positive and therefore physically realistic solutions. Equation 4 is rewritten in terms of pH as

$$\text{pH} = +6 - \log_{10} \{ \{ (\text{Net Ions}) + [ (\text{Net Ions})^2 + (4K_H K_1 P_{CO_2}) ]^{0.5} \} / 2 \} \quad (5)$$

where the +6 factor results from the fact that the  $\mu\text{eq/L}$  concentration unit is required for the terms in Eq. 5. Figure 1 illustrates solutions of Eq. 5 for  $5^\circ\text{C}$  and  $25^\circ\text{C}$  (used to determine equilibrium constants,  $K_H$  and  $K_1$ ), and various values of  $P_{CO_2}$ . For example, for typical analysis conditions (curve E) and Net Ions equal to -100, the calculated pH is 7.31. With curve A the pH is 5.84 and with curve F the pH is 8.02. For the remainder of this paper, curve E will be used.

From 1959 to 1964 the U. S. Public Health Service collected monthly precipitation samples at 39 locations throughout the continental United States. Equation 5 was used to calculate the pH values for this data set of 1295 samples.  $\text{Mg}^{++}$  was not reported so it was estimated by assuming it to be related to  $\text{Ca}^{++}$ , with the  $(\text{Ca}^{++})/(\text{Mg}^{++})$  ratio being assigned regional values based on a very limited data base (principally the data from Lodge, 1966). The regional ratio values,  $>1$  except for coastal locations, selected for the continental United States are shown in Fig. 2. The individual station ratios used to select the regional ratios are also indicated.

The calculated versus measured pH values for the 1959-64 U. S. Public Health Service data are shown in Fig. 3. The pH calculated from the median Net Ion value for each measured pH class (0.1 pH unit in width) is plotted with a solid circle on the sensitivity bars. For example there were 50 samples with a measured pH of 5.5, and the median Net Ion value for these 50 samples was -7.77, producing a calculated pH of 6.23. The regional ratios in Fig. 2 were used for the calculations since  $(\text{Mg}^{++})$  was not reported. The upper limit values of the sensitivity bars in Fig. 3 resulted when regional ratios equal to 0.5 times those in Fig. 2 were used in calculating the pH. Likewise the lower limits resulted when twice the regional ratio values were used to calculate the pH. The line segments which have been fitted to the data points in Fig. 3 can be used to correct the calculated pH values such that they will agree with the measured pH values. The correction equations for the three line segments are:

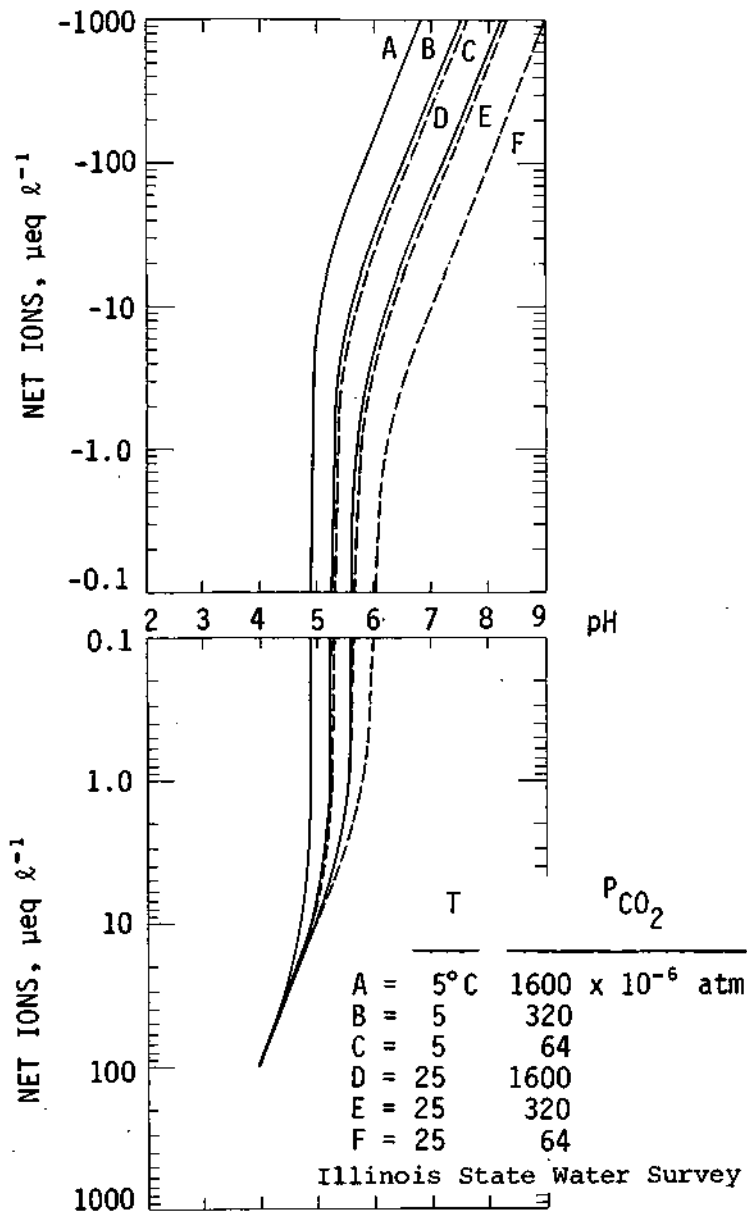


Figure 1. The concentration of Net Ions versus pH for precipitation samples with different values of T (temperature) and p<sub>CO2</sub>.



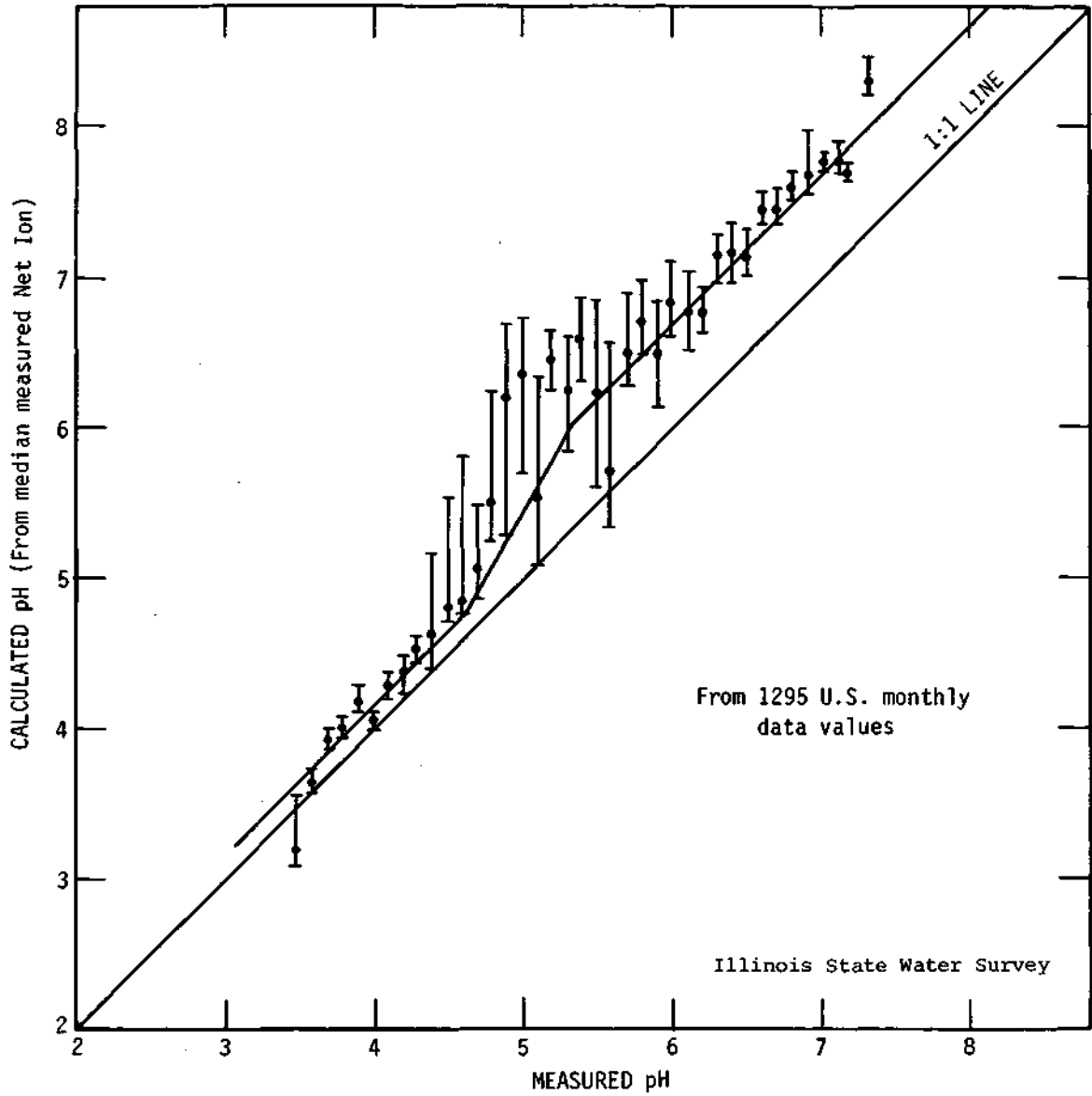


Figure 3. Calculated versus measured pH values for the 1959-64 U. S. Public Health Service data.

$$(a) \text{ pH (corrected) = pH (calculated) - C,} \quad (6)$$

where C = 0.70 for pH (calculated) > 6.0 and C = 0.15 for pH (calculated) < 4.8, and

$$(b) \text{ pH (corrected) = 0.54 pH (calculated) + 2.06,} \quad (7)$$

for 4.8 < pH (calculated) < 6.0.

The data reported by Granat (1972), for 1522 monthly precipitation samples from the European chemistry network, were also used to calculate the pH. In this case the measured alkalinities were used to calculate the pH values. Alkalinity (alk) is defined as

$$\text{alk} = (\text{HCO}_3^-) + (\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+). \quad (8)$$

Again, since  $(\text{CO}_3^{2-})$  and  $(\text{OH}^-)$  need not be considered for precipitation samples,

$$\text{alk} = (\text{HCO}_3^-) - (\text{H}^+) \quad (9)$$

and from Eq. 2. This can be rewritten as

$$\text{alk} = - \text{Net Ions.} \quad (10)$$

Thus for Granat's data, Eq. 5, with -alk substituted for Net Ions, was used to calculate the values which are plotted in Fig. 4. The lines corresponding to the empirical Eqs. 6 and 7 are shown on Fig. 4 and again fit the data quite well. A firm explanation as to why Eqs. 6 and 7 are needed for precipitation data is not yet available.

#### COMPARISON OF THREE MODELS TO CALCULATE pH

With respect to calculating pH, Eq. 1 can be compared with two other somewhat different approaches in the literature. Granat (1972) assumed that all the  $\text{Na}^+$  and  $\text{Cl}^-$  were due to sea salt and thus neither ion was included in his equations. Also the other ions were corrected for sea salt. Granat's final equation, expressed in the form of Eq. 1, was

$$\begin{aligned} (\text{Net Ions})_{\text{GRAN}} = & (\text{SO}_4^{2-} - \text{SSSO}_4^{2-}) + (\text{NO}_3^-) - (\text{Ca}^{++} - \text{SSCa}^{++}) - (\text{Mg}^{++} \\ & - \text{SSMg}^{++}) - (\text{NH}_4^+) - (\text{K}^+ - \text{SSK}^+). \end{aligned} \quad (11)$$

The SS prefix for an ion indicates that the quantity is the amount due to sea salt,  $\text{Na}^+$  being used by Granat as the reference sea salt ion.

Cogbill and Likens (1974) also corrected each ion for sea salt but included  $\text{Na}^+$  or  $\text{Cl}^-$  in the final equation. For example, if  $(\text{Na}^+)/(\text{Cl}^-)$  was greater than the ratio for sea water, then the excess  $\text{Na}^+$  was included in



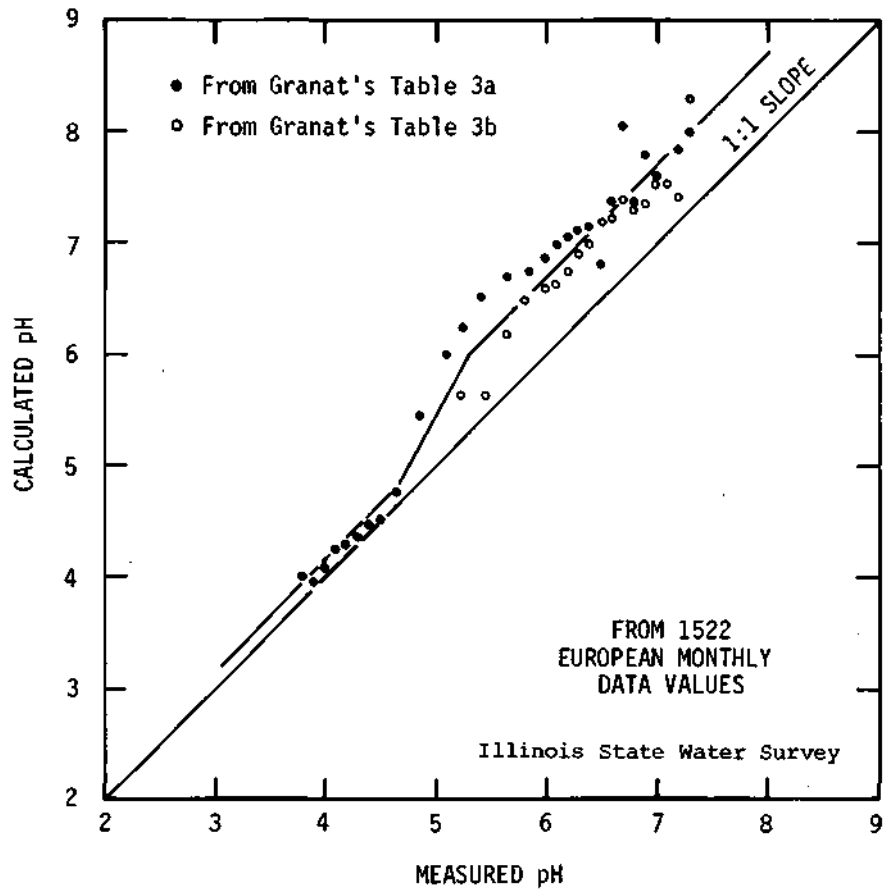


Figure 4. Calculated versus measured pH values for 1522 European monthly data values (Granat, 1972).

the equation using  $\text{Cl}^-$  as the base ion for making the sea salt correction. In this case, the final equation, expressed in the form of Eq. 1, was

$$\begin{aligned}
 (\text{Net Ions})_{\text{COG}} = & (\text{SO}_4^{2-} - \text{SSO}_4^{2-}) + (\text{NO}_3^-) - (\text{Ca}^{++} - \text{SSCa}^{++}) - (\text{Mg}^{++} \\
 & - \text{SSMg}^{++}) - (\text{NH}_4^+) - (\text{Na}^+ - \text{SSNa}^+) - (\text{K}^+ - \text{SSK}^+).
 \end{aligned}
 \tag{12}$$

Equations 11 and 12 were used in place of Eq. 1 to produce equations analogous to Eq. 5. The three pH equations were then applied to the same data set, namely Junge's 1955-1956 data for 63 sites in the United States (Junge, 1963).  $\text{Mg}^{++}$  was not reported by Junge so the regional ratios of  $\text{Ca}^{++}$  to  $\text{Mg}^{++}$  in Fig. 2 were used to estimate  $\text{Mg}^{++}$ , as previously discussed. To obtain annual averages for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , the quarterly values for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  reported by Junge (1958) were weighted with the quarterly precipitation at the sites. These results are tabulated in Table 1, along with other data to be discussed later in this paper. The site abbreviations in Table 1 are those used by Junge and Gustafson (1956).

The pH results for the three models are shown in Figs. 5 and 6. In Fig. 5 the pH values from Eq. 5 are plotted on the abscissa and the values, with the assumptions of Cogbill and Likens, are plotted on the ordinate. The agreement is very good with a linear correlation coefficient of  $r = 0.99$ . In Fig. 6, the results from Eq. 5 are compared with the pH values using Granat's assumptions. The agreement is not as good, with  $r = 0.90$  and the line of best fit being  $y = 0.96x$ . The pH values calculated with Granat's sea salt assumptions are generally lower than those calculated by Stensland with Eq. 5, a change which is in the same direction as that resulting from the empirical correction in Eqs. 6 and 7. Therefore, if the empirical corrections in Eq. 6 and 7 are not used, then the pH calculated with Granat's assumptions would probably agree better with measured pH values than if the assumptions of Cogbill and Likens or Stensland were used.

Although  $\text{pH}_{\text{Sten}}$  and  $\text{pH}_{\text{Cog}}$  in Fig. 5 agree very well, a problem still exists and is demonstrated with the data in Table 2. The first two columns contain data which were presented in Table 1 while the third column contains values from Fig. 3 of Cogbill and Likens (1974). For the data with an asterisk, the agreement between columns two and three is rather poor. This is quite important since these particular data points have been crucial in the argument that lower pH values extend further west and south in recent years versus the mid-1950's (Cogbill and Likens, 1974).

To further understand the data disagreements in Table 2, the Master's thesis by Cogbill was consulted (Cogbill, 1975). Equation (2) on page 6 of this document gives the excess  $\text{Na}^+$  as  $-([\text{C}^-] - 1.17[\text{Na}^+])$ , which is correct if  $(\text{C}^-)/(\text{Na}^+) > 1.17$ . Following this equation is found the statement, "Moreover, when the ratio of  $\text{C}^-$  to  $\text{Na}^+$  is greater than 1.17, all references to  $\text{Na}^+$  are changed to  $\text{C}^-$  and the notation in the additional term is reversed." This statement, taken literally, suggests that Cogbill might have used the term  $-([\text{Na}^+] - 1.17[\text{C}^-])$ , which is incorrect. Although the discussion by Cogbill (1975) is confusing, the following calculation was tried. For the Junge data, there is an excess of  $\text{Na}^{++}$  over that expected from sea salt,

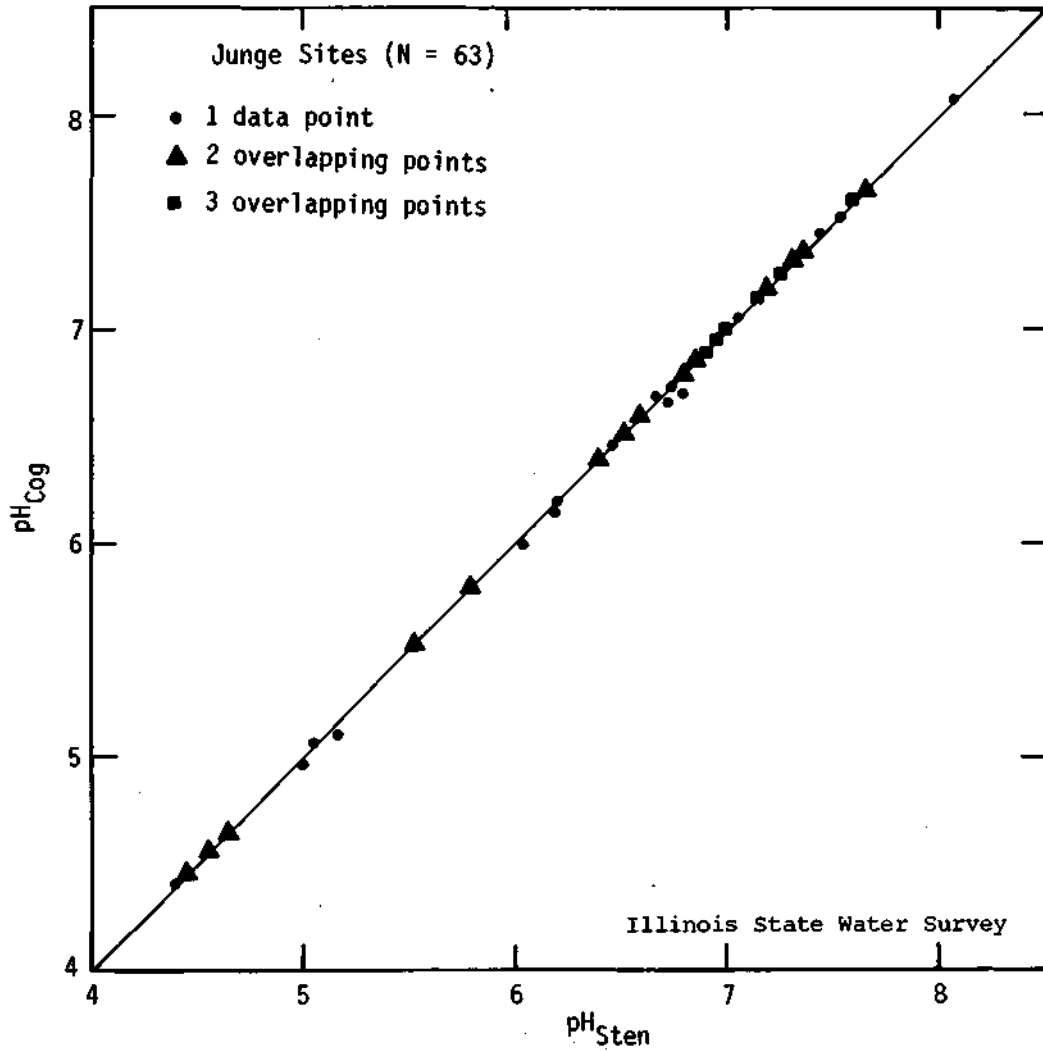


Figure 5. The pH calculated with the assumptions made by Cogbill and Likens versus the pH calculated with the assumptions by Stensland, for the 1955-56 Junge data.

Table 1. Calculations using Junge 1955-56 data.  
For Concentrations are in milligrams per liter.

Junge Sites	(NO <sub>3</sub> <sup>-</sup> )	(NH <sub>4</sub> <sup>+</sup> )	Esti- mated (Ca <sup>++</sup> / Mg <sup>++</sup> )	pH <sub>Sten</sub>	pH <sub>Cog</sub>	pH <sub>Gran</sub>	Correc- ted pH	Upper pH <sub>Sten</sub>	Lower pH <sub>Sten</sub>	Differ- ences of prev. 2 Col.	pH <sub>Sten</sub> (Mg <sup>++</sup> / Ca <sup>++</sup> )	pH <sub>Sten</sub> (Ca <sup>++</sup> / Ca <sup>++</sup> )	(Ca <sup>++</sup> / Sten= 0.2)
AK (Akron, OH)	1.05	.10	4	4.55	4.55	4.55	4.40	4.8	4.5	0.38	4.5	4.2	4.2
AL (Albany, NY)	.76	.05	4	4.65	4.65	5.60	4.50	4.9	4.6	0.30	4.6	4.3	4.4
AM (Amarillo, TX)	.53	.06	14	7.25	7.25	7.20	6.55	7.3	7.2	0.09	7.3	4.9	4.7
AQ (Albuquerque, NM)	.84	.09	14	7.65	7.65	7.65	6.95	7.7	7.6	0.08	7.7	5.4	4.5
BI (Bismark, ND)	.68	.20	4	6.95	6.95	6.70	6.25	7.1	6.8	0.29	7.5	4.8	4.9
BO (Boise, ID)	.43	.10	4	6.75	6.75	6.20	6.05	6.9	6.7	0.23	6.7	5.4	6.1
BR (Brownville, TX)	.35	.07	6	8.05	8.05	7.00	7.35	8.1	8.0	0.09	8.1	7.7	7.5
BS (Boston, MA)	.47	.07	4	4.40	4.40	4.35	4.25	4.5	4.4	0.10	4.4	4.3	4.3
BU (Burlington, VT)	1.12	.11	4	4.55	4.55	4.50	4.40	4.8	4.5	0.33	4.5	4.2	4.3
CA (Caribou, ME)	.52	.09	4	5.05	5.05	4.80	4.79	6.0	4.8	1.22	4.9	4.3	4.4
CH (Charleston, SC)	.22	.02	4	5.80	5.80	5.00	5.19	6.3	5.5	0.82	5.6	4.7	5.0
CO (Columbia, MO)	.58	.08	4	7.30	7.30	7.30	6.60	7.5	7.2	0.27	7.2	4.6	4.5
DE (Des Moines, IA)	.75	.15	4	7.45	7.45	7.40	6.75	7.6	7.4	0.25	7.4	4.6	4.3
EL (El Paso, TX)	.62	.25	4	7.60	7.60	7.50	6.90	7.7	7.5	0.23	7.5	5.1	4.5
EY (Ely, NV)	.39	.08	4	7.60	7.60	7.55	6.90	7.7	7.5	0.21	7.6	6.0	4.7
FO (Ft Worth, TX)	.55	.11	6	6.90	6.90	6.85	6.20	7.1	6.8	0.23	6.9	4.7	4.7
FR (Fresno, CA)	.43	.48	4	7.05	7.05	7.00	6.35	7.1	7.0	0.08	7.0	6.8	6.9
GI (Grand Island, NE)	.70	.11	4	7.60	7.60	7.55	6.90	7.7	7.5	0.21	7.5	6.3	4.9
GJ (Grand Junct., CO)	.65	.11	14	7.30	7.30	7.25	6.60	7.4	7.2	0.13	7.4	4.2	4.1
GL (glasgow, MT)	.43	.25	14	7.15	7.15	7.05	6.45	7.2	7.1	0.09	7.2	4.9	4.8
GO (Goodland, KS)	.54	.08	14	7.00	7.00	6.90	6.30	7.1	7.0	0.10	7.1	5.1	5.1
GR (Grand Rapids, MI)	1.04	.14	4	5.80	5.80	5.55	5.19	6.7	5.1	1.59	5.3	4.3	4.3
GV (Greenville, SC)	.34	.01	4	5.55	5.55	5.15	5.06	6.1	5.3	0.81	5.4	4.7	5.0
HA (Hatleras, NC)	.21	.02	.6	7.00	7.00	6.50	6.30	7.4	6.6	0.75	5.3	4.7	6.1
HE (Helena, MT)	.26	.03	4	6.60	6.60	6.35	5.90	6.9	6.3	0.54	6.4	4.5	4.6
HU (Huron, SD)	1.16	.21	4	7.25	7.25	7.20	6.55	7.5	7.1	0.33	7.2	4.3	4.2
IF (Int. Falls, MN)	.90	.12	4	6.70	6.70	6.55	6.00	6.9	6.5	0.46	6.6	4.5	4.6

IN (Indianapolis, IN)	.53	.07	4	6.85	6.85	6.70	6.15	7.1	6.6	0.44	6.7	4.4	4.4
JA (Jackson, MS)	.26	.02	6	6.50	6.50	6.20	5.80	6.6	6.4	0.25	6.5	5.0	5.4
JV (Jacksonville, FL)	.21	.04	4	7.00	7.00	6.75	6.30	7.1	6.9	0.24	6.9	5.2	5.5
LA (Las Vegas, NV)	1.15	.09	4	7.65	7.65	7.65	6.95	7.8	7.6	0.22	7.6	5.3	4.5
LI (Little Rock, AR)	.19	.05	14	7.35	7.35	7.30	6.65	7.4	7.3	0.08	7.4	5.8	5.1
LK (Lake Charles, LA)	.29	.02	6	7.20	7.20	7.10	6.50	7.3	7.1	0.16	7.2	5.9	5.7
LO (Lorado, TX)	.83	.11	6	7.55	7.55	6.90	6.85	7.7	7.5	0.21	7.6	4.2	4.0
MA (Madison, WI)	1.12	.26	4	6.95	6.95	6.75	6.25	7.2	6.8	0.33	6.9	4.6	4.6
ME (Medford, OR)	.27	.02	4	6.60	6.60	6.60	5.90	6.8	6.5	0.32	6.5	5.0	5.4
MG (Montgomery, AL)	.30	.03	4	6.40	6.40	5.95	5.70	6.6	6.3	0.31	6.3	5.3	6.1
MO (Mobile, Al)	.17	.02	6	6.35	6.35	5.20	5.65	6.5	6.3	0.19	6.4	5.1	6.0
NA (Nashville, TN)	.21	.01	14	6.50	6.50	6.10	5.80	6.6	6.4	0.17	6.6	4.7	4.8
NU (Nantuck.IS., MA)	.37	.02	.6	5.15	5.10	4.90	4.84	6.9	4.6	2.28	4.4	4.3	4.6
PO (Pocatello, ID)	.29	.02	4	6.85	6.85	6.75	6.15	7.1	6.7	0.35	6.8	4.6	4.7
RE (Redlands, CA)	.29	.14	4	6.20	6.20	6.10	5.50	6.5	6.0	0.42	6.1	5.0	5.7
RO (Roanoke, VI)	.84	.06	4	4.45	4.45	4.40	4.30	4.5	4.4	0.12	4.4	4.3	4.3
SA (Salem, OR)	.05	.05	4	6.05	6.00	5.55	5.35	6.3	5.9	0.37	5.9	5.1	6.1
SC (Scottsbluff, NE)	.70	.24	14	7.15	7.15	7.05	6.45	7.2	7.1	0.07	7.2	6.3	6.2
SD (San Diego, CA)	.59	.37	4	6.20	6.15	4.95	5.50	6.7	5.5	1.18	5.8	4.4	4.4
SH (Sheridan, WY)	.31	.08	14	6.80	6.80	6.75	6.10	6.9	6.8	0.11	6.9	4.9	5.0
SM (Santa Maria, CA)	.31	.49	4	6.95	6.95	6.70	6.25	7.0	6.9	0.08	6.9	6.8	6.9
SN (San Angelo, TX)	.87	.22	6	7.35	7.35	7.25	6.65	7.4	7.3	0.18	7.3	5.0	4.7
SP (Spokane, WA)	.20	.02	4	5.55	5.55	5.05	5.06	6.2	5.2	0.95	5.3	4.6	4.9
SS (S. St. Marie, MI)	.91	.11	4	6.90	6.90	6.85	6.20	7.1	6.7	0.47	6.8	4.3	4.3
ST (St. Cloud, MN)	1.19	.16	4	6.90	6.90	6.85	6.20	7.1	6.8	0.31	6.8	4.7	4.7
TA (Tatoosh, WA)	.18	.11	1	6.80	6.70	4.20	6.10	7.3	5.6	1.70	4.7	4.3	4.4
TL (Tallahassee, FL)	.16	.02	6	6.45	6.45	6.05	5.75	6.6	6.2	0.26	6.4	5.0	5.5
TP (Tampa, FL)	.14	.04	6	6.40	6.40	5.85	5.70	6.6	6.2	0.36	6.4	4.8	5.0
TU (Tuscon, AR)	.35	.08	14	7.15	7.15	6.85	6.45	7.2	7.1	0.07	7.2	6.3	6.3
WA (Washington, DC)	.54	.09	4	4.45	4.45	4.40	4.30	4.5	4.4	0.10	4.4	4.3	4.4
WC (Witchita, KA)	.50	.12	14	7.20	7.20	7.15	6.50	7.3	7.2	0.10	7.3	4.9	4.7
WE (West Palm B., FL)	.23	.07	4	6.70	6.65	6.30	6.00	6.9	6.6	0.29	6.6	5.0	5.5
WI (Winnemucca, NV)	.16	.02	4	7.25	7.25	6.85	6.55	7.3	7.2	0.17	7.2	6.6	6.6
WM (Williamsport, PA)	1.31	.09	4	4.65	4.65	4.45	4.50	5.2	4.5	0.68	4.6	4.2	4.2
YA (Yakima, WA)	.35	.13	4	6.80	6.80	6.15	6.10	6.9	6.7	0.19	6.7	5.9	6.4

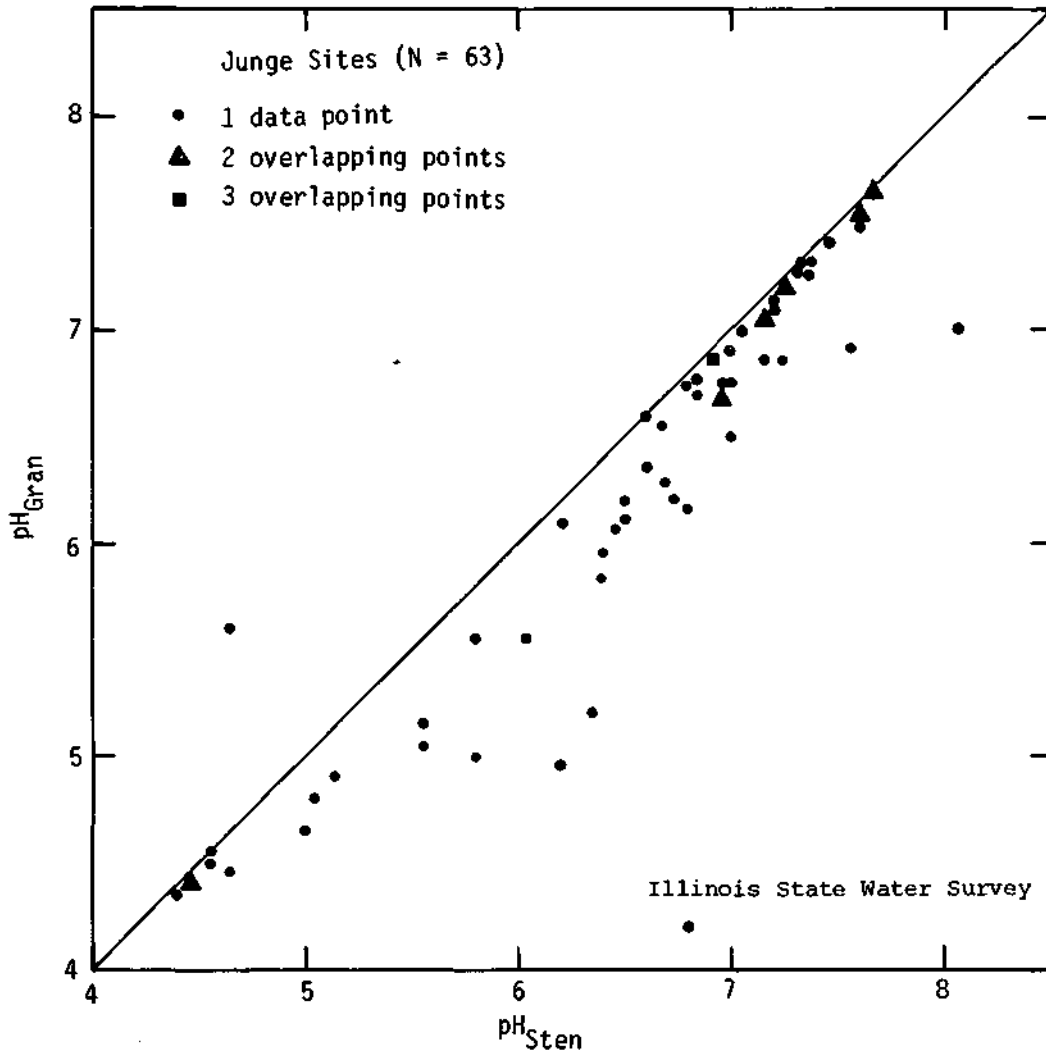


Figure 6. The pH calculated with the assumptions made by Granat versus the pH calculated with the assumptions by Stensland, for the 1955-56 Junge data.

Table 2. Calculations of pH for the Junge data.

<u>Junge Sites</u>	<u><sup>pH</sup>Sten</u>	<u><sup>pH</sup>Cog</u>	<u><sup>pH</sup>Cog-1974</u>
AK (Akron, OH)	4.55	4.55	4.45
AL (Albany, NY)	4.65	4.65	4.63
BU (Burlington, VT)	4.55	4.55	4.45
CA (Caribou, ME)	5.05	5.05	4.94
CH (Charleston, SC)	5.80	5.80	5.96
GR (Grand Rapids, MI)	5.80	5.80	5.35*
GV (Greenville, SC)	5.55	5.55	5.25
HA (Hatleras, NC)	7.00	7.00	6.00*
IN (Indianapolis, IN)	6.85	6.85	5.81*
MA (Madison, WC)	6.95	6.95	5.94*
MG (Montgomery, AL)	6.40	6.40	5.61*
NA (Nashville, TN)	6.50	6.50	5.73*
NU (Nantucket, MA)	5.15	5.10	5.42
RO (Roanoke, VA)	4.45	4.45	4.47
SS (S. St. Marie, MI)	6.90	6.90	5.76*
WA (Washington, DC)	4.45	4.45	5.09*
WM (Williamsport, PA)	4.65	4.65	4.42

for every site. The correct term for Eq. (12),  $[\text{Na}^+ - \text{SSNa}^+] = [(\text{Na}^+) - 0.86 (\text{Cl}^-)]$ , was replaced by the incorrect term -  $[(\text{Na}^+) - 1.17 (\text{Cl}^-)]$ . When this incorrect equation was applied to sites HA, MA, M6, and NA, values reasonably close to those in column three of Table 2 were indeed calculated.

#### pH CALCULATIONS WITH THE JUNGE DATA

The purpose of this section is to present pH isopleth maps for the 1955-56 Junge data, considering various assumptions, and sensitivity tests for these assumptions. The actual numerical data that were used are listed in Table 1. The isopleths on the figures to follow were produced by a computer program. The program used an objective map analysis technique based on a successive corrections scheme developed by Barnes (1964, 1973) and modified by Achtemeier (1978).

Figure 7 shows the location of the 62 Junge sites used in this present analysis, the Junge sites in Bermuda (BE) and Nova Scotia (SV) are not included. The one year average nitrate and ammonium ion concentrations using the precipitation weighted values mentioned earlier are displayed in Figs. 8 and 9. It is possible that the weighting scheme may have introduced some inaccuracy since a rain chemistry sample was probably not available for every rain and snow event. A more severe caution, though, must be placed on the values for some of the western sites where precipitation or chemical data were not available for several of the months. In particular, the ammonium and nitrate highs in California and Nevada, respectively, resulted from data for six months or less out of the twelve months of sampling.

The calculated pH shown in Fig. 10, and listed as  $\text{pH}_{\text{Sten}}$  in Table 1, resulted from using Eqs. 1 and 5, the ion concentration data available in Junge (1963), the average  $(\text{NO}_3^-)$  and  $(\text{NH}_4^+)$  in Table 1, and the  $(\text{Mg}^{++})$  from our best estimate of the  $(\text{Ca}^{++}/\text{Mg}^{++})$  ratio for each site. Pennsylvania and West Virginia are in the pH 4.5 region while essentially all sites west of a line from Alabama to Lake Michigan have pH 6.5, except for western Washington (the Spokane site).

The calculated pH shown in Fig. 11, and listed as  $\text{pH}_{\text{Cog}}$  in Table 1, resulted from using the same ion concentration data as for Fig. 10 but Eqs. 12 and 5 were used. The isopleth pattern in Figs. 10 and 11 are virtually identical with only very minor shifts evident in southwestern Washington and west of Florida. As pointed out with Table 2, Cogbill and Likens (1974) produced rather different calculated pH values for the northeast, with their pH = 5.60 isopleth enclosing a much larger geographic area than that shown in Fig. 11 (cf. Fig. 3 in Cogbill and Likens, 1974).

The calculated pH shown in Fig. 12, listed as  $\text{pH}_{\text{Gran}}$  in Table 1, resulted from using the same ion concentrations as for Fig. 10, but Eqs. 11 and 5 were used. When Fig. 10 and Fig. 12 are compared it is clear that Fig. 12 depicts a greater degree of precipitation acidity. Significantly lower pH levels appear for the extreme northwest, southern California and somewhat more generally



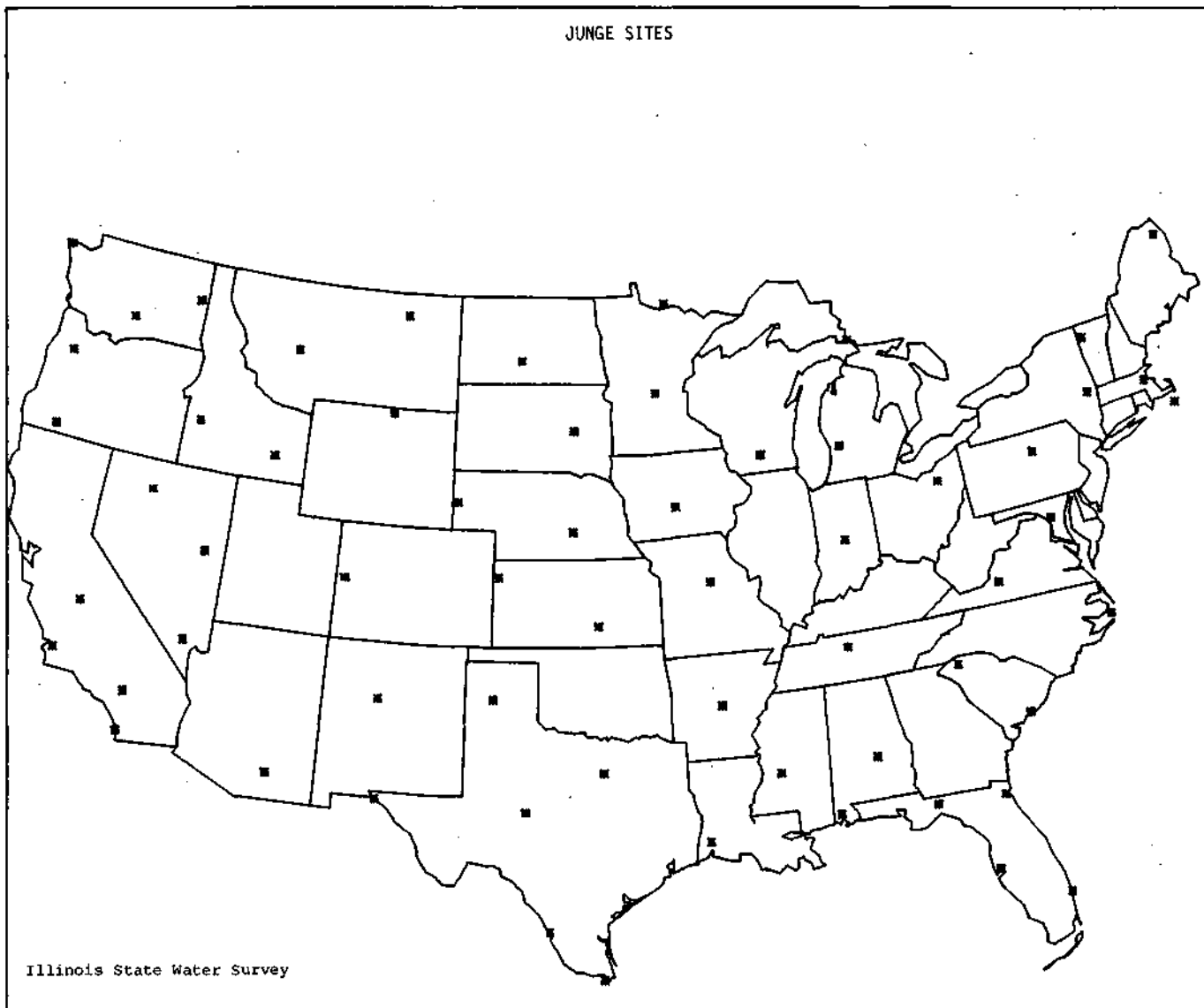
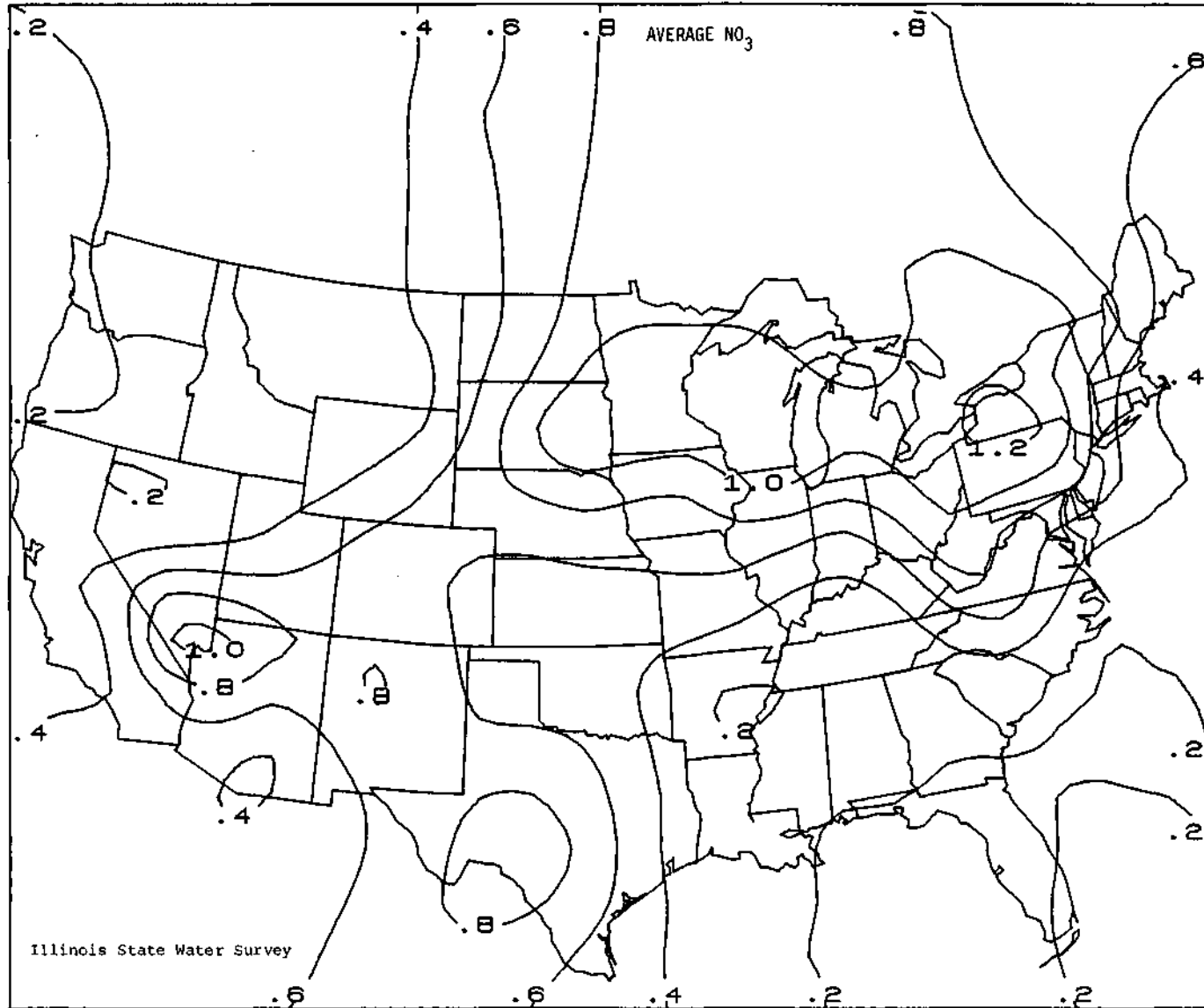


Figure 7. Location of the 1955-56 Junge sites.

Figure 8. Precipitation-weighted nitrate concentrations (Mg/ ) for the 1955-56 Junge data.



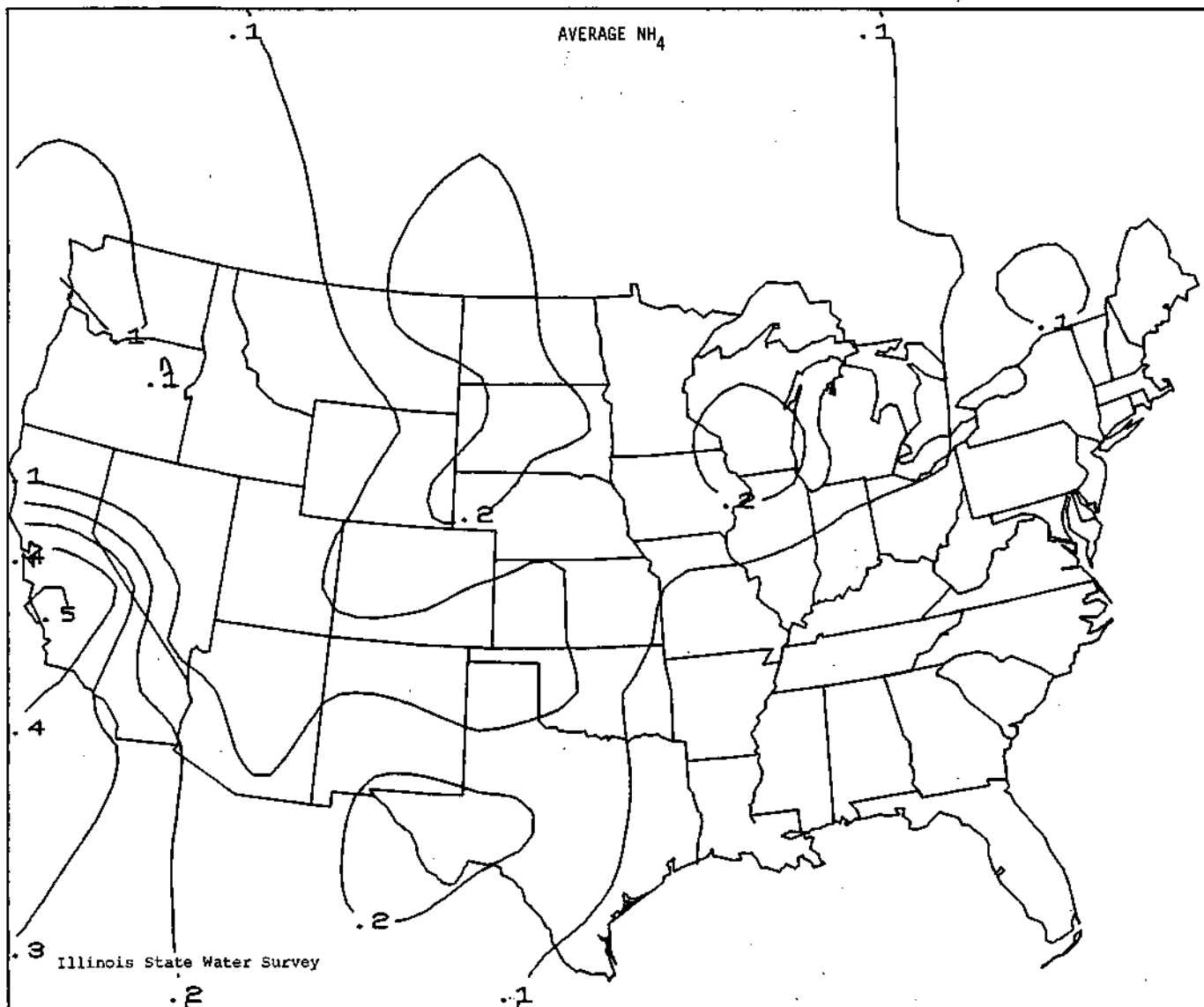
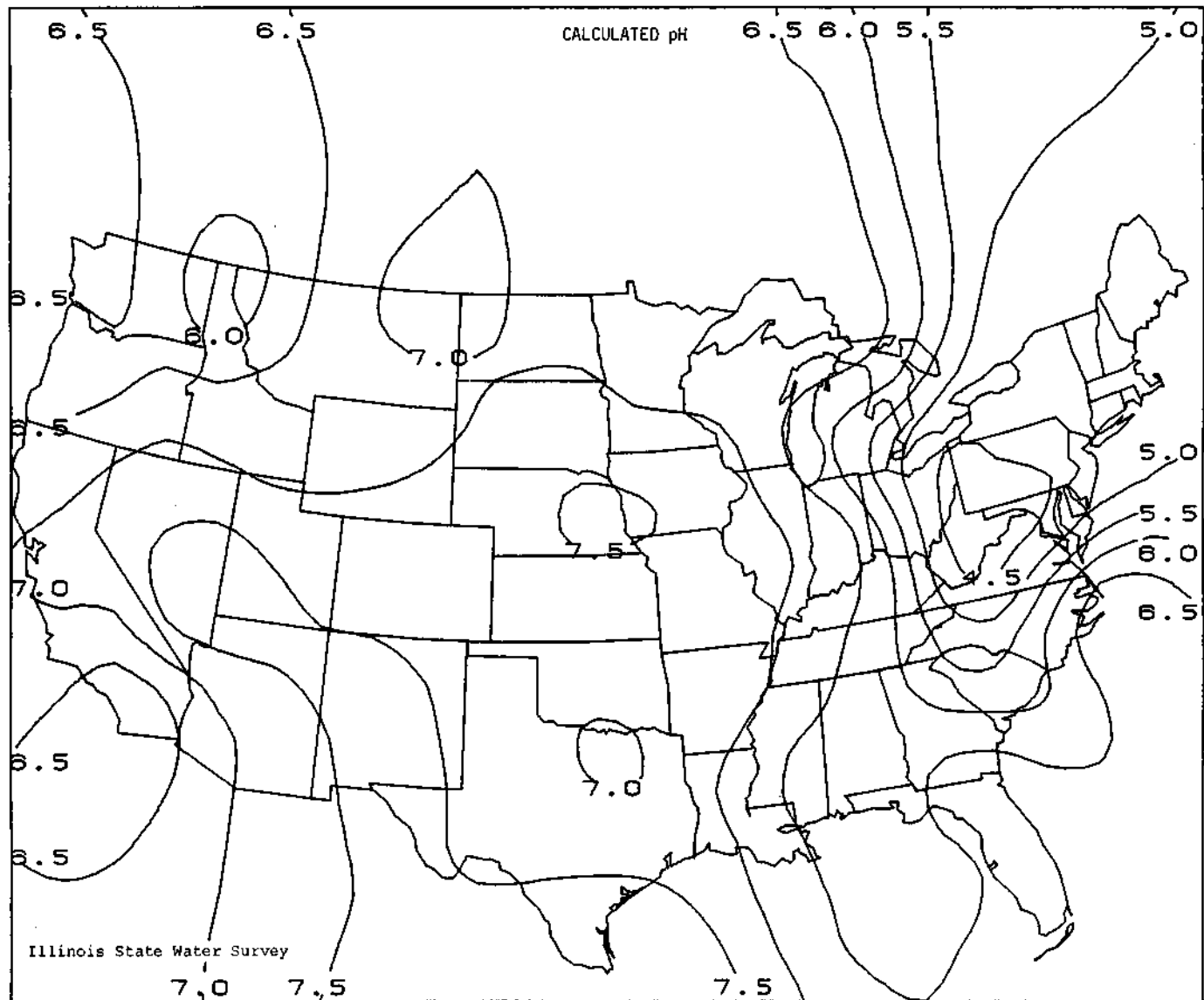
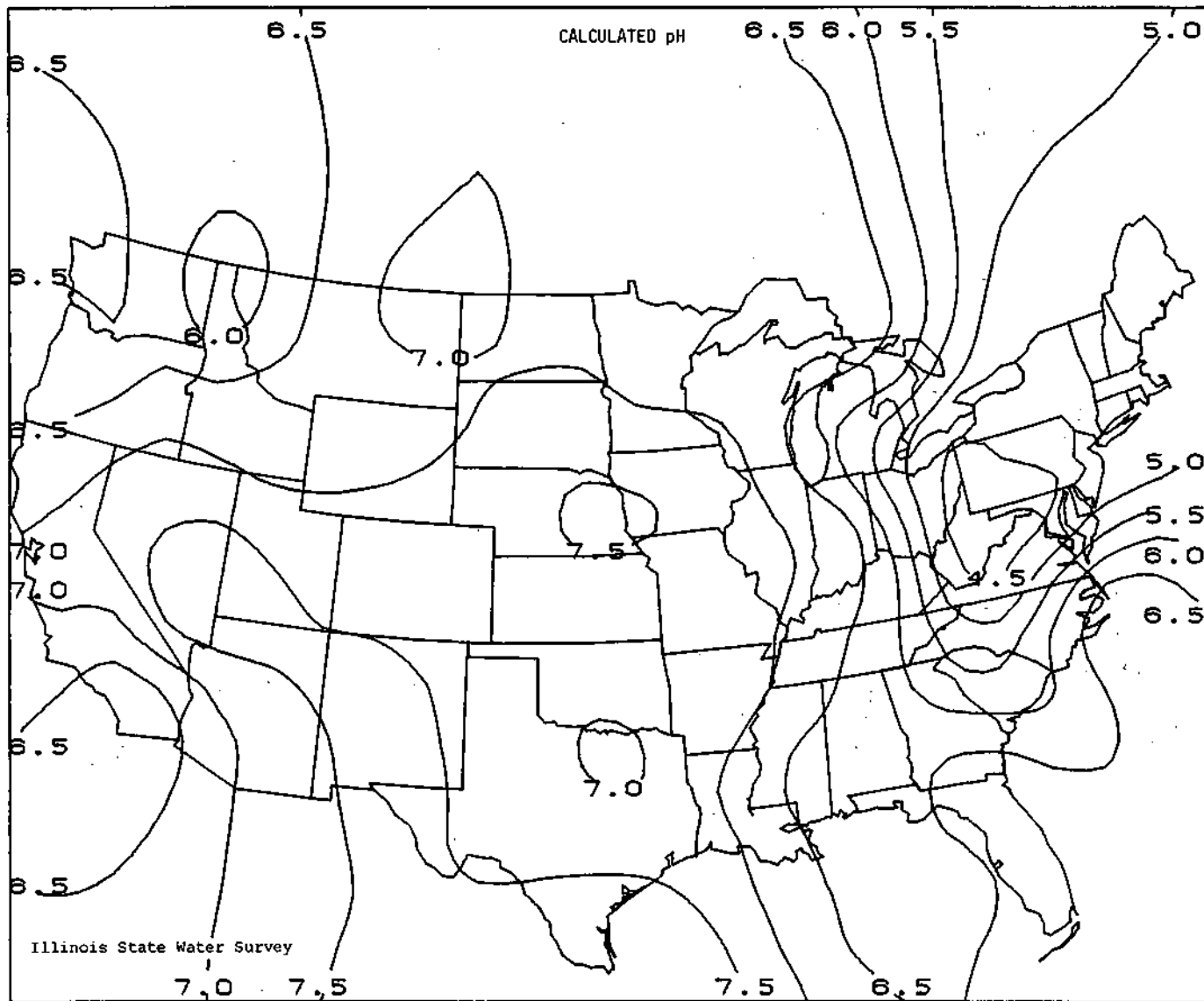


Figure 9. Precipitation-weighted ammonium concentrations (Mg/ ) for the 1955-56 Junge data.

Figure 10. pH values calculated for the 1955-56 Junge data, using Eqs. 1 and 5 and the data in the first three columns of Table I.

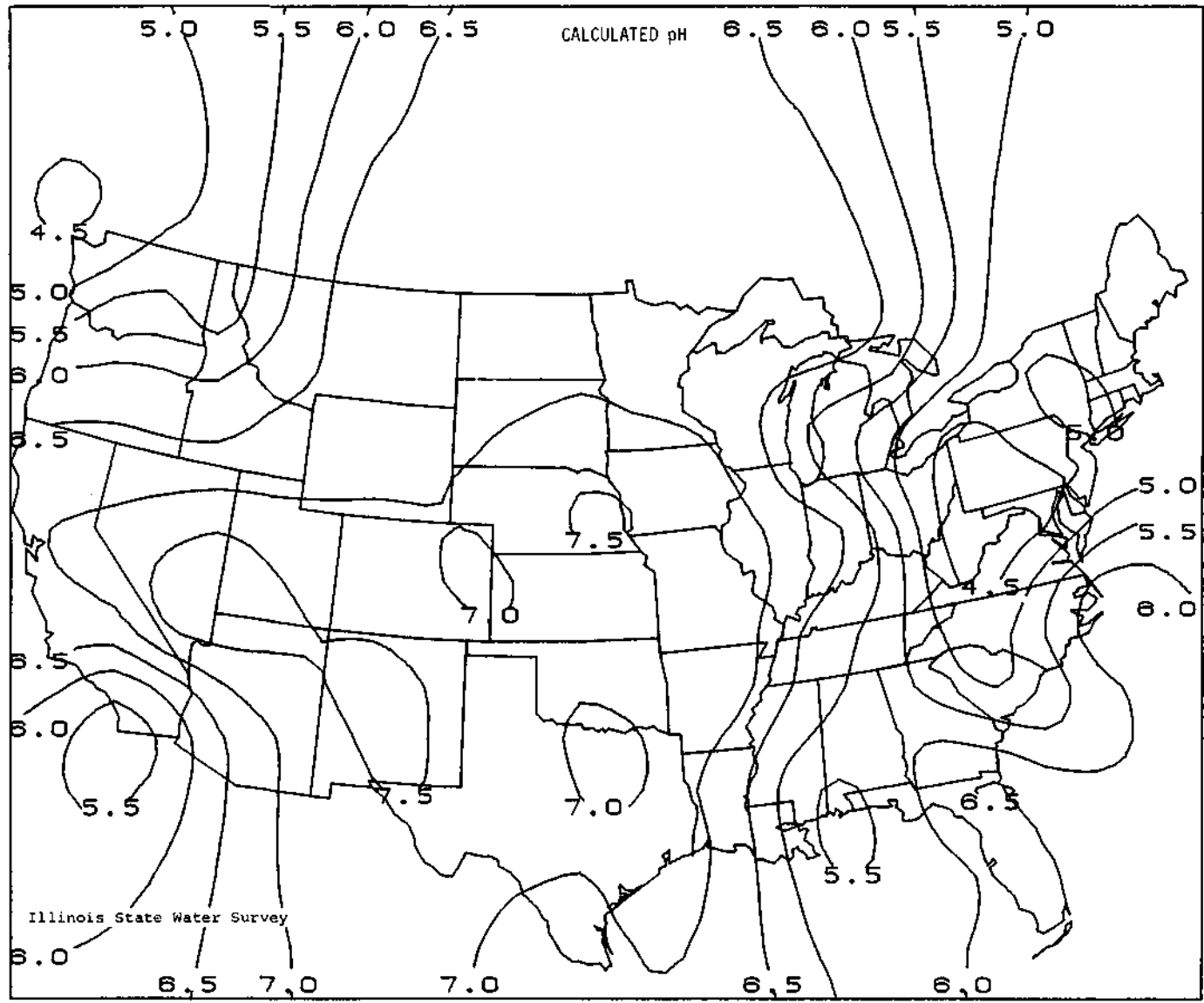




PHO2

Figure 11. pH values calculated for the 1955-56 Junge data using Eqs. 12 and 5.

Figure 12. pH values calculated for the 1955-56 Junge data using Eqs. 11 and 5.



for the east, with the pH 6 isopleth enclosing a much larger area in the east in Fig. 12 as compared to Fig. 10.

Finally, our best estimate of the pH of the precipitation in 1955-56, listed as "corrected pH<sub>sten</sub>" in Table 1, is shown in Fig. 13. These data are pH<sub>sten</sub> (cf. Fig. 10) corrected with the empirical Eqs. 6 and 7. In Fig. 13, the western states typically have pH values 7.0 while the pH 4.5 region covers much of the northeast.

The remaining figures in this section will illustrate the sensitivity of the pH patterns to the assumptions concerning the Mg<sup>++</sup> concentrations (cf. Figs. 14-17) and to the Ca<sup>++</sup> concentrations (cf. Figs. 18-19). Each of the Figs. 14-19 should be compared with Fig. 10 since Eqs. 1 and 5 were used in each case.

For Fig. 14 the Mg<sup>++</sup> concentrations were estimated by using (Ca<sup>++</sup>/Mg<sup>++</sup>) ratios equal to one half those listed in Table 1. Therefore (Mg<sup>++</sup>) for Fig. 14 was twice as large as for Fig. 10, and thus the general pattern is one of higher calculated pH levels. For Fig. 15, ratios twice those listed in Table 1 were used. Thus (Mg<sup>++</sup>) for Fig. 15 was one half as large as for Fig. 10 and therefore the pH levels are lower in Fig. 15. As a summary, Fig. 16 shows the pH values in Fig. 14 minus those in Fig. 15. The calculated pH is seen to be very sensitive to the (Ca<sup>++</sup>/Mg<sup>++</sup>) ratio at the Grand Rapids, MI site and at the Atlantic east coast and the west coast sites. The pH sensitivity for the coastal sites is to be expected since there the Mg<sup>++</sup> is of a greater magnitude and also more important in comparison to Ca<sup>++</sup>.

The results when a (Ca<sup>++</sup>/Mg<sup>++</sup>) ratio equal to 6 is applied at all sites is shown in Fig. 17. When this figure is compared to Fig. 10 it is again clear that the coastal area sites are most sensitive to the assumption related to (Mg<sup>++</sup>).

In previous Progress Reports it was pointed out that for an east central Illinois site, the present precipitation pH is about 4.0 compared to about 6.0 for 1954 (Stensland, 1977; Stensland, 1978). The large drop in the precipitation pH was found to be mainly due to the fact that the recent Ca<sup>++</sup> + Mg<sup>++</sup> concentrations were about 1/6 of those for 1954. Figure 18 shows the calculated pH values for the Junge data with the (Ca<sup>++</sup>) and (Mg<sup>++</sup>) for each site being 1/6 of the original values. Remember that (Mg) was estimated from the (Ca<sup>++</sup>/Mg<sup>++</sup>) ratios. When Fig. 18 is compared to Fig. 10, it is obvious that the pH values for the United States are very sensitive to (Ca<sup>++</sup> + Mg<sup>++</sup>). With the reduced Ca<sup>++</sup> and Mg<sup>++</sup> concentrations used for Fig. 18, the area with pH 5.5 includes most of the United States (>90%), and the area with pH 4.5 covering almost the entire northeast. Stensland (1978) has discussed the possibility that the sampling and analytical procedures produced the relatively high Ca<sup>++</sup> + Mg<sup>++</sup> values in the mid 1950's data, but concluded that this could be only a partial explanation. It was suggested that the drought years in the central United States in the 1950's may have been a prime cause for the high Ca<sup>++</sup> + Mg<sup>++</sup> levels. If the high Ca<sup>++</sup> + Mg<sup>++</sup> concentrations in the Junge data result from an extreme in the climate of the United States, then perhaps a more representative picture is found in Fig. 18 than in Fig. 10. If this hypothesis is accepted then Fig. 18 should be corrected with Eqs. 6 and 7 just as Fig. 13 was produced from Fig. 10.





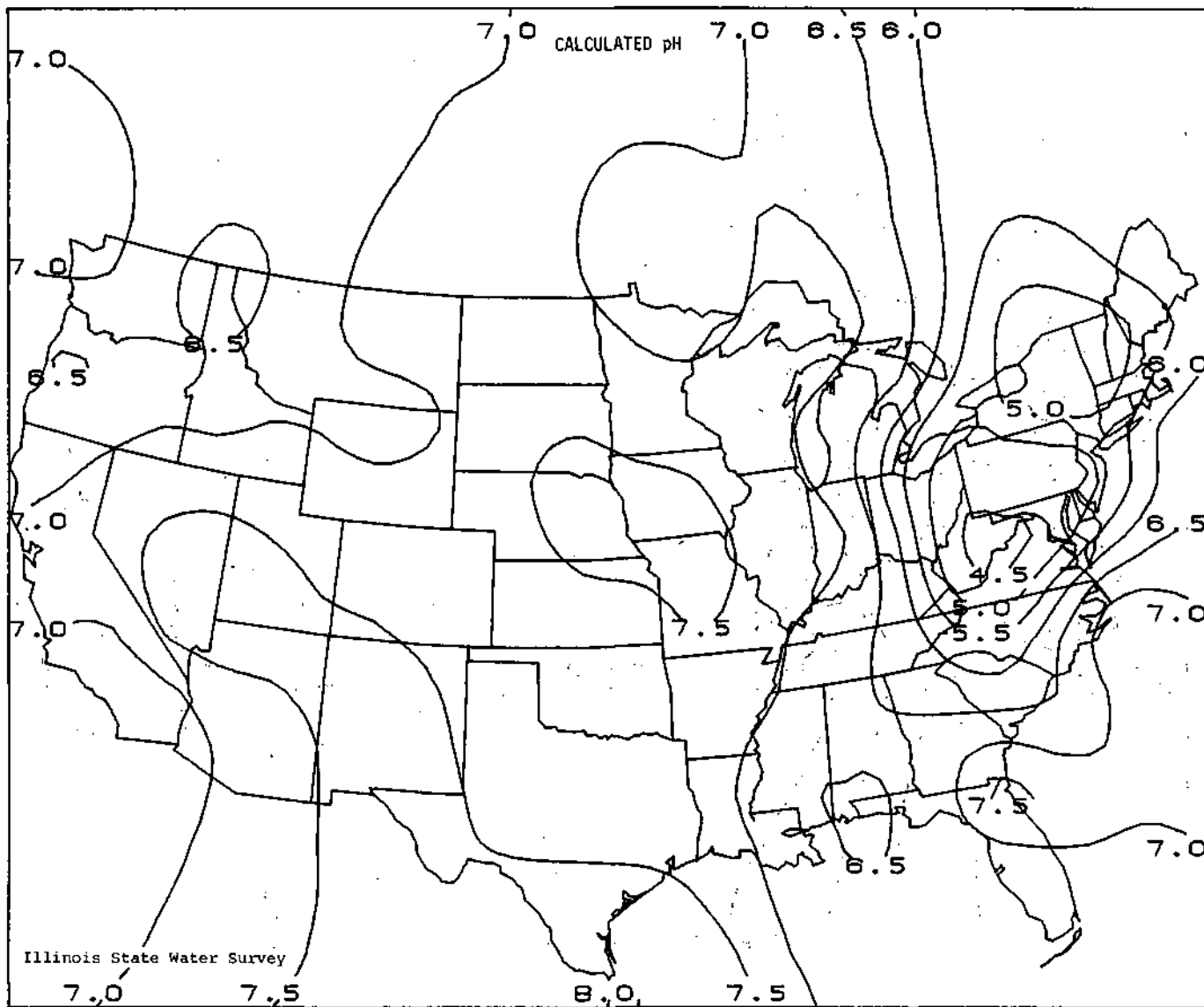
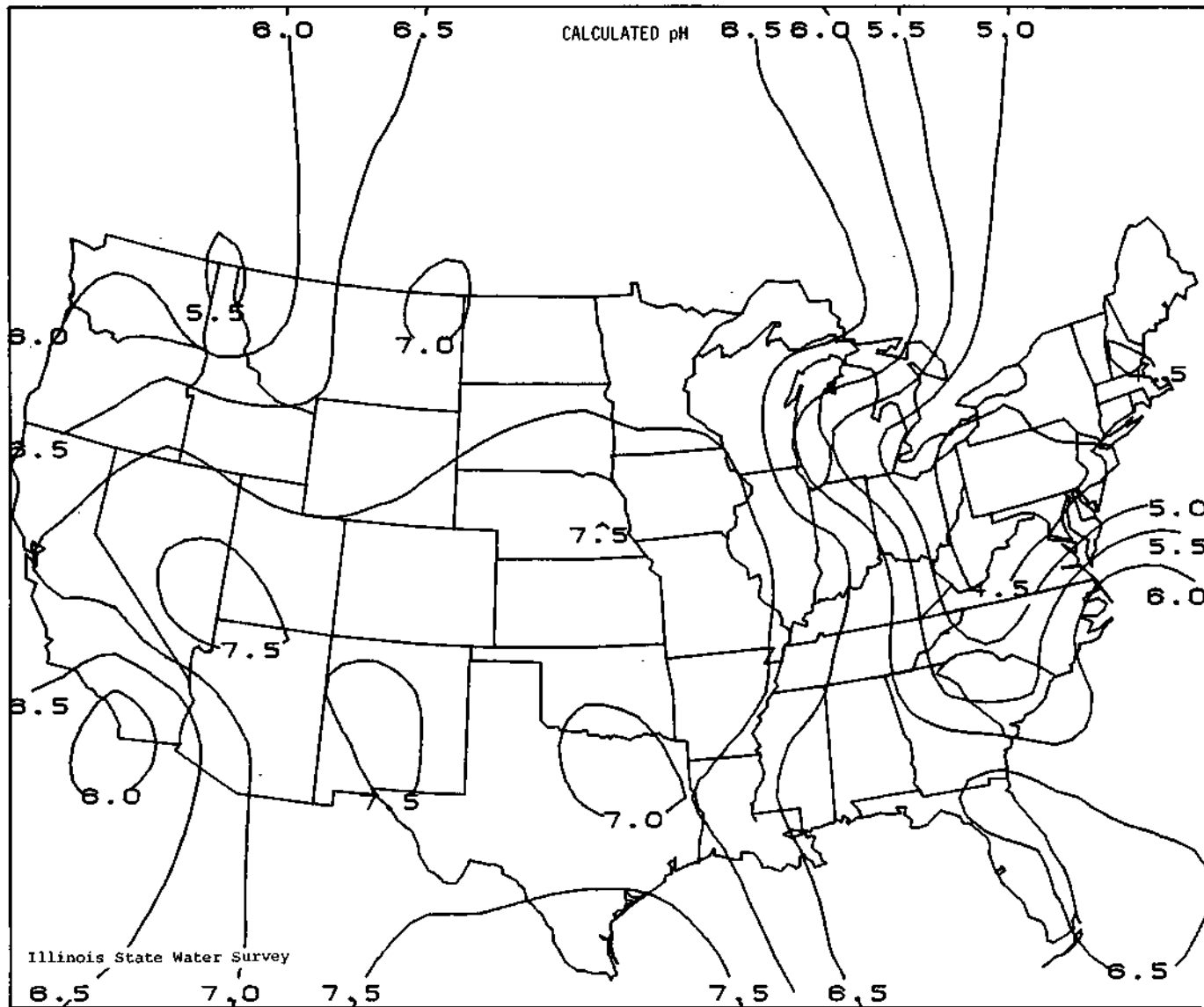


Figure 14. pH values calculated for the 1955-56 Junge data, using Eqs. 1 and 5 and one half the  $(Ca^{++}/Mg^{++})$  ratio values listed in Table I.

Figure 15. pH values calculated for the 1955-56 Junge data, using Eqs. 1 and 5 and twice the (Ca /Mg ) ratio values listed in Table 1.



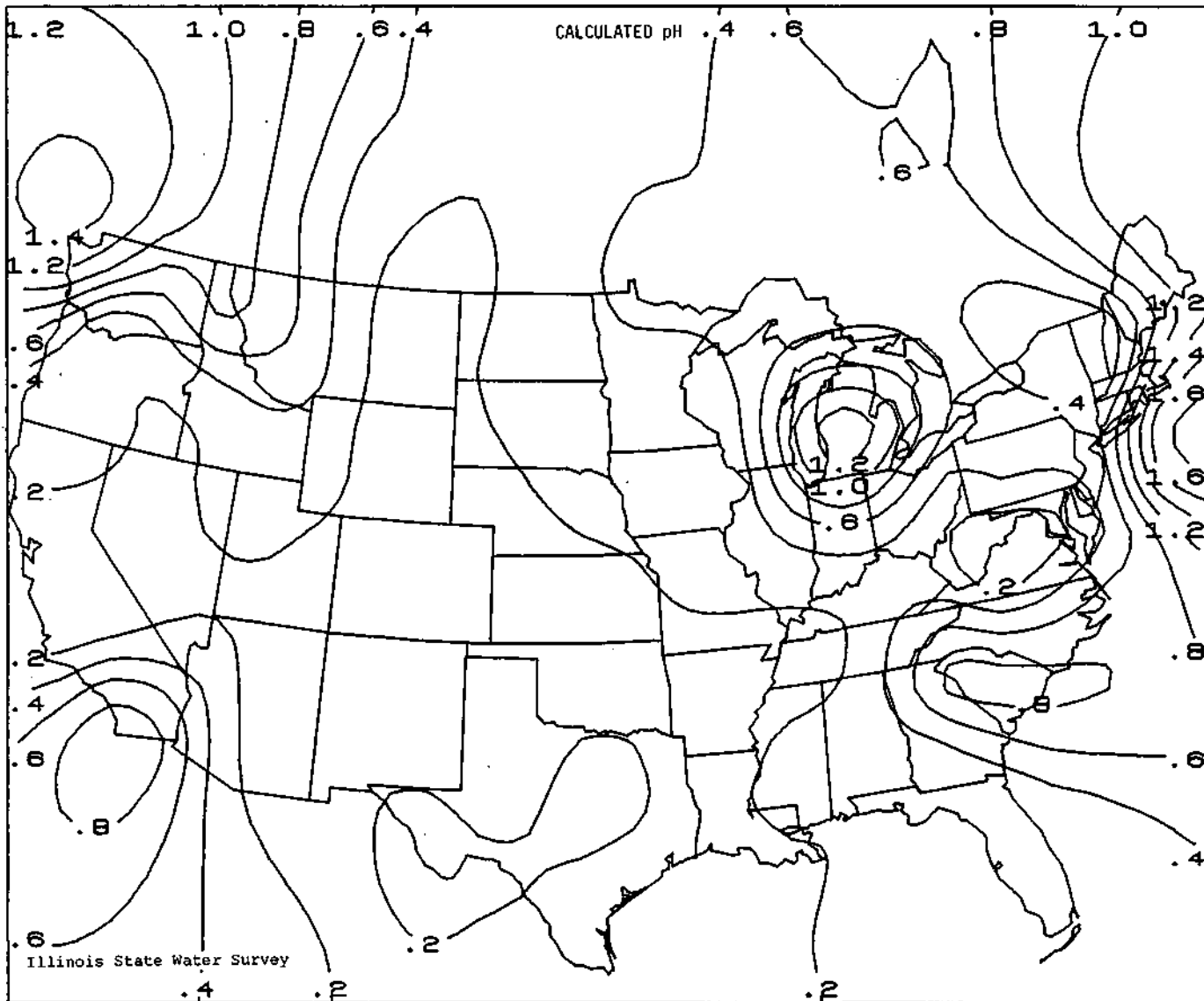
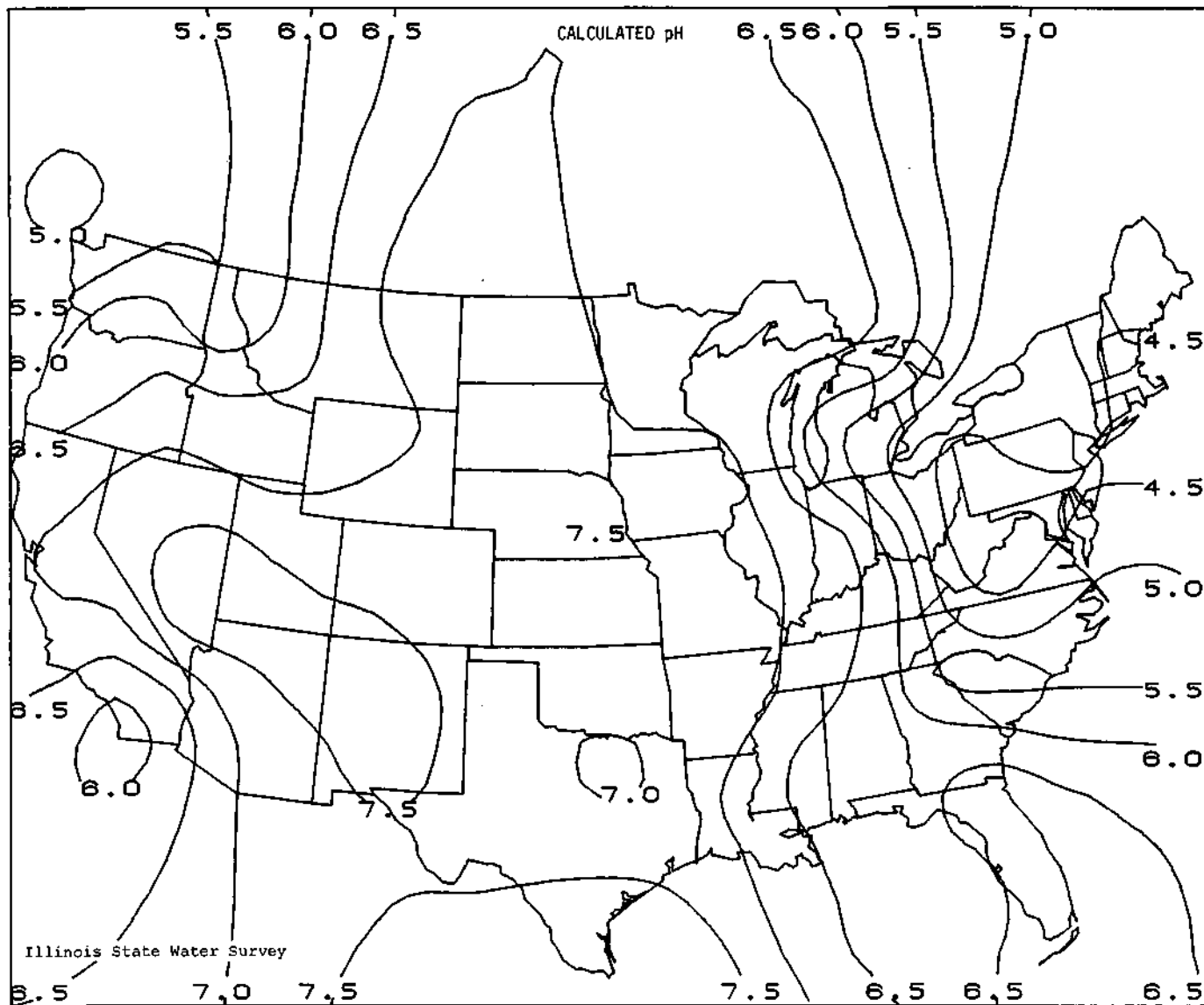


Figure 16. Difference between the pH calculated with twice the (Ca /Mg ) ratios in Table I and the pH calculated with one half the ratios.

Figure 17. pH values calculated for the 1955-56 Junge data, using Eqs. 1 and 5 and a ratio of  $\text{Ca}^{++}/\text{Mg}^{++} = 6$  at all the Junge sites.



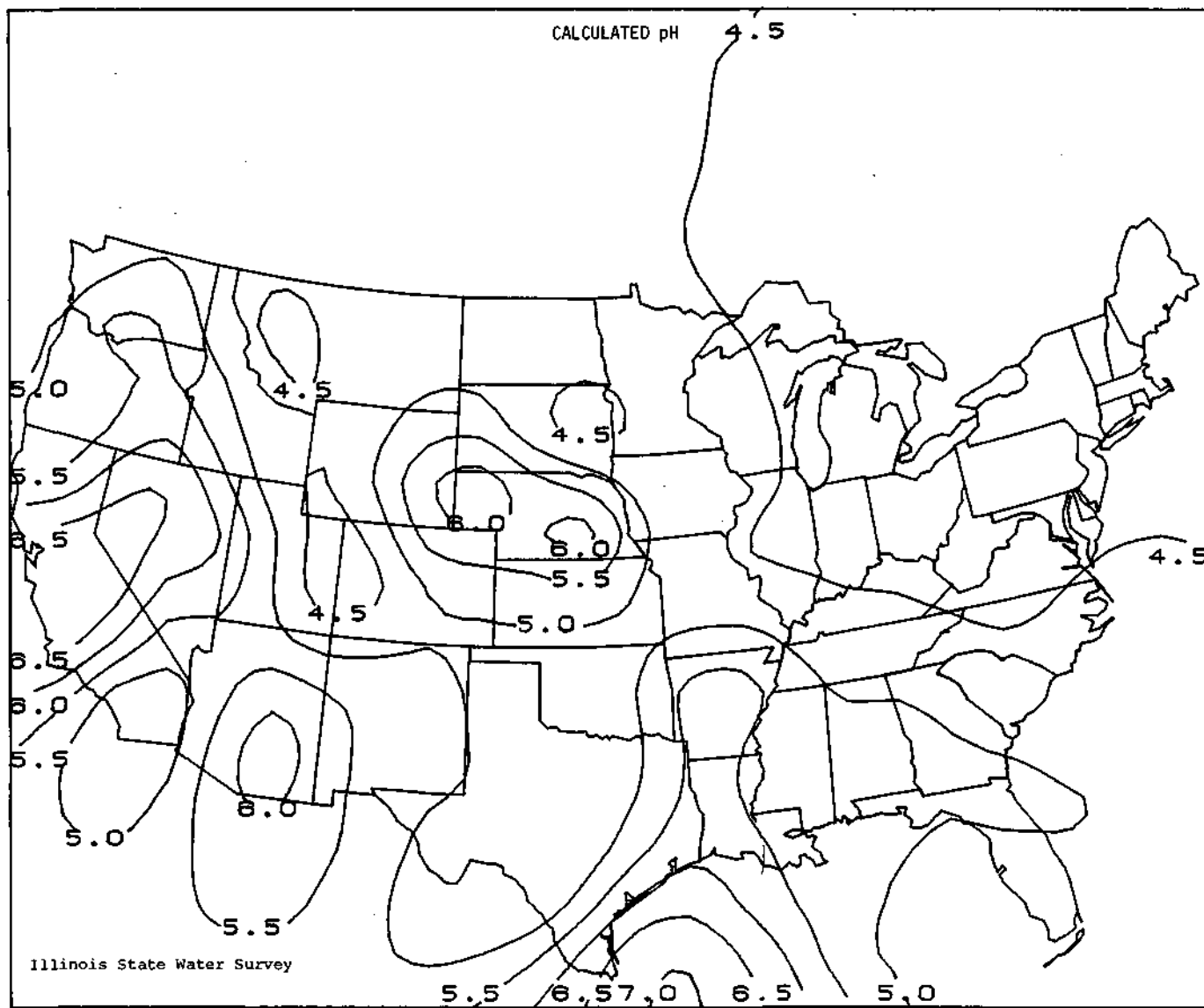


Figure 18. pH values calculated for the 1955-56 Junge data, using Eqs. 1 and 5 and  $\text{Ca}^{++}$  concentrations equal to 1/6 those reported by Junge.

Figure 19 displays the pH isopleths when all the Junge sites are assigned a  $\text{Ca}^{++}$  value of 0.2 mg/L, which is a typical 1977 value for central Illinois. This assumption produces even greater areas of low pH as compared to Fig. 18.

## CONCLUSIONS

Using an ion charge balance equation, the pH for the United States was calculated for the 1955-56 Junge data (cf. Fig. 10). The results are quite different than those reported previously by Cogbill and Likens (cf. Table 2).

A comparison of measured versus calculated pH values suggests that an empirical correction should be applied to the calculated pH values (cf. Eqs. 6 and 7). The pH isopleths in Fig. 13 include this empirical correction, and thereby provide the best estimate of the pH for 1955-56 in the United States.

A study of data for a central Illinois site has suggested that the 1955-56  $\text{Ca}^{++} + \text{Mg}^{++}$  levels were about six times higher than the current levels. When the ( $\text{Ca}^{++} + \text{Mg}^{++}$ ) for the Junge data were reduced by a factor of six, the calculated (but not empirically corrected) pH levels were much more acid. These data, in Fig. 18, show most of the United States with pH 5.5 and almost the entire northeast with pH 4.5. With the empirical correction the northeast would have pH 4.35.

Figure 18 demonstrates that the 1955-56 pH values were very sensitive to the  $\text{Ca}^{++} + \text{Mg}^{++}$  levels and this must be carefully considered if the 1955-56 data are used as a reference data set to look for "acid precipitation" trends. If the droughts of the mid 1950's produced the elevated  $\text{Ca}^{++} + \text{Mg}^{++}$  levels in the air and precipitation, then this climatic feature must be considered when evaluating effects of increased anthropogenic sulfur and nitrogen emissions.

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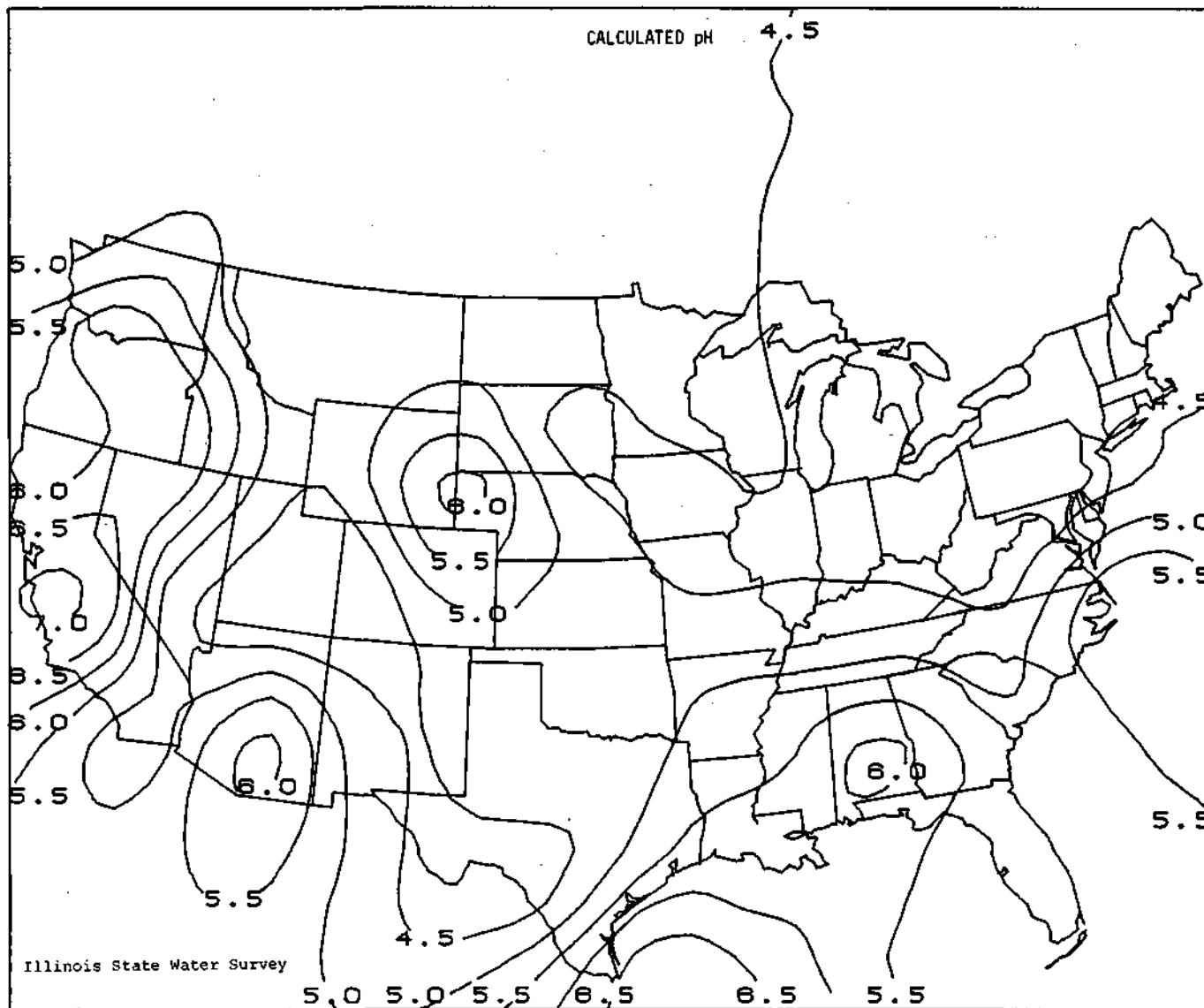


Figure 19. pH values calculated for the 1955-56 Junge data, using Eqs. 1 and 5 and  $(Ca^{++}) = 0.2 \text{ mg/}$  at all the Junge sites.

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CHAPTER 9

ATMOSPHERIC CHEMISTRY LABORATORY UPDATE

Mark E. Peden

FACILITIES

The ever expanding demands on the Atmospheric Chemistry Laboratory resulted in the addition of a new laboratory bay plus several equipment acquisitions during the past year. After undergoing extensive refurbishment, which included the installation of a laminar flow clean bench unit, the lab is currently being used for sample processing and preliminary chemical measurements. Instrumentation installed in the new lab includes three analytical balances, two specific conductance meters, pH meter, and six micro-filtration apparatus. A deionized water polishing system which delivers water of  $< 0.5$  umhos specific conductance at a rate of two liters, minute<sup>-1</sup> has also been incorporated into the renovation.

As a part of the ongoing effort to automate as many of the chemical measurements as possible, two accessories have been added to the existing array of instrumentation. The first, which provides for unattended specific conductance analysis at a rate of 30 samples per hour, employs a detector module interfaced to the existing Technicon AutoAnalyzer System. Measurements are made in an isothermal environment and displayed on a strip chart recorder. The analytical working range extends from 2-20,000  $\mu$ mhos with a 3% precision.

The second equipment acquisition provides automatic sample feed to the carbon furnace atomizer. Replacing the tedious and imprecise manual injection method, the new autosampler incorporates a standard impingement bead type nebulizer which deposits a uniform drop size aerosol into the carbon cuvette. The temperature of the cuvette during deposition averages 125°C thereby eliminating the normally required drying step.

Analysis speed averages 40 samples per hour with a precision of 2%. Manual injection typically allows for 20 samples per hour with a precision of 5%. The furnace autosampler is being utilized during SCORE-79 for zinc determinations at the  $\mu\text{g}\cdot\text{L}^{-1}$  level. Zinc deposition data will be used as a natural tracer to identify industrial sources affecting the precipitation chemistry network.

SCORE 1978 ANALYSIS PROGRESS

The Atmospheric Chemistry Laboratory processed a total of 1,348 precipitation and dry deposition samples generated during SCORE 1978. Included

in this number were 575 bulk samples, 383 wet-only, 270 dry deposition, and 120 sequential precipitation samples. Chemical analyses, which included pH, specific conductance,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{Cl}^-$  measurements, have been completed for all but the dry samples. The analytical results have been keypunched and computer checked to verify the accuracy of the lab measurements. Preliminary data synthesis, combining chemical results with meteorological observations, has yielded new information regarding the spatial and temporal variability of  $\text{SO}_4^-$  and  $\text{H}^+$  ions. In addition, detailed analysis of the terrestrial components found in precipitation, such as  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{K}^+$ , will reveal the key role played by airborne soil dust in the neutralization of acidic rainfall. The July 1, 1978 case study reported on in Chapter 6 is one such example.

CHAPTER 10

IONIC STABILITY OF PRECIPITATION SAMPLES:  
WET-ONLY COLLECTION

Loretta M. Skowron and Mark E. Peden

INTRODUCTION

Over the past few years the chemical analysis of precipitation has become an integral part of research related to weather modification, the acid rain phenomenon, the effects of atmospheric deposition on terrestrial and aquatic ecosystems, local and regional transport of pollutants and nutrients in the troposphere, and historic documentation of pollutant levels. Accurate data are necessary to ensure valid conclusions in effects research, as well as for the promulgation of regulatory guidelines.

Data quality is a function of sample collection, handling, and storage as much as it is dependent upon the accuracy of laboratory analyses. The ionic stability of precipitation samples with respect to collection and storage has been recently investigated. Data have qualitatively shown the effects of extraneous particulate matter, meteorological events, sample type (bulk vs. wet-only, event vs. weekly), and storage time. All the samples which displayed changes in ionic concentration showed the same pattern: an increase in pH with a concomitant rise in the terrestrial components such as  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . Wet-only event samples were the most stable. Filtration of the precipitation was the most effective means of sample preservation; refrigeration was minimally effective for relatively "clean" samples (Peden and Skowron, 1978).

In April, 1978, we continued our study, focusing our attention on the changes occurring during the first two weeks after collection. Since wet-only samples were shown to be the most stable, they were used exclusively in this study. No preservation techniques were employed because the purpose of this experiment was to quantify ionic concentration changes rather than to compare samplers or storage methods. Emphasis was placed on immediate analyses because our previous study indicated that most concentration changes took place during the first ten days of storage. This is a critical period between sample collection and arrival in a laboratory where stabilizing techniques can be employed.

EXPERIMENTAL

Samples were collected on the roof of the Illinois State Water Survey (ISWS) in Champaign, Illinois, during April 1978. Wet-only samples were

acquired utilizing a wet-dry collector of the design published by the Department of Energy, Environmental Measurements Laboratory (Volchok and Graveson, 1975). Collection containers were cylindrical five liter polyethylene buckets with 19.5 cm diameter openings.

Samples were stored at room temperature (25°C) in their original collection vessels without using any techniques to help them retain ionic integrity. Sample collection times ranged from seven hours to seven days.

Chemical analyses were performed within a few hours after collection, the next day, and then as often as time permitted, usually 3-4 times during the first week. Atomic absorption spectroscopy was used to determine  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Na}^+$ . Hydrogen ion concentration was measured with a pH meter and micro-combination electrode. Specific conductance was measured with a manually balanced AC bridge.

## RESULTS AND DISCUSSION

Figures 1-4 represent data from four samples, each having a different exposure time. Different ionic concentrations in  $\text{mg L}^{-1}$  (ppm) are plotted against time after collection on a semi-logarithmic scale. Percentages given represent changes from the original concentrations.

A sample exposed for a little more than a week is depicted in Fig. 1. During this period the mean daily temperatures were in the mid-40°F range and winds were from the east at 5-10 mph. Approximately 555 mL (0.72") of rain which fell during the 4th, 7th, and 8th days, were collected and analyzed. The concentrations of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  changed most during the first day after collection and then seemed to stabilize. After ten days these cations showed an increase of 8% over their original concentrations. The relatively small changes and early stabilization of these terrestrial components can be explained either by: 1) the particulate to sample volume ratio is low due to the large amount of rain, or 2) most of the changes in concentration had already occurred during the approximately one week sampling period.

Figure 2 represents a sample that was exposed for approximately two days. This period had mean daily temperatures in the 50°F range, 5-10 mph winds, and light rains. About 189 mL (0.24") of precipitation were collected. The hydrogen ion concentration and specific conductance did not change significantly, but the measured cations increased. After 18 days  $\text{Ca}^{++}$  increased by 29%,  $\text{Mg}^{++}$  by 11%, and  $\text{Na}^+$  by 39%. The concentrations of these ions are also rather high when compared with levels usually encountered in rain from the Champaign area. This is indicative of airborne soil dust contamination which was not diluted very much with the small rainfall amount.

Another sample with a small rainfall amount, ~ 112 mL (0.14"), was collected as an event after ~ 19 hours. Figure 3 illustrates the dramatic changes in ionic concentrations which occurred during the two week storage

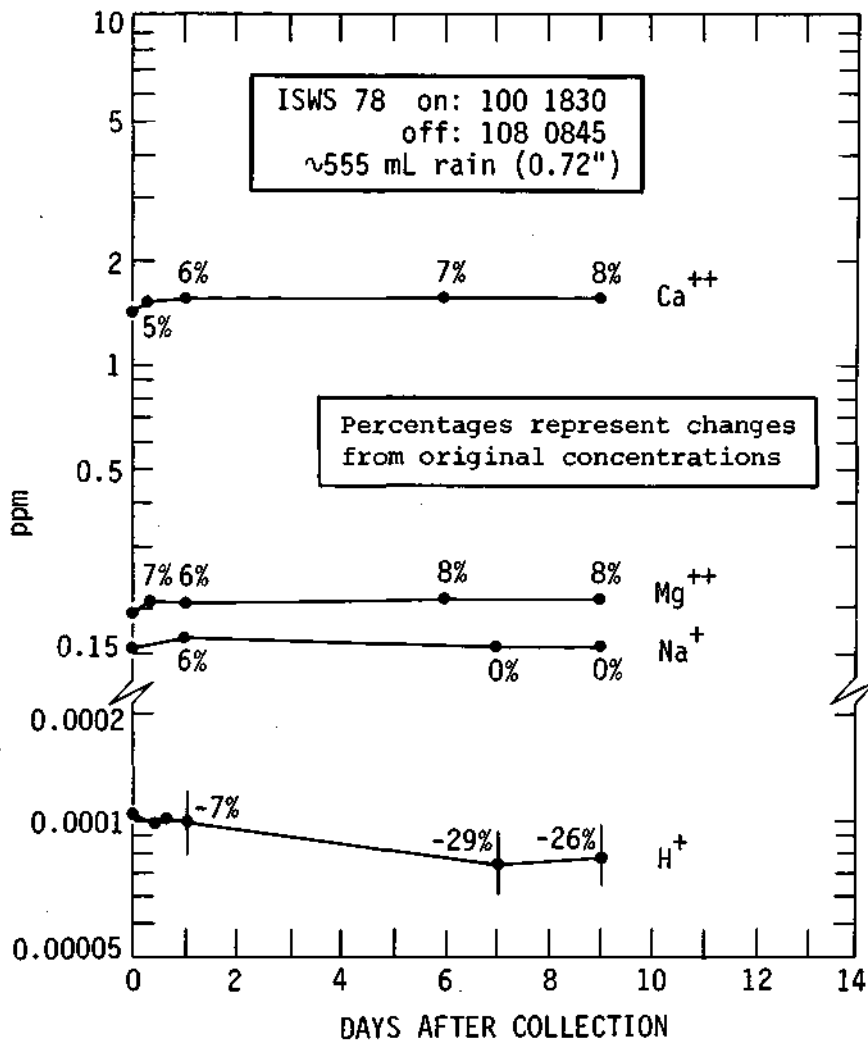


Figure 1. ionic concentration changes of rain sampled with a HASL wet-dry collector. Exposure time was 7 days, 9 hours, 35 minutes. The sample was unfiltered and stored in the original collection vessel at 25°C

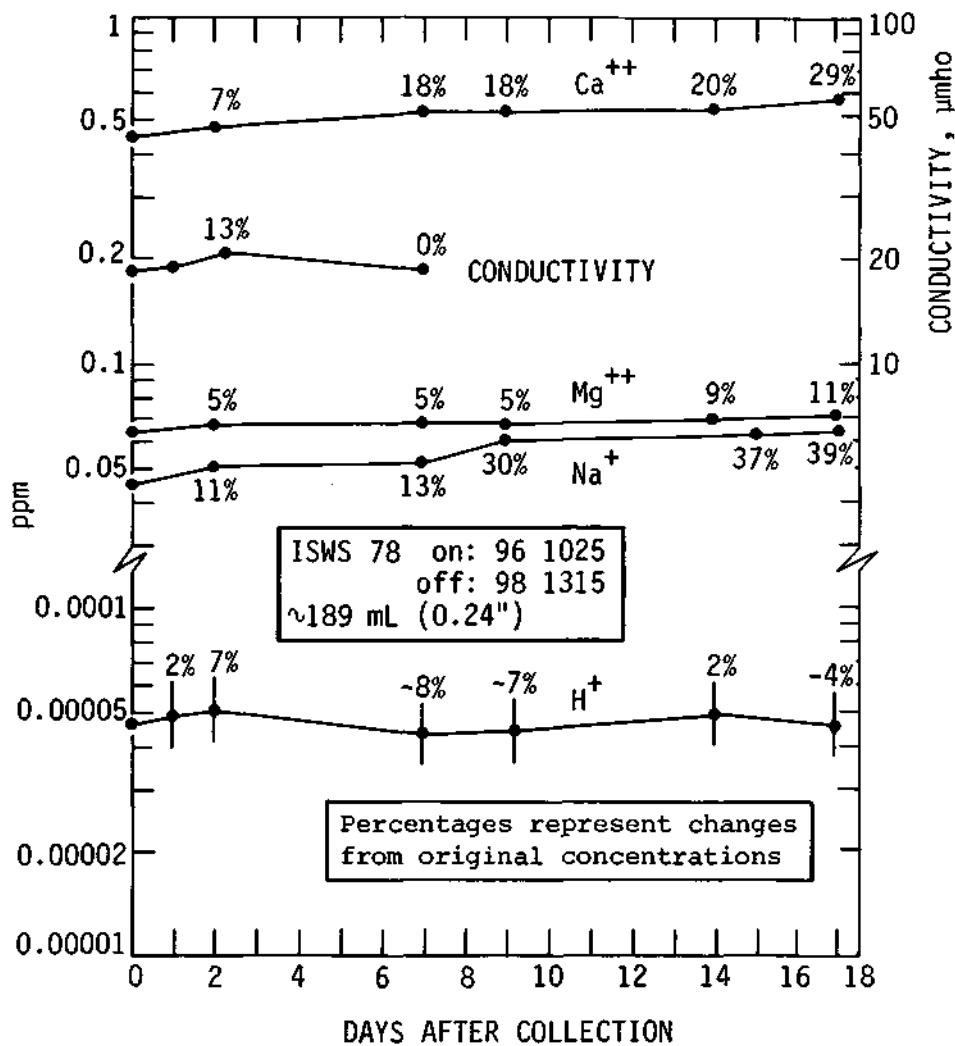


Figure 2. Ionic concentration changes of rain sampled with a HASL wet-dry collector. Exposure time was 2 days, 3 hours, 15 minutes. The sample was unfiltered and stored in the original collection vessel at 25°C.

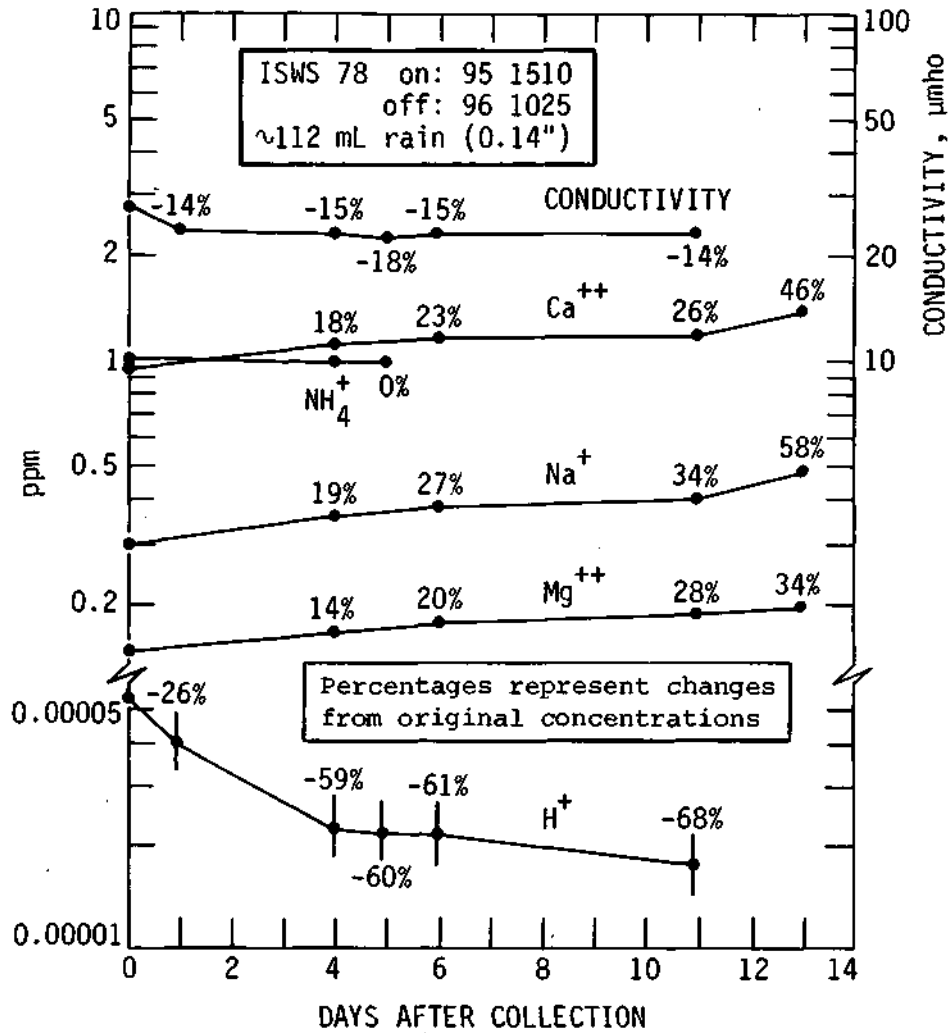


Figure 3. Ionic concentration changes of rain sampled with a HASL wet-dry collector. Exposure time was 19 hours, 15 minutes. The sample was unfiltered and stored in the original collection vessel at 25°C.

period after collection. Conductivity decreased by ~ 15% and seemed to stabilize after the first day. The hydrogen ion concentration decreased by ~ 60% within the first four days and then stabilized.  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Na}^+$  concentrations increased by 46%, 34%, and 58%, respectively, and did not display any leveling off tendencies after 14 days. Three analyses for  $\text{NH}_4^+$  made during the first week showed no changes. These are the types of changes we have routinely encountered in small volume samples with a heavy dust loading.

Figure 4 depicts a "true" event sample having an exposure time of ~ 7 hours. Again the ionic concentration changes were significant and began immediately, the fastest rates occurring during the first day. The  $\text{H}^+$  ion concentration changed the most during the first seven days and then stabilized after the seventh day. If a line is extrapolated through the first four measurements of  $\text{H}^+$  concentrations, the decrease in ions seems to be an exponential function of time during the first seven days of storage. The  $\text{Na}^+$  concentration increases an average of 19% and was stable after one week.  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  increased 65% and 44%, respectively, after 18 days. Once again the largest rate of increase took place during the first two days after collection.

#### SUMMARY RECOMMENDATIONS

It is clear that the measured ionic concentrations in wet-only samples are still subject to changes, despite the elimination of most dry deposition. Different rain samples changed by different degrees, and the variables affecting these changes are numerous: wind speed, relative humidity, temperature, ground cover, soil composition, topography, and rainfall amounts. Small samples are less able to dilute aerosol dust loadings. They display relatively high ionic levels overall as well as large changes in the concentrations of terrestrial components such as  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ .

The first few hours after the cessation of rainfall are the most critical when making assessments of ionic stability. Hydrogen ion concentration decreased exponentially during the first day. The greatest rates of increase of  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Na}^+$  took place during the first week.

Event sampling followed immediately by analysis or a preservation technique is the optimal method of obtaining accurate data for the documentation of terrestrial components and hydrogen ions. Further research needs to focus on quantifying concentration changes over a shorter time scale (hourly) than ever before as well as defining the influences of atmospheric variables. The results from this work will be invaluable in planning future measurement programs and evaluating the validity of existing data.



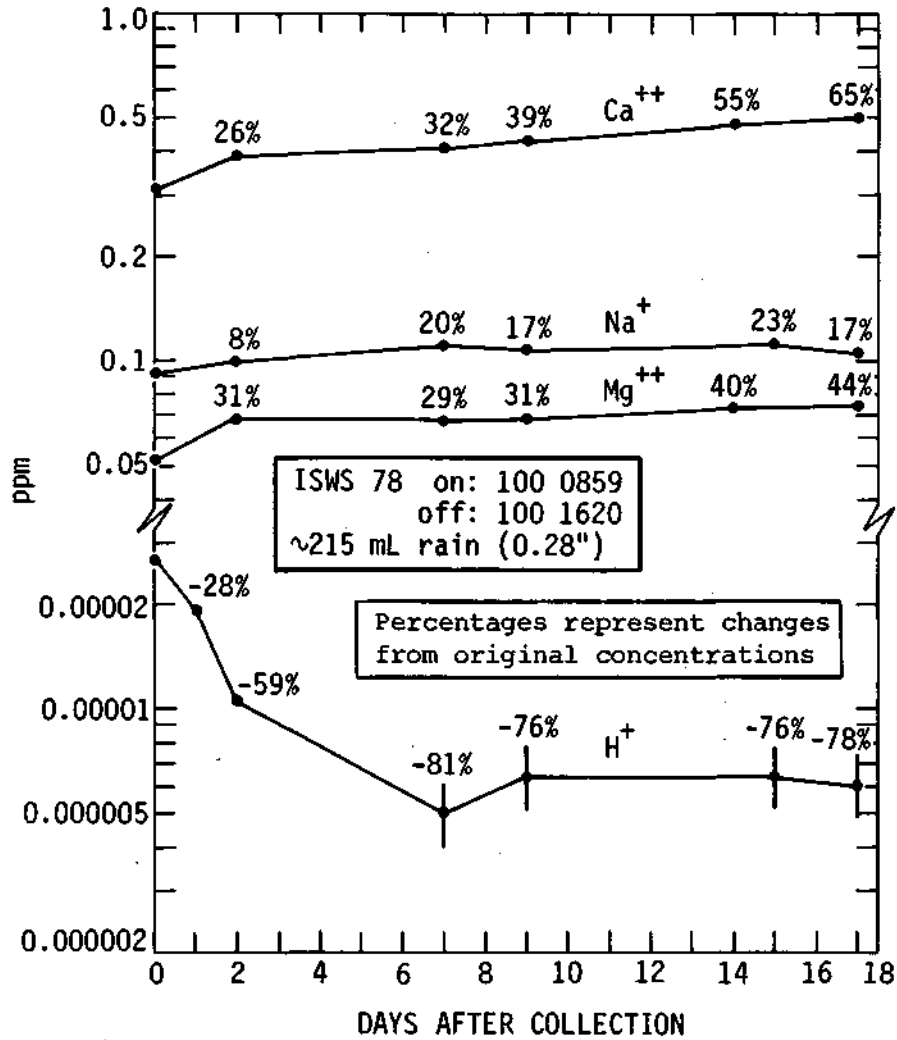


Figure 4. Ionic concentration changes of rain sampled with a HASL wet-dry collector. Exposure time was 7 hours, 19 minutes. The sample was unfiltered and stored in the original collection vessel at 25°C.

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## APPENDIX

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