THE HISTORY AND CHARACTER OF ACID PRECIPTATION IN EASTERN NORTH AMERICA[1]

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ABSTRACT

The history and present distribution of precipitation acidity in eastern North America is reviewed. Precipitation chemistry from the 1920's indicates heavy ionic deposition, but low acidity (calculated) in Tennessee (pH 7.4) and New York (pH 6.15). However, high acidity was apparently widespread over northeast North America by 1955-56 and measured pH's below 4.5 were observed earlier. The geographic distribution of acid precipitation has spread through the present. Yearly average pH values for 1972-73 are not significantly different in New York and New Hampshire, indicating a regional consistency in acid (pH 4.10) deposition. Summer acidity is currently lower in Tennessee than in the Northeast. Precipitation chemistry of individual storms reveals some local variation even within a 3 km range, but a storm in central New York is generally homogenous over 70 km.

INTRODUCTION

While the history of precipitation acidity in Europe is well documented (Oden 1968), little is known about its geographic spread or time trends in North America. Only two synoptic surveys of precipitation chemistry have been carried out (Junge 1958, Junge and Werby 1958, Lodge et al. 1968) and annual surveys are available for only a few locations (Herman and Gorham 1957, Gambell and Fisher 1966, Pearson and Fisher 1971, Likens 1972, Likens and Bormann 1974). Significantly, all recent surveys show a wide area of low pH over the northeastern United

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States. This paper summarizes the history and describes the geographic distribution of the acidity of precipitation in North America. This information can be used to assess historical acidity values, dates of changes, and the approximate magnitude of recent perturbations. Such information is essential for gauging possible effects of this phenomenon.

Early reports on precipitation chemistry frequently lack data on pH. Where missing, other chemical determinations were used to predict pH using the method of Cogbill and Likens (1974). Briefly, a stoichiometric relationship is derived using the chemical components found in precipitation, and an exact ionic balance predicts the acidity. This approach allows the history of precipitation acidity to be expanded and is combined with actual measurements of alkalinity and pH. Additionally, detailed sampling within the eastern United States is used to elucidate the spacial variability of present-day acidity and to establish statistical procedures for analysis of acid precipitation data.

HISTORY OF ACIDITY

The earliest data for which pH determination is possible are from Tennessee (MacIntire and Young 1923). All parameters needed for pH prediction, except Na^+, were measured periodically from 1917 to 1922. Employing either the MacIntire and Young's (1923) subtraction-derived Na^+ concentration or the sea-salt (Cl^-) equivalent Na^+ concentration produces a predicted pH of approximately 7.3. Endpoint titrations performed on these Knoxville, Tennessee, samples yield an estimated pH of 7.0 using Granat's (1972) theoretical alkalinity curve or 7.5 using his empirical alkalinity curve. Other titrations from stations across Tennessee during this same period show alkalinity-predicted pH determinations from 6.7 to 7.9.

Numerous other precipitation acidity values have been reported. In Blacksburg, Virginia, from 1923 to 1928 all rain samples tested showed a distinct "alkaline reaction" (Ellett and Hill 1929). Collison and Mensching (1932) determined HCO_3 concentrations of samples from Geneva, New York between 1919 and 1928. Using the carbonic acid-bicarbonate equilibrium equation, the average calculated pH is 6.15 with annual averages ranging from 5.46 to 6.36. Also, all the chemical data from the 1920's indicate heavy deposition of SO_4^{--} and particulates, but that the pH was at or above the expected normal value of 5.6 (the CO_2 equilibrium point).

Houghton (1955) found that cloud water pH at the top of Mt. Washington averaged 4.5 between 1937 and 1940. This survey also recorded the earliest known precipitation pH, a 5.9 reading in one rainstorm in Brooklin, Maine, on 22 August 1939 (H.G. Houghton, personal communication to G.E. Likens). Values of individual raindrop pH show that a 4.2 pH occurred in Washington, D. C. in 1949 and raindrop pH from

1952-53 outside Boston, Massachusetts, averaged 4 (Landsberg 1954).

Cogbill and Likens (1974) used the 1954-55 precipitation chemistry data from Junge's synoptic network to produce a map of predicted pH (Figure 1). This map shows a regional pattern of pH below 5.6 in

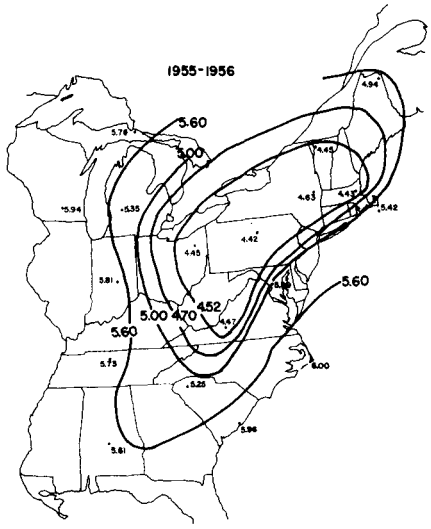

Figure 1. Distribution of predicted pH in 1955-56 (based on Junge 1958 and Junge and Werby 1958). Lines are placed at intervals of 10 μeq/l H^+, thus 5.6 is approximately neutral (=0 μeq/l), while each line lower indicates an increase of 10 μeq/l acidity.

eastern North America with the highest acidity (pH less than 4.52) centered over the New England and Middle Atlantic states. A second synoptic survey (Lodge et al. 1968, Pearson and Fisher 1971) formed the basis for predicting pH in 1965-66 (Cogbill and Likens 1974, see Figure 2). Also included on this map are acutal pH measurements from 1962-63 from the Southeast (Gambell and Fisher 1966). The same distribution of acidity seen 10 years earlier is found in 1965-66, but the acidity has spread south and west. The present pattern of pH acidity is obtained using measured pH values in eastern North America in 1972-73 (Kramer 1973, J. Miller personal communication, Cogbill and Likens 1974, see Figure 3). The region of high acidity (pH less than 5.6) has continued to spread and now covers all eastern North America

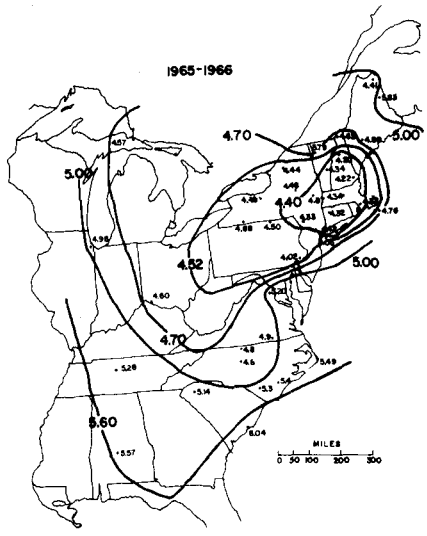

Figure 2. Distribution of predicted pH nominally for 1965-66 (based on Lodge et al. 1968, Gambell and Fisher 1966, and Pearson and Fisher 1971).

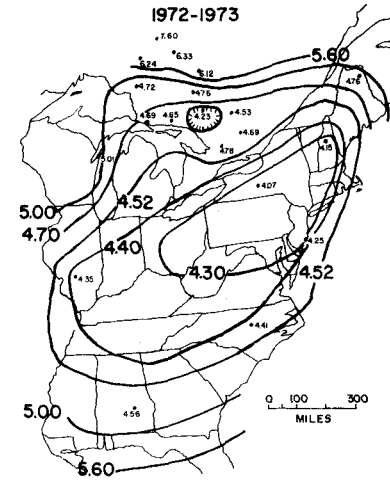

Figure 3. Distribution of observed pH during 1972-73 (based on Kramer 1973, J. Miller, personal communication (NOAA/EPA), and Cogbill and Likens 1974).

except the tip of Florida and northern Canada. Certain locations in the middle of the acid precipitation region display pH readings as low as 4.0.

Historically, highly acid precipitation has been prevalent over eastern North America since at least 1955. Low pH readings occurred in 1949 and probably earlier in some locations. While a source for acidity was present in the form of H_2SO_4 by 1939, indications are that there was no regional acid precipitation in 1928.

TIME TRENDS IN ACIDITY

The change of acidity is best illustrated by comparing predicted pH in 1955-56 to that measured 10 years later at the same locations. Nine stations at the periphery of the acid center occur in both surveys and permit an estimate of the spread of the acidity. Average increase in acidity at these sites was 12 μeq/l (about one isoline) over the 10 year period. This is about the accuracy of the prediction process. Two stations were included in all three synoptic surveys and they are located at the northern limit of the acid pattern. Caribou, Maine, had

an annual average pH of 4.94, 4.63, and 4.76 in 1955-56, 1965-66, and 1972-73 respectively. Concurrently, Sault Ste. Marie, Michigan, exhibited a change in pH from 5.76 to 4.76 to 4.69.

Two continuous series of precipitation chemistry data have been taken from 1966 to the present. The first is from the network of nine stations serviced by the United States Geologic Survey (USGS 1965-72) and the second is from Hubbard Brook, New Hampshire. Measured pH, averaged over the seven inland sites has remained between 4.30 and 4.66 in New York. In New Hampshire samples show a lower, but generally consistent pH between 4.04 and 4.19 (Likens and Bormann 1974). All these studies taken together indicate a definite spread of acidity over the past twenty years and a moderate, but irregular, decrease in pH in northeast North America.

GEOGRAPHIC VARIABILITY

I investigated the variability of precipitation acidity at locations within the extensive and consistent center of acid deposition. In 1972-73 56 individual storms were sampled at Ithaca, Aurora, and Geneva, New York (see Likens 1972, Cogbill and Likens 1974). Data for the same period from two locations in the Hubbard Brook Experimental Forest, New Hampshire was also collected (G.E. Likens, personal communication). In addition, weekly summer samples were taken at four locations in New Hampshire, including an altitudinal series up Mt. Moosilauke (from 215 m to 1370 m), and three locations in Great Smoky Mountains National Park, Tennessee (from Gatlinburg at 440 m to Newfound Gap at 1520 m). The pH of all samples was promptly measured with an Orion 401 pH meter standardized to 4.01 and 7.00. The Tennessee samples were from an area recently affected by acid precipitation and form a comparison for the Northeast samples.

All data were averaged using H^+ concentrations and compositing was accomplished by weighted averaging by precipitation amount. However, frequency distributions of the precipitation H^+ concentration in 82 storms throughout the year in New York and 40 weekly samples from New Hampshire show a log-normal distribution (X^2=8.99, d.f.=9, $p > .25$ and X^2 =5.24, d.f.=6, $p > .5$ respectively); that is, the pH is normally distributed. For this reason, all statistical tests are based on logarithmic transformations of the H^+ concentration, or equivalently the arithmetic mean and standard deviation of the pH values.

Local variation of pH over some 70 km was tested using the average seasonal pH values at the three central New York sites. A two-way factorial analysis of variance (ANOVA) (seasons by sites) demonstrates a significant difference ($p < .01$) between seasons, but no significant difference between sites. Winter had the highest pH (average 4.24)

while summer had the lowest (average 3.92). The pH at the three sites varied from 4.07 to 4.10. The logarithmic standard deviation per determination (s) was 0.06 pH units indicating that the overall variance over 70 km is very small. A two-way ANOVA (sites by storms) on 16 matched storms throughout the year at all three New York sites also failed to indicate significant differences as storms pass from one site to another, but a statistically significant difference ($p < .005$) between storms was found. The standard deviation per determination (s) is 0.16 pH units indicating that storms tend to add variation, but averaging over a year at a site reduces this variation (see s=0.06 above). In New Hampshire six summer storms were sampled at four sites less than 3 km apart. The two-way ANOVA (sites by storms) indicate a significant difference between both sites ($p < 005$) and storms ($p < .005$). Thus, under certain circumstances even over a short distance, there is considerable variability to precipitation pH in the same storm (in this case 3.83 to 4.02 site average). The standard deviation per determination (s=0.12) shows less variation than was seen between storms in central New York, but more variation over 3 km due to local sources than over 70 km in New York. Finally, ANOVA tests between sites spaced more than 1 km apart up mountainsides in New Hampshire (6 sites by 3 storms) and Tennessee (3 site one-way) show no significant differences between pH at sites on the same altitudinal series.

Differences between pH values at sites over 500 km apart indicate the magnitude of regional changes in precipitation acidity. A year of pH determinations at 5 sites, three in central New York and two at Hubbard Brook, New Hampshire were tested by one-way ANOVA. No significant difference between sites was found although the New Hampshire data show higher values (average pH 4.15 to 4.18) than New York values (4.04 to 4.11). However, the variation between the New York sites and the overall standard deviation per determination (s=0.27) show the tendency of local variation and small regional changes to obscure any differences over large distances. A one-way ANOVA using summer pH determinations in Tennessee, New York and New Hampshire yields a statistically significant difference between Gatlinburg (average pH= 4.18), Ithaca (average pH= 3.91), and Hubbard Brook (average pH= 3.96). By least significant differences, it is observed that the Tennessee pH is significantly higher in accord with its peripheral location, and the Northeast data is statistically indistinguishable. Significantly, the components of acidity (derived from the predictive pH relationship; Cogbill and Likens 1974) are about 62% H_2SO_4, 32% HNO_3, and 6% HCl at all three locations in the eastern United States. This indicates a quantitative difference over a distance of 1500 km, but little qualitative difference in precipitation chemistry across the regional pattern.

CONCLUSIONS

In summary, there is a regional pattern of acid precipitation covering almost all of eastern North America. This distribution is spreading to the south and west with some intensification at its center in the northeast United States. This concentric pattern existed in 1955-56, originating sometime after the 1920's. Highly acid precipitation (pH less than 4.52) was observed in 1949 and there is an indication that a source existed in 1939. Generally two historic types of precipitation chemistry in eastern North America emerge: sometime before 1950 precipitation was burdened with a heavy ionic load, but low acidity; since at least 1950 precipitation has had a lower ionic, but greater acidity load than before.

Individual storms and seasons differ significantly in acidity among themselves and sites even within 3 km show considerable local variation. However, acidity at sites over 500 km apart shows a regional (and annual) consistency in H^+ concentration. Peripheral areas indicate the spreading of acidity, but maintain higher pH values than central locations. The present distribution of acid precipitation (pH less than 5.6) seems well established. The bounded zone now covers a wide area, but it cannot yet be predicted how widespread and intense acid precipitation will become.

REFERENCES

Cogbill, C. V. and G. E. Likens. 1974. Acid precipitation in the northeastern United States. WATER RESOUR. RES. 10:1133-1137.

Collison, R. C. and J. E. Mensching. 1932. Lysimeter investigations: II. Composition of rainwater at Geneva, New York, for a 10-year period., N. Y. STATE AGR. EXPT. STA., TECH. BULL. 193. 19 pp.

Ellett, W. B. and H. H. Hill. 1929. Effect of lime materials on the outgo of sulfur from Hagerstown silt loam soil. J. AGR. RES. 38:697-711.

Gambell, A. W. and D. W. Fisher. 1966. Chemical composition of rainfall in eastern North Carolina and southern Virginia. GEOL. SURVEY WATER SUPPLY PAPER 1535-K. 41 pp.

Granat, L. 1972. On the relation between pH and the chemical composition in atmospheric precipitation. TELLUS 24:550-560.

Herman, F. A. and E. Gorham. 1957. Total mineral material, acidity, sulfur, and nitrogen in rain and snow at Kontville, Nova Scotia. TELLUS 9:180-183.

Houghton, H. G. 1955. On the chemical composition of fog and cloud water. J. METEOROL. 12:355-357

Junge, C. E. 1958. The distribution of ammonia and nitrate in rain-water over the United States. AMER. GEOPHYS. UNION TRANS. 39:241-248

Junge, C. E. and R. Werby. 1958. The concentration of chloride, sodium, potassium, calcium, and sulphate in rain water over the United States. J. METEOROL. 15:417-425.

Kramer, J. R. 1973. FATE OF ATMOSPHERIC SULFUR DIOXIDE AND RELATED SUBSTANCES AS INDICATED BY CHEMISTRY OF PRECIPITATION. Dept. Geology, McMaster Univ., Hamilton, Ont. 143 pp.

Landsberg, H. E. 1954. Some observations of the pH of precipitation elements. ARCHIV FÜR METEROLOGIE, GEOPHYSIK U. BIOKLIMATOLOGIE. SER A., 7:219-226.

Likens, G. E. 1972. The chemistry of precipitation in the central Finger Lakes region. Cornell Univ. Water Resources and Marine Science Center. Ithaca N.Y. TECH. REP. 50. 47 pp.

Likens, G. E. and F. H. Bormann. 1974. Acid Rain: A serious regional environmental problem. SCIENCE 184:1176-1179.

Lodge, J. P. Jr., K. C. Hill, J. B. Pate, E. Lorange, W. Basbergill, A. L. Lazrus, and G. S. Swanson. 1968. CHEMISTRY OF UNITED STATES PRECIPITATION. Final report on the national precipitation sampling network. Laboratory of Atmospheric Sciences, National Center for Atmospheric Res. Boulder, Colorado. 66 pp.

MacIntire, W. H. and J. B. Young. 1923. Sulfur, calcium, magnesium, and potassium content and reaction of rainfall at different points in Tennessee. SOIL SCI. 15:205-227.

Pearson, F. J. Jr. and D. W. Fisher. 1971 Chemical composition of atmospheric precipitation in the northeastern United States. GEOL. SURV. SUPPLY PAPER 1535-P. 23 pp.

USGS (United States Geologic Survey) 1965-72. WATER RESOURCES FOR NEW YORK, PART 2 WATER QUALITY RECORDS. U. S. Dept. of the Interior.