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PRECIPITATION CHEMISTRY TRENDS IN THE NORTHEASTERN UNITED STATES

by

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INTRODUCTION

Gases and particles injected into the atmosphere by natural or anthropogenic sources are returned to the earth's surface through wet and dry removal processes. Therefore historical trends of the concentrations of the various trace substances in precipitation can serve as an indication of the changes in the levels of these substances in the air.

This paper will examine three topics related to the precipitation chemistry data base for the United States. First, since the pH of precipitation is of major interest, techniques to calculate this quantity will be considered. This calculation is necessary when the pH was not reported, as is frequently the case for the older data sets. Next, the changes in the precipitation chemistry for a central Illinois site will be discussed. This site is at the western edge of present high atmospheric sulfate levels, and thus it is interesting to examine changes in the precipitation pH at this site and the reasons for them. The third and final topic will be to consider changes in the sulfate and nitrate at this central Illinois site and other sites further East, and to compare these changes to the time trends in the anthropogenic source emissions.

METHODS TO CALCULATE PRECIPITATION pH

The 1954 data set to be discussed in the next section of this paper did not include pH measurements so the following procedure has been used to calculate the pH.[1,2] In a rain or melted snow

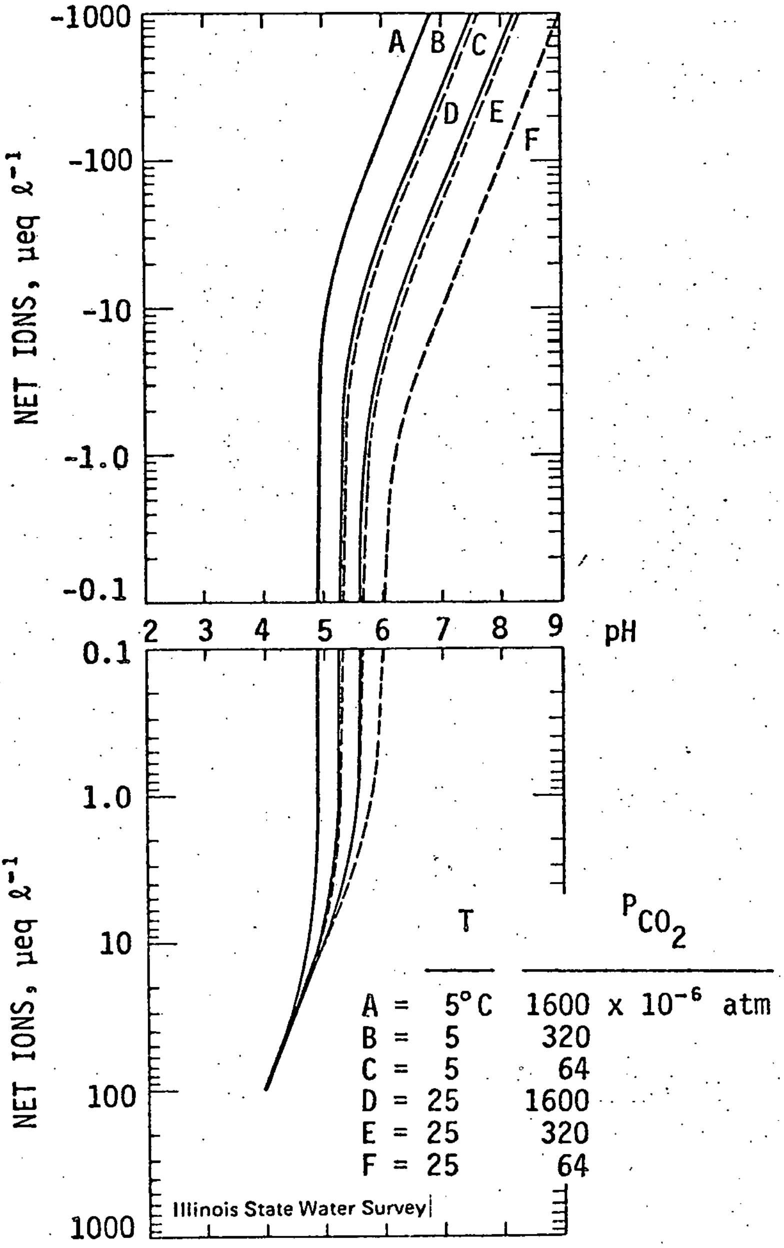

Figure 1. The concentration of Net Ions versus pH for precipitation samples with different values of T (temperature) and P_{CO_2} (from ref. 2).

limited data base. The ratio was >>1 except along the sea coasts. The results of these calculations are shown in Figure 2, where the median of the calculated pH values for each measured pH class (0.1 unit in width) are plotted. The line segments which have been fitted to the data points can be used to correct the calculated pH solution, a charge balance is maintained. If a term called Net Ions is defined as

$$(\text{Net Ions}) = (SO_4^{=})+(NO_3^{-})+(Cl^{-})-(Ca^{++})-(Mg^{++})-(NH_4^{+}) -(Na^{+})-(K^{+}), \quad (1)$$

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

$$(H^{+})-(HCO_3^{-})=(\text{Net Ions}), \quad (2)$$

with each concentration in units of microequivalents per liter ($\mu eq/\ell$). Although Eq. 2 is not exactly correct, since some ions have not been included, 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 $(HCO_3^{-}) \simeq 490\ (OH^{-})$ and for samples with $pH<8$, $(CO_3^{=})<<(HCO_3^{-})$. Thus, the two ions OH^{-} and $CO_3^{=}$ 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

$$(HCO_3^{-})=K_H K_1 P_{co_2}/(H^{+}) \quad (3)$$

where K_H is the constant in Henry's Law and K_1 is the first dissociation constant of CO_2 in water (for 25°C, $K_H = 0.034 \times 10^{+6}$ $\mu eq/\ell/atm$ and $K_1 = 4.5 \times 10^{-1}$ $\mu eq/\ell$). Substituting Eq. 3 into Eq. 2 and solving the quadratic equation for (H^{+}) gives

$$(H^{+})=\{(\text{Net Ions}) \pm [(\text{Net Ions})^2 + (4K_H K_1 P_{co_2})]^{0.5}\}/2. \quad (4)$$

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

$$pH=+6-\log_{10}\{\{(\text{Net Ions})+[(\text{Net Ions})^2+(4K_H K_1 P_{co_2})]^{0.5}\}/2\} \quad (5)$$

where the +6 factor results from the fact that the $\mu eq/\ell$ concentration unit is required for the terms in Eq. 5. Figure 1 illustrates Eq. 5 for a variety of temperature T and P_{co_2} values. Curve E was used to calculate the pH for the 1954 data.

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. Mg^{++} was not reported so it was estimated by assuming it to be related to Ca^{++}, with the $(Ca^{++})/(Mg^{++})$ ratio being assigned regional values based on a very

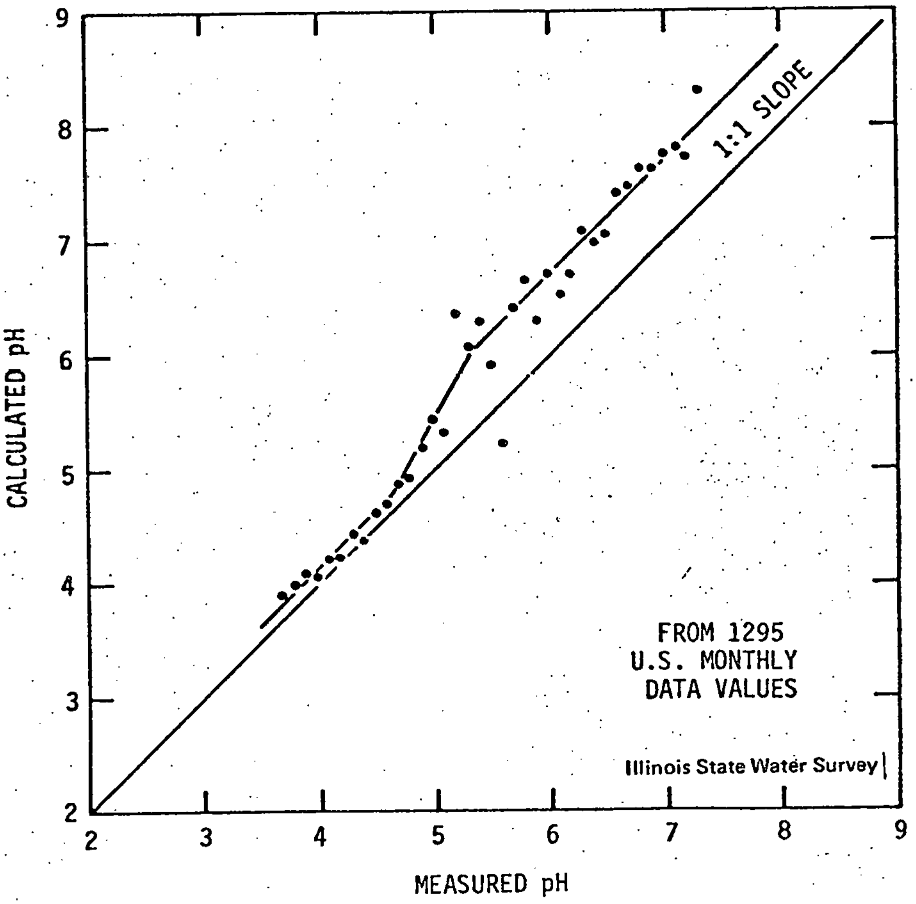

Figure 2. Calculated pH versus measured pH for monthly precipitation samples (from ref. 2).

values such that they will agree with the measured pH values. The equations for the three line segments are

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

where C = 0.70 for pH (calculated) ≥ 6.0 and C = 0.15 for pH (calculated) ≤ 4.8, and

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

for $4.8 < \text{pH (calculated)} < 6.0$. The data reported by Granat,[3] for about 1500 monthly samples from the European chemistry network, were also used to prepare a graph like Figure 2. Equations 6 and 7 also fit the Granat data very well. A firm explanation as to why Eqs. 6 and 7 are needed for the precipitation data is not yet available.

Finally, with respect to calculating pH, Eq. 1 can be compared with two other somewhat different approaches in the literature.

Granat[3] assumed that all the Na^+ and 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

$$(\text{Net Ions})_{\text{GRAN}}=(SO_4^=-SSSO_4^=)+(NO_3^-)-(Ca^{++}-SSCa^{++})-(Mg^{++}-SSMg^{++})-(NH_4^+)-(K^+-SSK^+). \quad (8)$$

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

Cogbill and Likens[4] also corrected each ion for sea salt but included Na^+ or Cl^- in the final equation. For example, if $(Na^+)/(Cl^-)$ was greater than the ratio for sea water, then the excess Na^+ was included in the equation and the base ion for making the sea salt correction was Cl^-. In this case the final equation, expressed in the form of Eq. 1, was

$$(\text{Net Ions})_{\text{COG}}=(SO_4^=-SSSO_4^=)+(NO_3^-)-(Ca^{++}-SSCa^{++})-(Mg^{++}-SSMg^{++})-(NH_4^+)-(Na^+-SSNa^+)-(K^+-SSK^+). \quad (9)$$

Equations 8 and 9 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.[5] Mg^{++} was not reported by Junge so regional ratios of Ca^{++} to Mg^{++} were used to estimate Mg^{++}, as was previously discussed. Also, Junge reported only quarterly values for NH_4^+ and NO_3^-. Thus, these values were weighted with the quarterly precipitation at the sites to produce annual averages for NO_3^- and NH_4^+.

The pH results are shown in Figures 3 and 4. In Figure 3 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 the linear correlation coefficient $r = 0.99$. In Figure 4, 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 Figure 2. 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.

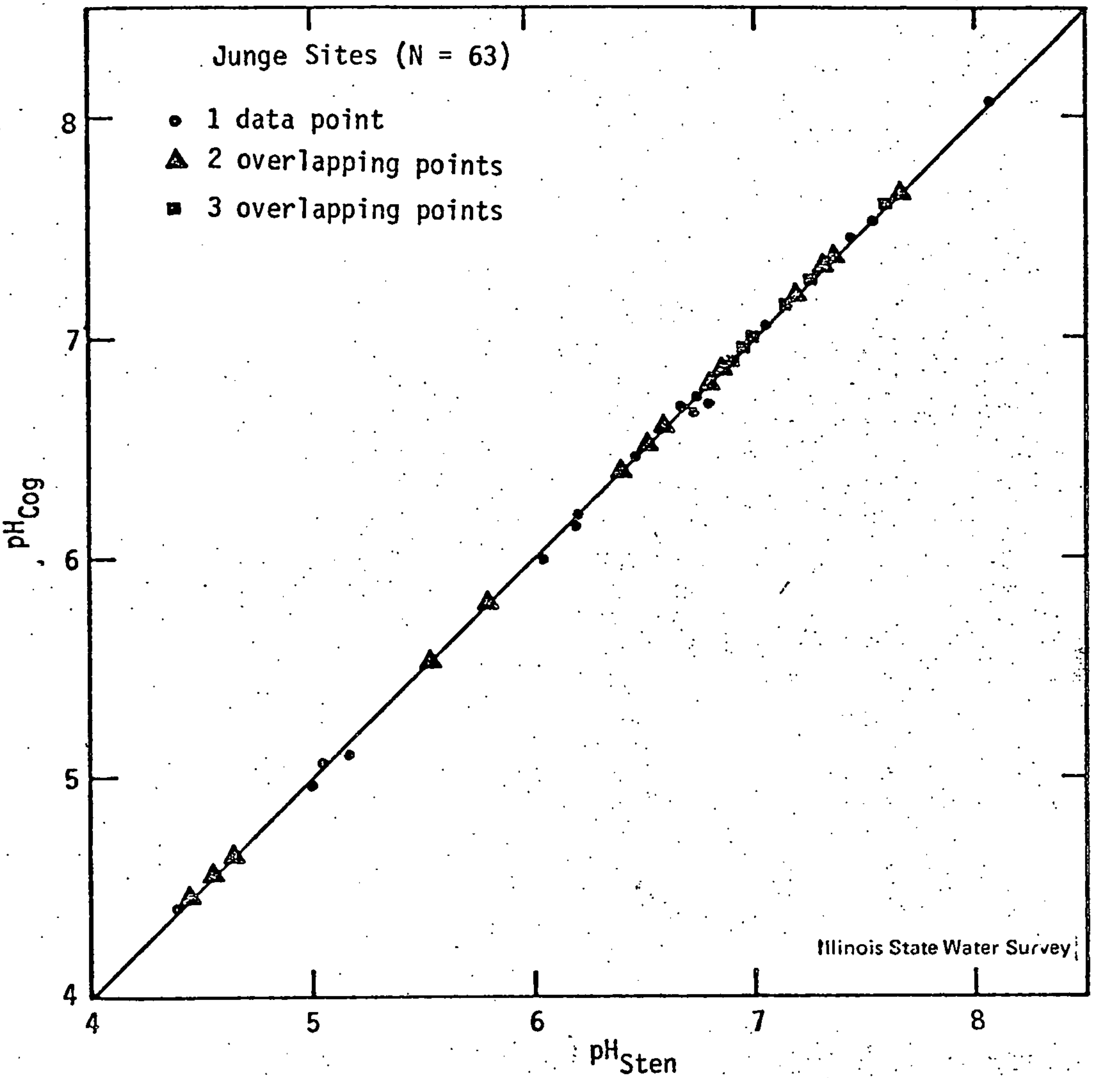

Figure 3. The pH calculated with the assumptions made by Cogbill and Likens versus the pH calculated with the assumptions by Stensland, for the 1955-56 Junge data (from ref. 2).

PRECIPITATION CHEMISTRY IN CENTRAL ILLINOIS IN 1954 AND 1977

The difference in the precipitation chemistry for a rural, east-central Illinois site in 1954 as compared to 1977 was investigated to ascertain whether or not the precipitation became more acidic and if so, why.* The 1954 data set[6] was unique for its time

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*This topic is covered in more detail in reference 1 and in a paper that has been submitted to the Journal of the Air Pollution Control Association.

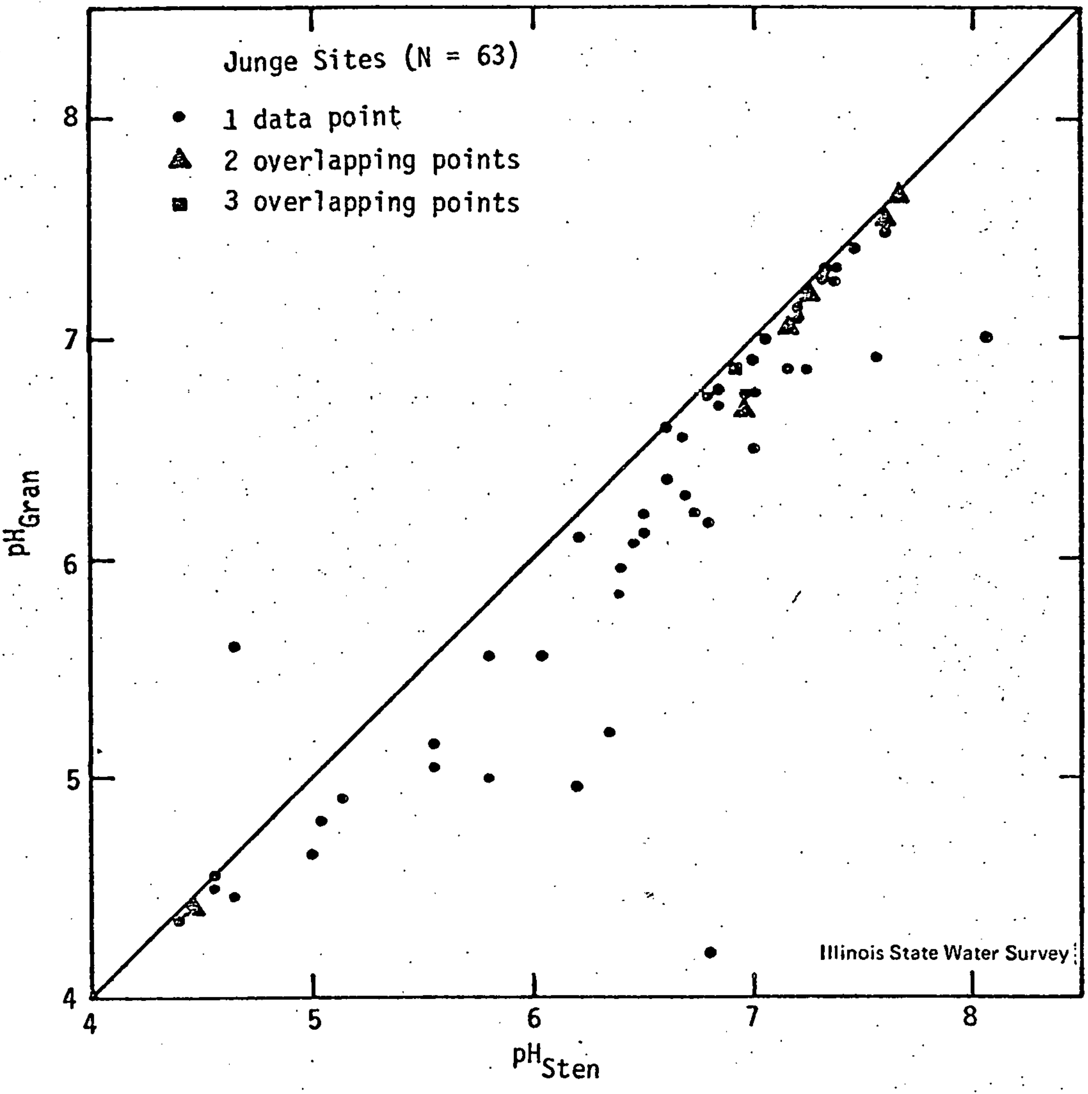

Figure 4. The pH calculated with the assumptions made by Granat versus the pH calculated with the assumptions by Stensland, for the 1955-56 Junge data (from ref. 2).

because the manual sampling technique carefully eliminated any dry deposition and because individual precipitation events were analyzed. The sampling site in both 1954 and 1977 was at the Champaign-Urbana airport (referred to as CMI), located 7 kilometers south of Champaign and surrounded by cultivated fields except for a golf course to the east. The data sets were collected from October 26, 1953 to August 12, 1954 and from May 15, 1977 to February 6, 1979. For convenience the two sets will be referred to as the 1954 data and the 1977 data.

For the 1977 study an automatic collector, which exposed the wet-side bucket only during the time of precipitation, was used. The polyethylene bucket was changed within 24 hours of the end of the precipitation event and then brought immediately to the laboratory where pH and conductivity were measured followed by sample filtration with a 0.45 micrometer membrane filter. The ions $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Mg^{++}, K^+, and Na^+ were determined by standard methods on AutoAnalyzer and atomic absorption instruments. The sampling and analysis procedures for the 1954 data are described in detail in the Larson and Hettick paper.[6]

From about May 15 to September 30 the landscape around CMI is mostly green due to the corn and soybean crops. In the fall season most of the farmland is tilled, producing a brown landscape. Since the local dust conditions thus may be quite different for the two periods, the precipitation chemistry data for 1977 was divided into the *green* period events and the *brown* period events. The data for pH show that this potential dust effect was not large for the 1977 data set. Due to the relatively small number of data points for 1954 these events were not divided into *brown* and *green* periods. Three other types of data separation were carried out. First, in the 1954 data there were six precipitation events wherein consecutive samples were taken, so a volume-weighted average was computed for each ion. These average values were used in the subsequent analyses. Second, there were six events, also in the 1954 data, where the sample collection began after the precipitation had started. Because the chemical concentrations are highest at the beginning of precipitation events, these six samples were given special consideration. Third, for the 1977 samples the procedures allowed very small samples to be analyzed and these data were also noted separately.

The precipitation pH was not reported for the 1954 data so Eqs. 5, 6, and 7 were used to calculate the pH. The frequency distributions of the calculated pH for 1954 and for the measured pH for 1977 are presented in Figure 5. It can be seen that the median pH does not change significantly when the smaller samples are included, but the *green* period pH is somewhat lower than the *brown* period pH. The 1977 combined *brown* and *green* period median pH, for events ≥ 0.70 mm, is 4.1. This compares with the calculated median pH of 5.9 for the 1954 data. If those 1954 samples with precipitation at the beginning are excluded, the 1954 median pH is 6.05. The more basic precipitation in 1954 could have resulted from low levels of acidic ions (e.g., sulfate and nitrate) or from high levels of basic ions (e.g., calcium and magnesium). This issue is addressed with the data in Table 1. For this table the small precipitation samples (<0.70 mm) were not included.

For sulfate in 1977 the median was 80 μeq/ℓ for the *brown* period, 65 μeq/ℓ for the *green* period, and 70 μeq/ℓ for the combined *brown* and *green* period. The median for 1954 was 50 μeq/ℓ, but when samples with precipitation at the beginning were excluded the 1954 median was 60 μeq/ℓ. As with sulfate, the 1977 nitrate values had a somewhat larger median for the *brown* period. The nitrate median was 38 μeq/ℓ for the *brown* period, 28 μeq/ℓ for the *green* period and 30 μeq/ℓ for the combined *brown* and *green* periods. The 1954 median nitrate value was 18 μeq/ℓ while the exclusion of samples with precipitation at the beginning increased the median to 20 μeq/ℓ. The hardness, defined as the sum of calcium and magnesium

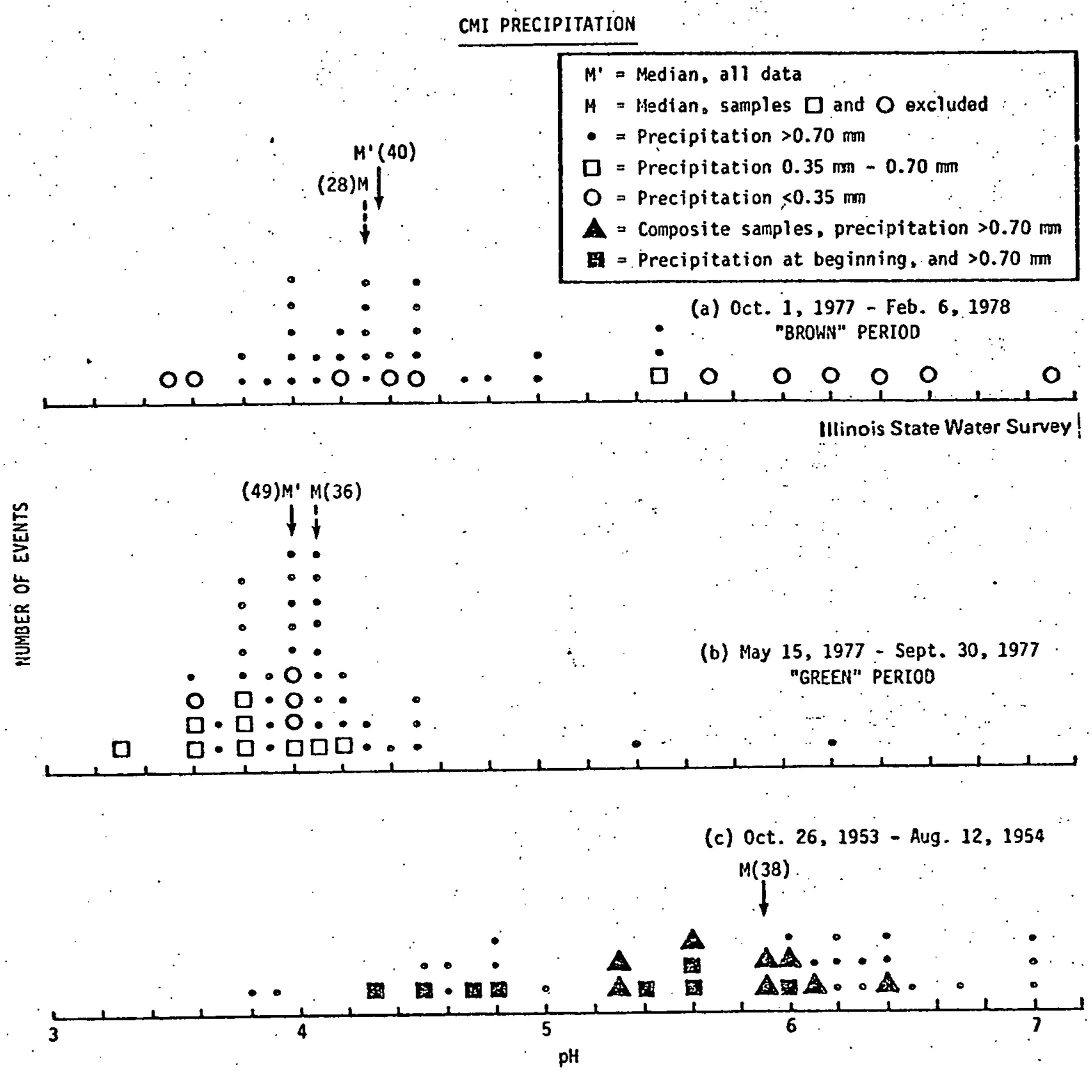

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Figure 5. Frequency distribution of measured pH for 1977 precipitation events and calculated pH for 1954 precipitation events. The numbers in parentheses indicate the number of data points from which the median was obtained (from ref. 1).

concentrations ($Ca^{++} + Mg^{++}$), was reported for the 1954 data and therefore is the quantity presented in Table I. The median hardness value for 1977 for the combined *green* and *brown* period was 10 μeq/ℓ, with the *brown* period median being 15 μeq/ℓ and the *green* period value being 10 μeq/ℓ. For 1954, the median hardness value was 65 μeq/ℓ, but when samples with precipitation at the beginning are excluded the median was 82 μeq/ℓ. Of the nine 1954 events with hardness greater than 100 μeq/ℓ, two were in the *green* period and seven in the *brown* period.

Table I. Ion concentrations (μeq ℓ^{-1}) and pH for precipitation samples (<0.70 mm).

	($SO_4^=$)	(NO_3^-)	($Ca^{++} + Mg^{++}$)	pH
Ill., 1954[a]	60	20	82	6.05[b]
Ill., 1977[a]	70	30	10	4.1

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[a] Median values for CMI event samples.
[b] Includes the empirical correction for calculated pH. Without this correction the value would be about 6.75.

With the data summarized in Table I there can be little question that the CMI samples in 1954 were much more basic than the 1977 samples. Although both $SO_4^=$ and NO_3^- were apparently lower in the 1954 samples, it was the high concentrations of soil related species, Ca^{++} and Mg^{++}, which produced the high pH in 1954. If the $Ca^{++} + Mg^{++}$ concentration in 1954 had been 10 μeq/ℓ (the 1977 level), the pH would have been 4.17 instead of 6.05. The median pH = 6.05 for 1954 includes the empirical correction in Eqs. 6 and 7. Without this correction the 1954 median pH value would have been about 6.75, and 4.34 with the 1977 level of $Ca^{++} + Mg^{++}$.

The high 1954 $Ca^{++} + Mg^{++}$ concentration could have resulted from problems in the chemical analysis procedures, or may be indicative of higher ambient air levels of these elements in 1954. Recent work at the Illinois State Water Survey has shown that the $Ca^{++} + Mg^{++}$ levels in rain can rise considerably with time if the samples are not filtered.[7] The 1977 samples were filtered but most of the 1954 samples were not. There are other preliminary data, however, which suggest that the absence of filtering will not account for the majority of the increase in the 1954 pH levels compared to the 1977 values.

Assuming now that the reported Ca^{++} + Mg^{++} values were accurate for the precipitation falling in 1954, one must then conclude that more calcium and magnesium were present in the atmospheric aerosols in 1954 than in 1977. A possible source could have been the dust from rural gravel roads, if they were more common in 1954. Also the types of crops grown and the size of the machinery used to cultivate the fields has changed in the CMI area since 1954. This could have modified the local dust levels to some extent, but no quantitative assessment is available. The final suggestion offered for the elevated Ca^{++} +Mg^{++} levels in the atmospheric aerosols is that the years 1953-1954 were very dry in many states of the Midwest and the Plains, and thus more susceptible to soil erosion by the wind, as compared to 1977. For instance, in 1954 the precipitation was -33% (below normal) in Oklahoma, -25% for Kansas, -14% for Nebraska, -13% for Missouri, +9% for Iowa, and -6% for Illinois. Research is now in progress to more fully investigate the possibe relation between droughts and elevated basic ions in precipitation.

SULFATE AND NITRATE TRENDS IN THE NORTHEASTERN UNITED STATES

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; (c) and wet and dry removal of the compounds from the atmosphere. 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 section will examine annual average values for source emissions estimates and for precipitation quality, for the northeastern United States for the mid-1950's versus the late 1970's.

The analysis presented in this section was undertaken because precipitation chemistry data have recently become available for the 1977-1978 period and therefore can be compared with existing data from 1954-55/56.[8] The locations of the sampling sites used in this analysis are shown in Figure 6. The MAP3S network[9] 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.[10] 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 an event precipitation chemistry collection program near Champaign, Illinois in May 1977, and this site (CMI) provided data for this analysis.[1] In addition, the ISWS study at the same site from October 1953, to August 1954, provided historical data for this analysis.[6] The Junge network was in operation from July 1955 to June 1956, and provided the remainder of the historical data.[5,11]

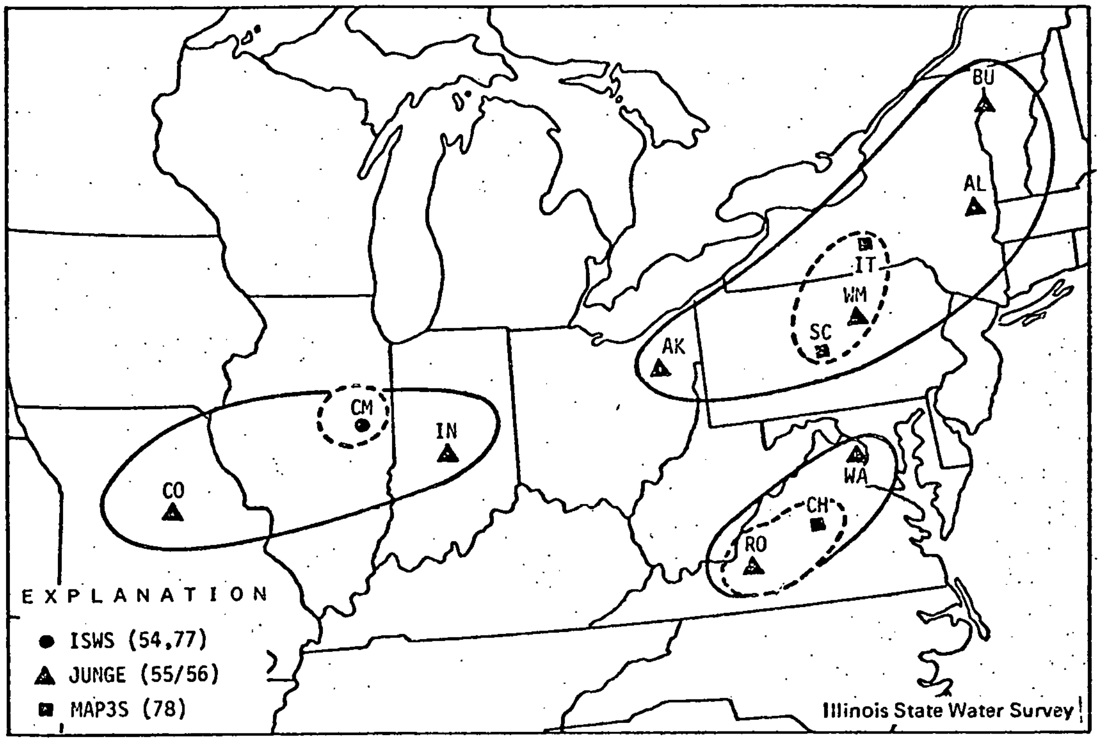

Figure 6. Location of precipitation chemistry sampling sites in the northeastern United States. The dashed lines enclose the primary sites being compared while the solid lines enclose additional sites for which data are presented (from ref. 8).

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 6 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, a 1.2 meter diameter stainless steel funnel being uncovered and well rinsed at the beginning of the events. Finally, the 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 II 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.

Table II. Median concentrations and sample volume weighted average concentrations for the MAP3S samples (mg/ℓ) (from ref. 8).

	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

The sulfate and nitrate concentration data for the sites shown in Figure 6 are presented in Tables III and IV. Accurate sample volumes were not available for the 1954 ISWS data. Therefore for all the ISWS data in Tables III and IV (site CMI) the median concentra-

Table III. Sulfate concentrations in precipitation (mg/ℓ as $SO_4^=$) and ratios of recent values to historical values (from ref. 8).

MIDWEST

1977/78	Ratio	1954	1955/56
CMI: 3.79	(1.2)	CMI: 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 IV. Nitrate concentrations in precipitation (mg/ℓ as NO_3^-) and ratios of recent values to historical values (from ref. 8).

MIDWEST

1977/78	Ratio	1954	1955/56
CMI: 1.85	(1.5)	CMI: 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

tions are given. For the Junge data the monthly compositing procedure produced sample volume weighted concentrations. Since the Junge data and the MAP3S data are to be compared, the MAP3S sample volume weighted averages are listed in Tables III and IV instead of the median values.

The upper portion of Table III 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 IV. The basic feature to note in the tables is the sulfate ratios are near one, while those for nitrate are greater than one. These trends will now be compared to the source emissions trends.

The emissions data which are presented in this section 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 precipitation quality sites in the northeastern United States. A study of the geographical distribution of the 1972 emissions data has shown that the EPA air quality regions I-IV (basically the eastern United States) contributed 80% of the total nitrogen oxide emissions.[12] 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.

It is generally accepted that the anthropogenic sources dominate over natural sources for industrialized areas such as the Northeast. Of the various sources categories, fossil fuel combustion at stationary sources dominates for the sulfur oxides.[13] In 1970 about 78% of the sulfur oxides were emitted from these sources. Steam electric power plants were the major stationary sources and they contributed 57% of the total sulfur oxide emissions. In total, coal combustion accounted for about 65% of the total sulfur oxide emissions. For nitrogen oxides, gasoline combustion in motor vehicles accounted for 34% of the total emissions in 1970 while coal, fuel oil, and natural gas combustion in stationary sources accounted for 44% of the total.[13]

The time trend of the estimated emissions is summarized in Table V. The EPA report providing the data for the lower half of Table V warned that the earlier estimates (upper half of Table V) had not been calculated in exactly 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 exactly. The data in these tables are expressed as SO_2 and NO_2. In Table VI the data from Table V have been 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 VI shows that nitrogen oxide emissions have increased much more than sulfur oxide emissions. From mid-1950 to 1976, nitrogen oxides increased from about 11 to 23 million metric tons per year,

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

	1940	1950	1960	1970
Nitrogen Oxides[a]	7.2	9.4	12.7	20.6
Sulfur Oxides[a]	19.5	21.6	21.1	30.8

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

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[a] Source: Reference #13 (p. 4, Table 1)
[b] Source: Reference #14 (p. 5-1, Table 5-1)

Table VI. Normalized emissions estimates as calculated from Table V (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

a factor of 2.1. At the same time, sulfur oxides increased from about 20 to 27 million metric tons per year, a factor of 1.3. The relatively small increase in the sulfur oxide emissions is explained by the fact that natural gas and low sulfur oil and coal have become more heavily used since the mid-1950's.[15] The larger growth rate in the nitrogen oxide emissions is due to the large increases in energy consumption for electric power and transportation. From 1955 to 1970 the former increased by a factor of 2.6 and the latter by a factor of 1.6.[15]

CONCLUSIONS

The results in this paper suggest that at present the best approach to calculating the pH of a precipitation sample is to assume that a charge balance exists and then to apply an empirical correction, as expressed in Eqs. 6 and 7. With this approach the

1977 central Illinois samples are shown to be much more acid than those from 1954. The primary reason for this pH decrease is the decreased concentration of calcium and magnesium in the samples.

For the mid-1970's compared to the mid-1950's the source emissions estimates for the United States were up by a factor of 1.3 for sulfur and 2.1 for nitrogen. During this same time interval the sulfate concentrations for the precipitation chemistry sites in the northeastern United States remained about the same and the nitrate concentrations increased by factors varying from 1.3 to 1.8. Since the emissions estimates increased more than the precipitation concentrations, it would seem that a smaller fraction of the pollutants were being removed over the northeast by wet processes in the mid-1970's than in the mid-1950's. This could be a result of the trend towards the use of taller stacks. However, the data presented in this paper are very limited both spatially and temporally so the conclusion should be considered as rather speculative.

ACKNOWLEDGMENTS

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