EFFECT OF SNOWMELT ON THE QUALITY OF FILSON CREEK AND OMADAY LAKE, NORTHEASTERN MINNESOTA

WITH A SECTION ON

PRELIMINARY EVALUATION OF METHODS FOR DETERMINATION OF SULFATE CONCENTRATION IN PRECIPITATION AND OTHER DILUTE SOLUTIONS

U. S. GEOLOGICAL SURVEY
WATER-RESOURCES INVESTIGATIONS 81-66

PREPARED IN COOPERATION WITH THE
U. S. ENVIRONMENTAL PROTECTION AGENCY

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

50272-101

REPORT DOCUMENTATION PAGE

1. REPORT NO.

2.

3. Recipient's Accession No.

4. Title and Subtitle Effect of snowmelt on the quality of Filson Creek and Omaday Lake, northeastern Minnesota, with a section on Preliminary evaluation of methods for determination of sulfate concentrations in precipitation and other dilute solutions

5. Report Date September 1981

6.

7. Author(s) D. I. Siegel

8. Performing Organization Rept. No. USGS/WRI 81-66

9. Performing Organization Name and Address

U.S. Geological Survey
Water Resources Division
702 Post Office Building
St. Paul, Minnesota 55101

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.

(C)

(G)

12. Sponsoring Organization Name and Address

U.S. Geological Survey
Water Resources Division
702 Post Office Building
St. Paul, Minnesota 55101

13. Type of Report & Period Covered

14.

15. Supplementary Notes

Prepared in cooperation with the U.S. Environmental Protection Agency

16. Abstract (Limit: 200 words)

Concentrations of major constituents were determined in the surface water, ground water, and precipitation in Filson Creek watershed to evaluate the effects of acid precipitation on surface-water quality during snowmelt. Concentrations of sulfate increased in Filson Creek and Omaday Lake during snowmelt from less than 2 to 12 milligrams per liter in 1977 and from less than 2 to 4 milligrams per liter in 1979. Hydrogen-ion activity increased from $10^{-6.5}$ to $10^{-5.0}$ during snowmelt in 1977 and from $10^{-6.5}$ to $10^{-6.0}$ in 1979. The magnitude of the increases of sulfate and hydrogen-ion concentrations depend on the (1) timing of the snowmelt, (2) concurrent precipitation, and (3) antecedent soil-moisture conditions. Alkalinity and concentrations of total calcium, magnesium, and sodium in the creek during snowmelt reflect the simple dilution of streamflow with more dilute precipitation. The mixing process is defined by hyperbolic curves of concentration versus discharge and can be modeled by use of a mass-balance equation. Concentrations of silica and total potassium in the creek during snowmelt are less than that at base flow because of dilution and uptake by diatoms and plants, respectively.

A quality-assurance study was made to determine the accuracy and precision of the turbidimetric, complexometric (methylthymol blue), and ion-chromatographic methods used to determine concentrations of sulfate in water.

17. Document Analysis a. Descriptors

*Chemical anlaysis, *Acidity, *Base flow, *Snowmelt, *Calcium,
*Calcium, *Magnesium, *Sodium, Precipitation

b. Identifiers/Open-Ended Terms

*Filson Creek, *Omaday Lake, *Minnesota

c. COSATI Field/Group

18. Availability Statement

No restriction on distribution

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages 90

22. Price

(See ANSI-Z39.18)

See Instructions on Reverse

OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

EFFECT OF SNOWMELT ON THE QUALITY OF FILSON CREEK AND OMADAY LAKE, NORTHEASTERN MINNESOTA

By D. I. Siegel

With a section on

PRELIMINARY EVALUATION OF METHODS FOR DETERMINATION OF SULFATE CONCENTRATION IN PRECIPITATION AND OTHER DILUTE SOLUTIONS

By D. I. Siegel, L. E. Anderson, and J. A. Rogalla

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 81-66

Prepared in cooperation with the

U.S. ENVIRONMENTAL PROTECTION AGENCY

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

September 1981

UNITED STATES DEPARTMENT OF THE INTERIOR

JAMES G. WATT, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information write to:

District Chief
U.S. Geological Survey
702 Post Office Building
St. Paul, Minnesota 55101

CONTENTS

Page
Abstract 1
Introduction 1
Acknowledgments 2
Purpose 2
Watershed description 2
Data-collection and laboratory methods 6
Hydrology 10
Water quality 14
  Ground water 14
  Surface Water 14
    H^+ ion and sulfate 14
    Nitrogen species 31
    Alkalinity 34
    Silica 38
    Chloride 40
    Potassium 42
    Calcium, magnesium, and sodium 42
Dilution model for water-quality changes at snowmelt 45
Summary 48
Preliminary evaluation of methods for determination of sulfate concentration in precipitation and other dilute solutions, by D. I. Siegel, L. E. Anderson, and J. A. Rogalla 49
  Introduction 49
  Description of methods for determining sulfate concentrations 49
  Comparison of methods 51
  Summary 62
References 62
Water-quality data 67

ILLUSTRATIONS

Figure 1. Map showing location of study area 3
2. Map showing generalized topography of the Filson Creek watershed 4
3. Map showing vegetation in the Filson Creek watershed 5
4. Map showing generalized thickness of surficial materials in Filson Creek watershed 7
5. Map showing bedrock geology of the Filson Creek watershed 8
6. Map showing location of instrumentation and sample sites 9
7. Hydrographs of mean daily discharge of Filson Creek at site F1, January 1976 to July 1979 11
8. Graph showing water levels in observation wells in peat, April to November 1977 12

ILLUSTRATIONS—Continued

Page

Figure 9. Graphs showing water levels in observation wells, March to June 1979 13

10. Semi-logarithmic plots of ground-water quality in April 1976 and 1977 and in May 1979 15

11. Graphs showing field pH along Filson Creek and Omaday Lake, January to August 1976-79 16

12. Graphs showing concentrations of sulfate in Filson Creek and Omaday Lake, January to August 1977-79 21

13. Graphs showing concentrations of nitrate plus nitrite in Filson Creek and Omaday Lake, January to August 1976, 1977, and 1979 32

14 Graph showing concentrations of sulfate and nitrate plus nitrite in successive 1-liter fractions of melted snow, April 1979 33

15. Graph showing concentration of nitrate plus nitrite versus discharge at F1, January to August 1976, 1977, and 1979 34

16. Graph showing concentration of alkalinity (as bicarbonate) versus discharge at F1, January to August 1976-79 35

17. Graphs showing concentrations of bicarbonate in Filson Creek and Omaday Lake, January to August 1976-79 36

18. Graph showing potentiometric titrations of alkalinity in Filson Creek and Omaday Lake, May 1977, and March and April 1979 37

19. Graph showing potentiometric titrations of alkalinity in Omaday Lake, December 1976 and January 1977 37

20. Graphs showing concentration of silica in Filson Creek and Omaday Lake, January to August 1976-79 39

21. Graph showing concentration of silica versus discharge at F1, January to August 1976-79 40

22. Graphs showing concentrations of chloride in Filson Creek and Omaday Lake, January to August 1976-79 41

23. Graph showing concentration of chloride versus discharge at F1, January to August 1976-79 42

24. Graphs showing concentrations of total potassium in Filson Creek and Omaday Lake, January to August 1977-79 43

25. Graphs showing concentrations of total calcium in Filson Creek and Omaday Lake, January to August 1977-79 44

26. Graph showing concentration of total calcium versus discharge at F1, January to August 1977-79 45

27. Graphs showing variations in concentrations of total calcium, magnesium, sodium, and bicarbonate as a function of streamflow at site F1, Janaury to August 1976-79 47

28. Graph showing concentrations of sulfate in Filson Creek and discharge hydrograph of Filson creek near its mouth, March 16 to June 8, 1979 60

29. Graph showing daily mass transport of sulfate by Filson Creek, April 12 to May 25, 1979 61

TABLES

Page

Table 1. Summary statistics of ground-water quality, January to August 1976-79 17

2. Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79 24

3. Estimated sulfate budgets for Filson Creek watershed above site F1, March to June, 1977 and 1979 30

4. Model parameters for constituents affected by snowmelt dilution, Filson Creek, January to August 1976-79 46

5. Methods used to determine concentration of sulfate 50

6-10. Summary statistics of the concentration of sulfate in:

  6. Water collected in March 1979, from Filson Creek 52
  7. Filson Creek water with a 5 mg/L addition of sulfate 53
  8. Filson Creek water with a 1 mg/L addition of sulfate 54
  9. Precipitation collected in March 1979, near Filson Creek 55
  10. Precipitation with a 0.5 mg/L addition of sulfate 56

11. Ratio between the determined and true addition of sulfate to Filson Creek water and precipitation 57

12. Summary statistics of the concentration of sulfate determined in de-ionized water with a 5 mg/L addition 58

CONVERSION FACTORS

Multiply SI (metric) unit	By	To obtain inch-pound unit
millimeter (mm)	0.039	inch (in)
meter (m)	3.28	foot (ft)
kilometer (km)	0.62	mile (mi)
square kilometer (km^2)	0.386	square mile (mi^2)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
liter per hectare per day (L/ha)/day	0.10	gallon per acre per day (gal/acre)/d
kilogram per hectare (kg/ha)	0.89	pound per acre (lb/acre)

The following abbreviations are used throughout the report: n = number of samples; s.d. = standard deviation; c.v. = coefficient of variation.

EFFECT OF SNOWMELT ON THE QUALITY OF FILSON CREEK AND OMADAY LAKE, NORTHEASTERN MINNESOTA

By D. I. Siegel

ABSTRACT

Concentrations of major constituents were determined in the surface water, ground water, and precipitation in Filson Creek watershed to evaluate the effects of acid precipitation on surface-water quality during snowmelt. Concentrations of sulfate increased in Filson Creek and Omaday Lake during snowmelt from less than 2 to 12 milligrams per liter in 1977 and from less than 2 to 4 milligrams per liter in 1979. Hydrogen-ion activity increased from $10^{-6.5}$ to $10^{-5.0}$ during snowmelt in 1977 and from $10^{-6.5}$ to $10^{-6.0}$ in 1979. The magnitude of the increases of sulfate and hydrogen-ion concentrations depend on the (1) timing of the snowmelt, (2) concurrent precipitation, and (3) antecedent soil-moisture conditions. Alkalinity and concentrations of total calcium, magnesium, and sodium in the creek during snowmelt reflect the simple dilution of streamflow with more dilute precipitation. The mixing process is defined by hyperbolic curves of concentration versus discharge and can be modeled by use of a mass-balance equation. Concentrations of silica and total potassium in the creek during snowmelt are less than that at base flow because of dilution and uptake by diatoms and plants, respectively.

A quality-assurance study was made to determine the accuracy and precision of the turbidimetric, complexometric (methylthymol blue), and ion-chromatographic methods used to determine concentrations of sulfate in water. Results suggest that the ion-chromatographic method is more accurate and more precise in the detection of sulfate at concentrations of 5 milligrams per liter or less. To obtain accuracy with either the turbidimetric or the complexometric methylthymol blue method, color blanks and turbidity should be determined if concentrations of sulfate are expected to be low, such as in precipitation, or where water is colored by organic material. Interference by color and turbidity is not a factor in the ion-chromatographic method.

INTRODUCTION

Studies in both the United States and Scandanavia have documented that acid precipitation causes changes in the water quality and ecology of poorly buffered lakes and streams. In particular, the pH of surface waters has decreased because of acid precipitation in Canada (Beamish, 1976), Scandanavia (Braekke, 1976), and the Adirondack Mountains of New York (Schofield, 1976a). The increase in acidity has resulted in a reduction of the diversity of zooplankton (Almer and others, 1974), benthos (Hendrey and Wright, 1976), and fish (Beamish, 1976; Schofield, 1976b). Precipitation in northeastern Minnesota and adjacent areas in Canada is also acidic, with pH commonly less than 5.2 (Gorham, 1976; Eisenreich and others, 1978; Glass and Loucks, 1980); and there is concern about the ecology and water quality of lakes and streams in the BWCA (Boundary Waters Canoe Area), a protected wilderness, and other parts of the Superior National Forest (Glass, 1980). Glass and Loucks (1980) found that the mean annual pH of precipitation near the BWCA is already near the point where damage to aquatic life begins, and that acid deposition is at similar levels to those associated with the onset of acidification of lakes in Sweden.

The effect of acid precipitation on surface waters is greatest in spring when acidity and trace metals can be concentrated during the first part of snowmelt (Gjessing and others, 1976; Haapala and others, 1975; Henrikson and Wright, 1977). Siegel (1979) found that the concentrations of hydrogen ions (henceforth referred to as H^+) and sulfate in Filson Creek and Omaday Lake, northeastern Minnesota, increased at snowmelt during the drought of 1976-77, described by Matthai (1979). The increase was probably caused by the concentration of acidity in the snowpack.

A section documenting the results of a preliminary quality-assurance study on the accuracy and precision of three methods commonly used to determine sulfate has been added to this report at the request of the U.S. Environmental Protection Agency.

ACKNOWLEDGMENTS

The work and assistance of L. E. Anderson, J. A. Rogalla, L. J. Heines, C. S. Sandburg, J. A. Isle, T. H. Roush, F. Boettcher, and G. E. Glass of the U.S. Environmental Protection Agency Environmental Research Laboratory, Duluth, Minn., in the collection and analysis of water samples is gratefully acknowledged.

PURPOSE

The purposes of this report are to (1) determine whether changes in sulfate and H^+-ion concentrations in Filson Creek are typical of the snowmelt period or whether they represent a response only to drought, and (2) evaluate changes in concentrations of other major constituents during snowmelt. This report documents the results of chemical analyses of water collected from Filson Creek and Omaday Lake during snowmelt in 1979. These analyses of major constituents, in conjunction with previous water-quality data from 1976-78 (U.S. Geological Survey, 1977; Mustalish, unpublished data on file with Minnesota Environmental Quality Board, 1978; Siegel, 1981b) bracket the range of water-quality changes to be expected from dilution and sulfate acidity in Filson Creek watershed (see water-quality data).

WATERSHED DESCRIPTION

Filson Creek and Omaday Lake are in Superior National Forest 13 km southeast of Ely, Minn. (fig. 1). Filson Creek watershed above the U.S. Geological Survey gage is 25.2 km^2 in area; it contains one major tributary and Omaday and Bogberry Lakes (fig. 2). The watershed is predominantly forested. During the past 75 years most of the original forest cover of white, jack, and red pine (Marschner, 1974) has been cut and replaced by a mixed upland forest (Sather, 1978) consisting of aspen, birch, spruce, and other conifers (fig. 3). About 30 percent of the watershed is wetland consisting of fens and black spruce swamp.

The physiography of the watershed reflects both the bedrock topography and surficial material deposited by Pleistocene glaciation (Olcott and Siegel, 1978). Altitudes range from more than 536 m east of Bogberry Lake in the eastern part of the basin to less than 440 m near the mouth of the stream. Topographic features trend northeast-southwest and reflect both bedrock ridges in the Precambrian Duluth Complex and the general direction of Wisconsin Glaciation. South and southwest of Bogberry Lake, the general trend is broken by an east-west bedrock ridge that partly outlines the southern boundary of the watershed.

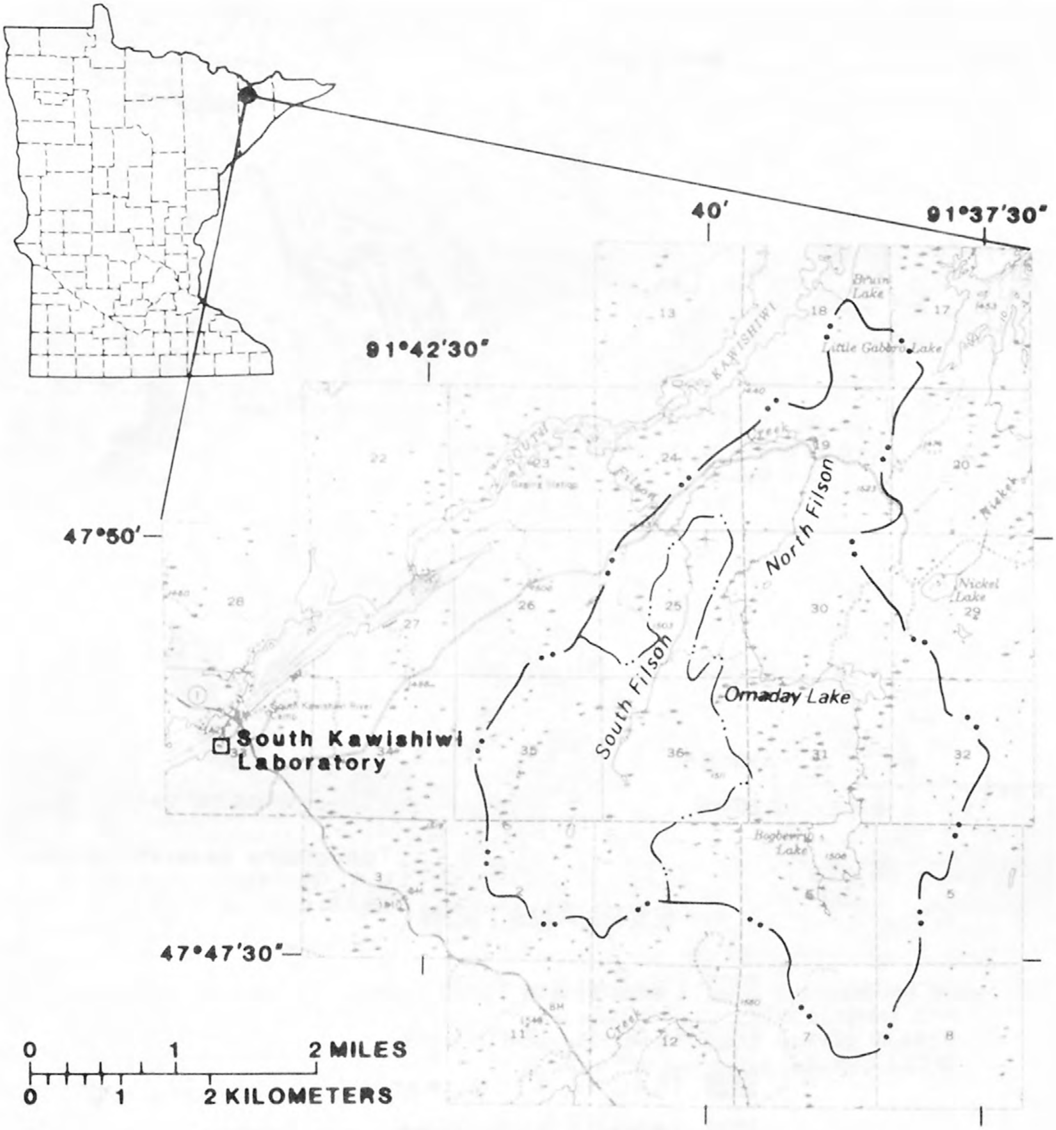
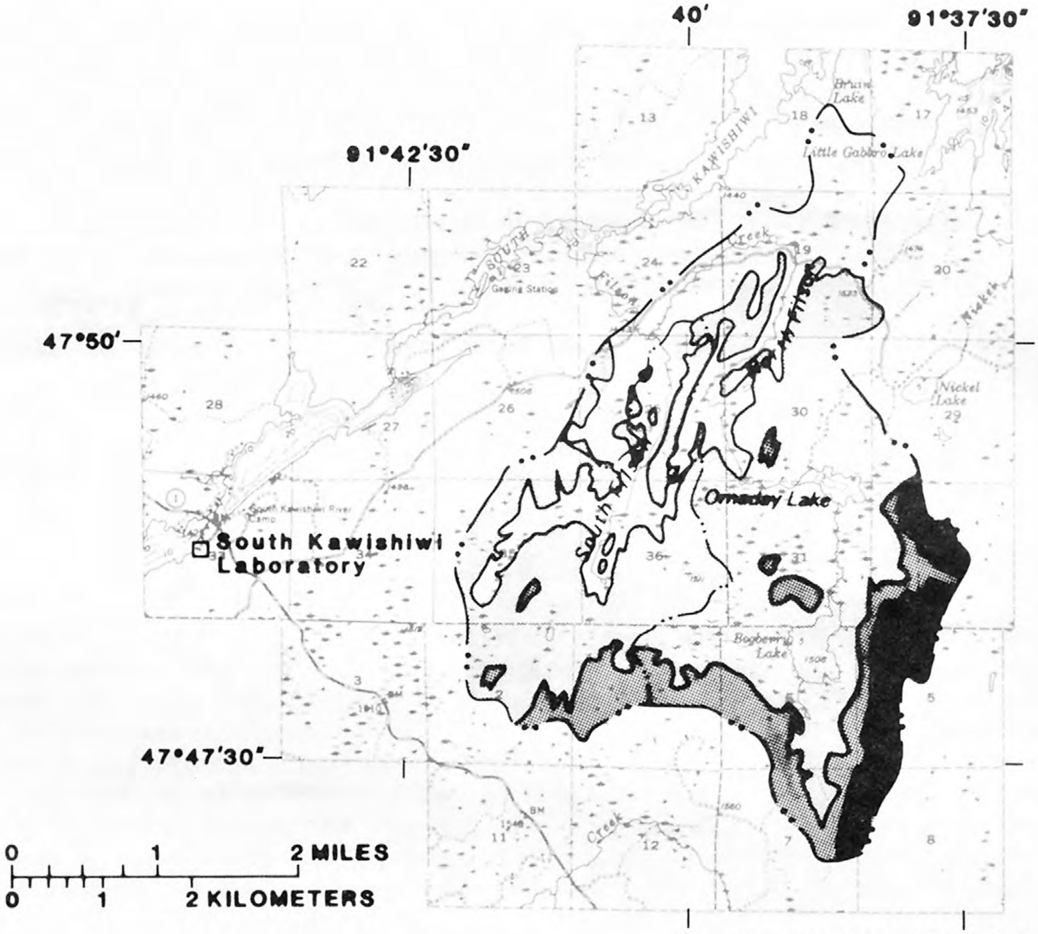


Figure 1.--Location of study area

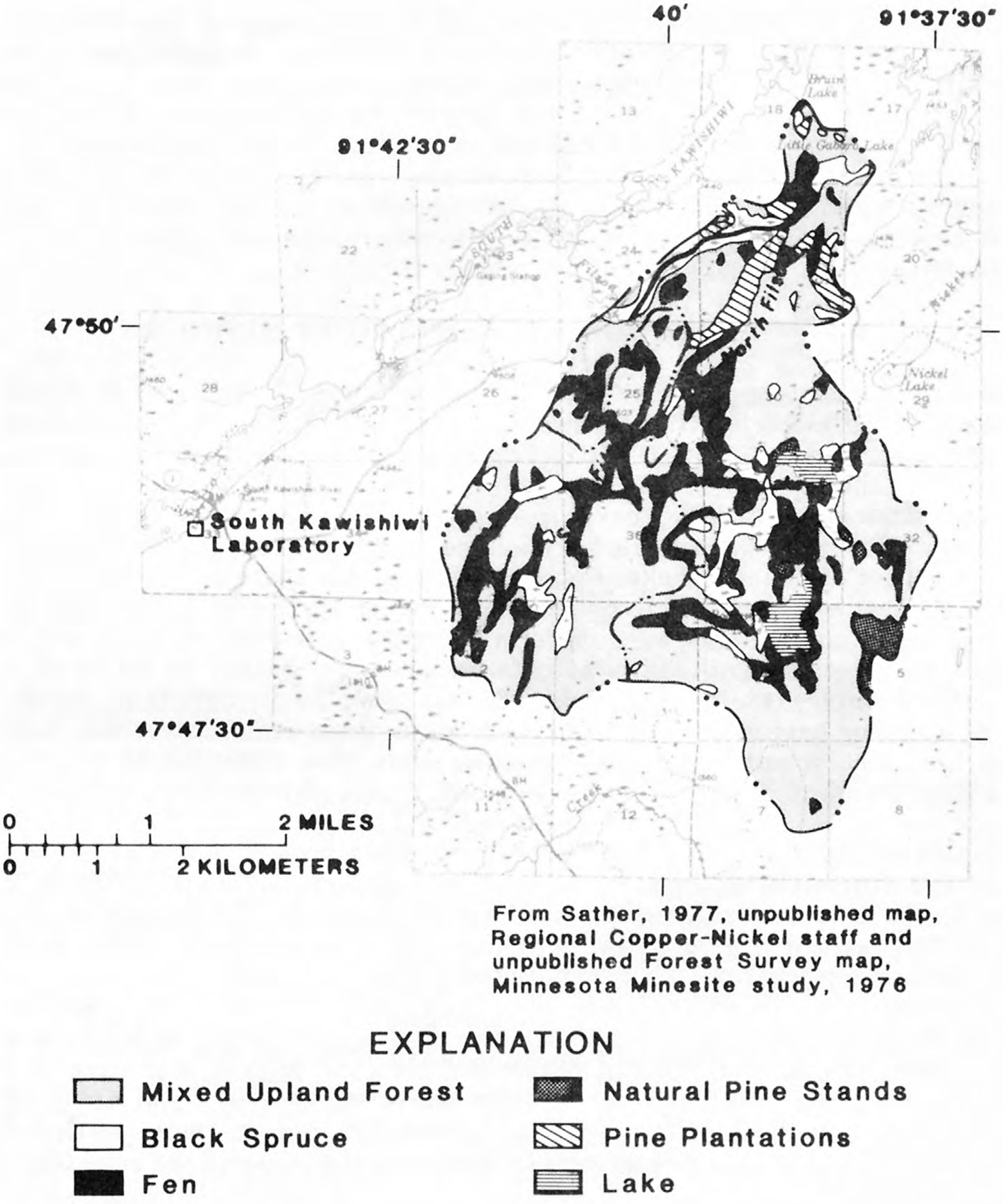


Topography generalized from
U.S. Geological Survey
Gabbro Lake 1:62,500, 1957

EXPLANATION

☐ Less than 1500 feet
░ 1500 to 1540 feet
▒ 1540 to 1600 feet
▓ 1600 to 1700 feet
█ Greater than 1700 feet
—— ·· —— Watershed boundary
—— · —— Subwatershed boundary

Figure 2.--Generalized topography of the Filson Creek watershed



From Sather, 1977, unpublished map, Regional Copper-Nickel staff and unpublished Forest Survey map, Minnesota Minesite study, 1976

Figure 3.--Vegetation in the Filson Creek watershed

Ten to 15 percent of the watershed is rock outcrop (Cooper, 1978). The remainder is covered by drift and Holocene surficial materials generally less than 1.5 m thick (Prettyman, 1976; Stark, 1977; Olcott and Siegel, 1978), but as thick as 15 m in wetland areas (fig. 4).

The mineralogy of the drift reflects the underlying and nearby types of bedrock. Ninety percent of the watershed (fig. 5) is underlain by rocks of the Duluth Complex (Green and others, 1966). These rocks are mostly composed of calcic plagioclase, with minor amounts of olivine, orthopyroxene, clinopyroxine, and iron and titanoferric oxides. Typically, the composition of the rock is troctolite (Green and others, 1966; Cooper, 1978), but can vary from anorthosite to gabbro. The northern part of the watershed is underlain by the Precambrian Giants Range Granite. Most of the granite consists of microcline, hornblende, and highly altered oligoclase (Green, 1970). A mineralized zone that contains both copper and nickel sulfide minerals occurs at the contact between the Giants Range Granite and the Duluth Complex (fig. 5).

DATA-COLLECTION AND LABORATORY METHODS

The data in this report come from several sources. From January through July 1976, samples were collected (fig. 6) biweekly at the gaging station of Filson Creek (F1) and monthly near the outlet of Omaday Lake (F4). Samples were also collected from December 1976 through July 1977, January to February 1978, and March through June 1979 at four sites along Filson Creek, Omaday Lake, and the mouth of the tributary to Filson Creek. The creek was sampled (1) between Omaday Lake and Bogberry Lake (F6), (2) near the outlet of Omaday Lake (F4), and (3) both immediately upstream from F3 and within the mineralized zone (F1) to determine if changes in the concentrations of H^+ ion, sulfate, and other constituents were uniform along the creek and to determine if oxidation of sulfide minerals significantly affects the chemical quality of the creek near the mouth. The tributary to Filson Creek (F2) was sampled to determine water-quality changes of a stream having no mineralized bedrock or lakes in its watershed. Sampling in 1977 was biweekly, monthly in 1979. Samples were also collected at F1 at variable intervals from March to July 1977 by the Regional Copper-Nickel Study Staff.

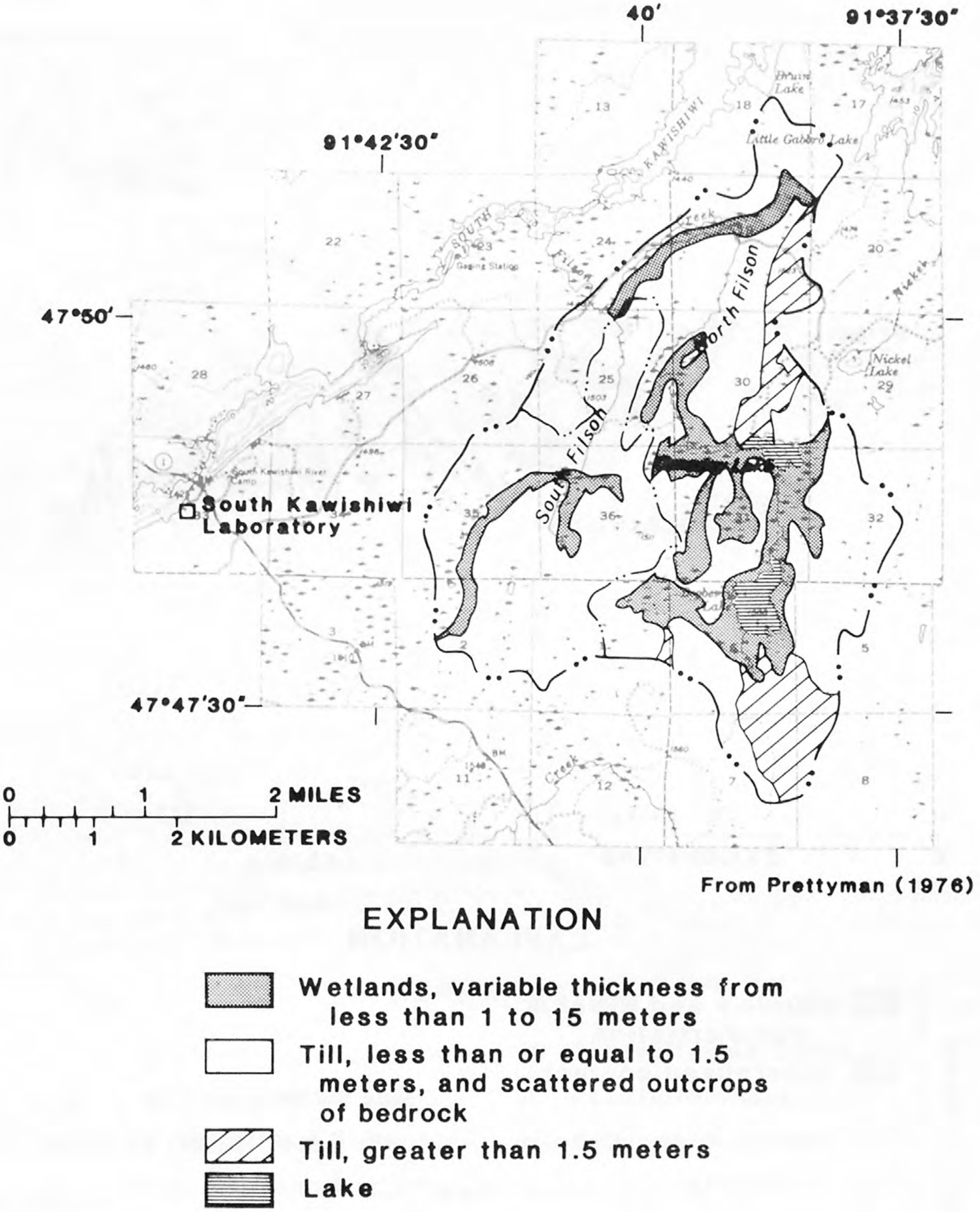
Samples collected in 1976-77 were analyzed by methods in Brown and others (1974), Skougstad and others (1979), and American Public Health Association (1974). Samples collected in 1979 were analyzed by methods of the U.S. Environmental Protection Agency (1979), except for chloride, nitrate, and sulfate, which were analyzed by Dionex[1/] (Dionex Corporation) ion chromatography.

Ground-water and surface-water samples (see water-quality data) were analyzed for pH, calcium, magnesium, sodium, potassium, chloride, sulfate, and nitrate. Samples of ground water were collected periodically during spring 1977 and 1978 from four piezometers set at the base of the peat, one piezometer in drift 100 m northwest of the watershed boundary, and two piezometers in drift over the mineralized zone (fig. 6).

Bulk precipitation was collected biweekly from March to July 1977 in three polypropylene precipitation collectors (fig. 6) similar to that described by Likens and others (1967). Precipitation was collected by a funnel 80 mm in diameter, which was fitted to a

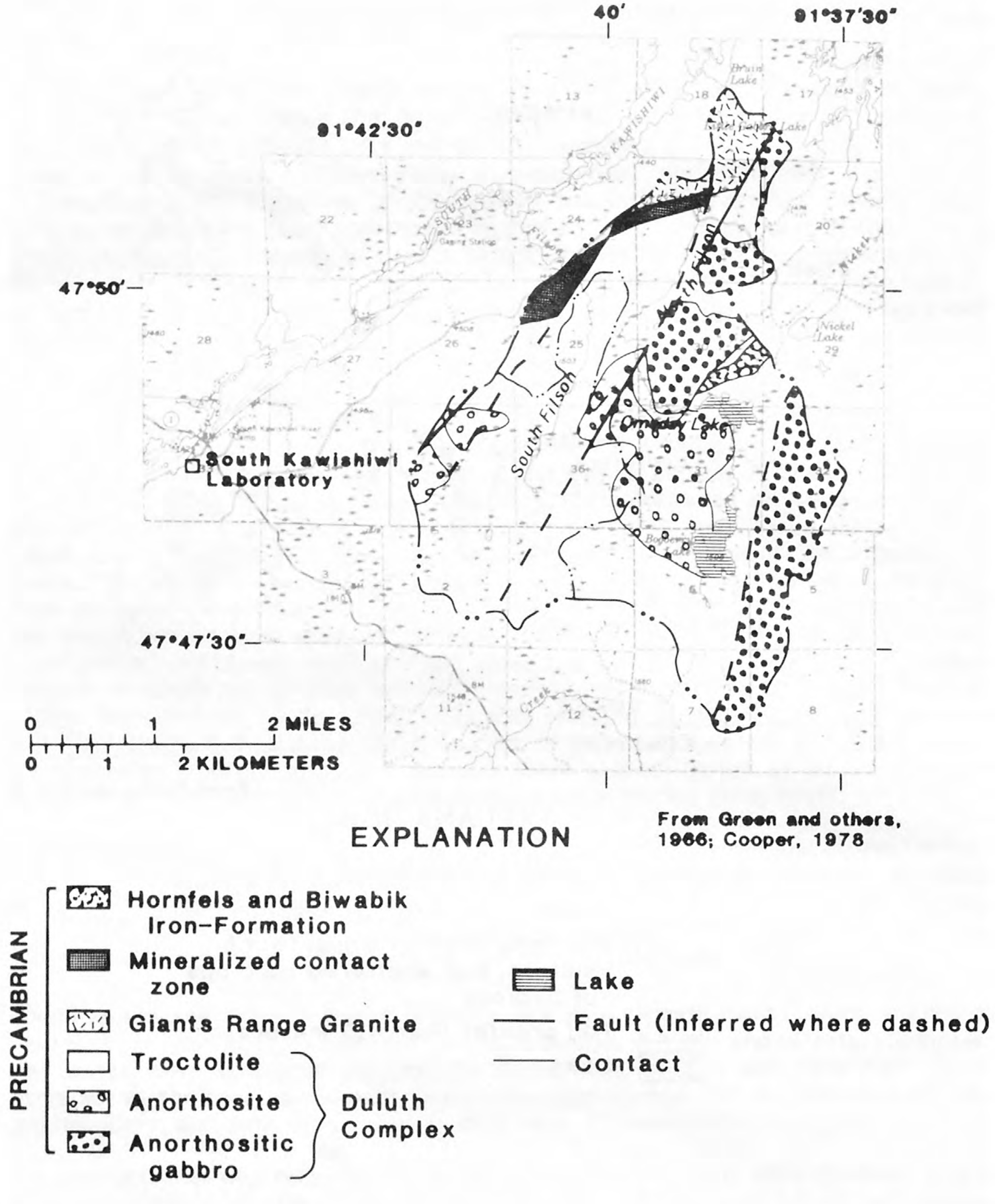
---

[1/] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.



From Prettyman (1976)

Figure 4.--Generalized thickness of surficial materials in Filson Creek watershed



From Green and others, 1966; Cooper, 1978

Figure 5.--Bedrock geology of the Filson Creek watershed

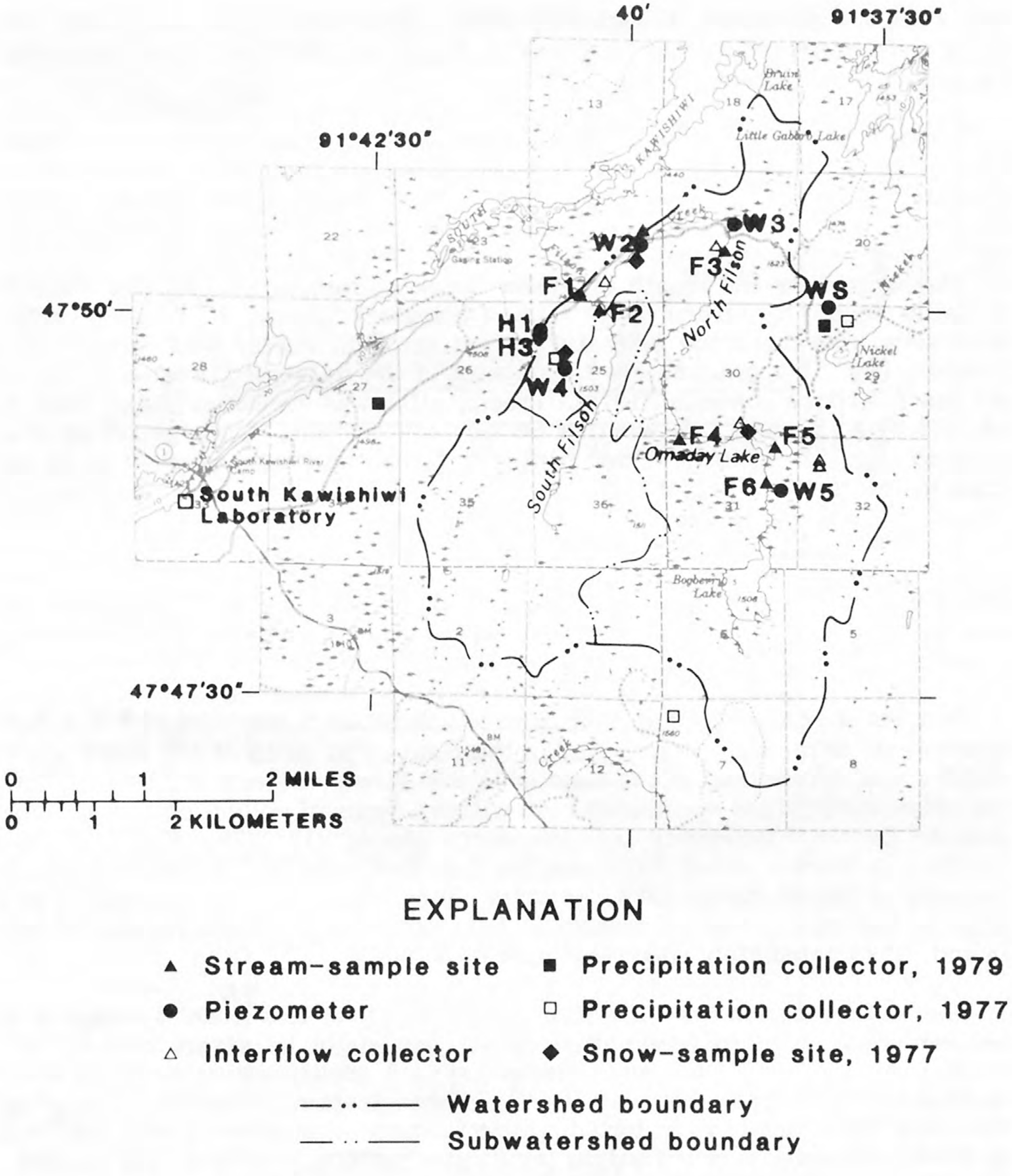


Figure 6.--Location of instrumentation and sample sites

liter bottle mounted at ground level. Acid-washed Whatman No. 70 filter paper was placed in the funnel to remove particulate material and to prevent insects and dry debris from entering the sample bottle. The filter was held in place by a second funnel. All equipment was rinsed with de-ionized water between samplings. Precipitation was collected weekly from March through July 1979, 1.5 km west of the watershed. Bulk snow samples were collected at four locations on March 20, 1977, at 8 locations on March 13, 1980, and at 6 locations on March 19, 1980.

Samples of precipitation were analyzed for pH, total sulfate, and nitrate in 1979 and for pH and total sulfate in 1977 (see water-quality data). All ground-water samples were filtered through acid-washed commerical 0.45-micrometer filters. Precipitation and surface-water samples were not filtered.

Discharge near the mouth of Filson Creek at sample site F1 was measured by a continually recording stream gage (U.S. Geological Survey, 1977; 1978; 1979; 1980). Precipitation was measured daily 1975-77 at the U.S. Forest Service South Kawishiwi Laboratory (fig. 6), approximately 2.5 km west of the watershed (Regional Copper-Nickel Study Staff, written commun., 1978). Precipitation was measured weekly from March to June 1979 by a standard U.S. Weather Service nonrecording rain gage 1.5 km west of the watershed (fig. 6). The moisture content of the snow was determined by two snow courses in March 1976 (Regional Copper-Nickel Study Staff, written commun., 1978) and by three snow courses on March 13 and March 19, 1980.

All statistics were done by use of the SAS Institute statistical analysis system (1979). Data sets in 1976 and 1977 include data collected in July because the effects of snowmelt on sulfate concentration can extend to that time (Siegel, 1981a). Samples were not collected in July 1979.

Samples were collected at approximately midstream locations of 0.5-m depths, and measurements of pH were determined in the field. The depth of the creek is about 1 m. Alkalinity was determined in the field or within 2 hours of collection in 1977 and 1978. All samples were chilled and transported within 6 hours of collection to the Limnological Research Center, University of Minnesota during 1977-78; U.S. Forest Service Laboratory in Winton during 1979; and the U.S. Environmental Protection Agency (EPA) Laboratory in Duluth during 1979. Samples collected in 1975-76 were mailed to the U.S. Geological Survey Central Laboratory in Lakewood, Colo. Alkalinity was determined in 1976 and 1979 immediately upon receipt of the samples.

The determination of sulfate at concentrations less than 5 mg/L is difficult (American Public Health Association, 1974), especially in waters colored by organic material such as Filson Creek and Omaday Lake. A quality-assurance study was made to determine sulfate at low concentrations. Concentrations of sulfate discussed in this report were determined by the turbidimetric technique (American Public Health Association, 1974). Reported concentrations less than 2 mg/L may be up to 100 percent in error and may be considered as "less than 2 mg/L."

HYDROLOGY

Filson Creek responds rapidly to snowmelt at the beginning of April when maximum daily air temperatures are above freezing. Discharge measured at F1 (U.S. Geological Survey, 1977; 1978; 1979) increased from less than 0.15 m^3/s at base flow to about 3.0 m^3/s (fig. 7) at the peaks of the snowmelt that occurred from March to May in 1976 and

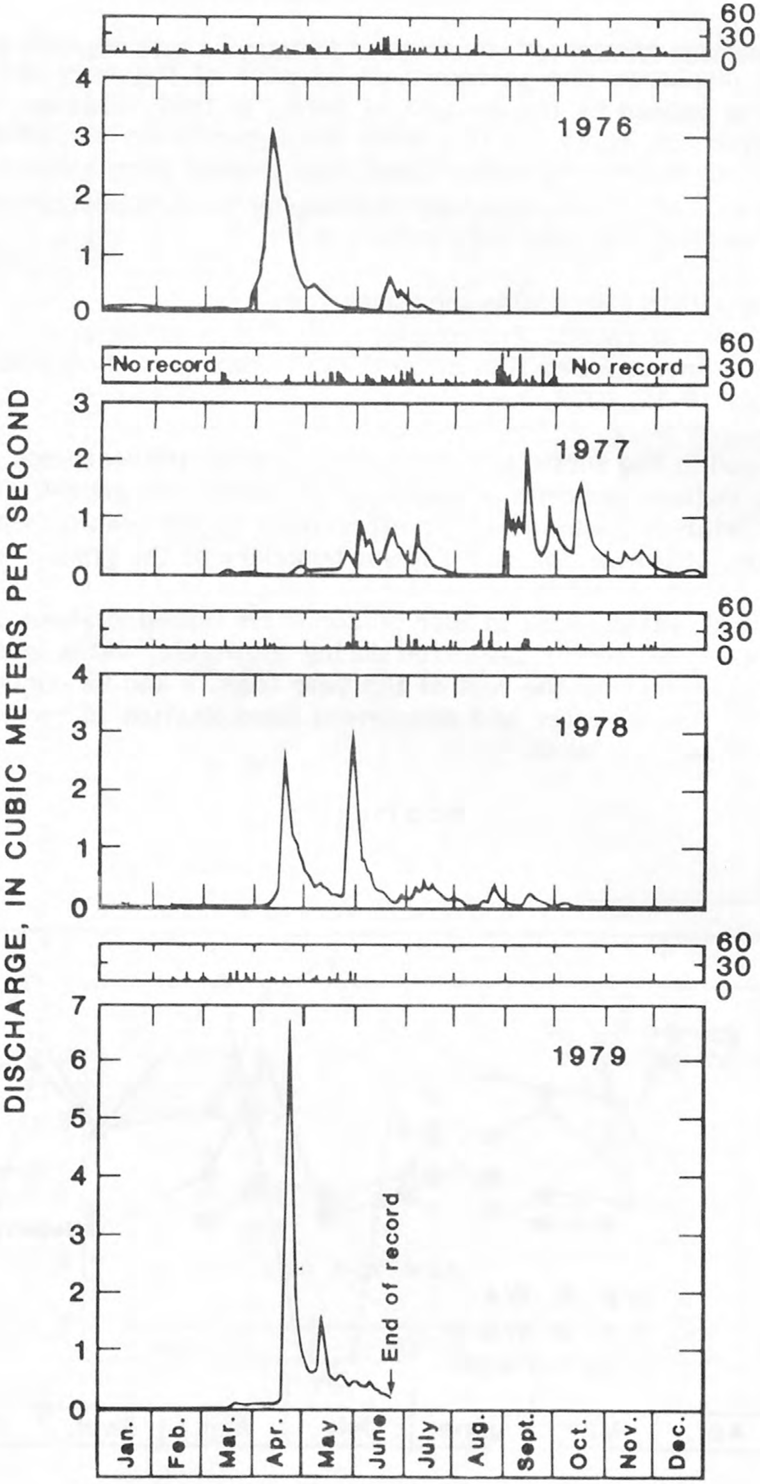


Figure 7.--Hydrographs of mean daily discharge of Filson Creek at site F1, January 1976 to July 1979. Precipitation 1976 and 1977 at South Kawishiwi Laboratory and at Winton in 1978 and 1979

1978. Filson Creek was frozen to its bed from January to late March 1977, and there was little increase in discharge due to snowmelt because of the very dry antecedent soil-moisture conditions caused by the drought of 1976. In 1979, however, heavy snowfall in February and March and rapid melting with concurrent rain caused a record flood of greater than 6 m^3/s. Before the major flood peak, runoff from a short melting period in early March (National Oceanographic Atmospheric Administration, 1978) briefly increased discharge from less than 0.03 to 0.11 m^3/s.

Discharge in Filson Creek also increases fairly rapidly after storms, once the thin till and wetlands are saturated. For example, discharge during brief storms in June and July 1976 and 1977 increased within several days from less than 0.05 to 0.7 m^3/s. A small storm on May 10-12, 1979, increased streamflow to 0.9 m^3/s.

Water is found in the surficial materials underlying the wetlands and within discontinous and poorly defined deposits of surficial till, sand, and gravel. The bedrock under the surficial materials is assumed to be effectively impermeable to ground-water flow (Siegel and Ericson, 1980) and forms the lower boundary of the ground-water system.

Hydrographs of water levels in four piezometers installed about 1 m into peat indicate that once wetlands become saturated during snowmelt, water levels remain near or above the land surface during the rest of the year (figs. 8 and 9). Once the wetlands are saturated, additional melt water and concurrent precipitation to the wetlands is quickly discharged to the creek and lakes.

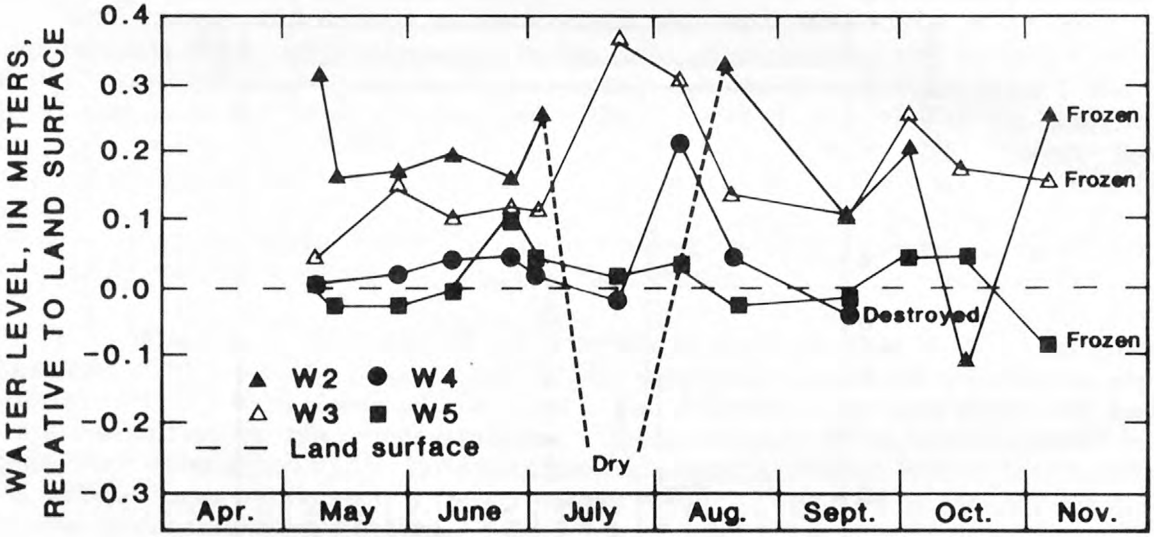


Figure 8.--Water levels in observation wells in peat, April to November 1977

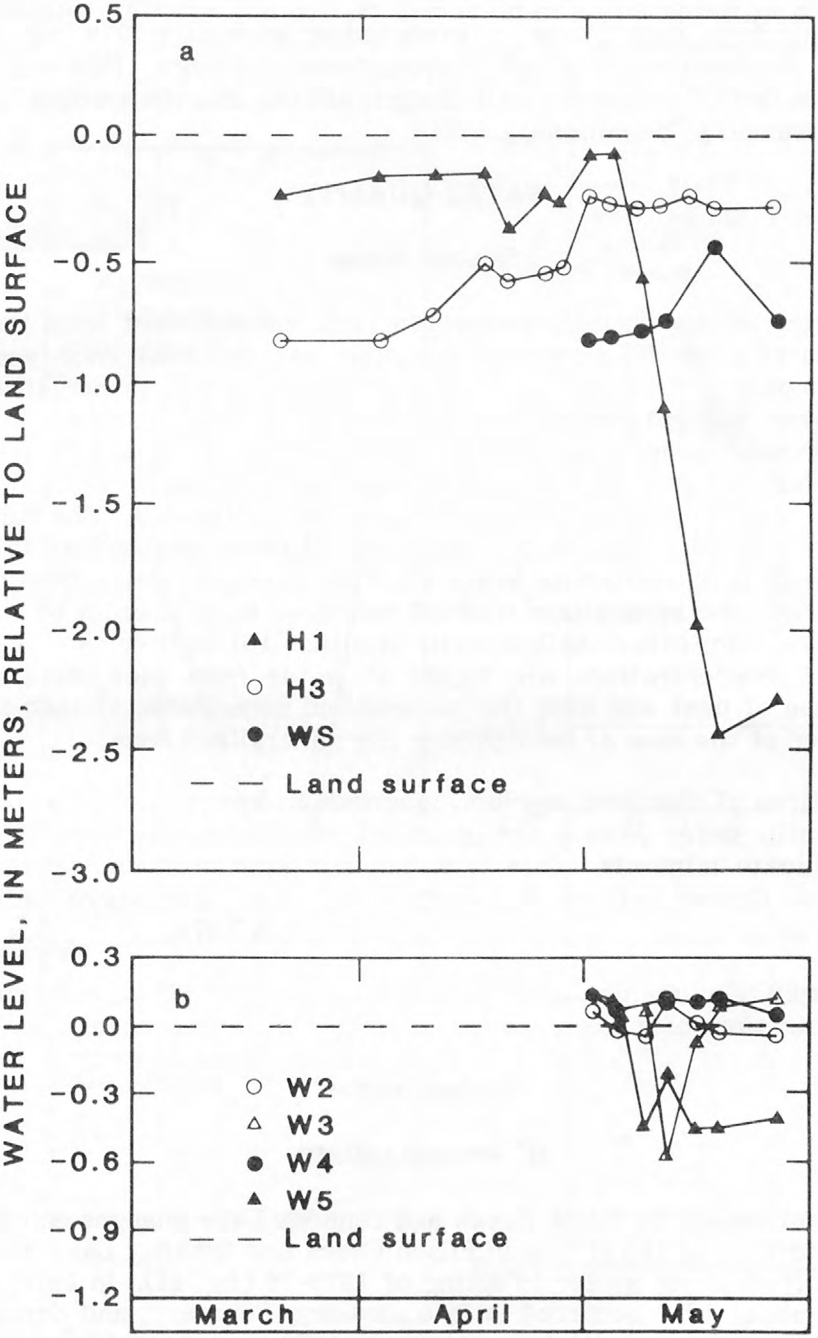


Figure 9.--Water levels in observation wells, March to June 1979. Wells illustrated in part a are in drift, in part b are in peat

Hydrographs of water levels in piezometers WS, H1, and H3, installed in drift near the watershed boundary, show a rise in levels during snowmelt 1979 (fig. 9), which indicates that some snowmelt water is lost to ground-water storage. However, the extent of these discontinous drift deposits is small (Siegel, 1981a), and the amount of water lost to storage can be assumed to be minimal.

WATER QUALITY

Ground Water

Ground-water quality during snowmelt in 1979 was different from that in 1976 and 1977. Unfortunately, the frequency of sampling was different each year and, consequently, the comparison between years must be qualitative rather than statistically rigorous. However, several general conclusions can be made. Based on the chemical composition expressed as milliequivalents, ground water is generally a mixed calcium magnesium bicarbonate type, except near the mineralized zone, where sulfate milliequivalents can equal or exceed bicarbonate milliequivalents (fig. 10). The sulfate in ground water near the mineralized zone is probably derived from local oxidation of copper and nickel sulfide minerals in bedrock or in the till. For example, water from piezometer H1 placed in drift above the mineralized bedrock has more than an order of magnitude more sulfate than water from other shallow wells in either till (H3) or sand and gravel (WS). Similarly, sulfate concentrations are higher in water from piezometers W2 and W3, placed at the base of peat and over the mineralized zone (table 1) than in piezometers W4 and W5, placed at the base of peat outside the mineralized zone.

Concentrations of dissolved calcium, magnesium, and sodium in water from H1 are also greater than in water from other piezometers and are indicative of the enhanced dissolution of silicate minerals (table 1) by sulfuric acid produced by the oxidation of sulfide minerals. Concentrations of bicarbonate, silica, and major cations generally changed little in water from drift or wetlands during May 1979.

The frequency of sampling was not adequate in spring 1977 to determine the rate of change in concentrations of major constituents in ground water during snowmelt.

Surface Water

H^+ ion and sulfate

The chemical quality of Filson Creek and Omaday Lake changes considerably during snowmelt. The activity of the H^+ ion in Filson Creek and Omaday Lake varied more than an order of magnitude from winter to spring of 1976-79 (fig. 11). In 1976, maximum H^+-ion activities of about 10^{-5} occurred in late January, February, and during snowmelt in April and May. The minimum H^+-ion activity in 1976 was about 10^{-7} at F1 during base flow in early January and late March. In 1977, a drought year, H^+-ion activity increased at F1 from a minimum of $10^{-6.5}$ at the beginning of April to a maximum of about $10^{-5.0}$ in mid-May and then decreased to about $10^{-6.5}$ by June. Smaller increases occurred at other sample sites in 1977 except at F6, where the H^+-ion activity remained about the same. Increase in H^+-ion activity during snowmelt in 1977 was similar to that observed in 1976 and 1977. The greatest H^+-ion activity, about 10^{-5}, was during the short melting period in March. Activity decreased after March to base-flow activity of about $10^{-6.5}$ until the major snowmelt flood peak from mid-April to May, when H^+-ion activity increased again to about $10^{-5.0}$.

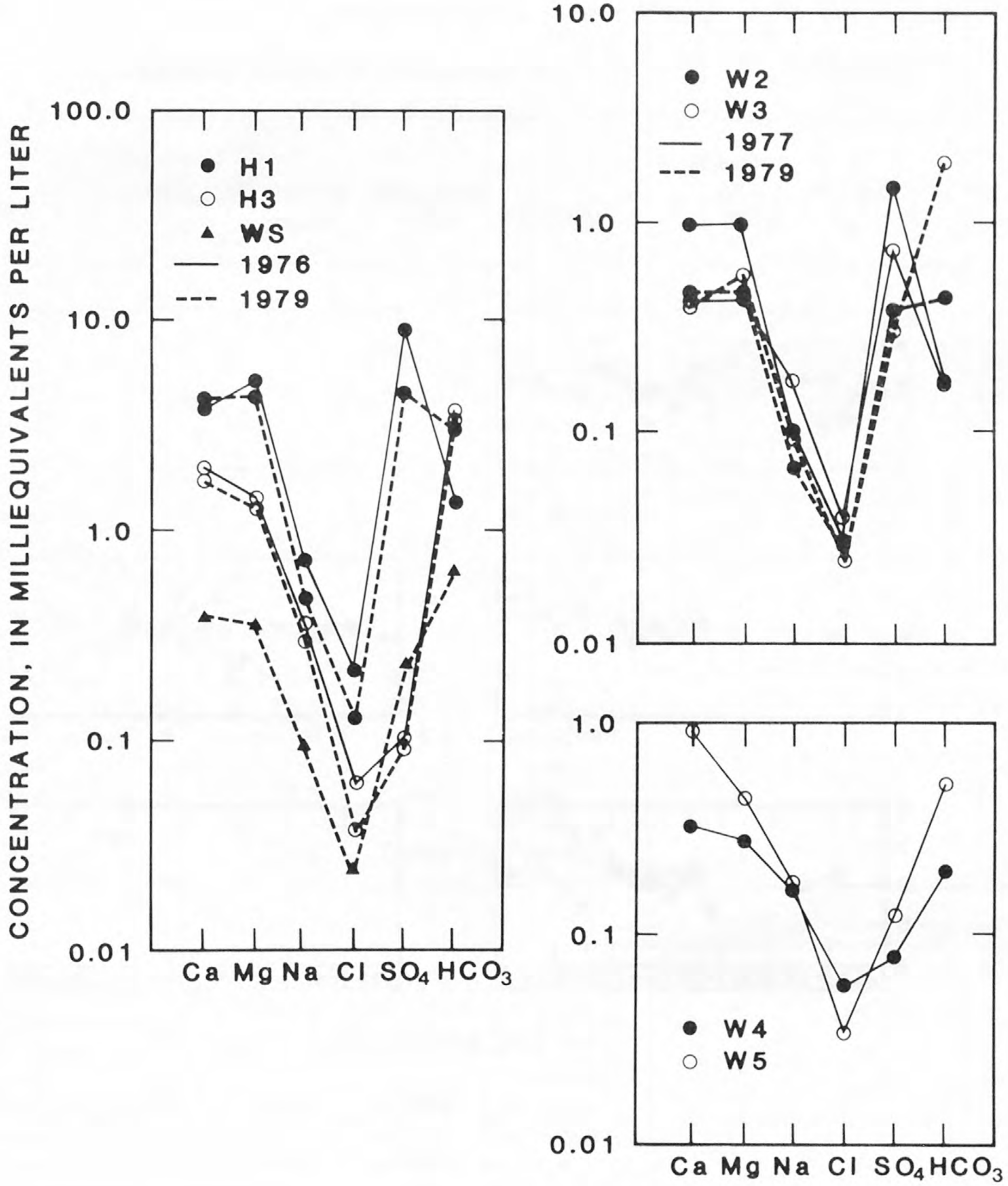


Figure 10.--Semi-logarithmic plots of ground-water quality in April 1976 and 1977 and in May 1979. Data for wells W4 and W5 are for 1977. Data for 1979 are mean concentrations

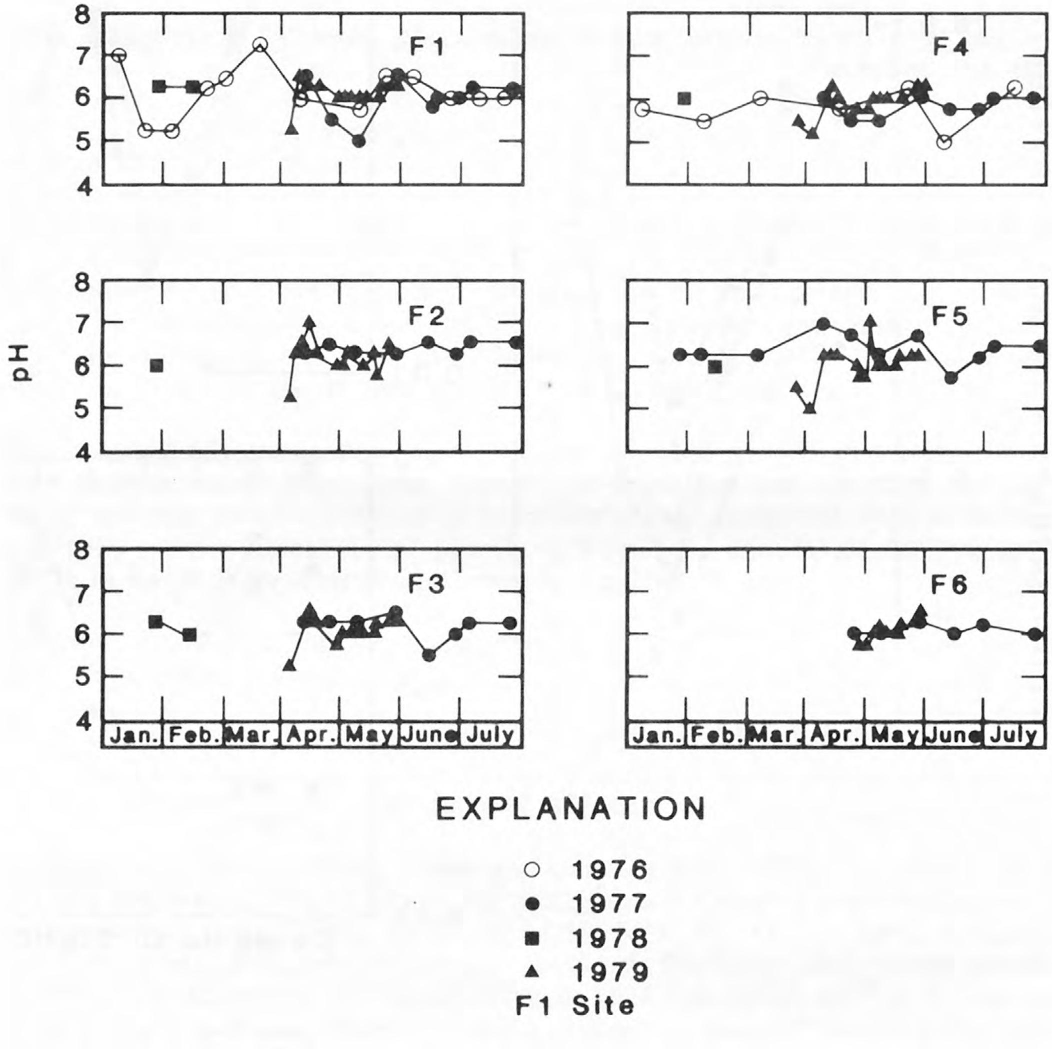


Figure 11.--Field pH along Filson Creek and Omaday Lake, January to August 1976-79

Table 1.—Summary statistics of ground-water quality, January to August 1976–79

(All concentrations in milligrams per liter except where noted)

Variable	Number of samples	Minimum value	Maximum value	Variable	Number of samples	Minimum value	Maximum value
Well H1 1976							
Bicarbonate	2	72.0	98.0	Dissolved sodium	2	16.0	18.0
Sulfate	2	450.0	450.0	Dissolved potassium	2	6.0	10.0
Chloride	0	—	—	Silica	1	17.0	17.0
Dissolved calcium	2	74.0	76.0	H^+ ion as pH, in units	1	5.9	5.9
Dissolved magnesium	2	60.0	63.0				
Well H1 1979							
Bicarbonate	4	176.0	186.6	Dissolved sodium	3	10.7	11.4
Sulfate	5	18.5	287.0	Dissolved potassium	3	5.3	5.6
Chloride	5	3.0	4.3	Silica	5	14.6	16.4
Dissolved calcium	3	83.0	89.0	H^+ ion as pH, in units	4	7.9	7.2
Dissolved magnesium	3	50.0	53.0				
Well H3 1976							
Bicarbonate	3	216.0	236.0	Dissolved sodium	3	7.5	9.3
Sulfate	3	3.5	4.7	Dissolved potassium	3	2.4	4.1
Chloride	0	—	—	Silica	2	23.0	24.0
Dissolved calcium	3	34.0	46.0	H^+ ion as pH, in units	2	7.1	6.7
Dissolved magnesium	3	16.0	18.0				
Well H3 1979							
Bicarbonate	6	92.7	212.4	Dissolved sodium	5	6.5	6.7
Sulfate	6	0.5	13.5	Dissolved potassium	5	2.0	2.1
Chloride	5	1.0	.14	Silica	5	16.9	17.9
Dissolved calcium	5	35.5	39.8	H^+ ion as pH, in units	6	7.9	7.3
Dissolved magnesium	5	14.9	15.4				

Table 1.—Summary statistics of ground-water quality, January to August 1976-79—Continued

Variable	Number of samples	Minimum value	Maximum value	Variable	Number of samples	Minimum value	Maximum value
Well WS 1979							
Bicarbonate	5	37.0	43.3	Dissolved sodium	5	2.1	2.4
Sulfate	5	10.5	12.1	Dissolved potassium	5	1.1	1.2
Chloride	5	0.7	0.9	Silica	5	2.7	7.1
Dissolved calcium	5	7.3	8.0	H^+ ion as pH, in units	5	8.0	7.3
Dissolved magnesium	5	4.0	4.6				
Well W2 1977							
Bicarbonate	2	11.0	33.0	Dissolved sodium	2	2.8	4.3
Sulfate	2	30.0	72.0	Dissolved potassium	2	0.3	1.7
Chloride	2	0.8	1.1	Silica	2	16.0	24.4
Dissolved calcium	2	14.0	20.0	H^+ ion as pH, in units	4	6.2	5.4
Dissolved magnesium	2	6.4	11.4				
Well W2 1978							
Bicarbonate	4	23.5	30.1	Dissolved sodium	3	1.6	1.7
Sulfate	6	6.6	27.4	Dissolved potassium	3	0.1	0.1
Chloride	5	0.8	1.2	Silica	4	13.1	15.5
Dissolved calcium	3	9.5	9.8	H^+ ion as pH, in units	5	7.1	5.8
Dissolved magnesium	3	5.4	5.6				
Well W3 1977							
Bicarbonate	4	11.0	49.0	Dissolved sodium	5	1.3	10.0
Sulfate	5	14.0	44.0	Dissolved potassium	5	0.7	17.8
Chloride	5	0.8	10.6	Silica	5	10.0	19.6
Dissolved calcium	5	5.8	11.7	H^+ ion as pH, in units	6	6.5	5.9
Dissolved magnesium	5	4.3	14.0				

Table 1.—Summary statistics of ground-water quality, January to August 1976–79—Continued

Variable	Number of samples	Minimum value	Maximum value	Variable	Number of samples	Minimum value	Maximum value
Well W3 1979							
Bicarbonate	5	92.0	158.5	Dissolved sodium	3	2.2	2.3
Sulfate	6	12.4	17.8	Dissolved potassium	3	0.4	0.5
Chloride	5	0.6	1.1	Silica	5	9.2	10.3
Dissolved calcium	3	6.9	8.8	H^+ ion as pH, in units	4	7.3	7.3
Dissolved magnesium	3	6.5	7.1				
Well W4 1977							
Bicarbonate	3	11.0	16.0	Dissolved sodium	3	1.7	5.6
Sulfate	3	2.0	6.4	Dissolved potassium	3	2.1	2.9
Chloride	3	0.2	5.0	Silica	3	23.0	34.0
Dissolved calcium	3	6.0	7.5	H^+ ion as pH, in units	3	5.7	5.6
Dissolved magnesium	3	3.1	3.6				
Well W4 1979							
Bicarbonate	0	---	---	Dissolved sodium	0	---	---
Sulfate	4	3.6	14.8	Dissolved potassium	0	---	---
Chloride	5	2.9	5.2	Silica	5	8.5	11.8
Dissolved calcium	0	---	---	H^+ ion as pH, in units	0	---	---
Dissolved magnesium	0	---	---				
Well W5 1977							
Bicarbonate	4	18.0	45.0	Dissolved sodium	4	3.1	6.4
Sulfate	3	1.0	11.0	Dissolved potassium	4	0.7	10.4
Chloride	3	0.8	2.1	Silica	3	13.4	20.2
Dissolved calcium	5	7.5	54.5	H^+ ion as pH, in units	5	6.1	5.4
Dissolved magnesium	3	4.8	6.3				

Table 1.—Summary statistics of ground-water quality, January to August 1976–79—Continued

Variable	Number of samples	Minimum value	Maximum value	Variable	Number of samples	Minimum value	Maximum value
			Well W5 1979				
Bicarbonate	1	6.1	6.1	Dissolved sodium	0	---	---
Sulfate	1	8.0	8.0	Dissolved potassium	0	---	---
Chloride	2	---	---	Silica	1	11.8	11.8
Dissolved calcium	0	---	---	H^+ ion as pH, in units	1	6.5	6.5
Dissolved magnesium	0	---	---				

H^+-ion activity does not correlate well with increases in discharge in Filson Creek because H^+-ion increase during snowmelt is caused by (1) the general dilution of creek water by snowmelt, which generally has pH one unit lower than that of the creek and (2) a larger and transient increase in activity caused by the leaching of acidity from the snowpack during the first part of snowmelt. The increase in H^+-ion activity at snowmelt is relatively independent of discharge and more dependent on the intensity and timing of the first part of snowmelt. Least squares regressions between H^+-ion activity and discharge show no correlation at 0.01 level of significance.

The increase in H^+-ion activity at snowmelt is approximately synchronous with an increase in the concentration of sulfate. The concentration of sulfate in Filson Creek and Omaday Lake is generally less than 2 mg/L (Siegel, 1979; 1981a). During snowmelt in April and early May, sulfate concentrations generally increased from less than 2 mg/L to an average of 12 mg/L at all sites in 1977 and from less than 2 to 4 mg/L in 1979 (fig. 12).

By mid-May 1977, sulfate concentrations were declining, and by mid-June concentrations were less than 2 mg/L. Sampling in 1979 was discontinued during the first week in June, when sulfate concentrations had not yet returned to presnowmelt levels. However, sulfate in a sample collected at F1 on August 31 was less than 1.0 mg/L, a concentration near that measured at base flow in early April.

Siegel (1979; 1981a) attributed the increase in H^+-ion and sulfate concentrations during snowmelt 1977 to the selective leaching of sulfate acidity from the snowpack, similar to that found at snowmelt in Scandanavia (Haapala and others, 1975; Gjessing and others, 1976; Henriksen and Wright, 1977). Because of the drought, there was little overland flow when snowmelt began. Most of the initial snowmelt infiltrated into the till and wetlands. After the till and wetlands were saturated, interflow water having high sulfate concentrations from the initial snowmelt entered the creek and Omaday Lake. The increases were greatest in 1977 at sites not in wetlands, F1, F5, and F4. Increases in sulfate and H^+-ion concentrations were least at sites F6 and F3, both in fens. There were

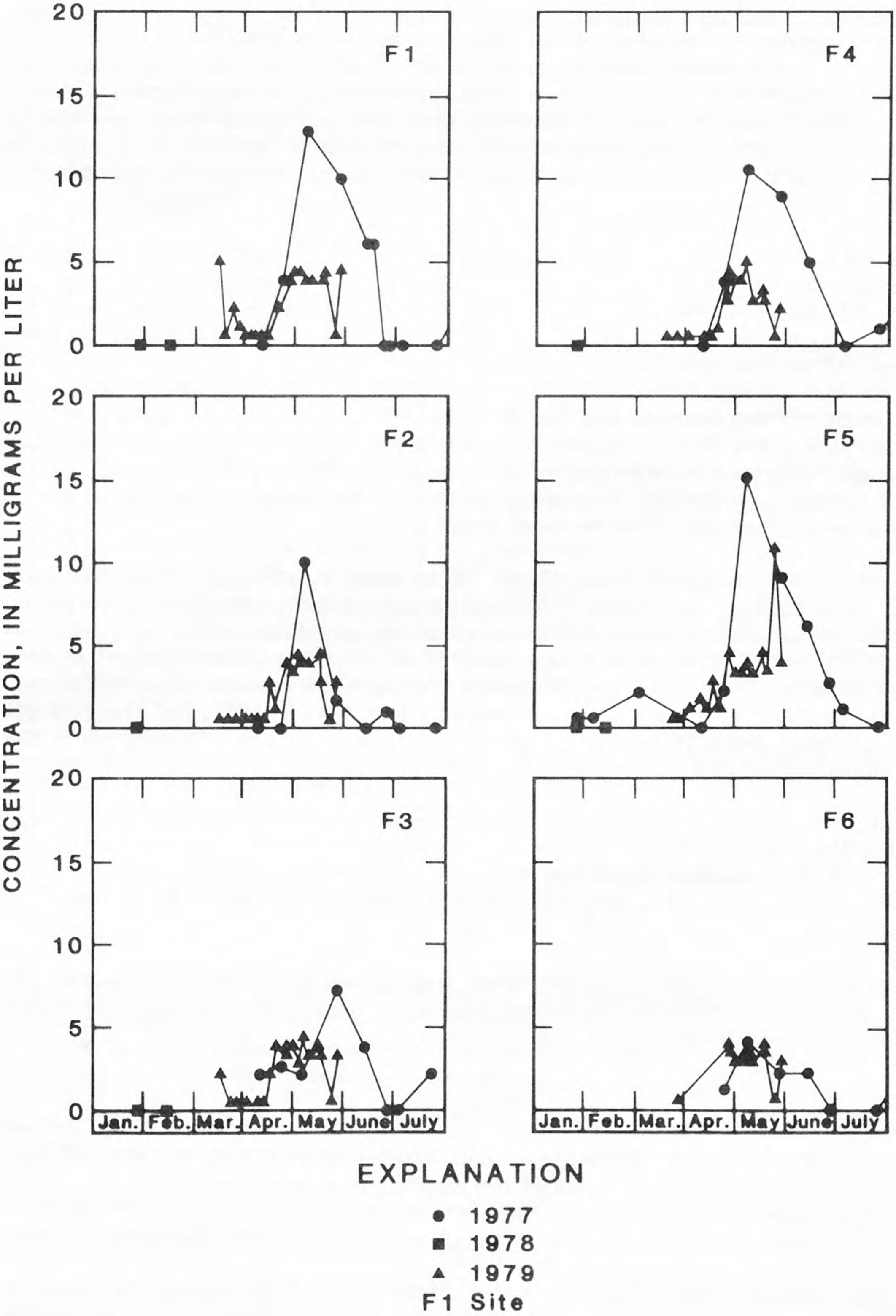


Figure 12.--Concentrations of sulfate in Filson Creek and Omaday Lake, January to August 1977-79

no systematic increases in sulfate concentration and H^+-ion concentration from headwater sites and across the mineralized zone to the mouth, even though concentrations of sulfate and H^+ ion were greatest in ground water in drift over the mineralized zone. The lack of systematic increases of these constituents along the creek implies that neither sulfide oxidation near the mineralized zone nor ground-water discharge are the mechanisms that cause the increases in sulfate at snowmelt. Sulfate concentrations also increased at site F2, the tributary to Filson Creek that has no mineralized bedrock within its watershed.

In 1979, the average concentration of sulfate in the bulk snowpack before significant melting in mid-March was 1.18 mg/L (s.d.=0.14, n=8). Maximum daily air temperatures at Winton, 25 km northeast of the watershed, exceeded freezing on March 5 and 6. Assuming similar air temperature at Filson Creek, it is likely that some of the sulfate deposited before this date was leached from the snowpack.

A short melting period from March 16-22, 1979, decreased the water content of the snowpack from 150 to 86 mm (determined on March 13 and March 19, respectively), while the average sulfate concentration of the snowpack decreased from 1.18 to 0.6 mg/L (n=6). Synchronous with the decrease of sulfate in the snowpack was the slight increase of sulfate concentrations in the creek of about 2 mg/L.

Most of the snowmelt from March 16 to April 3, 1979, probably did not go into storage. Total runoff from March 16 to April 3 was 3.8 mm, compared to 64 mm of snowmelt. The difference between the amounts of snowmelt and creek discharge, about 60 mm, is effectively the same as that estimated as the total storage deficit at the end of the 1976 drought (Siegel, 1981a). Because 1978 was not a drought year, the storage deficit at freeze-up in 1978 had to be considerably less than in 1977, and the bulk of the 60 mm of snowmelt probably left the watershed as flow across the channel ice in the creek or overland flow.

The increase in sulfate concentrations in Filson Creek and Omaday Lake was greatest during the major snowmelt period from mid-April to May. Calculations were done to determine if ground-water discharge to the creek during snowmelt, rather than leaching of sulfate acidity from the snowpack, could have caused the sustained increase in sulfate concentrations.

Ground-water discharge to the creek was calculated "liberally" because of uncertainties in the assumptions. Calculations were based on a simple two-dimensional application of Darcy's law:

$$Q = KIA$$

where:

Q = ground-water discharge, in cubic meters per second,
K = hydraulic conductivity of the aquifer, in meters per day,
I = hydraulic gradient, and
A = area, in meters squared, through which the aquifer discharges to the creek.

It was assumed that (1) ground water discharges to both sides of the creek along its entire 13-km length, (2) the saturated thickness of the peat is about 1 m, (3) the hydraulic conductivity of the saturated fabric peat is 4 m/d (Boelter, 1966), and (4) the hydraulic gradient is about 7 m/km (Siegel and Ericson, 1980).

These estimates are liberal because (1) wetlands are not present along the entire length of the creek, (2) the hydraulic conductivity of decomposed peat is probably an order of magnitude less than cited, and (3) the hydraulic gradient is probably closer to 1 m/km within the wetlands proper. Because the till is thin and the underlying bedrock has low hydraulic permeability, it is assumed that ground-water discharge from these sources is negligible. Ground-water discharge from the wetlands was calculated as 8.6×10^{-3} m^3/s.

Assuming that the average concentration of sulfate in the wetland ground water was 12 mg/L, ground-water discharge would have had to be 30 percent of the total flow, or at least 1.2 m^3/s to raise the sulfate concentrations in the creek from 2 to 4 mg/L at the peak of discharge. This is at least 2 orders of magnitude greater than the liberally calculated amount of ground-water discharge to the creek.

Similarly, cation and bicarbonate concentrations were significantly greater in ground water (tables 1 and 2) than in Filson Creek during snowmelt in both 1977 and 1979. This further suggests that ground-water discharge was minimal. If ground-water discharge to the creek caused the observed increases in sulfate concentrations, similar increases in the concentrations of cations and bicarbonate would also be observed.

In 1979, concentrations of sulfate in the creek remained at about 4 mg/L even after the initial increase in response to snowmelt. The concentration of sulfate in precipitation from April 20 to June 6 averaged about 4.2 (n=11, s.d.=0.82), and storm runoff to the creek during the snowmelt recession probably maintained sulfate concentrations near 4.0 mg/L. With the decline of precipitation in June, sulfate concentrations in the creek also began to decline. By August, sulfate concentrations were less than 1 mg/L, typical of base flow.

Cummulative monthly estimates of the chemical budget for sulfate during snowmelt have been used to determine whether sulfate deposited by precipitation is retained in the watershed or is chemically at steady state.

Monthly chemical mass deposition on the watershed was calculated from

$$m_i = 0.01\, C_i P_m$$

where:

m_i = monthly deposition of constituent i, in kilograms per hectare per month,
P_m = monthly precipitation, in millimeters, and
C_i = average concentration of constituent i in precipitation collected during the month, in milligrams per liter.

The constant, 0.01, is a conversion factor of millimeters of precipitation to liters and milligrams per liter to kilograms per hectare.

Monthly mass chemical loss from the watershed by streamflow was calculated from

$$m_i = 0.0345\, Q_m C_i$$

where:

m_i = monthly loss of constituent i, in kilograms per hectare per month,
Q_m = monthly discharge, in cubic meters, and
C_i = monthly average concentration of constituent i, in milligrams per liter.

Table 2.—Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79

(Concentrations in milligrams per liter)

Variable	Number of samples			Mean			Standard deviation			Minimum value			Maximum value		
	1976	1977	1979	1976	1977	1979	1976	1977	1979	1976	1977	1979	1976	1977	1979
SITE F1															
Field pH, in units	13	13	13	5.9	5.8	6.0	1.7	2.6	1.2	7.3	6.6	6.6	5.3	5.0	5.3
Alkalinity (as bicarbonate)	13	21	20	16.3	7.9	13.2	5.0	3.3	11.0	8.0	1.2	3.0	25.0	13.4	41.5
Sulfate	0	11	19	—	4.6	2.6	—	3.8	1.8	—	2.0	0.5	—	13.0	5.2
Chloride	13	15	19	1.5	0.7	1.1	0.6	0.3	0.3	0.5	0.4	0.5	2.6	1.5	1.5
Nitrate + nitrite	7	10	19	0.4	1.0	0.6	0.3	1.4	0.4	0.1	0.2	0.1	0.7	4.4	1.6
Total calcium	0	23	20	—	3.6	3.3	—	0.9	1.6	—	2.5	1.9	—	5.6	7.9
Dissolved calcium	11	7	0	3.7	2.5	—	0.8	0.9	—	2.4	1.5	—	4.7	4.0	—
Total magnesium	0	23	20	—	2.5	2.2	—	0.7	0.9	—	1.6	1.3	—	3.8	3.6
Dissolved magnesium	11	11	0	2.6	1.5	—	0.7	0.6	—	1.8	1.1	—	3.6	2.6	—
Total sodium	0	19	20	—	1.3	1.0	—	0.2	0.3	—	1.0	0.6	—	2.0	1.5
Dissolved sodium	11	13	0	1.2	1.3	—	0.5	0.2	—	0.0	1.1	—	1.6	1.8	—
Total potassium	0	19	20	—	0.6	0.7	—	0.5	0.3	—	0.2	0.3	—	1.7	1.4
Dissolved potassium	12	13	0	0.4	0.4	—	0.2	0.3	—	0.0	0.2	—	0.7	1.0	—
Silica	13	11	19	7.4	6.4	8.0	3.5	2.8	2.5	1.5	1.0	3.2	12.0	11.0	11.9

Table 2.—Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79—Continued

Variable	Number of samples		Mean		Standard deviation		Minimum value		Maximum value	
	1977	1979	1977	1979	1977	1979	1977	1979	1977	1979
SITE F2										
Field pH, in units..........	9	14	6.4	6.0	0.1	1.3	7.0	6.9	6.2	5.3
Alkalinity (as bicarbonate)..........	9	19	9.3	11.0	4.1	9.0	5.0	3.3	16.0	25.8
Sulfate	9	19	2.7	2.1	2.7	1.6	1.0	0.5	10.0	4.3
Chloride	9	19	0.9	1.1	0.4	0.3	0.4	0.5	1.6	1.6
Nitrate + nitrite	0	19	—	0.5	—	0.5	—	0.1	—	1.8
Total calcium.............	9	19	3.5	2.8	0.9	1.0	2.0	1.8	4.7	4.4
Dissolved calcium	5	0	2.1	—	0.3	—	2.0	—	2.6	—
Total magnesium..........	8	19	2.7	2.0	0.8	0.7	1.8	1.3	4.1	3.1
Dissolved magnesium	4	0	1.3	—	0.3	—	1.0	—	1.8	—
Total sodium	9	19	1.6	0.9	0.4	0.2	1.2	0.6	2.5	1.2
Dissolved sodium..........	4	0	1.1	—	0.1	—	1.0	—	1.3	—
Total potassium...........	9	19	0.6	0.6	0.3	0.4	0.3	0.1	1.2	1.3
Dissolved potassium	4	0	0.5	—	0.1	—	0.3	—	0.6	—
Silica....................	9	19	8.5	8.8	2.5	3.2	4.6	2.8	12.3	12.8

Table 2.—Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79—Continued

Variable	Number of samples		Mean		Standard deviation		Minimum value		Maximum value	
	1977	1979	1977	1979	1977	1979	1977	1979	1977	1979
SITE F3										
Field pH, in units..........	6	10	6.1	6.1	0.2	0.4	6.3	6.5	6.0	5.7
Alkalinity (as bicarbonate)..........	6	12	7.7	8.6	2.8	4.7	5.0	4.6	12.0	22.9
Sulfate	6	12	2.2	2.8	1.0	1.1	1.0	0.5	4.0	4.0
Chloride	6	12	1.1	1.0	0.7	0.4	0.5	0.5	2.4	1.6
Nitrate + nitrite	0	12	—	0.2	—	0.1	—	0.1	—	0.4
Total calcium.............	5	12	3.3	2.7	0.4	0.7	2.8	2.2	4.0	5.0
Dissolved calcium	3	0	2.0	—	0.4	—	1.7	—	2.4	—
Total magnesium..........	5	12	2.2	1.9	0.6	0.7	1.6	1.6	3.3	4.0
Dissolved magnesium	3	0	1.6	—	0.1	—	1.5	—	1.7	—
Total sodium	5	12	1.4	0.9	0.2	0.2	1.1	0.6	1.6	1.3
Dissolved sodium	3	0	1.1	—	0.1	—	1.1	—	1.2	—
Total potassium...........	5	12	0.3	0.7	1.1	0.4	0.6	0.4	3.1	1.9
Dissolved potassium	3	0	0.4	—	1.3	—	0.6	—	2.9	—
Silica....................	6	12	4.5	5.0	1.6	2.0	2.9	1.8	7.0	7.8

Table 2.—Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79—Continued

Variable	Number of samples			Mean			Standard deviation			Minimum value			Maximum value		
	1976	1977	1979	1976	1977	1979	1976	1977	1979	1976	1977	1979	1976	1977	1979
SITE F4															
Field pH, in units......	7	8	14	5.5	5.7	5.8	3.4	1.3	1.5	6.3	6.1	6.2	5.0	5.3	5.2
Alkalinity (as bicarbonate)......	7	8	16	13.6	5.9	8.4	5.0	2.5	5.9	8.0	3.0	1.1	23.0	10.0	22.2
Sulfate	0	7	16	—	4.8	2.2	—	3.8	1.6	—	1.0	0.5	—	10.8	5.0
Chloride	7	8	16	1.4	1.1	1.1	0.4	0.5	0.3	0.7	0.4	0.6	2.0	1.7	1.6
Nitrate + nitrite	2	0	16	0.3	—	0.4	0.2	—	0.5	0.1	—	0.1	0.4	—	1.7
Total calcium.........	0	8	16	—	3.9	2.7	—	0.5	1.1	—	2.9	1.8	—	4.8	4.8
Dissolved calcium	5	6	0	3.4	2.4	—	0.9	0.7	—	2.2	1.7	—	4.4	3.6	—
Total magnesium......	0	8	16	—	2.6	1.8	—	0.5	0.6	—	2.0	1.2	—	3.5	3.0
Dissolved magnesium ..	5	6	0	2.3	1.6	—	0.7	0.6	—	1.5	1.1	—	2.9	2.5	—
Total sodium	0	8	16	—	1.5	0.9	—	0.3	0.2	—	1.1	0.5	—	2.1	1.3
Dissolved sodium......	5	6	0	1.3	1.3	—	0.6	0.3	—	0.6	1.0	—	2.0	1.7	—
Total potassium.......	0	8	16	—	0.9	0.7	—	0.5	0.3	—	0.3	0.3	—	1.9	1.4
Dissolved potassium ...	5	6	0	0.4	0.8	—	0.2	0.4	—	0.1	0.3	—	0.7	1.5	—
Silica................	7	8	16	4.7	5.5	6.6	2.6	2.3	2.1	1.4	1.8	2.7	7.3	8.1	9.6

Table 2.—Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79—Continued

Variable	Number of samples		Mean		Standard deviation		Minimum value		Maximum value	
	1977	1979	1977	1979	1977	1979	1977	1979	1977	1979
SITE F5										
Field pH, in units	11	16	6.3	5.9	0.4	1.9	7.0	6.9	5.8	5.1
Alkalinity (as bicarbonate)	11	18	9.8	8.3	5.3	5.5	5.0	2.1	19.0	20.0
Sulfate	11	18	3.9	3.1	4.5	2.3	0.5	0.5	15.0	10.8
Chloride	11	18	1.1	1.0	0.4	0.4	0.5	0.2	1.6	1.5
Nitrate + nitrite	0	18	—	0.4	—	0.4	—	0.1	—	1.5
Total calcium	11	18	4.3	2.7	2.4	1.0	2.1	0.6	7.8	4.4
Dissolved calcium	4	0	2.0	—	0.1	—	1.9	—	2.0	—
Total magnesium	11	18	3.2	1.7	1.7	0.6	1.5	0.4	5.8	2.8
Dissolved magnesium	4	0	1.3	—	0.1	—	1.2	—	1.4	—
Total sodium	11	18	2.0	0.9	0.9	0.2	1.1	0.2	3.4	1.2
Dissolved sodium	4	0	1.2	—	0.1	—	1.1	—	1.4	—
Total potassium	11	18	0.7	0.6	0.2	0.3	0.4	0.1	0.9	1.4
Dissolved potassium	4	0	0.7	—	0.1	—	0.6	—	0.9	—
Silica	11	18	3.3	6.1	2.4	3.0	1.0	0.9	8.6	16.0

Table 2.—Summary statistics of water quality of Filson Creek and Omaday Lake, January to August 1976-79—Continued

Variable	Number of samples		Mean		Standard deviation		Minimum value		Maximum value	
	1977	1979	1977	1979	1977	1979	1977	1979	1977	1979
SITE F6										
Field pH, in units	8	13	6.1	5.9	0.7	1.8	6.6	6.6	5.6	5.1
Alkalinity (as bicarbonate)	8	18	7.1	10.6	2.2	7.9	4.0	3.2	10.0	24.8
Sulfate	8	18	3.0	2.4	1.8	1.5	2.0	0.5	7.0	4.3
Chloride	8	18	1.1	1.1	0.5	0.4	0.5	0.5	1.8	1.9
Nitrate + nitrite	0	18	—	0.5	—	0.6	—	0.1	—	2.3
Total calcium	8	18	3.0	2.8	0.7	1.1	2.1	1.9	4.2	5.0
Dissolved calcium	4	0	2.1	—	0.1	—	2.0	—	2.3	—
Total magnesium	8	18	2.5	1.8	1.3	0.7	1.5	1.2	5.4	3.2
Dissolved magnesium	4	0	1.2	—	0.1	—	1.0	—	1.3	—
Total sodium	8	18	1.5	0.9	0.4	0.2	1.2	0.6	2.5	1.3
Dissolved sodium	4	0	1.2	—	0.1	—	1.1	—	1.3	—
Total potassium	8	18	0.9	0.6	0.2	0.2	0.6	0.3	1.1	1.1
Dissolved potassium	4	0	0.7	—	0.1	—	0.6	—	0.8	—
Silica	8	18	5.2	6.5	3.0	2.5	0.8	2.1	10.2	10.4

The constant, 0.0345, is a conversion factor of monthly discharge of cubic meters to liters and concentration from milligrams per liter to kilograms per hectare.

Storage of melt water in 1979 was assumed to be negligible. Based on the estimated storage deficit, about 60 mm of snowmelt was assumed to have gone into storage at snowmelt 1977 (Siegel, 1981a). Sulfate in ground-water discharge to the creek was assumed to be negligible in both years.

The estimated budgets for sulfate (table 3) suggest that sulfate is retained in the watershed not only during summer, fall, and winter, when reducing conditions are likely in the wetlands, but to a lesser extent during major recharge to the wetlands at snowmelt. Sulfate retention was determined independently of the sulfate-analysis method. Total sulfate deposition from March to June (snowmelt and concurrent precipitation) in 1977 and 1979 was 6.4 and 8.9 kg/ha, respectively, while sulfate transported by the creek was 2.0 and 7.2 kg/ha. The difference between deposition and loss in 1977, +4.4 kg/ha, is twice that in 1979. Much of this mass went into temporary storage because of the storage deficit that existed in 1977 before snowmelt and does not in itself reflect permanent sulfate retention in the watershed during snowmelt. However, over 10 kg/ha of sulfate was retained from March to October 1977, indicating annual sulfate retention (Siegel, 1981a).

Table 3.—Estimated sulfate budgets for Filson Creek watershed above site F1, March to June, 1977 and 1979

(All units are in kilograms per hectare per year)

	Sulfate deposition	Sulfate transport	Net loss or gain of sulfate
March 1977........	1.8	Indeterminate	+1.8
April 1977.........	0.4	0.1	+0.3
May 1977	4.2	1.9	+2.3
Total	6.4	2.0	+4.4
March 1979........	3.8	0.1	+3.7
April 1979.........	2.8	4.5	-1.7
May 1979	2.3	2.6	-0.3
Total	8.9	7.2	+1.7

The net retention of +1.7 kg/ha between sulfate deposition and loss in 1979 suggests retention of sulfate even during snowmelt because the ground-water and surface-water storage capacity was probably filled during record snowmelt discharge. The discharge was about twice that of previous years.

Sulfate could be retained in the watershed by both the reduction of sulfate to relatively insoluble metal sulfides in the wetlands or by sulfate adsorption to sesquioxides in the till (Johnson and others, 1979). Filson Creek watershed, which is mostly overlain by till derived from underlying mafic gabbro and troctolite, retains sulfate. This may be roughly contrasted to the net loss of sulfate from Hubbard Brook watershed in New Hampshire, which is overlain by till derived mostly from gneiss (Johnson and others, 1969; Johnson and Cole, 1977). Both watersheds are forested, subject to acid precipitation, and have about the same climate. Although it is probable that sulfate is being adsorbed by sesquioxides in the till in Filson Creek watershed, experimental work is needed to determine the extent of such adsorption.

Nitrogen species

Concentrations of nitrate plus nitrite increased in Filson Creek and Omaday Lake during snowmelt (fig. 13). For example, concentrations at F1 increased during the short melting period in March 1979 from about 0.5 to 1.7 mg/L and from about 0.75 to 1 mg/L during the major snowmelt in April. The range of increase in nitrate plus nitrite concentrations was different at different sites in 1979. For example, at site F2 nitrate concentration increased most during the major snowmelt period, whereas at site F3 the concentrations of nitrate plus nitrite were maximum at the beginning of the major snowmelt in March.

Nitrate is leached from the snowpack during snowmelt. On March 13, 1979, the average concentration of nitrate in the snowpack in Filson Creek watershed was 2.3 mg/L (n=8, s.d.=0.34). One week after the short melting period, on March 19, the average concentration was 1.3 mg/L (n=8, s.d.=0.19). This represents a 57 percent reduction in concentration of nitrate in the bulk snowpack.

Unlike that of sulfate, concentrations of nitrate were greater in the creek at the beginning of the major snowmelt and were not coincidental or near coincidental with the discharge peak. This suggests that nitrate acidity was leached more rapidly from the snowpack than sulfate acidity.

Two bulk snow samples were collected in the Superior National Forest by EPA on April 2, 1979, to provide data on how rapidly sulfate and nitrate are leached from the snowpack during melting (fig. 14). The bulk snow samples were successively melted to 1-liter fractions, which were analyzed for concentrations of nitrate and sulfate.

Concentrations of sulfate in the first liter of melt water were 2 to 3 times greater than that of the bulk snowpack, while concentrations of nitrate were from 2 to 17 times greater. An average of 30 percent of the total sulfate mass and 18 percent of the total nitrate mass was removed from the snowpack in the first liter of snowmelt. These results are comparable to those obtained in similar experiments using snow from the Superior National Forest in March 1978 (Glass and Loucks, 1980). In that study, 21 percent of the total sulfate mass and 18 percent of the total nitrate mass were removed in the first 10 percent of snowmelt. Lag in the leaching of sulfate with respect to that of nitrate was not discernible. If these results can be assumed to represent the leaching of sulfate and nitrate acidity in the natural system, it would be expected that sulfate and nitrate in Filson Creek should increase at about the same time. Perhaps the difference in the timing of the concentration "peaks" could be resolved by installing field lysimeters to gather melt water in the field (Johannessen and Henriksen, 1978).

Concentrations of nitrate plus nitrite were also greater at or near snowmelt 1976 and 1977 compared with concentrations during base flow, but the frequency of sampling was not great enough to define the relationship between concentration and the timing of the melting. Nitrate plus nitrite concentrations show only fair dependence upon stream discharge (fig. 15) because concentrations of nitrate are dependent on the timing and extent of snowmelt as well as biological uptake at the onset of the growing season.

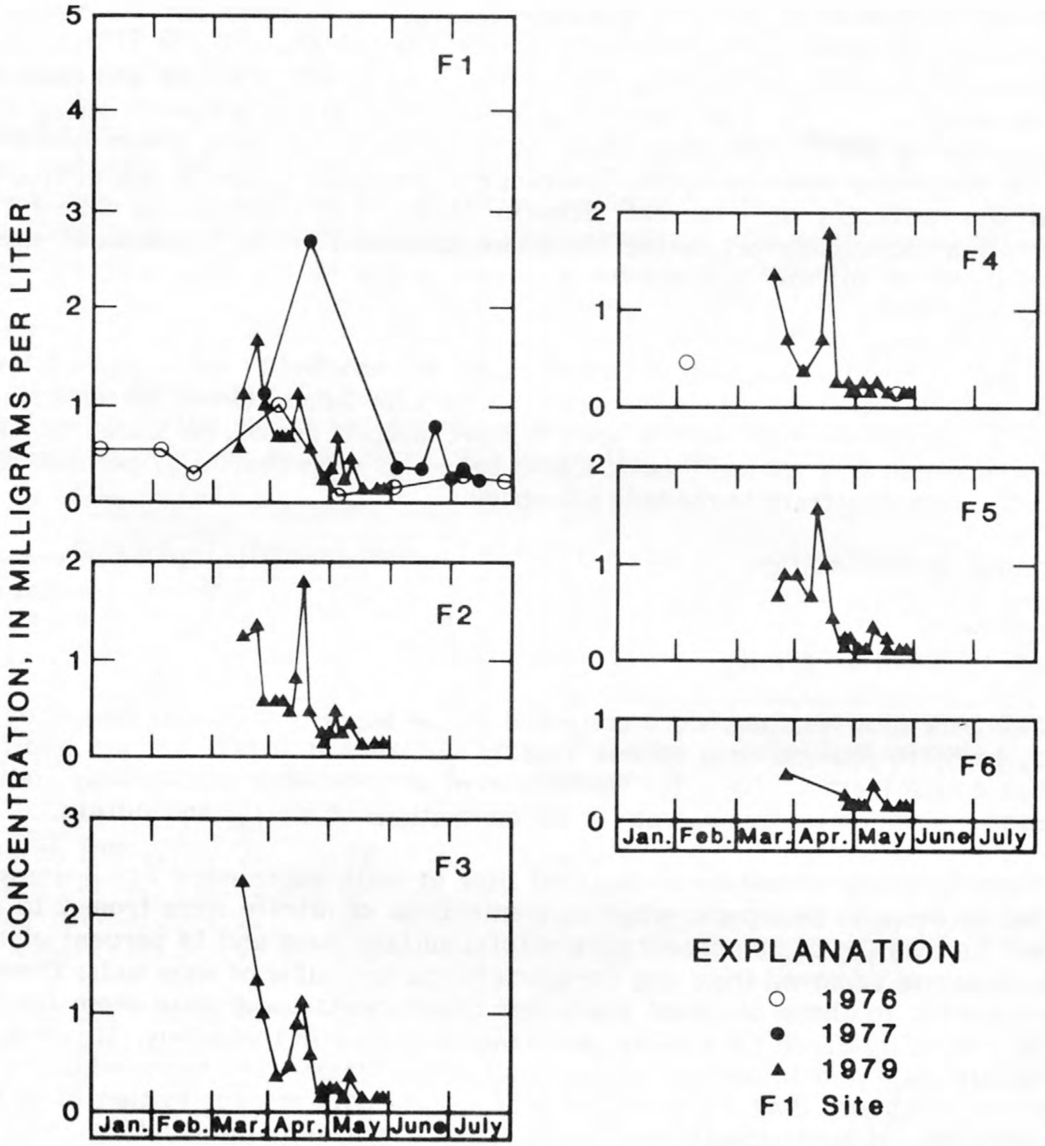


Figure 13.--Concentrations of nitrate plus nitrite in Filson Creek and Omaday Lake, January to August 1976, 1977, and 1979

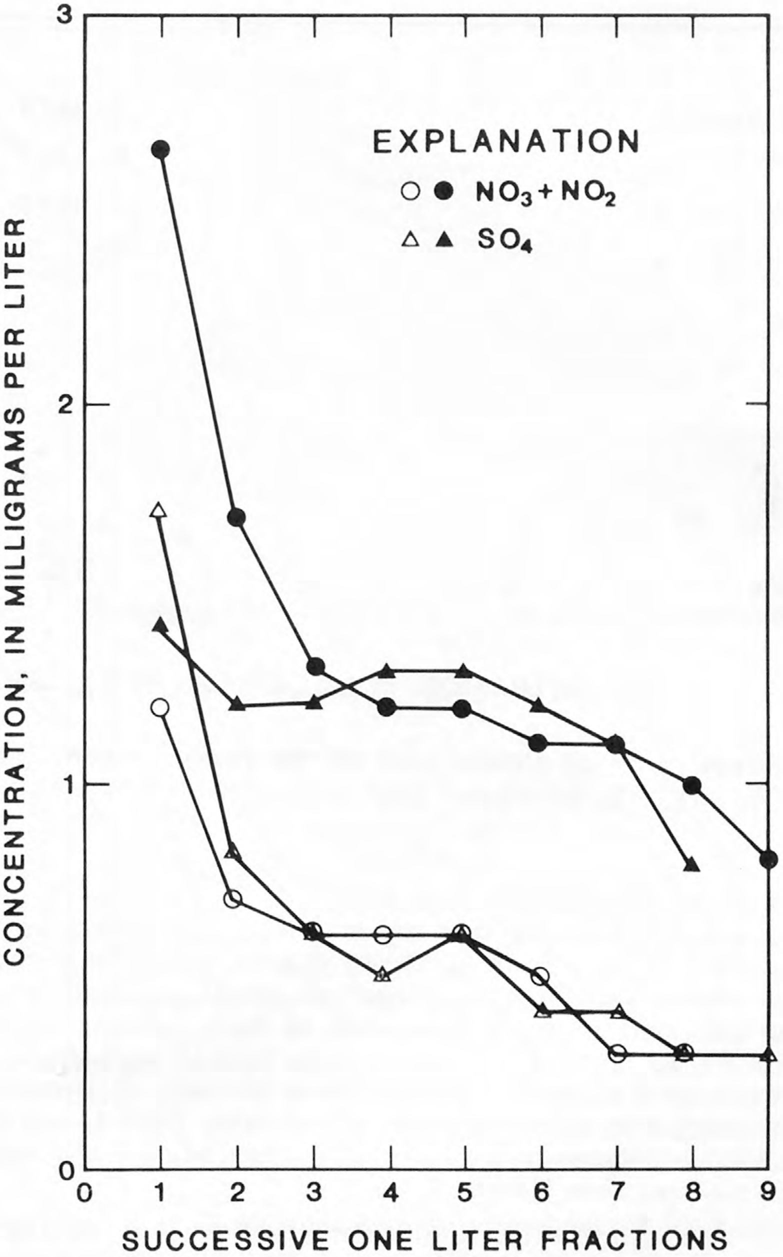


Figure 14.--Concentrations of sulfate and nitrate plus nitrite in successive 1-liter fractions of melted snow, April 1979. Solid points from snow collected at Snowpack Lake, open points from snow collected at Big Trout Lake

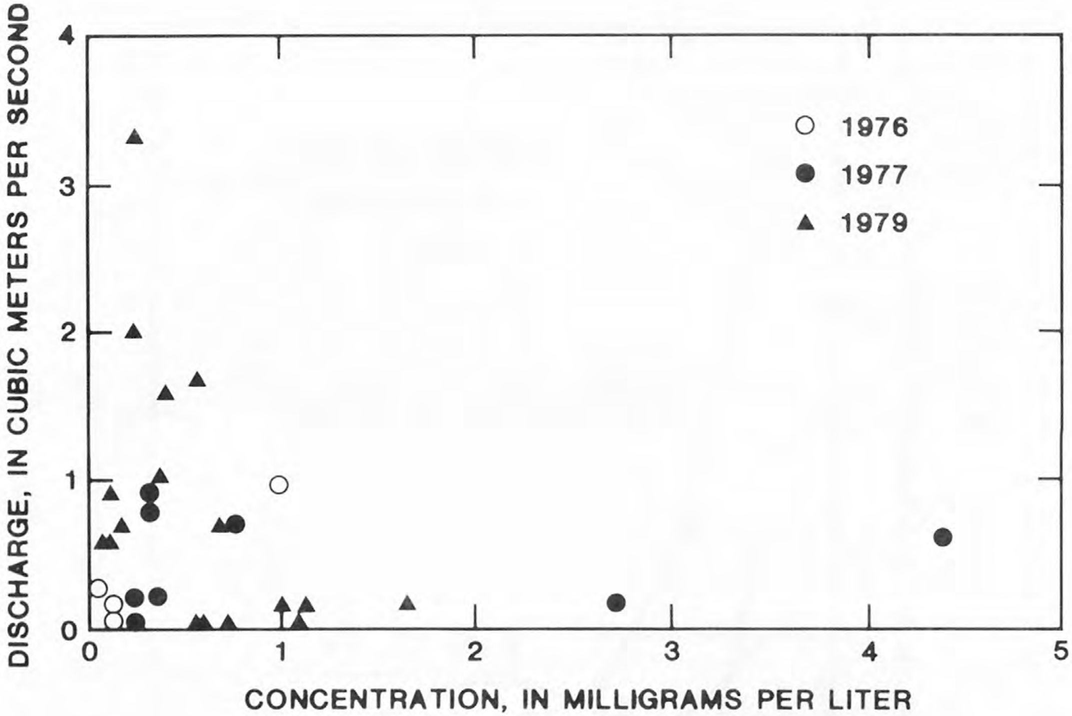


Figure 15.--Concentration of nitrate plus nitrite versus discharge at F1, January to August 1976, 1977, and 1979

Alkalinity

Alkalinity, defined as the milliequivalents of acid necessary to neutralize the titratable bases in a solution, declined exponentially with increases in streamflow in Filson Creek (fig. 16). Variations in alkalinity at snowmelt 1979 were more pronounced than in previous years because of a larger snowmelt. Alkalinity (as bicarbonate) decreased during snowmelt in April from over 15 mg/L to less than 5 mg/L (fig. 17). Alkalinity at sites F1, F2, and F5 decreased as much as 10 mg/L from March 16-23, and then increased by April 8 to near previous concentrations. It is probable that similar variations in alkalinity also occurred in March at sites F3, F4, and F6. The transient decrease in alkalinity is related to the increase in streamflow and consequent dilution of base flow by snowmelt between March 16-19.

During March and April 1976, total alkalinity decreased at site F1 from over 15 mg/L (as bicarbonate) to less than 10 mg/L. Alkalinity in 1977, a drought year, decreased at snowmelt in April and May at sites F1 through F5 from about 10 to less than 5 mg/L. Not enough samples were collected at F6 to determine a trend. Alkalinity in Omaday Lake (F5) prior to snowmelt in 1977 was about 15 mg/L, about the same as alkalinity at site F1.

Base flow virtually ceased by November 1976 and the creek froze to its bed by January 1977. The lower determinations of alkalinity in the initial samples collected in April 1977 reflect dilution by channel snowmelt of channel-ice melt water.

Significantly different analytical techniques were used in this study to determine alkalinity. Alkalinity was determined by potentiometric titration to (1) pH 4.5 in 1976, (2) the first inflection point in the pH-titrant curve, usually at pH 5.1, in 1977, and (3) by calculation from titrant volumes at both pH 4.5 and 4.2 in 1979.

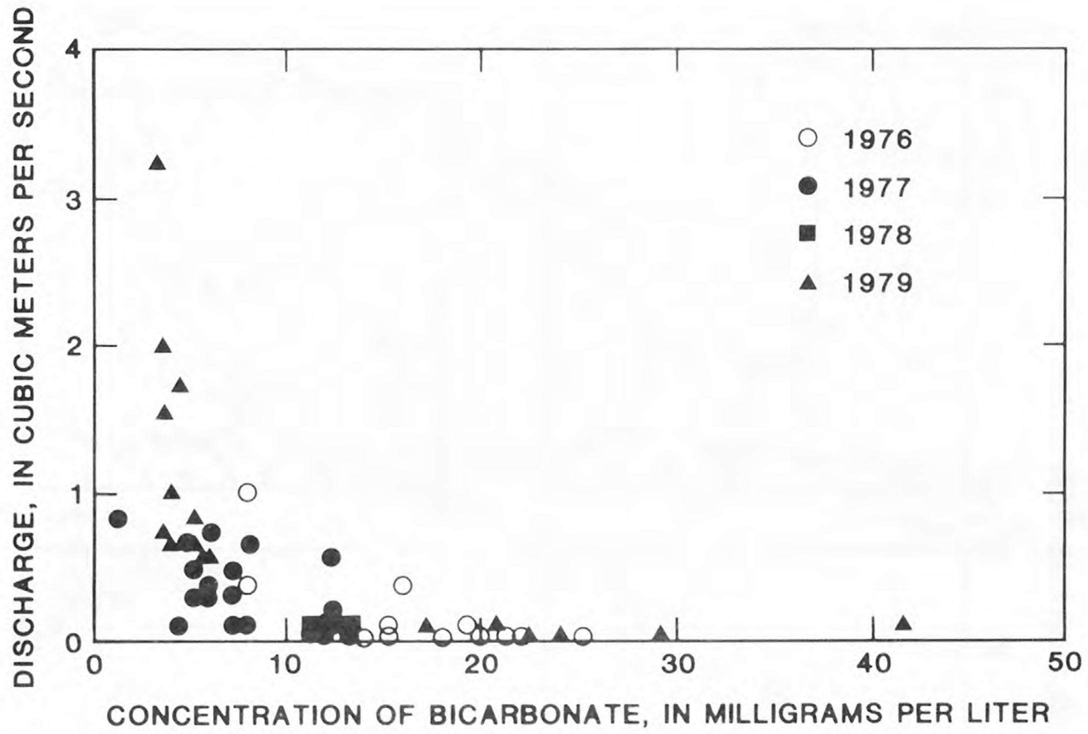


Figure 16.--Concentration of alkalinity (as bicarbonate) versus discharge at F1, January to August 1976-79

Interpretation of total-alkalinity data is further complicated by organic acids in the water. Organic acids are macroions of negatively charged organic colloids (Ong and others, 1970) that can contribute a significant part of total alkalinity in surface water associated with wetlands (Hem, 1975). At least 35 percent of the DOC (dissolved organic carbon) in water can be considered to be organic acids (R. L. Malcolm, oral commun., 1979). Filson Creek had an average of about 30 mg/L of DOC in 1977 (n=11, Mustalish, unpublished data on file in office of the Minnesota Environmental Quality Board, 1978). These concentrations of DOC are about an order of magnitude greater than those in streams that drain watersheds having no significant wetlands (Malcolm and Durum, 1976).

The effect of organic acids on total alkalinity is apparent from curves of potentiometric titrations (figs. 18 and 19). For example, the slope of the central part of titration curves for samples collected under ice on March 19, 1979, at F1, F2, and F5 was relatively flat. An indistinct inflection point occurs near a pH of 5.1. If bicarbonate was the major component of alkalinity in the waters, the curves would have more pronounced "S" shapes with a distinct inflection point between pH 4.3 and 5.2, depending on the ionic strength, temperature, and total alkalinity (Barnes, 1964; Stumm and Morgan, 1970).

Alkalinity decreases during snowmelt because of dilution and the addition of free acid, and the titration curves have much steeper slopes. For example, the inflection point on titration curves of samples collected on May 8, 1977, was at a pH of 5.1. This end point is near the theoretical bicarbonate end point calculated by Barnes (1964) for a solution with an ionic strength of about 10^{-4} and total carbonic species of 10 to 25 mg/L, which are conditions similar to those in Filson Creek.

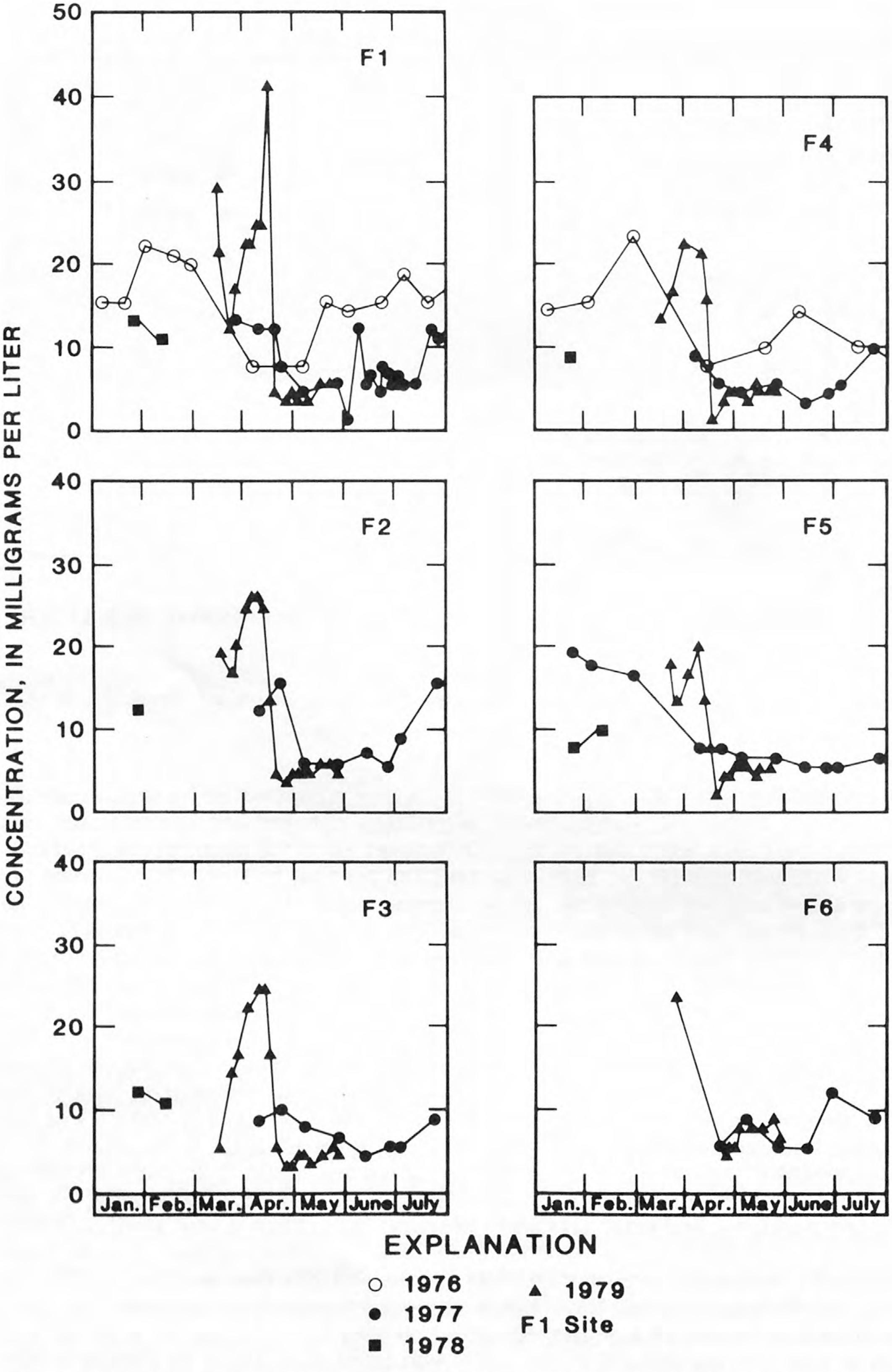


Figure 17.--Concentrations of bicarbonate in Filson Creek and Omaday Lake, January to August 1976-79

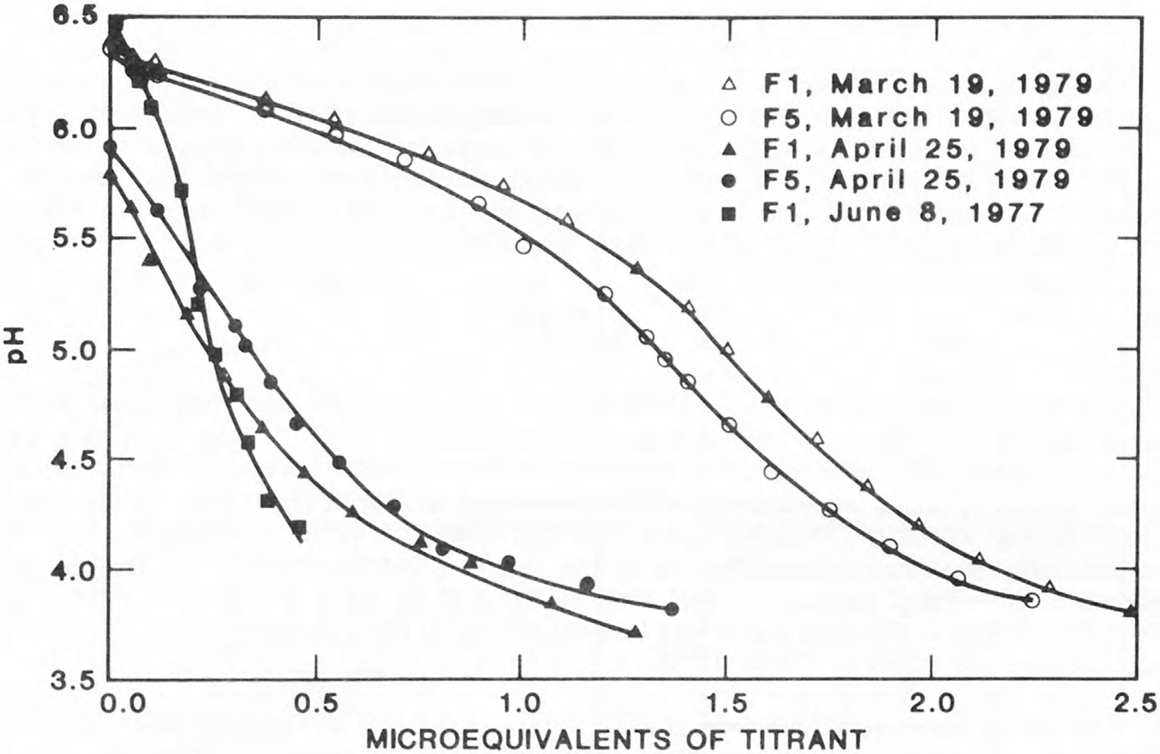


Figure 18.--Potentiometric titrations of alkalinity in Filson Creek and Omaday Lake, May 1977, and March and April 1979

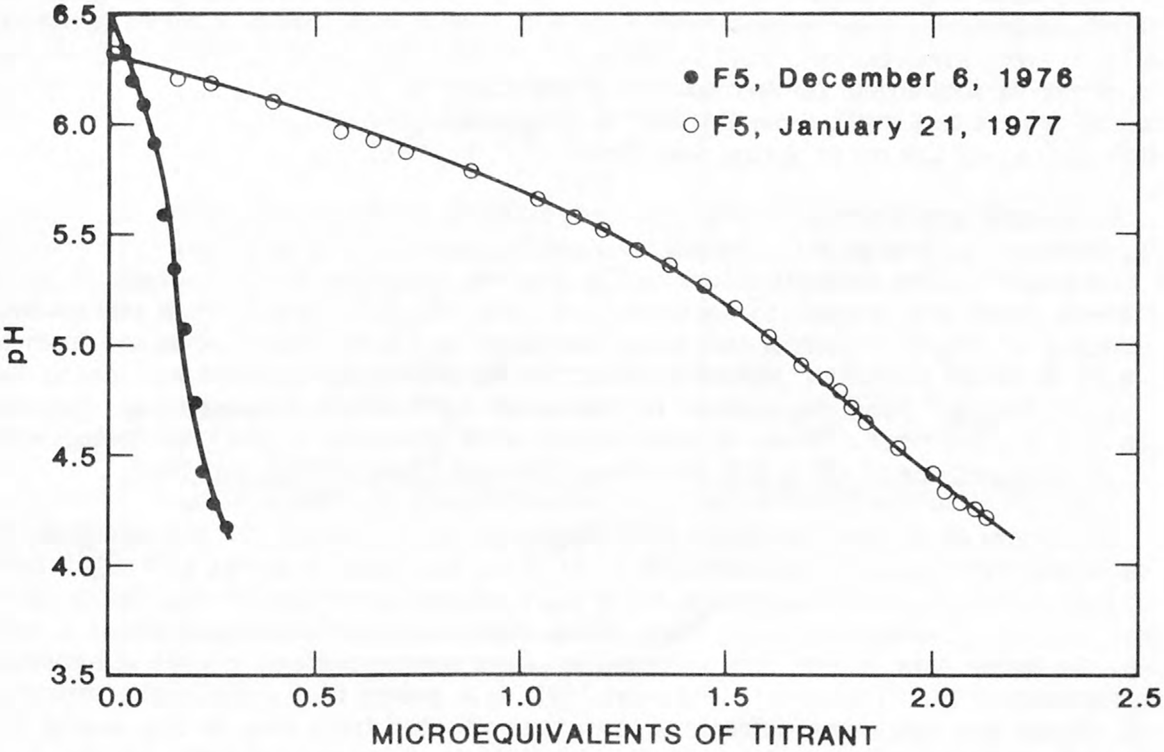


Figure 19.--Potentiometric titrations of alkalinity in Omaday Lake, December 1976 and January 1977

During snowmelt 1979, the titration curves had slopes intermediate between those for water collected during base flow 1979 and during snowmelt 1977. An inflection point can be inferred near pH 5.1, but the tail of the curve is skewed to greater milliequivalents of titrant per unit of pH decrease. Total alkalinity calculated from end points between pH 4.2 and 4.5 is twice as great as total alkalinity calculated from the end point of 5.1. Clearly, total alkalinity in this case is composed of both carbonate alkalinity and alkalinity contributed by organic acids.

Silica

The concentration of silica in Filson Creek is greatest at base flow under ice (fig. 20). For example, silica at F1 ranged from 10 mg/L in January to 12 mg/L in mid-March 1976. In January and February 1978, silica concentrations at F1 were 15 mg/L. Silica at F1 in 1979 was 13 mg/L immediately before snowmelt in March and April. Silica concentrations during winter in Omaday Lake (F5) and near the outlet of Omaday Lake (F4) were generally less than concentrations in the creek. Concentrations at F4 from January to March 1976 were 6 mg/L, one-half that at F1, and 10 mg/L in 1979, 20 percent less than at F1. Silica in Omaday Lake was less than 2 mg/L from January to March 1977 and 6 mg/L before snowmelt in March 1979.

The silica concentrations less than 7 mg/L at F4 and in Omaday Lake in winters 1976, 1977, and 1979 may reflect the uptake of silica by diatoms during the previous springs and summers. From April to October 1976, during the drought, silica concentrations declined in Filson Creek (F1) from 12 to 3.9 mg/L with declining discharge (U.S. Geological Survey, 1977). Although Omaday Lake was not sampled in 1976 except during December, data collected at F4 indicated that concentration of silica in the lake also declined. Silica at F4 decreased from 6 to less than 2 mg/L from April to September 1976 (U.S. Geological Survey, 1977). Silica in Omaday lake in December 1976 was only about 1 mg/L, indicating further loss of silica under the ice. Silica at F1, however, increased from 4 to 6 mg/L from October to December 1976 (Siegel, 1981b), indicative of a silica gain along the creek during base flow.

In January and February 1978, however, silica in Omaday Lake at F4 was about 15 mg/L, identical to that at F1. The high concentrations of silica in winter 1978 are difficult to explain. Silica concentrations in the lake and creek increased with discharge and lake levels from late August to early October 1977 (Siegel, 1981b), when storms broke the drought of 1976-77. During this time, discharge of Filson Creek increased from less than 0.03 to about 1.4 m^3/s. Before storms, the concentration of silica in Omaday Lake was about 5 mg/L. From September to December 1977, silica concentrations increased to greater than 10 mg/L. These concentrations were sustained in the lake during winter 1978. Concentrations of silica also increased in Filson Creek during fall 1977.

Silica concentrations decreased with discharge in 1976 and 1979. For example, during snowmelt 1979, silica concentrations at all sites decreased from 11 to 7 mg/L during the major flood peak and increased to 8 mg/L during recession of the floods before storms in May. During storms in May, silica concentrations decreased about 5 mg/L. Except for three data points, the decrease in silica concentrations in 1979 is hyperbolic with discharge (fig. 21). Many 1976 and 1977 data points plot outside the hyperbolic trend. These are silica concentrations in water collected from May to the second week in July and probably reflect uptake of silica by diatoms at ice-out (Wetzel, 1975).

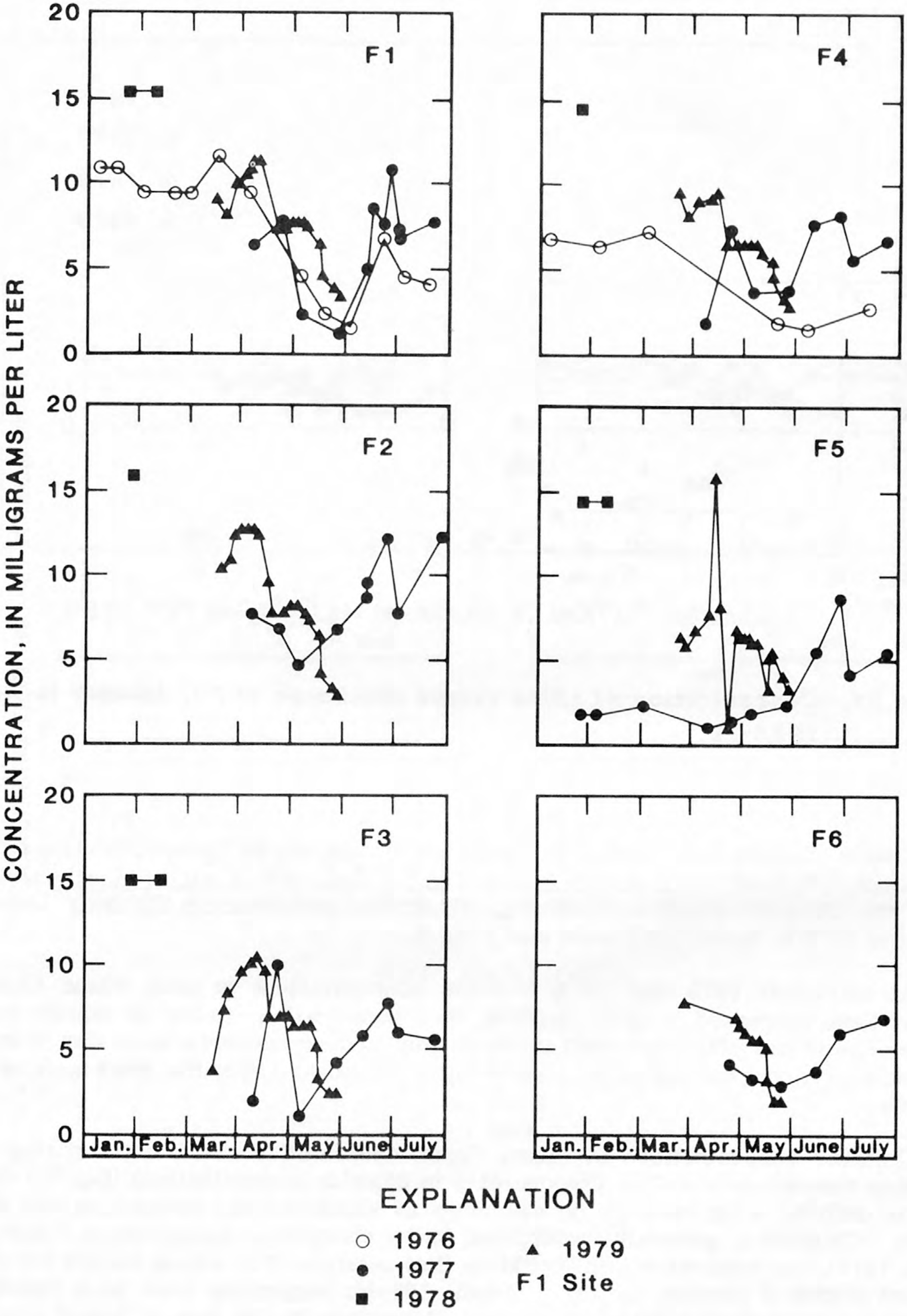


Figure 20.--Concentrations of silica in Filson Creek and Omaday Lake, January to August 1976-79

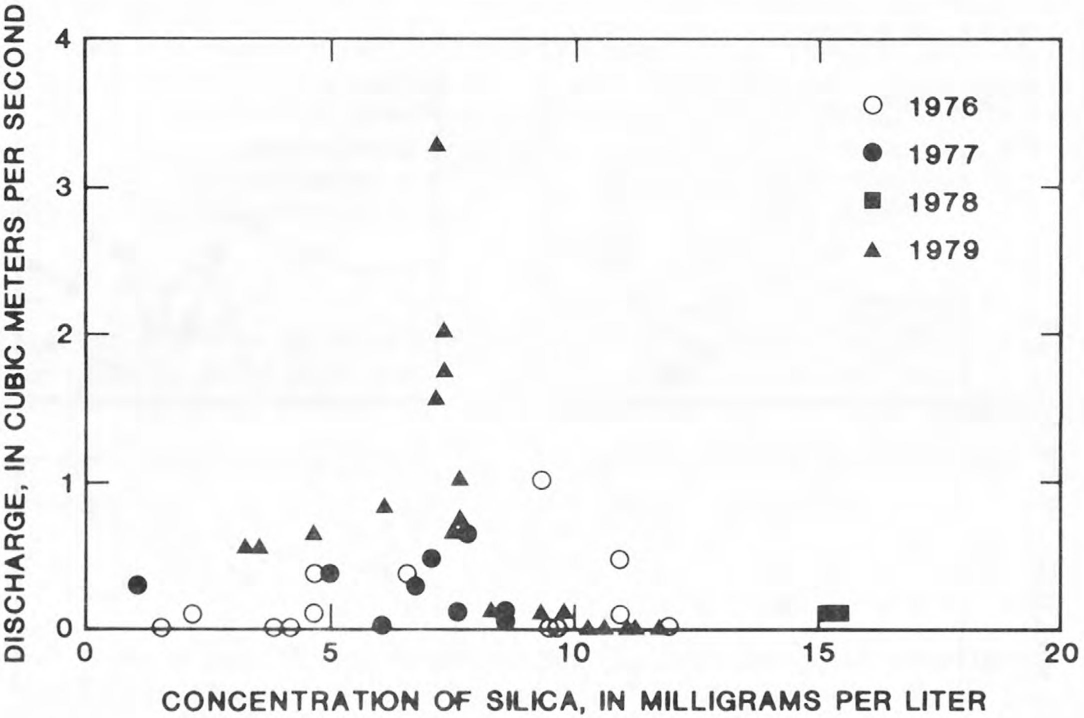


Figure 21.--Concentration of silica versus discharge at F1, January to August 1976-79

Chloride

Concentrations of chloride decreased 50 percent during snowmelt. Chloride concentrations in Filson Creek ranged from 1.5 to 2.5 mg/L during winter months and at low flow from June to October 1976 (fig. 22). Concentrations in Omaday Lake from December 1976 to March 1977 were also 2 mg/L.

At snowmelt 1976 and 1979, chloride concentrations in both Filson Creek and Omaday Lake decreased 1 mg/L. In 1979, the concentration of chloride quickly returned to base-flow values after snowmelt in April, only to decrease again with May storms. As with alkalinity, concentrations of chloride also decreased during the short melting period in March.

Chloride concentrations in Filson Creek decreased about 1 mg/L during storms from May through July 1977. The decrease in chloride concentrations (fig. 23) does not show as definite a dependence on discharge as alkalinity and concentrations of total cations. Chloride is generally considered to be chemically conservative (Cleaves and others, 1970), and concentrations should be flow related. The annual budget for chloride balanced within 5 percent in 1977 (Siegel, 1981b), suggesting that on a yearly basis chloride is indeed chemically conservative. Consequently, the lack of better correlation between chloride concentrations and discharge is unexplained.

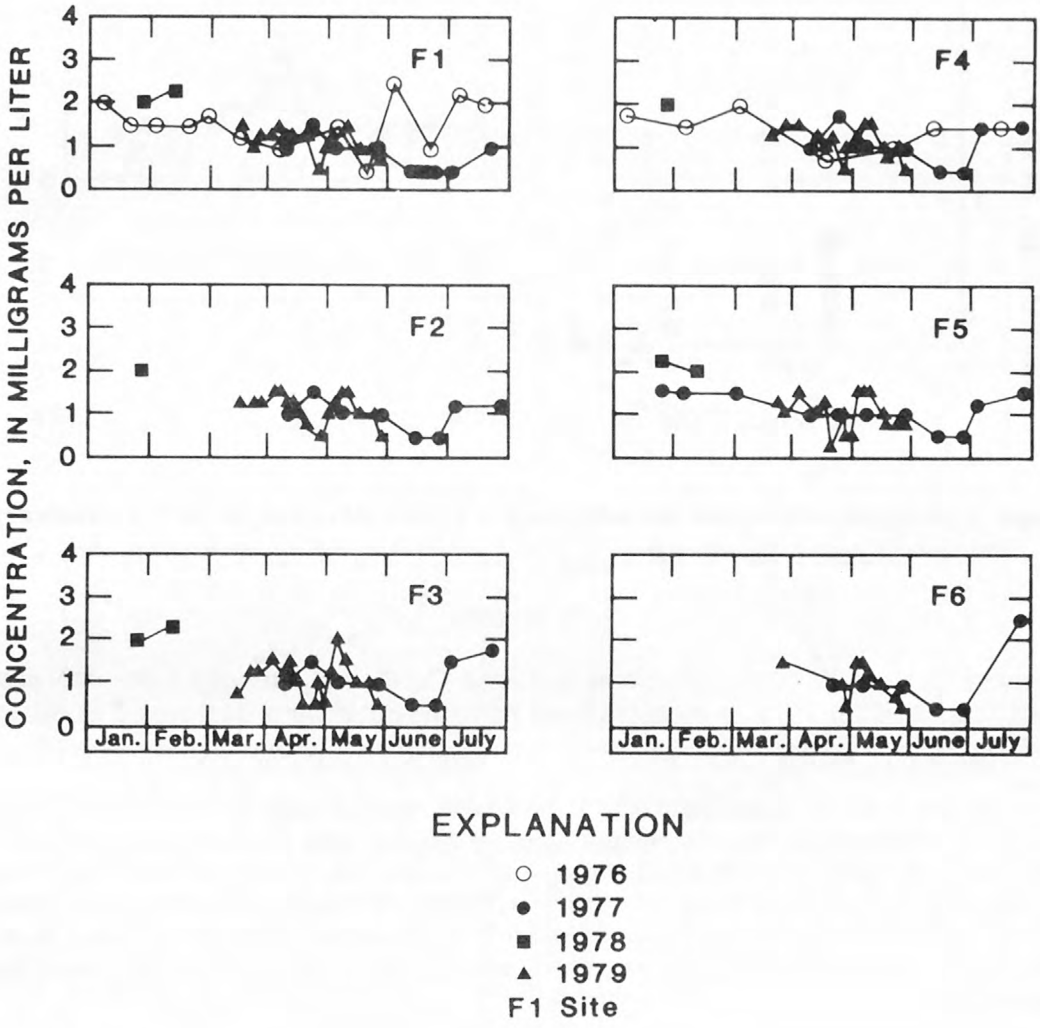


Figure 22.--Concentrations of chloride in Filson Creek and Omaday Lake, January to August 1976-79

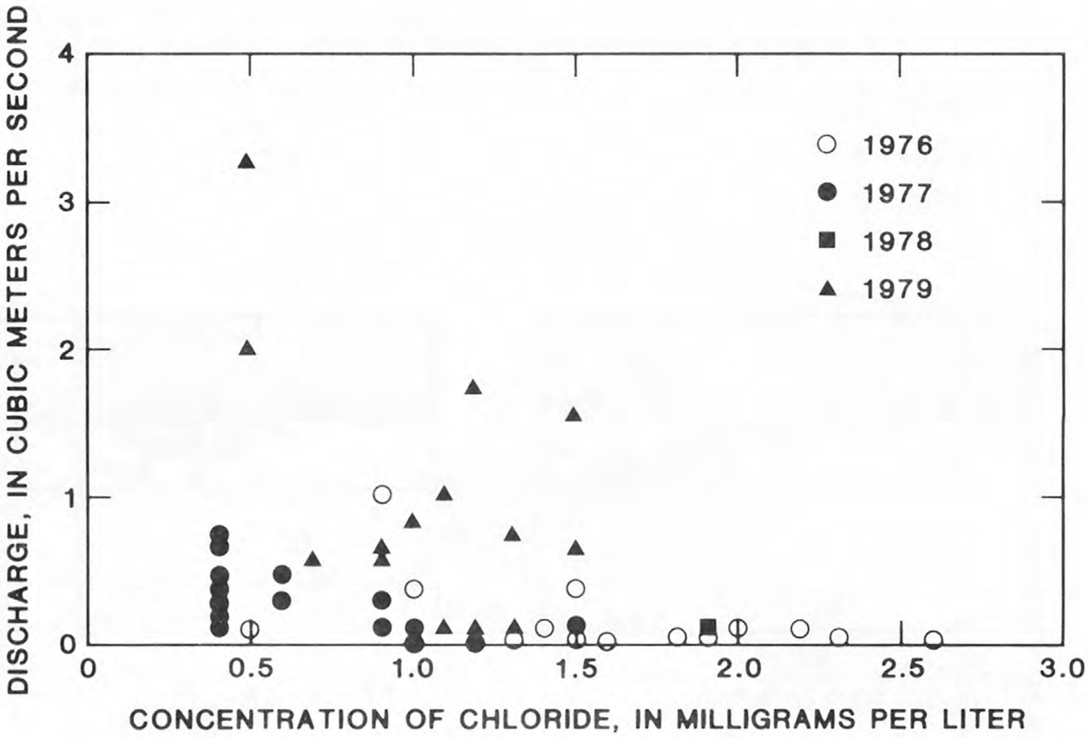


Figure 23.--Concentration of chloride versus discharge at F1, January to August 1976-79

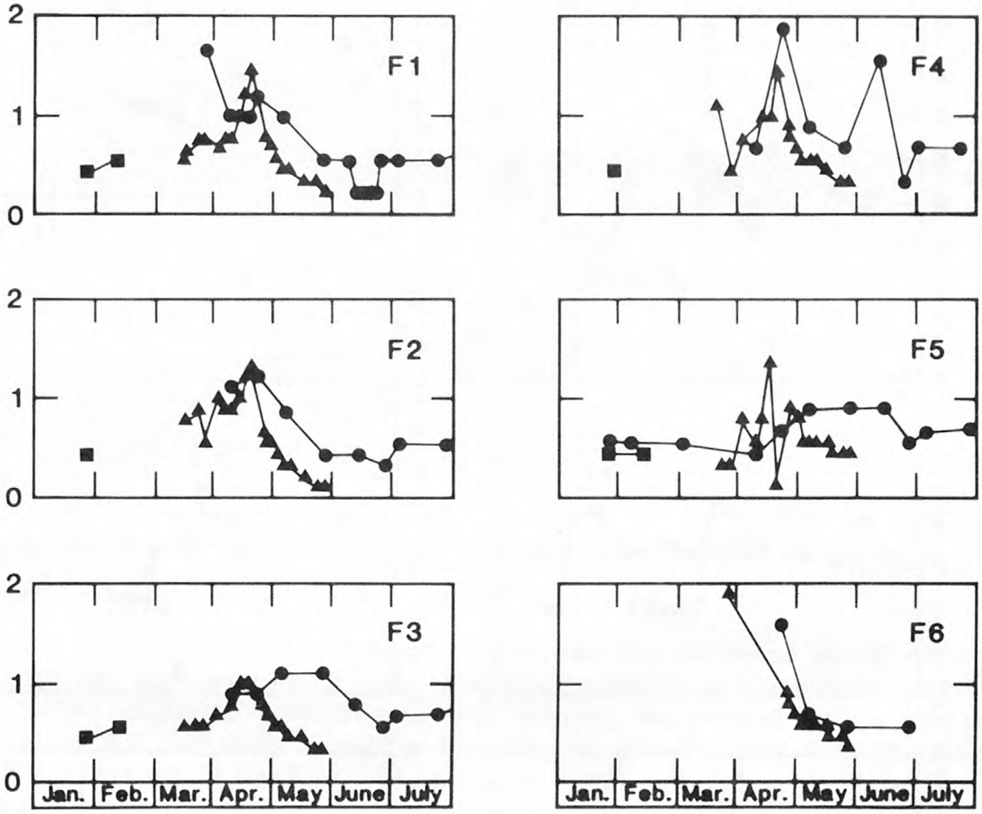
Potassium

Concentrations of total potassium in Filson Creek and Omaday Lake decreased with snowmelt (fig. 24). In 1979, concentrations of total potassium decreased at all locations from about 1.4 to 0.3 mg/L.

Concentrations of total potassium, however, varied unsystematically during snowmelt in 1977. Concentrations decreased at sites F1, F2, and F6, but increased at Omaday Lake (F5). Concentrations of total potassium at site F4, the mouth of the lake, varied widely, ranging from 0.3 to 2 mg/L. The variability of concentrations of potassium may reflect the unsystematic uptake of potassium, an essential nutrient (Likens and others, 1967), by biota immediately after snowmelt and during early spring when plant growth is at its maximum.

Calcium, magnesium, and sodium

Concentrations of dissolved calcium, magnesium, and sodium decrease with discharge at snowmelt. Concentrations of these cations in Filson Creek and Omaday Lake decreased during both the short snowmelt in March and the major snowmelt in April 1979. Concentrations of these constituents generally decrease hyperbolically with discharge. Figure 25 illustrates the trend for total calcium. Figure 26 illustrates the concentration variations in total calcium at all sample sites on the creek and the lake from January through July 1977-79.



EXPLANATION

● 1977

■ 1978

▲ 1979

F1 Site

Figure 24.--Concentrations of total potassium in Filson Creek and Omaday Lake, January to August 1977-79

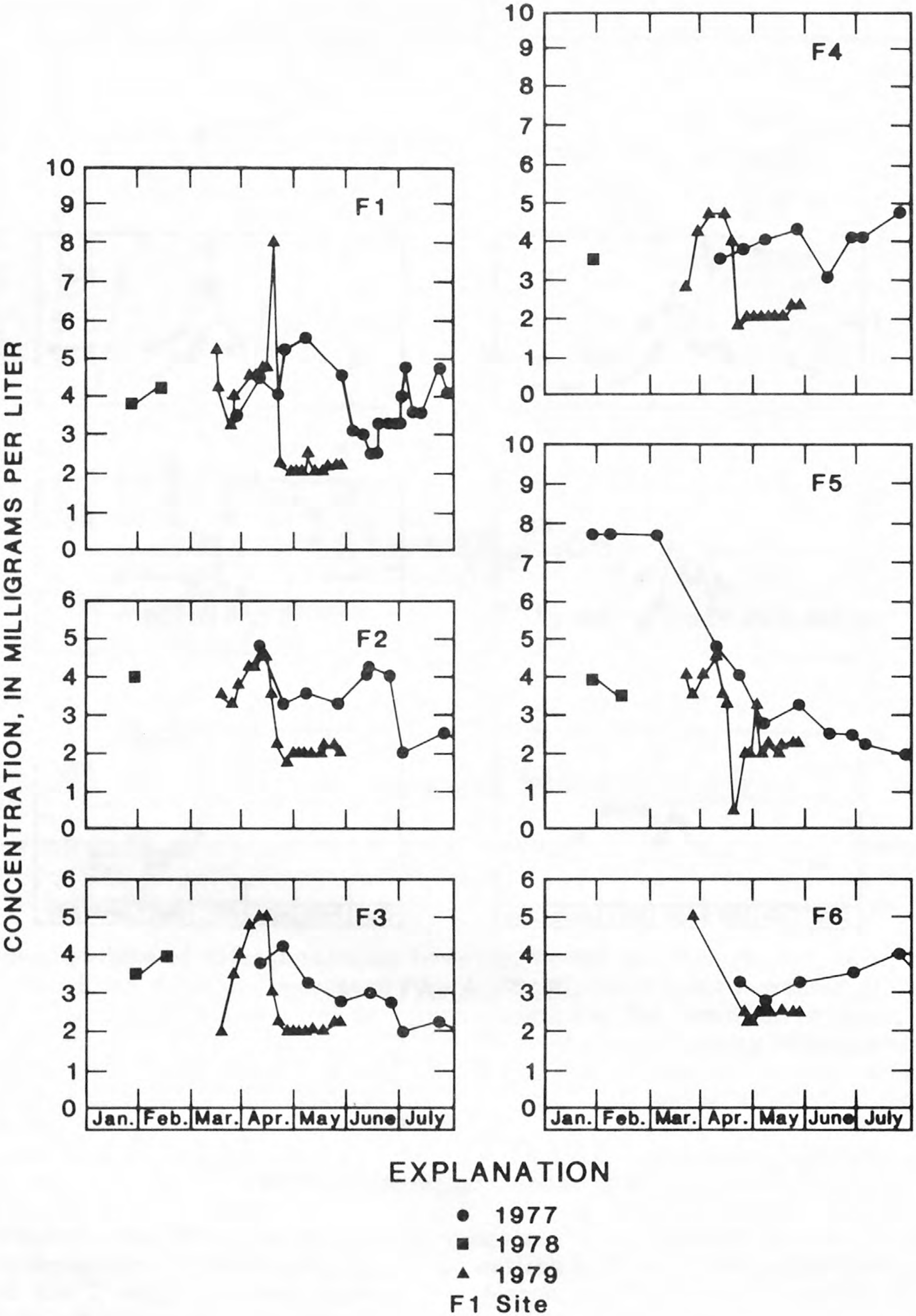


Figure 25.--Concentrations of total calcium in Filson Creek and Omaday Lake, January to August 1977-79

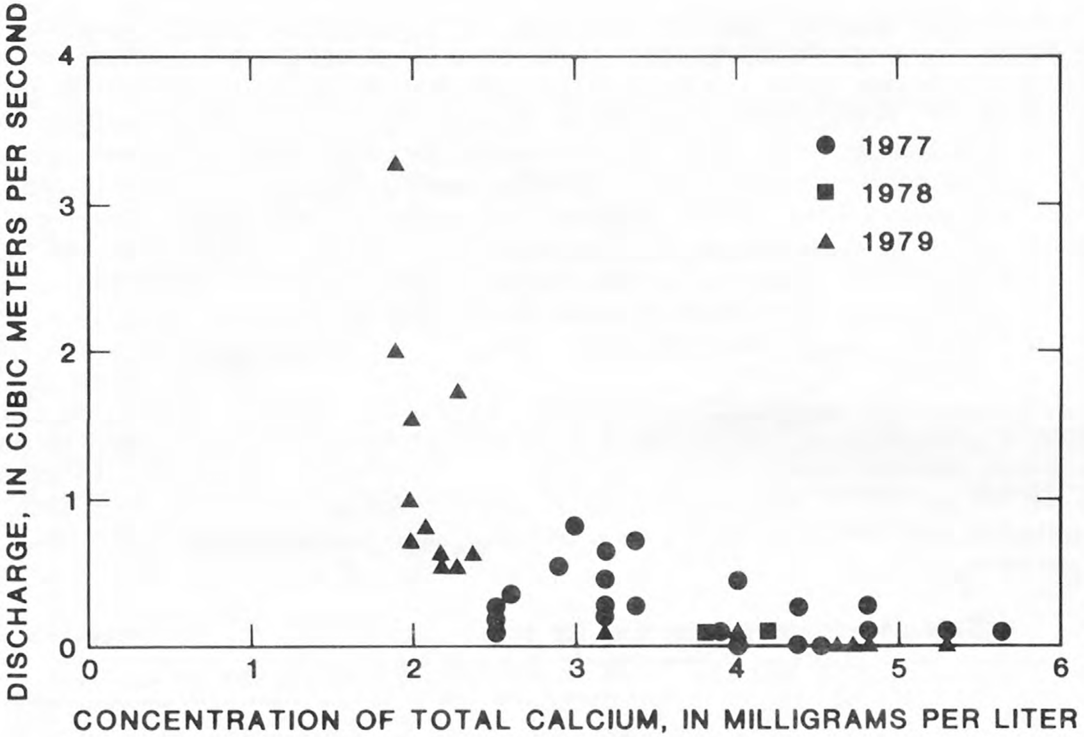


Figure 26.--Concentration of total calcium versus discharge at F1, January to August 1977-79

Concentrations during the drought in 1977 did not decrease during snowmelt as in 1979 because the snowmelt went into temporary storage in the soil and dry wetlands. However, total calcium, magnesium, and sodium concentrations in Omaday Lake decreased about 5.0, 3.0, and 1.7 mg/L, respectively, by early May. This probably reflects dilution of the lake water by snowmelt on the lake ice.

DILUTION MODEL FOR WATER-QUALITY CHANGES AT SNOWMELT

If decreases in concentrations of nonreactive components at snowmelt and during storms are mainly the result of dilution of base flow by precipitation, the dilution and mixing process at any time can be modeled by the mass balance equation (Johnson and others, 1969):

$$C_i = AC_b + Cp$$

where:

C_i = observed concentration of constituent i, in milligrams per liter,
A = $1/(1 + BQ)$, unitless,
C_b = the average concentration of constituent i at base flow minus the average concentration of constituent i in precipitation, in milligrams per liter,
Cp = the average concentration of constituent i in precipitation, in milligrams per liter,
B = a constant, which is equal to the ratio between the residence time for water moving through the watershed and the minimum volume of the water in the system at base flow, in liters per hectare per day, and
Q = discharge, in liters per hectare per day.

The model assumes that (1) the volume of water in the creek approaches a minimum value, *Vo*, when discharge approaches zero, (2) at any time the volume of water in the creek in excess of *Vo* is directly proportional to streamflow, and (3) there is a "characteristic" water quality at base flow. Linear-regression analysis between discharge and the discharge term "A" will determine which snowmelt-concentration variations can be described by a simple dilution model. Regression-curve intercepts will approximate precipitation water quality. As discharge gets larger, the term A gets smaller, and the base-flow water-quality term C_b becomes negligible. In the statistical analysis, the optimum values for B were determined by trial and error to achieve the best linear fit of the data. The value of the correlation coefficient and the slope of the line of regression (C_b) were rejected if F-tests for significance were not at the 0.01 level.

Results of the analysis (fig. 27) suggest that the hyperbolic distribution of concentrations of total calcium, sodium, and alkalinity (as bicarbonate) can roughly be described by a simple dilution model (table 4). The best correlations occurred with values of B from $10^{-4.0}$ to $10^{-5.0}$, about the same as independently determined from total annual precipitation and estimates of the average volume of surface water in the lakes, creek, and wetlands.

Table 4.—Model parameters for constituents affected by snowmelt dilution, Filson Creek, January to August 1976-79

	C_b	C_p	r[1]	log B
Total calcium	3.88	1.91	0.72	-4.3
Total magnesium	2.20	0.89	0.65	-4.3
Total alkalinity (as bicarbonate)	21	-0.69	0.71	-4.0
Total sodium	1.37	0.12	0.73	-4.7

[1] Regression coefficient.

The intercepts of the lines of regression for the discharge function against concentrations of total sodium and total calcium are about equal to the average concentrations of these constituents determined in precipitation collected in Filson Creek watershed in 1977 (Siegel, 1981a). The intercept of the regression line for alkalinity is below the origin because titrations to determine alkalinity in 1977 and 1978 gave results less than that used in either 1976 or 1979. Consequently, data for 1977 plot low on the diagram. If alkalinities in 1977 were only 10 percent greater, the regression line would intercept the ordinate of the diagram near the origin and fit the dilution model. There is no alkalinity in precipitation with pH less than 5.1, which is typical of precipitation on the Filson Creek watershed.

The large standard error of the estimate of the least squares regression line for total magnesium concentrations suggests that other mechanisms contribute to magnesium concentrations during snowmelt. The intercept of the regression line for total magnesium is greater than the average concentration of total magnesium in precipitation determined in 1977. This also suggests a geochemical or biological process in the watershed that contributes magnesium to the creek during snowmelt. Such a process or processes might include the release of magnesium from the dissolution of silicate minerals or the release of magnesium from decomposition of organic material during the winter.

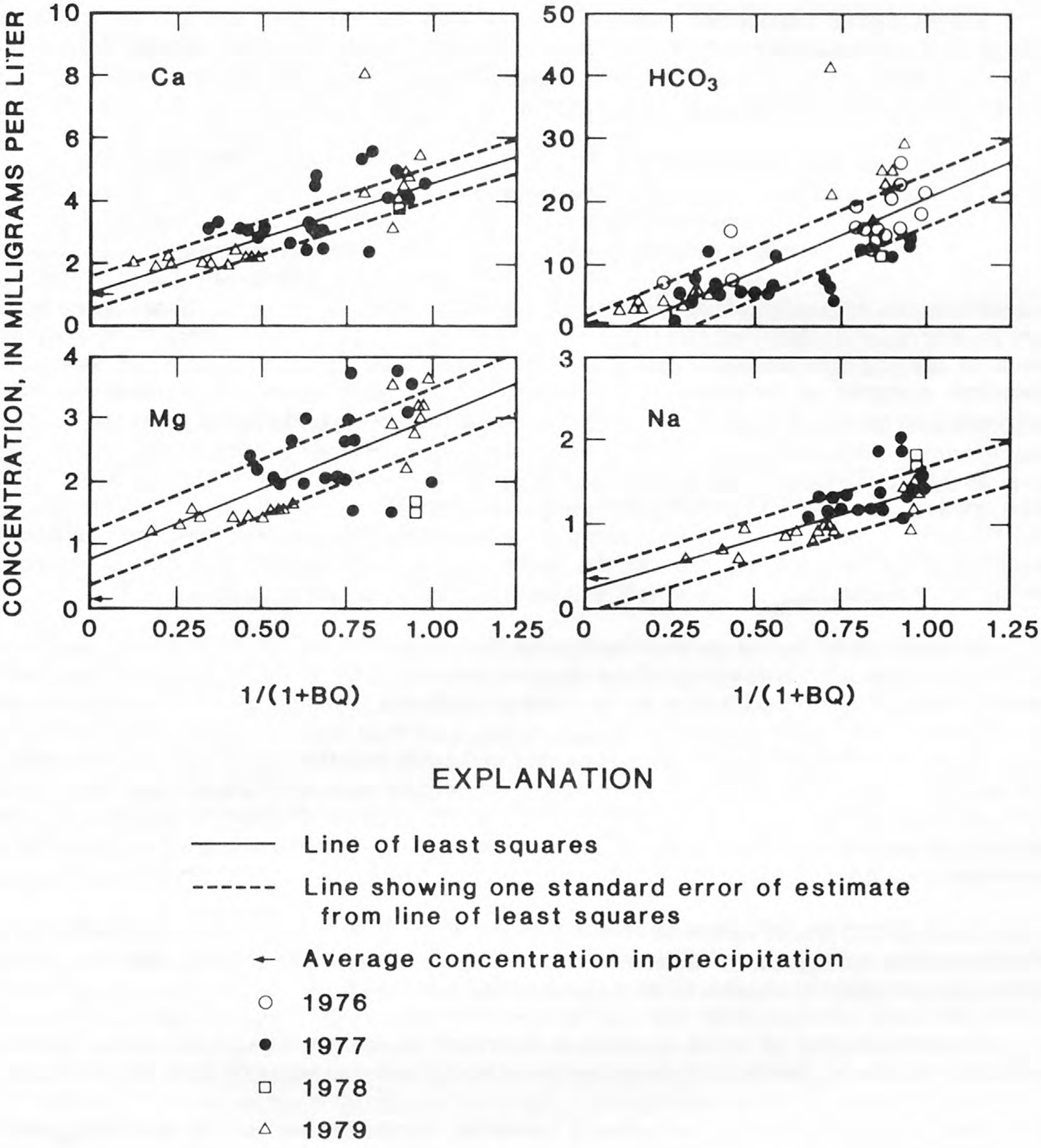


Figure 27.--Variations in concentrations of total calcium, magnesium, sodium, and bicarbonate as a function of streamflow at site F1, January to August 1976-79

SUMMARY

Filson Creek responded rapidly to snowmelt in 1976 and 1979 when streamflow increased from less than 0.15 m^3/s to as much as 2.5 and 5 m^3/s, respectively. During snowmelt 1977, streamflow did not increase because most of the snowmelt went into soil-moisture, lake, and ground-water storage.

Concentrations of sulfate and H^+ ion increased in Filson Creek and Omaday Lake during snowmelt. The magnitude of the increase depended on the timing of the snowmelt and antecedent soil-moisture conditions. Concentrations of sulfate increased from less than 2 to about 14 mg/L during snowmelt 1977 when, because of drought, all melt water was able to infiltrate into the soils and, hence, to the creek. In 1979, a wet year, concentrations of sulfate increased from about 2 to about 4 mg/L. Short warming periods in March, with rain before the major snowmelt at the end of April, probably leached much of the sulfate acidity from the snowpack. This melt water was not sampled for chemical analysis or measured as storm runoff because much of it probably left the watershed as overland runoff on the ice cover of the creek and frozen ground.

In 1977, H^+-ion activity increased from $10^{-6.5}$ to $10^{-5.0}$ during snowmelt, whereas pH increased from $10^{-6.5}$ to $10^{-6.0}$ during snowmelt 1979. The range of increased sulfate and H^+-ion concentrations at snowmelt 1977 and 1979 probably brackets the effects that leaching of sulfate acidity has on the water quality of Filson Creek and Omaday Lake during snowmelt.

Ground water near a mineralized zone that contains sulfide minerals has as much as 450 mg/L sulfate. However, sulfate concentrations at base flow in Filson Creek do not increase near the mineralized zone because ground-water discharge to the creek is small.

Changes of alkalinity (as bicarbonate) and total calcium, magnesium, and sodium in the creek during snowmelt roughly reflect the simple mixing of base-flow water quality with more dilute precipitation water. The mixing process defined by hyperbolic-shaped curves of concentration versus discharge can be modeled by use of a mass-balance equation.

Concentrations of silica decreased in the creek during snowmelt, probably because of the uptake of silica by diatoms in Omaday Lake and the creek, but the decrease cannot be adequately explained by a simple dilution model.

Concentrations of total potassium decrease at snowmelt in 1979, but, because of probable uptake by plants during spring growth, did not show simple flow dependence.

No clear dependence was found between discharge and chloride concentrations, although chloride concentrations generally decreased in the creek and lake during snowmelt in 1976 and 1979.

PRELIMINARY EVALUATION OF METHODS FOR DETERMINATION OF SULFATE CONCENTRATIONS IN PRECIPITATION AND OTHER DILUTE SOLUTIONS

By D. I. Siegel, L. E. Anderson, and J. A. Rogalla

Introduction

Sulfate concentrations in precipitation and base flow in Filson Creek are often less than 5 mg/L, near the detection limit of commonly used analytical methods. It is important to evaluate the accuracy and precision of these methods, especially when used to evaluate the effects of acid precipitation on dilute poorly buffered surface waters that contain colored humic material, such as lakes and streams in northern Minnesota.

The purpose of this section of the report is to document the results of a preliminary quality-assurance study on the accuracy and precision of three methods commonly used to determine sulfate. In addition, an evaluation is made of the relative amount of error in the calculations of sulfate mass discharged by Filson Creek during snowmelt 1979, when sulfate was determined by different methods.

Description of Methods for Determining Sulfate Concentrations

Six laboratories participated in the study. Four were operated by Federal agencies and one by a State agency. The sixth set were analyses done by the authors, at the Limnological Research Center Laboratory, University of Minnesota. Each laboratory was informed that the samples were part of a quality-assurance study to detect sulfate at low concentrations. Two laboratories used a manual turbidimetric method to determine sulfate, two laboratories used an automated complexometric methylthymol blue (MTB) method, one laboratory used both the turbidimetric and automated MTB methods, and one laboratory used the ion chromatograph (IC) method employing a Dionex AutoIon System 12 Analyzer. A brief summary of the techniques is given in table 5.

The accurate determination of sulfate in water at concentrations less than 10 mg/L is difficult. The turbidimetric method has a detection limit of 1 mg/L (American Public Health Association, 1975), but the limit for accurate determinations (c.v. = ±5 percent) may be as high as 10 mg/L (Appel and others, 1979). The MTB method has a detection limit of 5 mg/L (Skougstad and others, 1979), but may be as low as 2 mg/L, depending on modifications to the standard method (Peden and others, 1979). The IC method used here has a reported detection limit of about 0.1 mg/L (Wetzel and McNeil, 1979). However, a detection limit of 0.001 mg/L may be obtained from a 3- x 50-mm anion-concentrator column (Fulmer and others, 1979). This method gave better results than the MTB method in a quality-assurance study for the determination of sulfate in precipitation (Fishman and Pyen, 1979).

Even though the determination of sulfate by the turbidimetric and MTB methods is difficult at low concentrations, many sulfate concentrations less than 5 mg/L have been reported in the literature without any estimates of the probable error of the analyses. Similarly, calculations of sulfate mass budgets in watershed studies contain errors caused by analytical techniques as well as statistical errors associated with sampling.

Table 5.—Methods used to determine concentration of sulfate

Method	Summary of method	Reference
Turbidimetric method	Sulfate ion is precipitated in an acid solution with barium chloride to form barium sulfate crystals of uniform size. The absorbance of the barium sulfate suspension is manually measured by a spectrophotometer and the sulfate ion concentration is determined by comparison of the reading with a standard curve. For this study, Beckman Model 24 (laboratory A), Beckman Model ACTA-4 (laboratory E), and Zeiss PM2DL spectrophotometer (laboratory D) were used.	American Public Health Association (1975)
Complexometric methylthymol blue method (MTB)	The sample stream is automatically passed through a cation-exchange column before addition of an acid solution containing barium chloride and methylthymol blue (MTB). Sulfate ion is precipitated as barium sulfate. When the mixture is made basic, the remaining barium ions form a complex with MTB, and the absorbance of the uncomplexed MTB is directly proportional to the amount of sulfate originally present.	Skougstad and others (1979)
Dionex ion chromatographic method (IC)	Sample is centrifuged, spiked with sodium bicarbonate, and then passed through a strong base anion resin. Separated sulfate in the sample is then passed through a strong acid suppressor resin that converts the sulfate to sulfuric acid, the concentration of which is determined by specific conductance.	Wetzel and McNeil (1979)

The quality-assurance program was designed to evaluate these errors. As a part of the program, each laboratory received four samples of raw creek water, two samples of creek water with a 5 mg/L sulfate addition, two samples of creek water with a 1 mg/L sulfate addition, two standards of de-ionized water with a 5 mg/L sulfate addition, four samples of precipitation, and two samples of precipitation with a 0.5 mg/L sulfate addition. Laboratory D received two sets and analyzed both by the turbidimetric technique. Samples of creek water were not filtered and were chilled at about 4°C from the time of sampling to mailing. Laboratory B filtered the Filson Creek water samples before analysis, and laboratory F centrifuged samples. Bottles were randomly assigned to each set. Samples in each set were not analyzed in any predetermined sequence and were analyzed at different times.

This quality-assurance study was a preliminary evaluation of the precision and accuracy of determination of sulfate below or near the reported detection levels for the turbidimetric and MTB methods. The study tests whether or not these methods can be extended to get reasonable results at levels beyond their accepted determination limits, but does not test the accuracy or precision of these methods within the normal working ranges.

Comparison of Methods

The results show significant differences in concentration values determined by the methods (table 6). Average concentrations determined by the MTB method were 9.95 and 10.53 mg/L for raw Filson Creek samples, and 4.58 mg/L for filtered samples. This suggests that filtering partly removed a positive interference, probably the colored organic material and colloidal iron oxides.

The two laboratories that determined sulfate by the turbidimetric method (laboratories A and D) reported values less than reported detection limits, 2 and 0.5 mg/L, respectively, when color blanks were used in the analyses. The laboratory that did not use color blanks (laboratory E) reported an average concentration of 8.88 mg/L. Concentrations determined by the IC method averaged 2.13 mg/L in raw creek water.

The precision of the sulfate determinations by all methods in raw creek water was good (table 6), based on coefficients of variation of less than 5 percent. The coefficients of variation of the sulfate determinations in creek samples with additions (tables 7 and 8) were also near or less than 5 percent for laboratories B, C, E, and F. However, coefficients of variation for determination of sulfate spikes by the turbidimetric method ranged from 1.5 percent (laboratory E, 1 mg/L spike) to 108 percent (laboratory D, 1 mg/L spike).

The precision of determining sulfate concentrations in precipitation and in precipitation with 0.5 mg/L sulfate addition (tables 9 and 10) is poor except for the IC method. Coefficients of variation ranged from 9.6 percent for laboratory D (turbidimetric method) to 128 percent for laboratory B (MTB method). Coefficients of variation ranged from 0.0 to 9.0 percent for sulfate determined in precipitation by the IC method. Two laboratories that used the turbidimetric and one laboratory that used the MTB method reported sulfate concentrations in precipitation less than a detection limit.

The accuracy of the different methods was determined by taking the ratio of the difference between the mean sulfate determination of spiked and unspiked samples and the known value of the spike. If the determinations were completely accurate, the ratio would be unity. Accuracy was also evaluated by comparing the results of sulfate determination in a 5 mg/L standard prepared with de-ionized water.

The results (table 11) suggest that the IC method is the best method for determining sulfate at low concentrations in both Filson Creek and in precipitation. Fishman and Pyen (1979) obtained similar results for determinations of sulfate in precipitation. The concentration values determined for samples to which sulfate was added were nearly perfect by this method. The MTB and turbidimetric methods gave results that were consistently low for samples of the creek to which sulfate was added. Except for laboratory C these methods gave results that were too high for a 0.5 mg/L addition to precipitation. The IC method was both more accurate and more precise in the determination of the 5 mg/L sulfate standard (table 12).

Table 6.—Summary statistics on the concentration of sulfate in water collected in March 1979 from Filson Creek, Minnesota

Laboratory	A	B	C	D[1]		E[1]		F
Mean, in milligrams per liter	<2	4.58	9.95	<0.5	<0.5	10.50	8.88	2.13
Standard deviation ...	—	0.15	0.10	—	—	0.33	0.17	0.01
Coefficient of variation, in percent	—	3.7	1.0	—	—	3.1	1.9	0.5
Number of samples ...	4	4	4	4	4	4	4	4
Method	Turbidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC
Sample preparation ...	Unfiltered	Filtered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Centrifuged
Color blanks	Yes	No	No	Yes	Yes	No	No	No

[1] Replicate sample at this laboratory.

Table 7.—Summary statistics on the concentration of sulfate in Filson Creek water with a 5.0 mg/L addition of sulfate

Laboratory	A	B	C	D[1]		E[1]		F
Mean, in milligrams per liter	6.35	8.85	12.0	7.4	5.35	13.00	11.5	7.22
Standard deviation ...	0.49	0.07	0.0	1.13	2.05	0.0	0.70	0.0
Coefficient of variation, in percent	7.8	0.8	0.0	15.3	38.3	0.0	6.1	0.0
Number of samples ...	2	2	2	2	2	2	2	2
Method	Turbidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC
Sample preparation ...	Unfiltered	Filtered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Centrifuged
Color blanks	Yes	No	No	Yes	Yes	No	No	No

[1] Replicate sample at this laboratory.

Table 8.—Summary statistics on the concentration of sulfate in Filson Creek water with a 1 mg/L addition of sulfate

Laboratory	A	B	C	D[1]		E[1]		F
Mean, in milligrams per liter	<2	5.45	10.5	4.65	2.15	11.0	9.7	3.15
Standard deviation ...	—	0.07	0.71	5.02	1.48	0.0	0.014	0.03
Coefficient of variation, in percent	—	1.3	6.0	108	68.8	0.0	1.4	1.0
Number of samples ...	2	2	2	2	2	2	2	2
Method	Turbidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC
Sample preparation ...	Unfiltered	Filtered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Centrifuged
Color blanks	Yes	No	No	Yes	Yes	No	No	No

---

[1] Replicate sample at this laboratory.

Table 9.—Summary statistics on the concentration of sulfate in precipitation collected in March 1979 near Filson Creek, Minnesota

Laboratory	A	B	C	D[1]		E[1]		F
Mean, in milligrams per liter	<2	0.38	1.58	1.20	0.85	<2	<5	0.59
Standard deviation	—	0.48	0.39	0.12	0.30	—	—	0.05
Coefficient of variation, in percent	—	126	25.0	10.0	35.3	—	—	8.5
Number of samples	4	4	4	4	4	4	4	4
Method	Turbidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC
Sample preparation	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Centrifuged

---

[1] Replicate sample at this laboratory.

Table 10.—Summary statistics on the concentration of sulfate in preciptation with a 0.5 mg/L addition of sulfate

Laboratory	A	B	C	D[1]		E[1]		F
Mean, in milligrams per liter	<2	1.00	1.25	2.05	1.55	<2	<5	1.12
Standard deviation ...	—	0.14	0.35	1.34	0.25	—	—	0.00
Coefficient of variation, in percent	—	14.0	28.0	65.4	16.1	—	—	0.00
Number of samples ...	2	2	2	2	2	2	2	2
Method	Tubidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC
Sample preparation ...	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Centrifuged

[1] Replicate sample at this laboratory.

Table 11.—Ratio between the determined and true addition of sulfate to Filson Creek water and precipitation

Laboratory	A	B	C	D[1]		E[1]		F
Filson Creek water plus 5 mg/L addition...........	—	0.85	0.41	---	---	0.50	0.52	1.02
Filson Creek water plus 1.0 mg/L addition...........	—	0.87	0.55	---	---	0.50	0.90	1.02
Precipitation water plus 0.5 mg/L addition...........	—	1.24	-0.66	1.70	1.40	---	---	1.06
Method used.........	Turbidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC

[1] Replicate sample at this laboratory.

Table 12.—Summary statistics on the concentration of sulfate determined in de-ionized water with 5 mg/L sulfate

Laboratory	A	B	C	D[1]		E[1]		F
Mean, in milligrams per liter	4.85	4.55	5.00	5.20	5.65	3.25	5.70	5.09
Standard deviation	0.07	0.07	0.57	0.56	0.49	0.35	0.28	0.00
Coefficient of variation, in percent	1.4	1.5	11.4	10.8	8.7	10.8	4.9	0.00
Number of samples	2	2	2	2	2	2	2	2
Method	Turbidimetric	MTB	MTB	Turbidimetric	Turbidimetric	MTB	Turbidimetric	IC
Sample preparation	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Unfiltered	Centrifuged
Ratio of observed concentration to known concentration	0.97	0.91	1.00	1.04	1.13	0.65	1.14	1.02

[1] Replicate sample at this laboratory.

The better precision and accuracy shown by the IC results may, in part, reflect the personnel and other factors in the operation of laboratory F. In order to evaluate the importance of these factors, sulfate concentrations in dilute solutions would have to be determined by all three methods in a single laboratory.

The actual concentration of sulfate in raw Filson Creek water was determined to be less than 5 mg/L and probably close to 2 mg/L. This conclusion is based on the results of the turbidimetric analyses that ran color blanks and on results of the IC analyses. The color of the water probably interferred with the MTB and other turbidimetric analyses. Although it may not be practical to determine color blanks on a routine basis, it should be considered when low concentrations are expected.

Mass budgets for sulfate have been determined in many watershed studies (Cleaves and others, 1970; Likens and Bormann, 1974; Skartveit and Gjessing, 1979) but little emphasis has been given to the amount of error caused either by the analytical technique used to determine sulfate or by the sampling strategy. As part of this study, additional samples of Filson Creek water were collected near its mouth about every 3 days from March 16 to May 25, 1979, and analyzed for sulfate both by the turbidimetric (U.S. Forest Service laboratory, Winton, Minn.) and by IC methods (U.S. Environmental Protection Agency laboratory, Duluth, Minn.). These data, together with daily discharge data at the sampling site (U.S. Geological Survey, 1980), provide the means to determine whether differences in sulfate concentrations determined by different methods were significant with respect to mass-budget calculations.

Plots were prepared of streamflow and sulfate concentrations over time (fig. 28) and the mass transport of sulfate from Filson Creek watershed was calculated on a daily basis. Calculations were done by taking products of the daily discharge and concentrations of sulfate extrapolated from the data plots. Sulfate concentrations reported as less than 0.5 mg/L were assumed to be 0.5 mg/L.

Total sulfate loss from March 16 to May 25, 1979, was 7.05 and 6.44 kg/ha for calculations which, respectively, used the IC and turbidimetric data. The sulfate determined by the turbidimetric method was about 90 percent that determined by the IC method.

Plots of the concentration of sulfate over time are nearly identical, if the data determined by the turbidimetric method on March 18 and May 12 are considered anomalous (fig. 28). Concentrations of sulfate determined by the IC method are about 1.5 mg/L higher during base flow in March and early April than that determined by the turbidimetric method and from 0.2 to 1 mg/L less during and after snowmelt in mid-April.

The effect of these differences are small when the sulfate data are used to calculate sulfate mass transport for the period of study (fig. 29). Except from April 20-23 during early snowmelt, both the IC and turbidimetric methods determined sulfate concentrations that gave comparable results when used in mass-transport calculations. The difference in calculated mass transport from April 20-23 was 0.47 kg/ha, about 80 percent of the total difference between the methods for the period of study. Although the turbidimetric method determined that there were differences in the concentrations of sulfate from base flow to snowmelt, the magnitude of change determined was about two times less than what was probably present. This error was not significant in the mass-transport calculations because streamflow before snowmelt was several orders of magnitude less than at snowmelt.

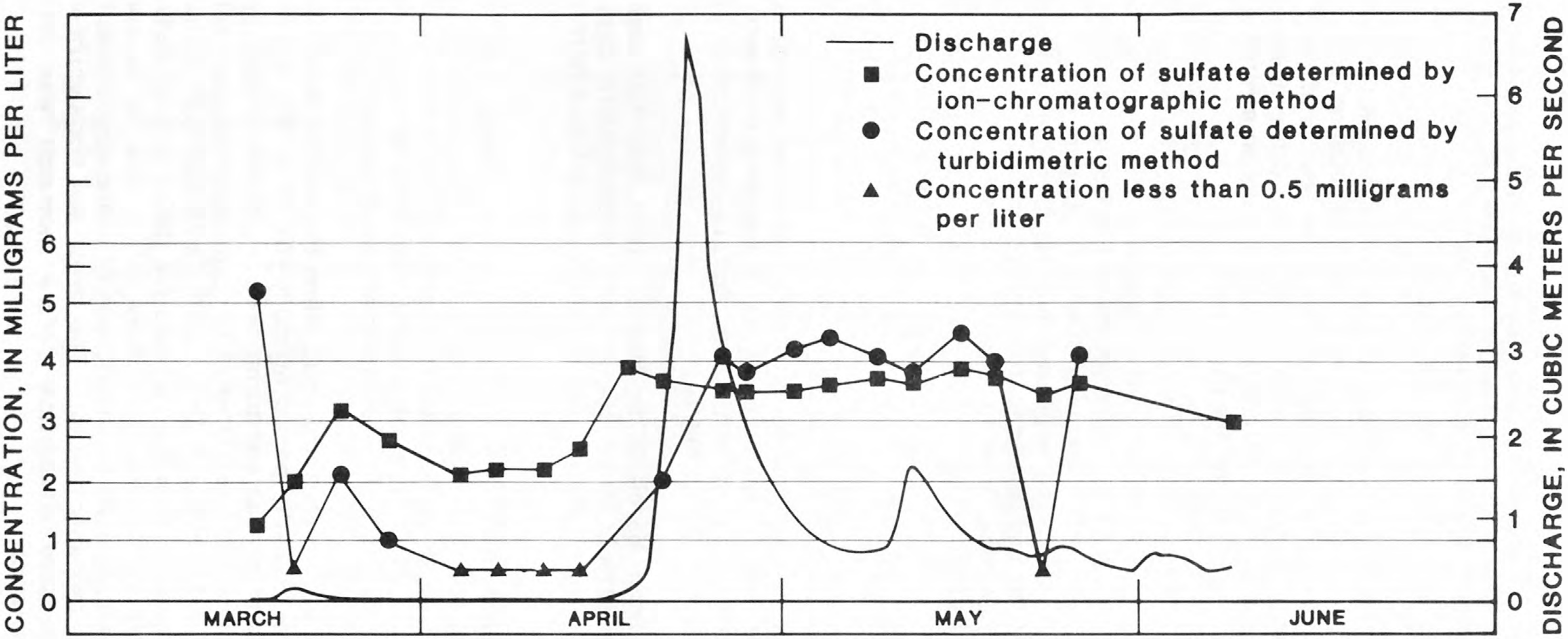


Figure 28.--Concentrations of sulfate in Filson Creek and discharge hydrograph of Filson Creek near its mouth, March 16 to June 8, 1979

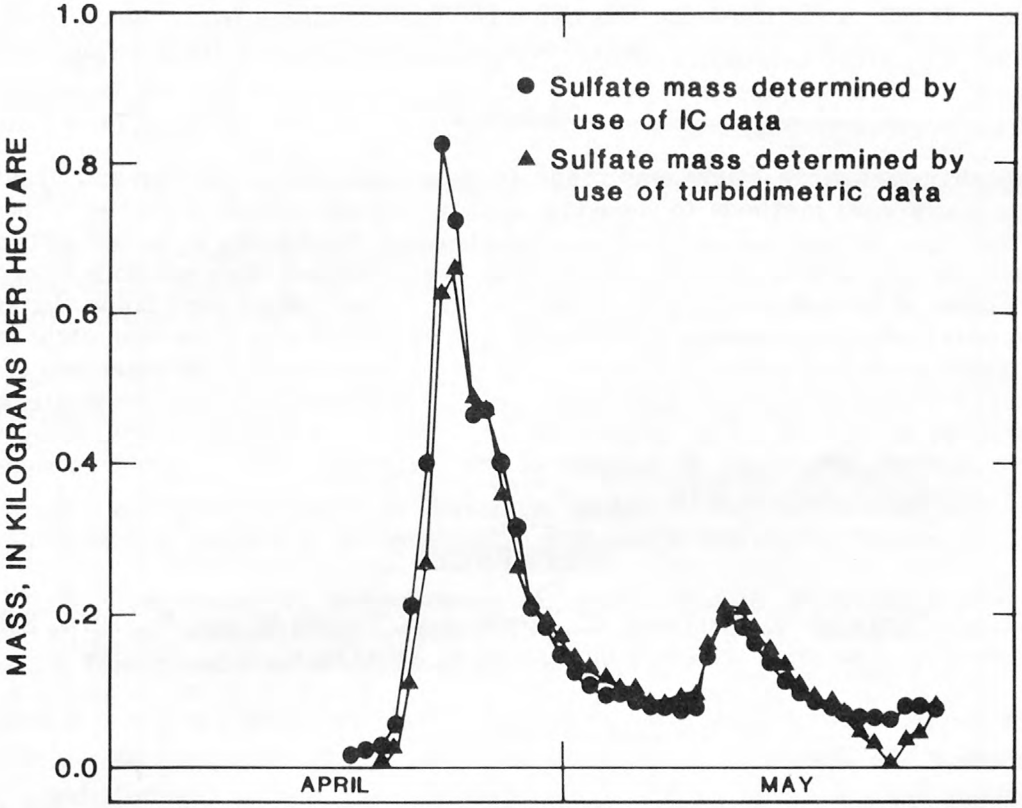


Figure 29.--Daily mass transport of sulfate by Filson Creek, April 12 to May 25, 1979

Greater error can occur in calculations of sulfate deposition when sulfate concentrations are determined by the turbidimetric method. In the quality-assurance program, about 0.5 mg/L of sulfate in precipitation (based on the IC results) either was not detected by the turbidimetric method or was overestimated by 1.4 to 2 times (table 9). Similarly, concentrations of sulfate determined in the precipitation samples spiked with 0.5 mg/L sulfate were overestimated by 1.4 to 1.7 times. In the mass-balance calculations used in this report, sulfate concentrations in precipitation in 1979 were determined by the IC method, whereas those in 1977 were determined by the turbidimetric method. Assuming the worst situation, sulfate deposition in 1977 could have been overestimated by 2 times. If this were the case, the net retention of sulfate from March to May 1977 would have been about 1.2 kg/ha, much closer to that determined for snowmelt 1979.

Summary

A quality-assurance study was made to determine the accuracy and precision of three commonly used methods to measure sulfate concentrations in water. The results suggest that the ion chromatographic method, used by laboratory F, is more precise and more accurate than either the turbidimetric or methylthymol blue methods to determine concentrations of sulfate at 5 mg/L or less. Results also suggest that color blanks should be run to obtain accurate results with the methylthymol blue and turbidimetric methods, and that the turbidimetric method is inaccurate and imprecise in the detection of sulfate concentrations below 2 mg/L. Calculated daily mass transport of sulfate in Filson Creek from March 16 to May 25, 1979, which used sulfate concentrations measured by the turbidimetric method, was about 90 percent of that calculated which used turbidimetric or ion chromatographic method data.

REFERENCES

Almer, B. W., Dickson, W., Ekstrom, C., Hornstrom, E, and Miller, V., 1974, Effects of acidification of Swedish Lakes: Ambio, v. 3, p. 330-336.

American Public Health Association, 1974, Standard methods for the examination of water and wastewater: Washington, D.C., 874 p.

____ 1975, Standard methods for the examination of water and wastewater: Washington, D.C., 877 p.

____ 1978, Standard methods for the examination of water and wastewater: Washington, D.C., 874 p.

Appel, B. R., and others, 1979, Improvement and evaluation of methods for sulfate analysis: U.S. Environmental Protection Agency 600/4-79-028, 197 p.

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

Beamish, R. J., 1961, Acidification of lakes in Canada by acid precipitation and the resulting effects on fishes: U.S. Department of Agriculture Forest Service Technical Report NE-23, p. 479-498.

____ 1976, Acidification of lakes in Canada by acid precipitation and resulting effects on fishes: Water, Air, and Soil Pollution, v. 6, p. 501-517.

Boelter, D. H., 1966, Hydrologic characteristics of organic soils in lakes states watersheds: Journal of Soil and Water Conservation 21, p. 50-53.

Braekke, F. H., ed., 1976, Impact of acid precipitation on forest and freshwater ecosystems in Norway: SNSF-projects, NISK, Aas-NLH, Norway, 111 p.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1974, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 160 p.

Cleaves, Emery T., Godfrey, A. E., and Bricker, O. P., 1970, Geochemical balance of a small watershed and its geomorphic implications: Geological Society of America Bulletin, v. 81, p. 3015-3031.

Cooper, Roger, 1978, Unpublished Ph. D. dissertation: University of Minnesota, 280 p.

Eisenreich, S. J., Hollod, G. J., and Langevin, S., 1978, Precipitation chemistry and atmospheric deposition of trace elements in northeastern Minnesota: Report to the Minnesota Environmental Quality Council, 149 p.

Fishman, M. J., and Pyen, G., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations 79-101, 30 p.

Fulmer, M. A., Penkrot, J., and Nadalin, R. J., 1979, Sodium, potassium, chloride, and sulfate analysis at PPB levels in water, in Mulik, J. D., and Sawick, E., eds., Ion chromatographic analysis of environmental pollutants: Ann Arbor Science, v. 2, 435 p.

Gjessing, E. T., Henriksen, A., Johannessen, M., and Wright, R. F., 1976, Impact of acid precipitation on freshwater chemistry, in Braekke, F. H., ed., Impact of acid precipitation on forest and freshwater ecosystems in Norway: SNSF project 1432 As. Res. Rep. FR 6/76, p. 65-68.

Glass, G. E., 1980, Susceptibility of aquatic and terrestial resources of Minnesota, Wisconsin, and Michigan to impacts from acid precipitation: Informational requirements, Proceedings of Continental Ecological Impact of Acid Precipitation, Sandefjord, Norway, March 1980.

Glass, G. E., and Loucks, O. L., eds., 1980, Impacts of air pollutants in wilderness areas of northern Minnesota: U.S. Environmental Protection Agency Report, EPA-600/3-80-044, 187 p.

Green, J. C., 1970, Lower Precambrian rocks of the Gabbro Lake quadrangle, northeastern Minnesota: Minnesota Geological Survey Special Publication, SP-13, 96 p.

Green, J. C., Phinney, W. C., and Weiblen, P. W., 1966, Geologic map of the Gabbro Lake quadrangle, Lake County, Minnesota: Minnesota Geological Survey Miscellaneous Map M-2.

Gorham, Eville, 1976, Acid precipitation and its influence upon aquatic ecosystems—an overview: U.S. Department of Agriculture Forest Service Technical Report NE-23, p. 425-548.

Haapala, H., Sepponen, P., and Meskus, E., 1975, Effect of spring floods on water acidity in the Kiiminkijoki area, Finland: Oikos 26, p. 25-31.

Hem, J. D., 1975, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 1473, 363 p.

Hendrey, G. R., and Wright, R. F., 1976, Acid precipitation in Norway: Effects on aquatic fauna: Proceedings, First Specialty Symposium on the Atmospheric Contribution to the Chemistry of Lake Water, International Association, Great Lakes Research, Orellia, Ontario, in Journal of Great Lakes Research, v. 2, p. 192-207.

Henriksen, A., and Wright, R. F., 1977, Effects of acid precipitation on a small acid lake in southern Norway: Nordic Hydrology 8, p. 1-10.

Johannessen, M. and Henriksen, A., 1978, Chemistry of snow meltwater: changes in concentration during melting: Water Resources Research 14, p. 615-619.

Johannessen, M., Dale, T., Gjessing, E. T., Henrikson, A., and Wright, R. F., 1975, Acid precipitayion in Norway: The regional distribution of contaminants in snow and the chemical concentration processes during snowmelt: Proceedings of Isotopes and Impurities in Snow and Ice Symposium, Grenoble, in International Association Scientific Hydrology Publication 118, p. 116-129.

Johnson, D. W., and Cole, D. W., 1977, Sulfate mobility in an outwash soil in western Washington: Water, Air, and Soil Pollution, v. 7, p. 489-495.

Johnson, D. W., Cole, D. W., and Gessel, S. P., 1979, Acid precipitation and soil sulfate adsorption properties in a tropical and in a temperate forest soil: Biotropica, v. 11, p. 38-42.

Johnson, N. M., Likene, G. E., Bormann, E. H., and Fisher, D. W., 1969, A working model for the variation in stream-water chemistry at the Hubbard Brook Experimental Forest, New Hampshire: Water Resources Research, v. 5, p. 1355-1363.

Likens, G. E., and Bormann, F. H., 1974, Acid rain: A serious regional environmental problem: Science, v. 184, p. 1176-1179.

Likens, G. E., Bormann, F. H., Johnson, N. M., and Pierce, R. S., 1967, The calcium, magnesium, potassium, and sodium budgets for a small forested ecosystem: Ecology, v. 78, p. 772-785.

Malcolm, R. L., and Durum, W. H., 1976, Organic carbon and nitrogen concentrations and annual organic carbon load of six selected rivers of the United States: U.S. Geological Survey Water-Supply Paper 1817-F, 21 p.

Marschner, F. J., 1974, The original vegetation of Minnesota, North-central forest experiment station: U.S. Department of Agriculture Forest Service, St. Paul, Minn., one sheet, 1:500,000.

Matthai, H. F, 1979, Hydrologic and human aspects of the 1976-77 drought: U.S. Geological Survey Professional Paper 1130, 84 p.

National Oceanographic and Atmospheric Administration, 1978, Climatological data for Minnesota, 1977: v. 27, no. 3, p. 1.

Olcott, P. G., and Siegel D. I., 1978, Physiography and surficial geology of the Copper-Nickel Study Region, northeastern Minnesota: U.S. Geological Survey Water-Resources Investigations 78-51, 22 p.

Ong, H. L., Swanson, V. E., and Bisque, R. E., 1970, Natural organic acids as agents of chemical weathering: U.S. Geological Survey Professional Paper 700-C, p. C130-C137.

Peden, M. E., Lorretta, M., and McGork, F. M., 1979, Precipitation sample handling, analysis, and storage procedures: Illinois State Water Survey, Research Report 4, COO-1199-57, p. 63-66.

Prettyman, D. H., 1976, Soil survey of the Kawishiwi area, Minnesota: U.S. Department of Agriculture Forest Service, 1 sheet, 1:62,000.

SAS User's Guide, 1979: SAS Institute Inc., Raleigh, N.C., 494 p.

Sather, Nancy, 1977, Unpublished map of forest types in the Copper-Nickel Study Region: Regional Copper-Nickel Study Group, Minnesota Environmental Quality Board.

Schofield, C. L., 1976a, Lake acidification in the Adirondack Mountains of New York, causes and consequences: U.S. Department of Agriculture Forest Service Technical Report NE-23, p. 499-500.

____ 1976b, Acid precipitation, effects on fish: Ambio, v. 5, p. 228-250.

Siegel, D. I., 1979, Sulfate contribution from snowmelt to Filson Creek watershed, northeastern Minnesota: EOS Transaction, American Geophysical Union, v. 60, no. 18, p. 259.

____ 1981a, The effect of snowmelt on the water quality of Filson Creek and Omaday Lake, northeastern Minnesota: Water Resources Research, v. 17, p. 238-242.

____ 1981b, Hydrogeochemistry and kinetics of silicate weathering in a gabbroic watershed: Filson Creek, northeastern Minnesota: Ph. D. Thesis, University of Minnesota, 275 p.

Siegel D. I., and Ericson, D. W., 1980, Hydrology and water quality of the Copper-Nickel Study Region, northeastern Minnesota: U.S. Geological Survey Water-Resources Investigations 80-739, 87 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Dunson, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Skartveit, Arvid, and Gjessing, T., 1979, Chemical budgets and chemical quality of snow and runoff during spring snowmelt: Nordic Hydrolgic, p. 141-154.

Stark, J. R., 1977, Surfical geology and ground-water geology of the Babbitt-Kawishiwi area, northeastern Minnesota: M.S. Thesis, University of Wisconsin, 101 p.

Stumm, W., and Morgan, J. J., 1970, Aquatic Chemistry: New York, Wiley-Interscience, 583 p.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and waste: Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA-600/4-79-020.

U.S. Geological Survey, 1977, Water Resources data for Minnesota, water year 1976: U.S. Geological Survey Water-Data Report MN 76-1, 896 p.

___ 1978, Water Resources Data for Minnesota, water year 1977: U.S. Geological Survey Water-Data Report MN 77-1, 276 p.

___ 1979, Water Resources data for Minnesota, water year 1978: U.S. Geological Survey Water-Data Report MN 78-1, 300 p.

___ 1980, Water Resources data for Minnesota, water year 1979: U.S. Geological Survey Water-Data Reoort MN 79-1, 267 p.

Wetzel, R. G., 1975, Limnology: W. B. Saunders Company, Philadelphia, Pa., 743 p.

Wetzel, R. A., and McNeil, L., 1979, Dionex ion chromatograph systems: Dionex Corporation, Sunnyvale, Calif., 171 p.

WATER-QUALITY DATA

FILSON CREEK AREA PRECIPITATION DATA

Date collected	Sample No.	SO_4 (mg/L)	Replicates			
3- 9-77*	SN	1.8	—	—	—	—
5- 8-77*	P1	5.8	—	—	—	—
5-27-77*	P1	3.2	—	—	—	—
6-11-77*	P2	2	—	—	—	—
	P3	0.9	—	—	—	—
6-25-77*	P2	1.4	—	—	—	—
	P3	1.0	—	—	—	—
4-20-79**	G_1	4.12	4.24	—	—	4.3
	G_1	4.24	4.33	—	—	—
	1	4.54	4.46	—	—	—
	2	4.31	4.37	4.33	—	—
5-11-79**	G_1	3.10	2.94	3.09	—	3.6
	G_2	4.10	4.17	4.12	4.10	—
	1	3.71	—	—	—	—
	2	3.21	3.13	—	—	—
6- 7-79**	G_1	4.39	4.37	—	—	—
	1	6.19	6.07	—	—	—
	2	4.70	—	—	—	—

* In 1977, samples P1 to P3 were collected in 1-liter bottles about one-half foot above ground level. Sample SN was a composite sample of 12 1-foot cores.

** In 1979, samples G_1 and G_2 were collected about 1 foot off the ground; Nos. 1 and 2 were about 5 feet from the ground. Sample collectors were 5-gallon open polyethylene buckets.

FILSON CREEK AREA SNOW SAMPLES — SPRING 1979

Sample No.	Date collected	Cover type	Remarks	NO_3 (mg/L)	SO_4 (mg/L)	pH
C201	3-13-79	Open	—	2.7	1.4	4.3
C202	3-13-79	do.	—	2.6	1.2	4.2
C203	3-13-79	Hardwood	—	2.4	1.2	4.4
C204	3-13-79	do.	—	2.3	1.2	4.3
C205	3-13-79	do.	—	1.9	1.0	4.5
C206	3-13-79	do.	—	1.8	1.0	4.5
C207	3-13-79	Pine	—	2.5	1.3	4.4
C208	3-13-79	do.	—	2.0	1.1	4.4
C501	3-19-79	do.	—	1.3	0.6	5.2
C502	3-19-79	do.	—	1.3	0.6	4.7
C503	3-19-79	Hardwood	—	1.3	0.6	4.6
C504	3-19-79	do.	—	1.5	0.7	4.7
C505	3-19-79	do.	—	1.0	0.5	4.8
C506	3-19-79	do.	—	1.4	0.6	4.6
C601	3-20-79	Open	C602 to C606 were combined for bulk snow sample in $SO_4^=$ QA.	1.1	0.4	4.7
C607	3-20-79	do.	—	1.6	0.8	4.5
C701	3-24-79	do.	Surface profile 1*	1.8	0.6	4.6
C702	3-24-79	do.	do. 2*	2.3	0.8	4.6
C703	3-24-79	do.	do. 3*	2.3	0.8	4.7
C704	3-24-79	do.	Bottom profile 4*	1.3	0.7	4.9

* Snowpack divided into four consecutive layers from surface to ground.

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER

(G = U.S. Geological Survey; H = Minnesota Department of Health; S = D. I. Siegel; E = U.S. Environmental Protection Agency; D = dissolved; T = total. All concentrations are in milligrams per liter, except pH, which is in pH units)

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE F1															
760106	G	7.1	15.0	.	2.0	0.66	.	3.8	.	2.9	.	1.40	.	0.5	11.0
760119	G	5.3	15.0	.	1.4	.	.	4.0	.	3.6	.	1.20	.	0.5	11.0
760203	G	5.3	22.0	.	1.6	0.66	.	4.1	.	3.3	.	1.60	.	0.6	9.5
760218	G	6.3	21.0	.	1.5	0.40	.	4.6	.	3.1	.	1.40	.	0.7	9.6
760302	G	6.5	20.0	.	1.8	.	.	4.5	.	3.1	.	1.50	.	0.5	9.7
760317	G	7.3	25.0	.	1.3	.	.	4.7	.	3.2	.	1.60	.	0.6	12.0
760406	G	5.9	8.0	.	0.9	0.66	.	2.6	.	1.8	.	1.00	.	0.7	9.4
760505	G	5.8	8.0	.	1.5	0.09	.	2.4	.	2.0	.	0.90	.	0.3	4.7
760520	G	6.5	15.0	.	0.5	.	.	3.0	.	1.9	.	1.00	.	0.2	2.2
760602	G	6.5	14.0	.	2.6	0.18	.	3.0	.	2.2	.	1.10	.	0.3	1.5
760622	G	6.1	16.0	.	1.0	.	.	.	.	.	.	.	.	.	6.6
760707	G	6.1	19.0	.	2.2	0.22	.	4.0	.	1.9	.	0.01	.	0.2	4.7
760720	G	5.9	15.0	.	1.9	.	.	.	.	.	.	.	.	0.0	4.2
770328	H	.	13.4	.	.	1.06	3.4	.	2.40	.	1.0	.	1.70	.	.
770409	S	6.56	12.0	2.0	1.0	.	4.5	.	2.00	.	1.6	.	1.00	.	6.2
770421	H	.	12.2	.	.	2.70	3.9	.	3.12	.	1.3	.	0.98	.	.
770423	S	5.51	8.0	4.0	1.5	.	5.3	.	3.60	.	2.0	.	1.20	.	7.6
770507	S	5.00	4.4	13.0	0.9	.	5.6	.	3.80	2.6	1.8	1.80	1.00	1.0	2.2
770527	S	6.60	5.1	10.0	0.9	.	4.4	.	3.80	2.6	1.8	1.80	0.60	0.6	1.0
770602	H	.	1.2	.	.	0.31	3.0	.	2.40	.	.	.	.	.	.

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

SITE F1—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
770609	H	.	12.2	.	.	4.38	2.9	.	2.64	.	1.3	.	0.50	.	.
770611	S	5.75	6.0	6.0	0.4	.	2.6	2.0	2.10	1.3	1.2	1.20	0.20	0.2	5.0
770612	S	.	.	.	0.4	.	2.5	.	2.10	1.2	1.2	1.20	0.20	0.2	.
770613	S	.	.	.	0.4	.	2.5	.	1.60	1.2	1.2	1.20	0.20	0.2	.
770616	S	6.12	7.0	6.0	0.4	.	2.5	2.0	1.60	1.2	1.1	1.10	0.20	0.2	8.6
770616	H	.	12.2	.	.	0.35	3.2	.	2.64	.	.	.	.	.	.
770618	S	.	.	.	0.4	.	.	.	.	.	1.3	1.30	0.20	0.2	.
770619	S	.	.	.	0.4	.	.	.	.	.	1.1	1.10	0.20	0.2	.
770621	H	5.90	4.9	.	.	0.75	3.2	.	2.11	.	1.3	.	0.50	.	.
770623	S	6.00	8.0	2.0	0.4	.	3.2	1.5	2.00	1.3	1.2	1.10	0.20	0.2	7.8
770625	S	6.05	7.0	2.0	0.4	.	3.2	3.2	2.00	1.1	1.2	1.20	0.20	0.2	11.0
770628	H	.	6.1	.	.	0.22	3.2	.	2.64	.	.	.	.	.	.
770702	S	6.25	7.0	2.0	0.6	.	4.8	4.0	3.00	1.1	1.3	1.30	0.60	0.6	6.8
770703	S	6.21	5.0	2.0	0.6	.	4.0	2.2	3.00	1.2	1.3	1.30	0.60	0.6	7.1
770705	H	.	6.1	.	.	0.31	3.4	.	2.18	.	.	.	.	.	.
770712	H	.	6.1	.	.	0.22	3.4	.	2.06	.	.	.	.	.	.
770723	S	6.35	12.0	2.0	1.0	.	4.8	2.7	3.60	1.2	1.4	1.40	0.60	0.6	7.7
770726	H	6.30	11.0	.	.	0.22	4.0	.	2.88	.	.	.	.	.	.
780128	S	6.20	13.0	2.0	1.9	.	3.8	3.8	1.60	1.6	1.7	1.70	0.40	0.4	15.5
780211	S	6.22	11.0	2.0	2.2	.	4.2	4.2	1.70	1.7	1.8	1.80	0.50	0.5	15.3
790316	E	.	29.0	5.2	1.5	0.58	5.3	.	3.62	.	1.4	.	0.54	.	11.9
790319	E	.	20.7	0.5	1.2	1.11	4.2	.	2.84	.	1.1	.	0.71	.	9.3
790323	E	.	12.7	2.1	1.1	1.64	3.2	.	2.19	.	0.9	.	0.80	.	8.3
790327	E	.	17.1	1.0	1.3	1.02	4.0	.	2.80	.	1.2	.	0.75	.	9.8
790403	E	5.30	21.9	0.5	1.3	0.62	4.5	.	3.03	.	1.5	.	0.70	.	10.4

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

SITE F1—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
790406	E	6.60	22.3	0.5	1.5	0.61	4.6	.	3.19	.	1.3	.	0.76	.	10.7
790410	E	6.35	24.0	0.5	1.2	0.71	4.7	.	3.26	.	1.3	.	0.81	.	11.2
790413	E	.	24.0	0.5	1.3	1.06	4.8	.	3.24	.	1.3	.	0.95	.	11.3
790417	E	6.30	41.5	.	.	.	7.9	.	3.58	.	1.4	.	1.26	.	.
790420	E	.	4.3	2.0	1.2	0.58	2.3	.	1.56	.	0.6	.	1.44	.	7.4
790425	E	5.90	3.0	4.1	0.5	0.22	1.9	.	1.25	.	0.6	.	0.83	.	7.2
790427	E	.	3.4	3.7	0.5	0.22	1.9	.	1.31	.	0.7	.	0.76	.	7.4
790501	E	6.00	4.1	4.2	1.1	0.35	2.0	.	1.39	.	0.8	.	0.65	.	7.6
790504	E	6.12	3.7	4.4	1.3	0.66	2.0	.	1.45	.	0.8	.	0.57	.	7.6
790508	E	6.08	4.0	4.1	1.5	0.18	2.4	.	1.50	.	0.9	.	0.49	.	7.5
790511	E	5.92	3.7	3.8	1.5	0.40	2.0	.	1.45	.	0.9	.	0.44	.	7.2
790515	E	5.90	5.2	4.5	1.0	0.13	2.1	.	1.44	.	0.9	.	0.38	.	6.2
790518	E	6.18	5.2	4.0	0.9	0.09	2.2	.	1.54	.	1.0	.	0.35	.	4.6
790522	E	6.34	6.1	0.5	0.9	0.09	2.3	.	1.64	.	0.9	.	0.29	.	3.5
790525	E	6.28	5.5	4.2	0.7	0.13	2.2	.	1.55	.	1.0	.	0.25	.	3.2

SITE F2

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
770409	S	6.36	12.0	2.0	1.0	.	4.7	.	4.10	.	1.20	.	1.10	.	7.8
770423	S	6.44	16.0	2.0	1.6	.	3.3	.	3.10	.	2.50	.	1.20	.	6.8
770508	S	6.35	6.0	10.0	0.9	.	3.6	.	3.00	.	1.80	.	0.90	.	4.6
770527	S	6.20	5.0	1.8	0.9	.	3.2	.	3.10	.	1.70	.	0.40	.	7.0
770612	S	6.38	7.0	2.0	0.4	.	4.2	2.0	2.10	.	1.60	.	0.40	.	9.4

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

SITE F2—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
770613	S	6.60	8.0	2.0	0.4	.	4.1	2.0	.	1.2	1.60	1.10	0.40	0.400	8.6
770625	S	6.25	6.0	1.0	0.4	.	4.1	2.1	2.40	1.0	1.60	1.00	0.30	0.300	12.3
770702	S	6.40	9.0	2.0	1.2	.	2.0	2.0	1.80	1.4	1.20	1.10	0.50	0.500	7.5
770702	S	6.40	15.0	2.0	1.2	.	2.6	2.6	2.00	1.8	1.30	1.30	0.60	0.600	12.1
780128	S	6.10	12.0	2.0	1.9	.	3.9	3.9	1.70	1.7	1.50	1.50	0.40	0.400	16.0
790319	E	.	19.3	0.5	1.2	1.24	3.6	.	2.51	.	0.90	.	0.76	.	10.3
790323	E	.	16.9	0.5	1.2	1.33	3.2	.	2.42	.	1.00	.	0.91	.	11.0
790327	E	.	19.8	0.5	1.2	0.58	3.8	.	2.74	.	1.10	.	0.52	.	12.1
790403	E	5.30	24.4	0.5	1.4	.	4.2	.	3.01	.	1.20	.	1.00	.	12.7
790406	E	6.20	25.4	0.5	1.6	0.53	4.3	.	3.14	.	1.10	.	0.93	.	12.8
790410	E	6.40	25.8	0.5	1.2	0.49	4.4	.	3.11	.	1.20	.	0.91	.	12.8
790413	E	6.90	23.9	0.5	1.2	0.80	4.4	.	3.04	.	1.10	.	1.03	.	12.2
790417	E	6.25	13.8	2.5	1.1	1.77	3.6	.	2.54	.	0.90	.	1.27	.	9.4
790420	E	.	4.1	1.1	0.7	0.44	2.3	.	1.56	.	0.60	.	1.28	.	7.5
790425	E	5.95	3.4	4.1	0.5	0.13	1.8	.	1.25	.	0.60	.	0.69	.	7.6
790427	E	.	3.3	3.7	0.5	0.18	1.8	.	1.32	.	0.70	.	0.61	.	7.8
790501	E	6.10	3.9	3.4	1.1	0.27	1.9	.	1.40	.	0.80	.	0.51	.	8.1
790504	E	6.35	4.0	4.3	1.3	0.44	1.9	.	1.50	.	0.80	.	0.43	.	8.2
790508	E	6.20	4.1	4.1	1.4	0.18	1.9	.	1.49	.	0.90	.	0.38	.	7.8
790511	E	6.07	3.9	3.7	1.5	0.35	1.9	.	1.45	.	0.90	.	0.35	.	7.4
790515	E	5.65	5.0	4.2	1.0	0.09	2.0	.	1.46	.	0.90	.	0.25	.	6.4
790518	E	6.26	5.0	2.8	1.1	0.09	2.2	.	1.54	.	1.00	.	0.21	.	4.1
790522	E	6.40	6.0	0.5	0.9	0.09	2.2	.	1.62	.	0.90	.	0.15	.	3.0
790525	E	6.34	4.8	2.8	0.6	0.09	2.0	.	1.53	.	1.00	.	0.11	.	2.8

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
						SITE F3									
770409	S	6.32	9.0	2.0	1.0	.	3.8	.	3.00	.	2.5	.	0.90	.	1.8
770423	S	6.25	10.0	3.0	1.6	.	4.2	.	5.40	.	1.6	.	0.90	.	10.2
770508	S	6.22	8.0	2.0	0.9	.	3.2	.	2.20	.	1.5	.	1.10	.	0.8
770527	S	6.58	7.0	7.0	0.9	.	2.8	.	2.60	.	1.6	.	1.10	.	4.2
770611	S	5.60	4.0	4.0	0.5	.	2.9	2.1	2.00	1.0	1.2	1.3	0.80	0.8	5.8
770625	S	6.08	5.0	2.0	0.5	.	2.8	2.0	2.00	1.3	1.2	1.1	0.60	0.6	7.5
770702	S	6.20	5.0	2.0	1.6	.	2.1	2.1	1.50	1.1	1.2	1.1	0.70	0.7	5.7
770723	S	6.15	9.0	2.0	1.8	.	2.3	2.3	1.50	1.2	1.2	1.3	0.70	0.7	5.4
780128	S	6.20	12.0	2.0	1.9	.	3.6	3.4	1.60	1.5	1.6	1.6	0.40	0.4	15.0
780211	S	6.10	11.0	2.0	2.2	.	4.0	4.0	1.70	1.7	1.7	1.7	0.50	0.5	15.2
790319	E	.	5.2	2.1	0.8	.	2.0	.	1.31	.	0.6	.	0.50	.	3.5
790323	E	.	14.1	0.5	1.2	1.33	3.6	.	2.32	.	1.0	.	0.60	.	7.3
790327	E	.	16.7	0.5	1.2	0.97	4.1	.	2.70	.	1.2	.	0.55	.	8.0
790403	E	5.15	22.4	0.5	1.5	0.35	4.7	.	2.96	.	1.3	.	0.68	.	9.4
790410	E	6.30	24.0	0.5	1.3	0.44	5.0	.	3.18	.	1.3	.	0.78	.	10.2
790413	E	6.60	24.8	0.5	1.4	0.93	5.0	.	3.22	.	1.3	.	0.92	.	10.4
790417	E	6.30	17.1	2.0	1.1	1.15	2.9	.	2.06	.	0.8	.	1.05	.	9.4
790420	E	.	6.1	3.7	0.6	0.53	2.2	.	1.31	.	0.6	.	0.99	.	6.6
790425	E	5.85	3.2	3.9	0.6	0.22	2.0	.	1.25	.	0.7	.	0.82	.	6.6
790427	E	.	3.4	3.2	1.1	0.09	2.0	.	1.31	.	0.7	.	0.77	.	6.7
790501	E	5.92	3.4	3.8	0.5	0.18	2.0	.	1.32	.	0.7	.	0.67	.	6.8
790504	E	6.08	3.9	3.0	1.3	0.27	1.9	.	1.38	.	0.7	.	0.61	.	6.5
790508	E	6.10	4.6	4.3	1.9	0.09	2.0	.	1.39	.	0.8	.	0.52	.	6.3
790511	E	6.00	3.8	3.1	1.4	0.35	2.0	.	1.35	.	0.8	.	0.46	.	6.2
790515	E	5.95	4.5	3.8	1.0	0.09	2.0	.	1.36	.	0.8	.	0.43	.	5.2

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE F3—Continued															
790518	E	6.20	4.9	3.1	1.0	0.09	2.1	.	1.41	.	0.9	.	0.40	.	3.4
790522	E	6.31	5.9	0.5	0.9	0.09	2.2	.	1.49	.	0.8	.	0.35	.	2.3
790525	E	6.34	4.9	3.5	0.6	0.09	2.2	.	1.42	.	0.9	.	0.30	.	2.1
SITE F4															
760106	G	5.8	14.0	.	1.7	.	.	4.1	.	2.9	.	1.4	.	0.4	6.7
760204	G	5.4	16.0	.	1.4	0.40	.	3.6	.	2.8	.	1.6	.	0.5	6.5
760305	G	6.1	23.0	.	2.0	.	.	4.4	.	2.7	.	2.0	.	0.7	7.3
760415	G	5.7	8.0	.	0.7	.	.	2.2	.	1.6	.	0.6	.	0.5	6.4
760519	G	6.2	10.0	.	1.0	0.13	.	2.6	.	1.5	.	0.7	.	0.1	1.9
760610	G	5.0	14.0	.	1.5	.	.	.	.	.	.	.	.	.	1.4
760713	G	6.3	10.0	.	1.5	.	.	.	.	.	.	.	.	.	2.6
770409	S	6.12	9.0	2.0	1.0	.	3.6	.	2.70	.	1.6	.	0.70	.	1.8
770508	S	5.44	4.0	10.8	0.9	.	4.0	2.6	2.60	2.5	1.7	1.7	0.90	0.9	3.6
770527	S	6.05	5.0	9.0	0.9	.	4.3	2.1	2.20	2.1	1.7	1.6	0.70	0.7	3.8
770423	S	5.38	6.0	4.0	1.7	.	3.8	.	3.10	.	2.1	.	1.90	.	7.1
770611	S	5.75	3.0	5.0	0.5	.	2.9	1.7	2.00	1.2	1.3	1.2	1.50	1.5	7.8
770625	S	5.83	4.0	.	0.4	.	4.0	2.6	2.00	1.3	1.1	1.1	0.30	0.3	8.1
770702	S	6.00	6.0	2.0	1.6	.	4.0	1.8	3.00	1.1	1.2	1.0	0.70	0.6	5.3
770723	S	5.92	10.0	1.0	1.4	.	4.8	3.6	3.50	1.6	1.2	1.0	0.70	0.6	6.6
780128	S	5.90	9.0	2.0	1.9	.	3.6	3.4	1.50	1.4	1.7	1.8	0.40	0.4	14.7
790320	E	.	13.8	0.5	1.2	1.32	2.7	.	1.94	.	0.8	.	1.07	.	9.6

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE F4—Continued															
790327	E	5.60	16.7	0.5	1.4	0.71	4.3	.	2.78	.	1.2	.	0.44	.	8.1
790403	E	5.20	22.2	0.5	1.6	0.35	4.8	.	2.98	.	1.3	.	0.80	.	9.1
790413	E	6.25	21.1	0.5	1.3	0.66	4.7	.	2.86	.	1.2	.	0.95	.	9.2
790417	E	5.94	15.6	0.7	1.1	1.73	4.0	.	2.62	.	1.1	.	1.05	.	9.6
790420	E	.	1.1	1.1	1.3	0.22	1.8	.	1.21	.	0.5	.	1.43	.	6.5
790425	E	5.75	3.3	4.4	0.6	0.22	2.0	.	1.32	.	0.7	.	0.85	.	6.5
790427	E	5.74	3.3	3.0	1.1	0.09	2.0	.	1.34	.	0.6	.	0.79	.	6.5
790501	E	5.73	4.1	3.7	0.9	0.09	2.0	.	1.31	.	0.7	.	0.69	.	6.5
790504	E	5.95	4.9	3.9	1.3	0.18	2.0	.	1.42	.	0.8	.	0.61	.	6.4
790508	E	5.99	4.6	5.0	1.5	0.09	2.0	.	1.39	.	0.8	.	0.54	.	6.3
790511	E	5.93	3.7	2.8	1.5	0.22	2.0	.	1.34	.	0.8	.	0.50	.	5.9
790515	E	5.90	5.1	3.1	1.1	0.09	2.0	.	1.36	.	0.8	.	0.44	.	5.3
790518	E	5.95	4.9	3.0	0.8	0.09	2.1	.	1.42	.	0.9	.	0.42	.	4.4
790522	E	6.15	4.9	0.5	0.9	0.09	2.2	.	1.50	.	0.8	.	0.37	.	3.4
790525	E	6.20	4.9	2.4	0.6	0.09	2.2	.	1.41	.	0.9	.	0.34	.	2.7
SITE F5															
770127	S	6.32	19.0	0.5	1.6	.	7.8	.	5.80	.	3.4	.	0.50	.	1.8
770205	S	6.30	18.0	0.5	1.6	.	7.8	.	5.80	.	3.2	.	0.60	.	1.6
770304	S	6.35	17.0	2.0	1.6	.	7.8	.	5.80	.	3.1	.	0.50	.	2.2
770409	S	6.95	8.0	2.0	1.0	.	4.8	.	2.70	.	1.6	.	0.40	.	1.0
770423	S	6.65	8.0	2.0	1.1	.	4.0	.	3.10	.	2.5	.	0.70	.	1.2
770508	S	6.28	7.0	15.0	0.9	.	2.8	.	2.70	.	1.7	.	0.90	.	1.7

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE F5—Continued															
770527	S	6.65	7.0	9.0	0.9	.	3.2	.	2.40	.	1.1	.	0.90	.	2.4
770611	S	5.75	5.0	6.0	0.5	.	2.6	2.0	2.00	1.4	1.4	1.4	0.90	0.9	5.5
770625	S	6.24	6.0	3.0	0.5	.	2.6	2.0	2.00	1.2	1.2	1.2	0.60	0.6	8.6
770702	S	6.50	6.0	1.0	1.2	.	2.2	2.0	1.50	1.2	1.2	1.1	0.70	0.7	4.2
770725	S	6.42	7.0	2.0	1.6	.	2.1	1.9	1.70	1.3	1.2	1.1	0.70	0.7	5.4
780128	S	6.18	8.0	2.0	2.2	.	3.9	3.9	1.60	1.5	1.8	1.8	0.40	0.4	14.7
780211	S	5.93	10.0	2.0	1.9	.	3.6	3.3	1.60	1.6	1.7	1.6	0.40	0.4	14.6
790323	E	.	18.3	0.5	1.2	0.71	4.1	.	2.55	.	0.9	.	0.32	.	6.4
790327	E	5.50	13.8	0.5	1.1	0.84	3.6	.	2.31	.	1.1	.	0.32	.	6.0
790403	E	5.10	16.6	1.0	1.4	0.84	3.9	.	2.51	.	1.2	.	0.79	.	7.0
790410	E	6.20	20.0	1.4	1.1	0.71	4.4	.	2.75	.	1.2	.	0.56	.	7.6
790415	E	6.35	13.7	1.2	1.1	1.55	3.5	.	2.12	.	1.0	.	0.77	.	15.9
790417	E	6.30	7.9	3.0	1.3	1.02	3.2	.	2.02	.	0.9	.	1.37	.	8.1
790420	E	.	2.1	1.1	0.2	0.44	0.6	.	0.36	.	0.2	.	0.10	.	0.9
790425	E	5.80	3.9	4.4	0.5	0.22	2.0	.	1.34	.	0.7	.	0.88	.	6.5
790427	E	5.90	3.9	3.4	1.1	0.09	2.1	.	1.39	.	0.7	.	0.85	.	6.8
790501	E	5.67	3.9	3.6	0.5	0.18	1.9	.	1.28	.	0.7	.	0.74	.	6.5
790504	E	6.92	6.0	3.2	1.4	0.13	3.2	.	1.48	.	0.8	.	0.61	.	6.3
790508	E	6.10	6.1	3.7	1.4	0.09	2.1	.	1.44	.	0.8	.	0.57	.	6.1
790511	E	6.07	5.5	3.5	1.5	0.35	2.2	.	1.41	.	0.8	.	0.54	.	5.7
790515	E	6.00	4.9	4.2	1.0	0.18	2.2	.	1.41	.	0.8	.	0.50	.	5.6
790518	E	6.30	5.0	3.1	0.8	0.09	2.1	.	1.44	.	0.9	.	0.46	.	4.8
790518	E	6.27	5.0	3.1	0.8	0.09	2.1	.	1.44	.	0.9	.	0.46	.	3.1
790522	E	6.37	6.1	10.8	0.8	0.09	2.2	.	1.49	.	0.8	.	0.42	.	3.9
790525	E	6.35	6.8	3.8	0.8	0.13	2.3	.	1.49	.	1.2	.	0.40	.	3.1

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE F6															
770423	S	6.01	5.0	1.0	1.1	.	3.2	.	2.30	.	1.6	.	1.50	.	4.3
770508	S	6.00	9.0	4.0	0.9	.	2.8	.	1.60	.	1.4	.	0.70	.	3.4
770527	S	6.18	6.0	2.0	0.9	.	3.2	.	2.00	.	1.4	.	0.60	.	2.9
770611	S	6.08	5.0	2.0	0.5	.	.	1.7	.	1.7	.	1.2	.	0.7	3.6
770625	S	6.29	12.0	2.0	0.5	.	3.5	2.4	2.00	1.5	1.3	1.1	0.60	0.6	6.0
770722	S	6.03	9.0	2.0	2.4	.	4.0	2.0	3.30	1.5	1.1	1.1	3.10	2.9	7.0
790327	E	.	22.9	0.5	1.6	0.44	5.0	.	4.00	.	1.3	.	1.91	.	7.8
790425	E	.	6.0	3.8	0.6	0.18	2.6	.	1.68	.	0.7	.	0.86	.	6.8
790427	E	5.75	4.6	3.4	1.1	0.09	2.2	.	1.59	.	0.6	.	0.83	.	6.9
790501	E	5.85	6.0	3.0	0.5	0.13	2.2	.	1.56	.	0.8	.	0.65	.	6.3
790504	E	6.05	7.6	2.6	1.4	0.13	2.4	.	1.71	.	0.9	.	0.61	.	5.8
790508	E	6.13	8.4	3.3	1.6	0.09	2.4	.	1.75	.	0.9	.	0.56	.	5.6
790511	E	6.10	7.9	3.0	1.2	0.31	2.5	.	1.69	.	0.9	.	0.54	.	5.4
790515	E	6.10	7.7	4.0	1.0	0.09	2.5	.	1.66	.	0.9	.	0.51	.	5.0
790518	E	6.10	8.0	3.1	0.9	0.09	2.6	.	1.71	.	1.0	.	0.48	.	3.4
790518	E	6.30	8.0	3.1	0.9	0.09	2.6	.	1.71	.	1.0	.	0.48	.	3.1
790522	E	6.30	8.5	0.5	0.8	0.09	2.5	.	1.78	.	0.8	.	0.42	.	1.9
790525	E	6.47	7.0	2.8	0.6	0.09	2.5	.	1.62	.	0.9	.	0.35	.	1.8
SITE H1															
42676	G	5.9	98.0	.	.	.	.	74	.	63	.	16.0	.	5.9	17.0
81676	G	.	72.0	.	.	.	.	76	.	60	.	18.0	.	9.7	.
50479	E	7.2	184.1	287.0	.	.	.	.	.	.	.	.	.	.	.
50879	E	7.2	185.4	286.0	4.2	.	.	89	.	53	.	11.4	.	5.3	15.6

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE H1—Continued															
51179	E	7.4	186.6	18.9	4.3	.	.	89	.	52	.	11.3	.	5.3	15.5
51579	E	7.9	175.5	259.0	4.1	.	.	83	.	50	.	10.7	.	5.6	15.5
51879	E	.	.	.	3.1	.	.	.	.	.	.	.	.	.	14.6
52679	E	.	.	224.0	3.0	.	.	.	.	.	.	.	.	.	16.4
SITE H3															
22476	G	7.1	236.0	.	.	.	.	46.0	.	18.0	.	9.3	.	4.1	23.0
42676	G	6.7	220.0	.	.	.	.	34.0	.	17.0	.	8.1	.	2.5	24.0
81776	G	.	216.0	.	.	.	.	40.0	.	16.0	.	7.5	.	2.4	.
50479	E	7.4	192.7	13.5	.	.	.	.	.	.	.	.	.	.	.
50879	E	7.4	212.2	5.9	1.4	.	.	39.8	.	15.4	.	6.5	.	2.1	16.9
51179	E	7.5	211.0	2.8	1.4	.	.	37.1	.	15.1	.	6.7	.	2.0	17.2
51579	E	7.7	212.4	1.4	1.2	.	.	35.9	.	15.0	.	6.6	.	2.0	17.4
51879	E	7.3	206.1	0.5	1.1	.	.	35.5	.	14.9	.	6.5	.	2.0	17.3
52679	E	7.9	205.0	4.2	1.0	.	.	36.2	.	15.0	.	6.7	.	2.0	17.9
SITE WS															
50879	E	8.0	37.0	11.3	0.9	.	.	7.4	.	4.6	.	2.2	.	1.2	2.7
51179	E	7.6	43.3	11.7	0.7	.	.	8.0	.	4.6	.	2.1	.	1.1	5.6
51579	E	7.6	40.8	12.1	0.9	.	.	7.9	.	4.5	.	2.1	.	1.2	4.2
51879	E	7.3	42.3	10.8	0.9	.	.	7.3	.	4.2	.	2.1	.	1.1	7.1
52679	E	7.3	40.0	10.5	0.7	.	.	7.6	.	4.0	.	2.4	.	1.2	5.3

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
SITE W2															
40977	S	5.4	.	.	.	.	.	.	.	.	.	.	.	.	.
42377	S	6.2	11.0	72.0	1.1	.	.	20.0	.	11.4	.	2.8	.	0.3	24.4
61177	S	6.2	.	.	.	.	.	.	.	.	.	.	.	.	.
62577	S	5.8	33.0	30.0	0.8	.	.	14.0	.	6.4	.	4.3	.	1.7	16.0
50479	E	6.7	.	27.4	.	.	.	.	.	.	.	.	.	.	.
50879	E	.	.	25.9	0.9	.	.	.	.	.	.	.	.	.	13.1
51179	E	6.4	30.1	19.8	0.8	.	.	9.8	.	5.6	.	1.6	.	0.1	15.2
51579	E	7.1	27.0	18.9	1.2	.	.	9.5	.	5.4	.	1.6	.	0.1	15.5
51879	E	5.8	23.5	6.6	1.1	.	.	.	.	.	.	.	.	.	.
52679	E	6.4	27.1	19.5	0.9	.	.	9.5	.	5.4	.	1.7	.	0.1	15.5
SITE W3															
40977	S	5.9	.	.	.	.	.	.	.	.	.	.	.	.	.
42377	S	6.3	11.0	34.0	1.6	.	.	8.7	.	5.4	.	4.2	.	0.7	17.4
51277	S	6.1	20.0	44.0	0.9	.	.	8.2	.	4.3	.	10.0	.	0.7	10.0
61177	S	6.5	.	34.0	0.8	.	.	11.7	.	7.7	.	7.0	.	1.0	11.0
62577	S	6.3	44.0	23.0	0.8	.	.	9.3	.	6.6	.	10.0	.	0.8	15.0
72277	S	6.1	49.0	14.0	10.6	.	.	5.8	.	14.0	.	1.3	.	17.8	19.6
50479	E	7.3	158.5	17.8	.	.	.	.	.	.	.	.	.	.	.
50879	E	.	.	14.8	1.1	.	.	.	.	.	.	.	.	.	9.7
51179	E	7.3	92.0	14.6	1.0	.	.	8.8	.	7.1	.	2.3	.	0.4	9.2
51579	E	7.3	107.9	14.6	0.8	.	.	8.5	.	7.1	.	2.3	.	0.4	9.2
51879	E	7.3	128.0	12.4	0.8	.	.	6.9	.	6.5	.	2.2	.	0.5	9.9
52679	E	.	152.0	15.9	0.6	.	.	.	.	.	.	.	.	.	10.3

CHEMICAL ANALYSES OF SURFACE WATER AND GROUND WATER—Continued

Date	Source	Field pH	HCO_3	SO_4	Cl	NO_3+NO_2 as NO_3	TCa	DCa	TMg	DMg	TNa	DNa	TK	DK	Reactive silica
							SITE W4								
61277	S	5.7	12	6.4	0.2	.	.	7.4	.	3.1	.	1.7	.	2.9	23.0
62577	S	5.6	11	2.0	0.8	.	.	6.0	.	3.6	.	4.3	.	2.7	34.0
72277	S	5.7	16	3.4	5.0	.	.	7.5	.	3.1	.	5.6	.	2.1	30.0
50879	E	.	.	11.6	5.2	.	.	.	.	.	.	.	.	.	8.5
51179	E	.	.	14.8	3.8	.	.	.	.	.	.	.	.	.	8.5
51579	E	.	.	3.6	3.8	.	.	.	.	.	.	.	.	.	11.2
52679	E	.	.	.	2.9	.	.	.	.	.	.	.	.	.	11.8
51879	E	.	.	9.4	3.1	.	.	.	.	.	.	.	.	.	10.4
							SITE W5								
42377	S	5.6	25.0	11	0.9	.	.	7.5	.	4.8	.	6.4	.	0.7	15.2
51277	S	5.6	18.0	.	.	.	.	.	.	.	.	.	.	.	.
52777	S	6.1	.	.	.	.	.	8.3	.	4.9	.	3.1	.	10.4	.
61177	S	5.9	45.0	1	2.1	.	.	10.6	.	6.3	.	3.7	.	6.7	13.4
62577	S	5.4	40.0	6	0.8	.	.	10.7	.	.	.	3.4	.	0.7	20.2
72277	S	.	.	.	.	.	.	54.4	.	.	.	.	.	.	.
50479	E	6.5	6.1	8	0.6	.	.	.	.	.	.	.	.	.	.
52679	E	.	.	.	2.9	.	.	.	.	.	.	.	.	.	11.8

☆ U. S. GOVERNMENT PRINTING OFFICE 1982—565-782/187