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**pH and Sulfate Data of
Rainwater July to August 1977
at the Biological Station,
St. Andrews, N.B.**

D.B. Sergeant and V. Zitko

Biological Station,
St. Andrews, N.B., EOG 2X0

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May 1978

pH AND SULFATE DATA OF RAINWATER JULY TO AUGUST 1977
AT THE BIOLOGICAL STATION, ST. ANDREWS, N.B.

by

D. B. Sergeant and V. Zitko

Fisheries and Environmental Sciences
Fisheries and Oceans Canada
Biological Station
St. Andrews, New Brunswick EOG 2X0

This is the ninth Manuscript Report in this series from
the Biological Station, St. Andrews, N.B.

ABSTRACT

Sergeant, D. B., and V. Zitko. 1978. pH and sulfate data of rainwater for July to August 1977 at the Biological Station, St. Andrews, N.B. Fish. Mar. Serv. MS Rep. 1468, 6 p.

pH and sulfate data of rainwater were obtained for the period July 26 to August 26, 1977, at a sampling site located at the Biological Station, St. Andrews. The average pH and sulfate (mg/L) were 3.88 and 2.30 respectively.

It was concluded that the precipitation was mainly acidic at this sampling site.

Key words: pH, sulfate, acid precipitation

RÉSUMÉ

Sergeant, D. B., and V. Zitko. 1978. pH and sulfate data of rainwater for July to August 1977 at the Biological Station, St. Andrews, N.B. Fish. Mar. Serv. MS Rep. 1468, 6 p.

Des données de pH et de sulfate ont été recueillies pour la période du 26 juillet au 26 août 1977, à un lieu d'échantillonnage situé à la Station de biologie à St-Andrews. Les moyennes de pH et de sulfate (mg/L) étaient 3.88 et 2.30 respectivement.

Nous avons conclu que la précipitation était surtout acide à ce lieu d'échantillonnage.

INTRODUCTION

Acid precipitation has been defined as precipitation having a pH less than 5.6-5.7, which is the pH of rainwater in equilibrium with atmospheric carbon dioxide at normal pressure (Barret and Brodin 1955; Cooper et al. 1976; Richardson and Merva 1976).

This study was prompted by the rising concern over the effects of acid precipitation on both flora and fauna. It was also conducted for comparison with the data obtained for this location during the same time period in 1976, when the authors participated in the Atmospheric Environment Service's Intensive Sulfates Study (AES ISS) (Anon. 1977). Comparison is also possible with the earlier unpublished data (Appendix 1) of Zitko and Carson in their study of trace elements, pH and sulfate at this location and in the vicinity.

The time interval chosen for the present study was the same July-August period as that of the AES ISS of 1976. This was done to allow a more relevant comparison of pH and sulfate data.

A major source of information on acid precipitation and its effects is found in the proceedings of a symposium of the USDA (Anon. 1976a) and a subsequent workshop (Anon. 1976b). Closer to St. Andrews, data are available for Caribou, Maine (Anon. 1975a), Saint John, N. B. (Anlauf et al. 1976), the northeastern United States (Jacobson et al. 1976), and for Washington, D. C. (Miller et al. 1976). References can also be found to work on modelling (Burton and Hidy 1974), individual raindrop pH and hailstone melt pH (Miller et al. 1976), regulations (Anon. 1975b), and on dry emissions (Whelpdale 1976).

METHODOLOGY

Rain samples were collected in a 1-liter polyethylene bottle connected directly to a 26-cm diameter polyethylene funnel. The bottle was enclosed in a weighted wooden box which was covered with a styrofoam ring, supporting the funnel. The collection apparatus was placed on the roof of the Station, well away from any above-roof projections. The funnel and the collection bottle were washed daily with distilled-deionized water to remove any traces of the previous sample (or dry fallout and bugs that may have accumulated during periods of no precipitation).

Samples were taken to the laboratory and their pH was measured at 22°C against standard buffer solutions (Fisher 4.01, 6.86 and 7.41). An Orion Model 801 digital pH meter equipped with an Orion (No. 91-02-00) combination pH electrode was used. Sample pH's were taken as

soon after sampling as possible and are subject to the usual tolerances (Lively 1975).

The samples were then stored under refrigeration until a sufficient number was accumulated to perform conveniently sulfate analysis. Sulfate was determined according to the turbidimetric method of Tabatabai (1974). The samples were not filtered prior to taking an aliquot for analysis as they did not appear to contain any particulate matter.

RESULTS AND DISCUSSION

The pH and sulfate data of the study are presented in Table 1. The number of millimeters of precipitation, recorded by the Station's standard rain gauge, is also given.

The data for the 1976 AES ISS are reproduced in Table 2 for comparison purposes.

Average pH was 4.68 in the AES ISS of 1976, and 3.88 in the present study. No event with pH greater than 5.7 was observed in 1977, but one event above this pH was observed in 1976. This was the sample that seemed to change between the time it was taken and the time it reached AES for analysis. The pH ranged from 2.99-4.74 in 1977, compared to 4.1-6.53 in the AES ISS of 1976.

Comparison of the 1976 and 1977 pH readings with other eastern seaboard locations can be made by reference to the compilation of pH and sulfate data in Table 3. St. Andrews data seem to agree better with those of the northeastern United States (to our south) than with data for more northern or eastern Canadian locations (which experienced rainfall of significantly higher pH during the AES ISS, with many readings above the pH 5.7 value of pure rainwater in equilibrium with atmospheric carbon dioxide). Generally the data at this site lend support to Summers and Whelpdale's (1976) identification of the Atlantic region as an area "where slight to moderately acidic precipitation appears to be falling over a large area" and "where extremely acid (pH < 4.0) precipitation has been detected".

No meteorological data were obtained for the period of our 1977 study but the trend found by Anlauf et al. (1976) for Saint John, N. B., would be expected to hold here as well. They observed pH's of 3.4 to 3.8 from southerly air flow and 4.33 from northerly flow.

Examination of the sulfate data from the St. Andrews studies indicates that it can vary significantly for the same period from one year to the next for the same location. At this location, readings from 0.23 to 34.0 mg/L have been recorded in the three studies.

Figure 1 (a, b, and c) graphically portrays the 1976 AES ISS and 1977 precipitation data

Table 1. 1977 precipitation data.

24-hr period ending 10.00 am	Precipitation (mm)	pH	SO ₄ ⁼ mg/L
July 31		4.74	0.75
Aug. 2	10.67	3.78	3.83
Aug. 6	2.54	3.92	1.83
Aug. 11	7.11	3.88	2.28
Aug. 12	0.51	2.99	3.08
Aug. 13	6.86	3.03	2.18
Aug. 15	5.08	4.04	2.18
Aug. 17	17.78	4.66	0.23
Aug. 18	33.02	4.09	2.05
Aug. 23	6.60	4.17	5.40
Aug. 25	2.54	3.41	1.53
Arithmetic average		3.88	2.30
Geometric average		3.84	1.81

^aJ. Hull et al. (unpub. data)

Table 2. 1976 AES ISS precipitation data.

24-hr period ending on	AES std rain gauge (mm)	pH	SO ₄ ⁼ mg/L
July 30	0.8	-	5.1
Aug. 2	11.9	4.47	2.2
Aug. 3	0.5	-	2.5
Aug. 7	2.3	4.10(4.2)	6.1
Aug. 8	6.1	- (3.86)	15.1
Aug. 9	10.7	4.95(5.03)	0.6
Aug. 10	4.6	6.53(7.35)	1.5
Aug. 11	1.0	- (3.92)	13.8
Aug. 15	0.3	- (4.3)	13.6
Aug. 16	24.4	4.31(4.2)	4.4
Aug. 28	8.9	3.81(3.95)	9.8
Aug. 29	3.8	4.56(4.6)	3.4
Arithmetic average		4.68(4.60)	6.51
Geometric average		4.61(4.51)	4.47

^aNumber in brackets was reading taken at our site prior to sending sample to AES.

Table 3. pH and sulfate values from other studies.

Location	Year of study	pH	SO ₄ ⁼ mg/L	Reference
St. Andrews, N. B.	1977	Avg. 3.88	Avg. 2.30	This study
St. Andrews, N. B.	1976	Avg. 4.68	Avg. 6.51	Anon. (1977)
St. Andrews, N. B.	May 1975 to March 1976	Avg. 4.22	Avg. 10.2	Zitko & Carson (unpub.)
Saint John, N. B.	1973	3.68-4.06	5.7-11.5	Anlauf et al. (1976)
Charlo, N. B.	1976	Avg. 5.93	Avg. 4.68	Anon. (1977)
Halifax, N. S.	1976	Avg. 4.52	Avg. 3.46	"
Sable Island	1976	Avg. 5.77	Avg. 7.53	"
Stephenville, Newfoundland	1976	Avg. 4.97	Avg. 6.62	"
Northeastern United States	1970-1971	3.9-5.8	--	Likens and Borman (1974)
Eastern US & N. Europe		4-5	--	Overrein (1977)
Caribou, Maine	1973	4.96	1.162	Anon. (1975a)
Washington, D. C.	1949	3.91-4.84		Miller et al. (1976)
Washington Airport	Landsberg's Study January to August	Individual Raindrops 4.1-6.2	--	"
Camp Station Washington D.C.	1960			
	1963	4.0	--	"
	1964	4.4		
	1965	4.6		
State of Maine	--	3.8-5.0		Boyce and Butcher (1976)
Yonkers, N. Y.	1974	3.4-4.9 (mean 4.1)	1-20	Jacobson et al. (1976)

^aRain and snow

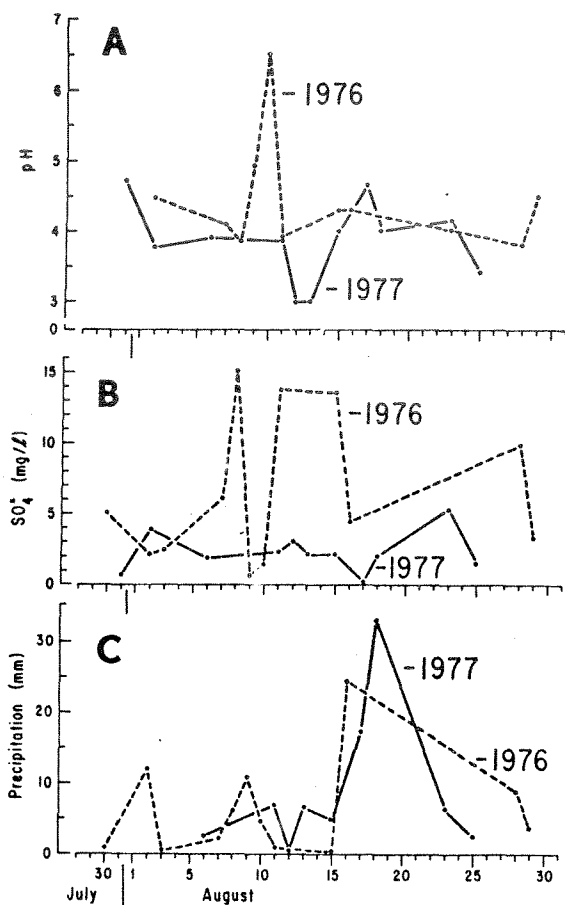


Fig. 1. Plots of pH, sulfate and millimeters of precipitation against time for the 1977 study and the 1976 AES ISS.
 ---- 1976 AES ISS Data
 ——— 1977 Data

for pH, sulfate and millimeters of precipitation.

From Figure 1 (b, c) there appears to be a negative correlation between sulfate concentration and millimeters of precipitation. Sulfate is highest when the millimeters of precipitation received are lowest. This suggests that sulfate washes out of the atmosphere at the start of the precipitation event and is then diluted by further precipitation.

Figure 1 (a, c) indicates that a similar correlation exists between pH and millimeters of precipitation, but it is not as noticeable as above.

In the 1976 AES ISS, the correlation between pH and sulfate values follows the general trend of high sulfate values accompanying low pH and vice versa. However, sulfate values do not entirely explain the acidity of most of the sample points and further experimentation (NO₃⁻ and Ca²⁺) would have been required to account for these pH values. There appears to be no correlation between sulfate and pH in the present study. The concentrations of sulfate were generally low. Additional data are needed on the presence of other strong acid anions.

CONCLUSIONS

Acidic precipitation (pH < 5.7) is falling at our location in southern New Brunswick. The occasional pH value above the equilibrium level of 5.7 was observed, but the average pH was 3.83, 4.68, and 3.88 in 1975-1977, and the concentration of sulfate was 10.2, 6.51, and 2.30 mg/L, respectively. The data are insufficient to make conclusions about trends of either pH or sulfate concentration.

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Appendix 1. pH and Sulfate in Precipitation at the Biological Station, St. Andrews, New Brunswick.^a

Date	Rainfall (mm)	pH	SO ₄ mg/L	Date	Rainfall (mm)	pH	SO ₄ mg/L
May 7, 1975	7	6.30	5.0	July 22, 1975	no data	4.60	34.0
" 22, "	1	3.00	4.5	" 27, 1975	9	4.90	<0.2
" 27, "	6	4.05		Aug. 2 "	no data	4.35	4.4
" 29, "	7	4.00	6.0	" 18 "	trace	3.50	30.0
June 4, "	1	3.50	2.9	Sept. 2-3 "	10	4.15	6.0
" 7-8 "	6	4.30		" 13 "	no data	4.80	7.0
" 14 "	21	4.75		Feb. 17, 1976	8	4.50	2.0
					(snow not counted)		
July 11 "	2	3.70	17.0	" 22, "	25	3.90	3.0
" 14 "	no data	4.14	14.0	Mar. 5, "	2	3.85	7.0

Average pH (calculated from average hydrogen ion concentration) = 3.83

Average sulfate concentration 10.2 mg/L (<0.2 value excluded)

Average sulfate deposition, as sulfur, 3.24 g/m² year.

^aReproduction of unpublished data of Zitko and Carson.