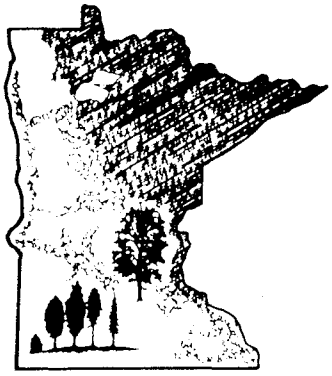

Minnesota Forestry Research Notes

No. 275
January 1980

SULFATE-SULFUR CONTENT AND pH OF RAINWATER AT A FORESTED SITE IN NORTHERN MINNESOTA

Edwin H. White and Charles F. Kramer*

ABSTRACT

Data are presented on SO_4-S and pH levels of wet plus dry fallout for 25 precipitation events from July 16 to November 11, 1977, on an area 17 km west of Cloquet, Minnesota. Average SO_4-S levels were 1.4 mg/l, and pH ranged from 4.0 to 6.6 with a median value of 5.5. No generally serious acidification of rainfall is indicated although individual rainfall events may be highly acidic.

Increasing acidity of precipitation has become a major environmental concern in several regions of the world including the United States. Likens and Bormann (8) and Likens et al. (9) have indicated increasing rainfall acidity in the northeastern United States over the past 20 years compared to the rest of the country. Rainfall pH's averaging 3 to 4 have been reported for locations in New York and New Hampshire with extreme values as low as pH 2.1 (3). Acidity of rainwater is a concern because of its effects on progressive acidification of soils, flora and fauna, corrosion of metals, and human health (4). A major symposium (4) has reviewed acidity of precipitation.

Sulfur dioxide, scavenged from the atmosphere and chemically transferred, provides major contributions to the acidity of rainwater. However, quantitative data on SO_4-S concentrations of rainwater are generally lacking for specific areas of northern Minnesota.

This paper presents the SO_4-S content and pH of rainwater plus dry fallout collected at the Cloquet Forestry Center 17 km southwest of Duluth, Minnesota, from mid-July to mid-November 1977. The data represent an initial sampling of acidity and SO_4-S of precipitation plus dry fallout in the study area.

METHODS

Five polyethylene bottles with 20-cm polyethylene funnels fitted with glass wool filters were used to collect combined dry and wet fallout from July 16 to November 11, 1977. The collection bottles were acid washed and thoroughly rinsed with distilled water after each sampling period. Duplicate samples were taken for analysis after bulking each storm. Total precipitation was measured using a standard U.S. Weather Service rain gauge.

After collection, the pH of each sample was potentiometrically determined without stirring or agitation after allowing the sample to sit for 3 minutes. Chemical analysis for SO_4-S was done by the Research Analytical Laboratory, Department of Soil Science, University of Minnesota using the EPA Automated Technician II Methylthymol Blue tentative method for the determination of sulfates in the atmosphere (2). Standard statistical procedures, including correlation analysis, were used to analyze the data (9).

*Professor and Research Plot Technician, respectively, Department of Forest Resources, College of Forestry, University of Minnesota, St. Paul, MN.

Published by the College of Forestry, 1530 North Cleveland Avenue, St. Paul, Minnesota 55108. E. Sucoff, editor.

RESULTS AND DISCUSSION

The rainfall plus dryfall had a median pH of 5.5 with extreme variations from 4.0 to 6.6 (Table 1). In the absence of major manmade pollutants, raindrops falling through the atmosphere will reach an equilibrium pH of approximately 5.7 from the absorption of atmospheric CO_2 which dissolves in water to produce the slightly acidic carbonic acid. The pH values exceeding 5.7 may be due to neutralization by calcerous dust from the west. Calcium bicarbonate may be an active ion-pair in these samples as evidenced by the relatively high calcium values of precipitation reported by Comerford and White (1). There was no significant correlation ($P \leq .05$) between the pH and SO_4-S levels indicating that for the majority of the storms additional mechanisms such as the carbonic acid system were involved in determining the combined pH of wet and dry fallout. There were several precipitation events wih pH values well below the carbonic acid equilibrium. Differences in pH among events are most likely related to storm and wind direction with higher pH's associated with rainfall and dryfall from less developed areas and lower pH's associated with rainfall and dryfall from industrialized areas which generate pollutants. Rainwater pH was not related to sampling date between July 16 and November 11 (Table 2).

The SO_4-S levels of the rainfall and dryfall were low relative to regions of the world experiencing acid rainfall problems. Average SO_4-S concentrations were 1.4 ppm and ranged from a low of 0.6 to a high of 5.4 ppm. Glass (6) has reported similar low levels of sulfate in precipitation at a forested site approximately 115 km north of the present study area. Gorham (7) has reported that the average SO_4 concentration for one year's precipitation in Minnesota is 1.4 ppm. Gardner (5) has reported the average SO_4-S content in 40 rainwater samples collected in the vicinity of Floodwood, Minnesota (32 km northwest of the sampling site in this study) as 1.8 ppm with a range of 0 to 11.2 ppm. In contrast, the average SO_4-S ion content in 300 rainwater samples collected in the vicinity of the Northern States Power Company's Sherco plant near St. Cloud, Minnesota (130 km southwest of the sampling site in this study) is 4.5 ppm with a range of 0.2 to 24.2 ppm (5).

Generally, the higher SO_4-S levels in the present study were associated with precipitation of less than a few millimeters (Table 1) although the negative correlation between millimeters of rainfall and SO_4-S was not significant (Table 2).

The data from the present study also indicate the total SO_4-S inputs by precipitation to a forest site in northern Minnesota. These data should prove valuable in assessing the impact of such forest management operations as full-tree harvesting on the sulfur cycle and site productivity. From mid-July to mid-November 1977 5 kg/ha of SO_4-S were added to the forest site by dryfall and rainfall. This amount for 5 months is consistent with the yearly total deposition of 10-15 kg/ha of SO_4-S (wet plus dry) measured in the Minnesota Copper-Nickel Study at a site 115 km north of the present study during the 2-year period of 1976 78 (6).

This study indicates acid rainfall is not a problem on the Cloquet Forestry Center although individual storms may be low in pH. Together with previous data (1, 5, 7, 11) the results suggest that the precipitation and dryfall falling on northern Minnesota have a relatively low sulfur content. However, other locations within the region may have serious SO_4-S or pH problems. Numerous studies (4) have reported wide extremes of rainfall pH and SO_4-S levels within a large geographic area caused by industrial inputs of atmospheric pollutants. The importance of local influences on rainfall acidity and ionic constituents has reinforced the need for quantitative site specific data such as that of the present study.

LITERATURE CITED

1. Comerford, N. B. and E. H. White. 1977. Nutrient content of throughfall in paper birch and red pine stands in northern Minnesota. Can. J. For. Res. 7(4):556-561.

2. EPA. 1978. Tentative method for the determination of sulfates in the atmosphere (automated technician II methylthymol blue procedure). Envir. Monitoring and Support Lab., EPA, Research Triangle, N.C.

3. Fisher, D.W., A. W. Gombell, G. E. Likens, and F. H. Bormann. 1968. Atmospheric contributions to water quality of streams in the Hubbard Brook Experimental Forest. Water Resource Res. 4(5):1115-1126.

4. Forest Service. 1975. Proceedings of the first international symposium on acid precipitation and the forest ecosystem. N.E. For. Exp. Sta., Upper Darby, PA. 1074 pp.

5. Gardner, D. 1979. Chemistry of rain in the vicinity of a sulfur dioxide point source in central Minnesota. M.S. thesis. Dept. Plant Pathology, Univ. Minn., St. Paul. 102 pp.

6. Glass, G. E. 1979. Impacts of air pollutants on wilderness areas of northern Minnesota. EPA, Envir. Res. Lab., Duluth, MN. 187 pp.

7. Gorham, E. 1961. Factors influencing supply of major ions to inland waters, with special reference to the atmosphere. Geol. Soc. Amer. Bull. 72, p. 795-840.

8. Likens, G. E. and F. H. Bormann. 1974. Acid rain: a serious regional environmental problem. Science 182 (4142):1176-1179.

9. Likens, G. E., F. H. Bormann, and N. M. Johnson. 1972. Acid rain. Environment 14(3):33-40.

10. Steele, R.G.D. and J.H. Torrie. 1960. Principles and Procedures of Statistics. McGraw-Hill Book Co., Inc., N.Y. 481 pp.

11. Verry, E. S. and D. R. Timmons. 1977. Precipitation nutrients in the open and under two forests in Minnesota. Can. J. For. Res. (1):112-119.

Table 1. Concentration of SO_4-S and pH of rainwater and dry fallout at the Cloquet Forestry Center in northern Minnesota, July 16 to November 11, 1977.

Sampling Date	Rainfall	pH	SO_4-S
	mm		mg/l
7/16	17	5.1	0.85
7/17	27	4.5	0.60
7/28	28	4.9	0.80
7/31	42	4.9	1.45
8/1	3	5.4	1.05
8/2	7	5.6	0.95
8/4	3	5.5	0.80
8/13	4	5.6	1.15
8/15	9	5.4	0.70
8/24	2	4.8	1.60
8/27	37	5.2	0.65
8/28	8	5.7	0.55
8/31	5	5.8	0.75
9/4	32	5.4	0.55
9/6	25	5.7	0.90
9/10	2	5.5	5.40
9/19	1	4.8	4.80
9/26	57	4.7	0.60
9/29	6	5.9	0.55
10/10	37	5.6	1.75
10/12	23	6.6	0.70
10/20	7	5.9	0.90
10/27	2	6.3	3.60
10/31	14	4.3	1.75
11/11	37	4.0	1.75
Average			1.41
S.D.			±1.29

Table 2. Correlation matrix (r values) among rainwater parameters.

	Time	Rainwater amount	Rainwater pH	Rainwater SO_4-S
Time	--			
Rainwater amount	.08	--		
Rainwater pH	.06	-.45*	--	
Rainwater SO_4-S	.31	-.33	-.05	--

* r value significant at $p \leq .05$, d.f. = 1, 24.

Published as Misc. Jour. Ser. Paper No. 1743 of the Univ. of Minn. Agr. Expt. Sta.