

METAL RELEASE FROM ACID SNOWMELT

by

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A Thesis

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

College of Natural Resources

UNIVERSITY OF WISCONSIN

Stevens Point, Wisconsin

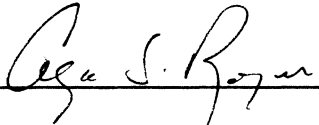
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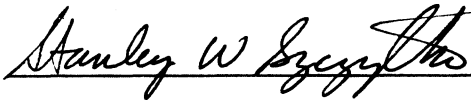
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## ABSTRACT

An investigation of seven Wisconsin lakes, five in the northern part of the state, (Bass, Buteau, Otter, Turtle, and Clara) and two in the central part, (Jacqueline, and University) was conducted for trace metal mobility in response to acid snowmelt. The five northern lakes are small oligotrophic, low alkaline, bog influenced lakes. This area was chosen due to it's combination of acid loading and geological sensitivity. The central Wisconsin site contains two lakes; a shallow soft water, lake, and a hard water, oligotrophic lake. This area has received more acidic precipitation than the northern lakes, but is more geologically resistant to inputs of acidic material.

Lake water samples were collected during ice cover, ice out (spring thaw), and late summer. Parameters measured included trace metals (Al, Cd, Cu, Fe, Ni, Zn), anions (SO<sub>4</sub>, NO<sub>2</sub>/NO<sub>3</sub>, Cl), alkalinity, hardness, and pH. Snow samples were also collected around each lake. In addition to the above mentioned parameters, acidity measurements were conducted on the snow samples. Sediment samples from each lake were analyzed for trace metal concentration.

Trace metals were analyzed using a Varian atomic absorption unit, using both the units flame and furnace modes depending on the sample. Anions (SO<sub>4</sub> and Cl) were analyzed on a Dionex ion chromatograph. NO<sub>2</sub>/NO<sub>3</sub> analyses were conducted using a Technicon Auto Analyzer II.

A laboratory sediment leachate study was also conducted using H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCL, H<sub>2</sub>CO<sub>3</sub>. In this study the pH of lake water in combination with sediments was decreased to 4.00 (equilibrium pH with H<sub>2</sub>CO<sub>3</sub> was 4.60). The trace metal concentration following this treatment was then measured and compared to values before acidification.

Trace metals increased following snow melt in all seven study lakes. There appears to be two major sources of these increases: the displacement of base metal ions from the soil/sediment by hydrogen ions contained within the percolating meltwater, and the snowpack itself. Whether the increases are the result of cation exchange or directly from trace metals contained within the snow, there is an increase of trace metals, approaching toxic levels, occurring during the spring thaw in these Wisconsin lakes. Considering the number of Wisconsin lakes with similar geology and acid loadings, the potential ecological damage is great.

Due to the similar nature of Jacqueline lake and the northern lakes, they responded similarly to inputs of acid snowmelt. Increases in alkalinity, hardness, pH, and trace metals appear to be caused by cation exchange reactions occurring between the meltwater which is high in hydrogen ion concentration and the soils and sediments of the watershed. As this meltwater percolates through the soil it displaces

cations and base metal ions carrying them into the lake, thus increasing the alkalinity, hardness, and pH. This may be indicative of a loss of this area's limited buffering capacity through leaching processes.

University lake was the only hard water lake included in this study and the only lake which showed a decrease in pH, alkalinity, and hardness values. This may be the result of meltwater entering the lake directly, due to the frost depth or nature of the surrounding soils, thus allowing the meltwater to express itself strongly within the water column. This would account for the decreases in pH, alkalinity, and hardness. In addition the relatively high concentration of alkalinity, and hardness found in University lake would require large amounts of base ions flushed into the system to show a significant increase.

Nitrate/nitrite concentrations decreased for all lakes following snowmelt, probably due to biological utilization as the meltwater percolated through the surrounding soil, along with early phytoplankton growth within the water column. Trace metal concentrations decreased later in the summer, likely due to adsorption and precipitation to the sediments.

## ACKNOWLEDGMENTS

Partial financial support for this study was provided by the Izaak Walton League and is much appreciated. I thank Mr. Joe Eliers, and the Wisconsin DNR for their assistance in site location and background information.

I am grateful to my advisor, Dr. Gerald Nienke, for his supervision and review of this thesis. I also thank the other members of my graduate committee, Dr. Aga S. Razvi and Dr. Stanley W. Szczytko, for their review of this thesis.

Many thanks are given to Dick Stephens and James Licari of the Environmental Task Force for their guidance and advice, along with full use of their facilities.

Finally, I would like to dedicate this thesis to a dear friend, Sarah Scharnoski, whose support, both technical and spiritual, made completion of this project possible.

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## INTRODUCTION

Acidic deposition is now a well-documented phenomenon that occurs over much of North America. Its main source is gaseous sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) emitted by industries and automobiles. These pollutants form sulfuric and nitric acids when reacting with water in the atmosphere. The main acid deposition impact region in the U.S. ranges from Minnesota to the eastern seaboard and from Florida to Maine. Air pollution produced in the industrialized Ohio River Valley is a significant source of the problem.

Wisconsin lies on the fringe of the acid deposition impact region. Both the amount of acid deposition and the rate at which it falls is lower in Wisconsin than in affected areas of New England. Additionally, the geology of Wisconsin provides some acid neutralizing capacity, but sensitive areas do exist in the northern half of the state. Based on 1980 precipitation data from the National Atmospheric Deposition Program (NADP), and others, northeastern Wisconsin is presently receiving acid precipitation with an average pH of 4.4, while northwestern Wisconsin precipitation has an average pH of 4.8. A decreasing gradient of rainfall acidity occurs in the state from east to west.

Environmental effects of acid precipitation depend on how much acid deposition an area receives (acid loading), and on how

sensitive the region is to acid loading (geological sensitivity). Wisconsin's situation regarding geologic susceptibility to acid deposition is unique. Only the northern half of the state is underlain by granite bedrock. However, the granite bedrock is overlain by as much as 100 meters of glacial till. This heterogeneous glacial till contains pockets of calcareous material (dolomite) which can provide some acid neutralizing capacity. Therefore, northern Wisconsin lakes located in this till show great variability in levels of alkalinity. Lakes located near dolomite deposits have relatively high alkalinities, while those not associated with such deposits generally have low alkalinities.

For approximately 4 1/2 months, most of northern Wisconsin is covered with a thick layer of snow. Which contains sulfuric ( $H_2SO_4$ ) and nitric ( $HNO_3$ ) acid which is released during the spring thaw. As the snow melts and enters the lakes and streams, acidity may increase tenfold. Metal ions may be released from lake sediments and surrounding soils during spring runoff due to depressed pH and increased solubility.

The concentration of metal ions in the aquatic environment is important due to the toxic nature of these ions to fish, benthos, and many other forms of aquatic life. These organisms are especially vulnerable during the spring of the year. Aluminum ions can suffocate emerging fry and fingerlings by

damaging their gills. Metal ions can cause decreased hatches for those amphibians that lay their eggs in the meltwater pools of early spring.

## LITERATURE REVIEW

## Effects of Acid Precipitation on Sensitive Waters

Lakes located in the United States northeast and northern midwest, and Sweden's west coast are similar since they receive acid precipitation and are generally low alkaline lakes. With bedrock geology consisting of low weathering minerals such as granites and gneisses, these lakes have a low ionic composition, especially low alkalinity, and are thus more sensitive to external influences. Their composition is highly dependent on atmospheric deposition. Precipitation in these regions can be distinctly acidic, with frequent pH values less than 4.0 (Glass 1980; Fisher 1968).

It is clear from data collected in the northeast that the hydrogen ion is one of the principal constituents of rain and snow in this area (Fisher 1968). When an acid precipitation occurs calcium, magnesium, and aluminum are lost from the watershed, while there is a net gain of hydrogen ions, nitrate, ammonium, sulfate, and sodium to the watershed. The net gain of hydrogen ions in the watershed is directly related to net losses of other cations from the watershed. The net uptake of nitrate and ammonium is most likely due to biological uptake such as denitrification and assimilation (Henriksen and Wright 1977). At the Hubbard Brook Experimental Forest

in New Hampshire, nitrate concentrations in the aquatic environment remained low throughout the summer and early autumn months, then began to rise in November. This increase was due to the leaching of nitrogenous byproducts from decaying vegetation.

Almer (1974), working on the western coast of Sweden, found that in lakes with pH values less than 5.0, the sulfate and potassium concentrations were similar, while the nitrogen and phosphorous concentrations decreased with pH. This decrease in phosphorous was probably due to precipitation with aluminum. Aluminum will easily precipitate dissolved phosphorous, with the strongest affinity occurring in the pH range of 5 to 6. Thus, lake water within this pH range may become more oligotrophic due to increased precipitation of phosphorous. In some acidified lakes, transparency has increased by more than ten meters, compared to before acidification. This increase in transparency depends on the precipitation of humus due to increased aluminum levels in connection with low pH (Dickson 1978).

Hydrogen ions in precipitation are exchanged with base metal ions, so that the base metal ions are leached from the watershed minerals. The pH of the solution is simultaneously increased by the incorporation of hydrogen ions from the percolating water into non-ionized dissolved silicic acid. Hydrogen ion inputs are approximately equal to

the total cation concentration found in the discharge waters. Therefore, the loss of calcium, magnesium, and aluminum from the watershed is mostly due to input of acidic precipitation, possibly through cation exchange reactions in the soils (Fisher 1968; Henriksen and Wright 1977).

The mobility of potassium, calcium, magnesium, iron, manganese, and aluminum is determined not only by the acidity of the precipitation, but the solubility of the mineral phase, the solubility of the cations in combination with anions in solution, the saturation state for the various cation exchanges, and availability of organic chelation agents (Norton 1981). Metal concentrations should increase in lakes undergoing acidification due to increased leaching of soils and sediments, especially for those less abundant elements. Norton (1981) found that considerable amounts of zinc can accumulate in aquatic ecosystems, and may be released upon acidification. However, zinc appears to be controlled by factors other than the hydrogen ion. Cronan (1979), in the Adirondack mountains, and Henriksen and Wright (1977) working in south and central Norway, found zinc concentrations to increase with decreasing pH. Zinc is mobilized from sediments where the pH becomes lower than 5.3, and is retained in alkaline soil (Hanson 1980). Norton (1981) found the solubility of iron bearing minerals to be strongly pH dependent and also dependent on the availability of organic chelation agents.

Copper showed only slightly higher concentrations in acidic lakes of the northeastern United States.

The availability of copper may have a strong relationship to organic matter content, especially allochthonous organic material which contains elevated copper concentrations (Norton 1981).

#### Characteristics of Acid Snow and Spring Shock

The term "spring shock" has been used to describe the rapid release of acids from a snowpack during the period of the spring thaw, and may cause a temporary decrease in the pH of poorly buffered lakes and streams. Most of the acidity within the snowpack is from  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Two factors make their relative importance to spring time acidification of lakes and streams uncertain: the stability of  $\text{NO}_2/\text{NO}_3$  and  $\text{SO}_4$  in the snowpack, and the amount of  $\text{HNO}_3$  biologically utilized during the melt period (Johannessen, Henricksen 1978; Jeffries and Synder 1982). Cadle (1984) found that no significant loss of any of the snow components occurred before the spring thaw. Rain occurring during the snowmelt period tended to dilute the concentration of hydrogen ion and nitrate, and to increase the concentration of sulfate (Cadle, 1984). Martin (1984) found that  $\text{HNO}_3$  was utilized rapidly during the spring melt period. Further studies by Cadle (1984) in northern Michigan indicated that nitrate was either biologically utilized or retained in the soil, whereas the concentration of sulfate had a

large peak value in concentration during the spring thaw, suggesting that release of sulfate from soil may be occurring.

Johannessen and Henriksen (1975,1978) demonstrated that concentrating of chemical variables within the snow pack does occur during the snowmelt process and may be due to adsorption onto the snow crystals surfaces. Snow crystals are formed in relatively clean air masses and the pollutants are adsorbed onto the surfaces as the snow passes through polluted air. These pollutants could be lost with the first wave of meltwater to enter the aquatic system (Fletcher 1970), but further concentration of pollutants may be the result of alternate melting and freezing during winter. The first meltwater presumably forms near the surface and may later freeze, either because of a change in air temperature or due to contact with colder snow as the meltwater percolates through the snowpack. This process may lead to the formation of essentially pure ice and concentrated meltwater, which eventually runs off into the aquatic environment (Johannessen and Henriksen 1978). Cadle (1984) found that 50 percent of the acidic species within the snowpack were released during the first 17 percent of snowmelt. Johannssen and Henriksen (1978) reported that the first 30 percent of snowmelt contained 44 to 76 percent of the total amount of all chemical components studied.

Other pollutants contained in the snow, such as heavy metals, are also released during the melting process, and

consequently increase in the surface waters (Hultberg 1977). In New York, the acid released from melting snow reduced stream pH from 5.5 to 4.5, and increased aluminum concentrations from 0.2-0.4 mg/l to as much as 1.0 mg/l (Driscoll, et al., 1980).

#### Biological Implications of Metal Ions in Aquatic Systems

Increases in metal concentrations have been associated with decreasing pH levels in acidic lakes and streams, apparently as a result of increased metal solubility. Living organisms require the availability of trace metals in sufficient quantities to supply nutritional requirements, but the margin between adequacy and toxicity for many metals may be narrow. Thus, any environmental factor that reduces or enhances organism accumulation of a trace metal potentially has major biological significance.

Acute metal toxicosis in aquatic organisms has been attributed to the coagulation or precipitation of mucus on the gills and to cytologic damage to the gills. The physiologic mechanism of death from either cause is related to a breakdown in gas exchange at the gills. Burton, et al., (1972) studied acute zinc toxicosis in rainbow trout (Salmo gairdneri) and were able to support the hypothesis that modification of the gas exchange process at the gills creates hypoxia at the tissue level, which appears to be the major physiologic change preceding death.

Physical gill damage and heavy mortality of brook

trout (Salmo fontinalis) fry occurred with 0.05 mg Al/l at pH levels 4.4 to 5.2. Aluminum toxicity varied with pH level, increasing with increasing pH (Driscoll, et al., 1980).

Holcomb and Benoit (1978) found that the maximum acceptable concentration of zinc in soft water was between 0.14 and 0.26 mg Zn/l. Benoit and Holcomb (1978) determined that for fathead minnow (Pimephales promelas) the threshold level for significant adverse affects was between 0.078 and 0.145 mg Zn/l. Brungs (1976) found an 83% reduction in egg production in the fathead minnow with zinc concentrations of 0.018 mg Zn/l. The maximum concentration considered safe for cadmium, copper, and nickel for the fathead minnow are 0.037 mg Cd/l, 0.017 mg Cu/l, and .380 mg Ni/l (Pickering and Gast 1984; Mckim and Benoit 1975). Biesinger (1972) uses *Daphina magna* as a representative of invertebrate acute and chronic toxicosis produced by several metals. The median lethal concentration for zinc is 0.280 mg/l, with 16% reproductive impairment at 0.070 mg/l.

Mount (1973) showed that the toxicity of a given concentration of trace metals to the fathead minnow varies with changing pH. In studies where a constant trace metal concentration was used, the survival of fathead minnows was not affected at pH 7.5. Lower egg production and hatchability occurred at pH 5.9. and at pH 5.2 to 4.5 females did not spawn. Test results of metal toxicity performed at higher pH values may therefore yield safe levels that are too high for acidic waters. Beamish (1976) reports

that although fish and other aquatic organisms are responding to an acid stress modified by metal toxicity, there does not appear to be any justification for considering that the failure of reproduction and ultimate extinction of aquatic populations have resulted primarily from the toxic effects of heavy metals alone. Aquatic organisms are being stressed by an association of factors of which acid is the principal stressing agent as well as controlling the concentration of less important factors.

## MATERIALS AND METHODS

### Study Area

Five northern lakes, Bass, Buteau, Clara, Otter, and Turtle, are located in a region of north central Wisconsin known as the Harrison Hills Recreational Area (Fig. 1). The area consists of several hundred acres of mixed hardwood forest, and is characterized by many hills and small lakes.

This area was chosen due to its combination of acid loading and geological sensitivity. The area is presently receiving precipitation with an average pH of 4.60. The watershed is underlain by granite containing patches of ground moraine. In addition, these study lakes possess properties which enhance their susceptibility to acid deposition. They are low alkaline, oligotrophic lakes, with a high Canadian susceptibility index (CSI) (Table 1). A lake with a CS

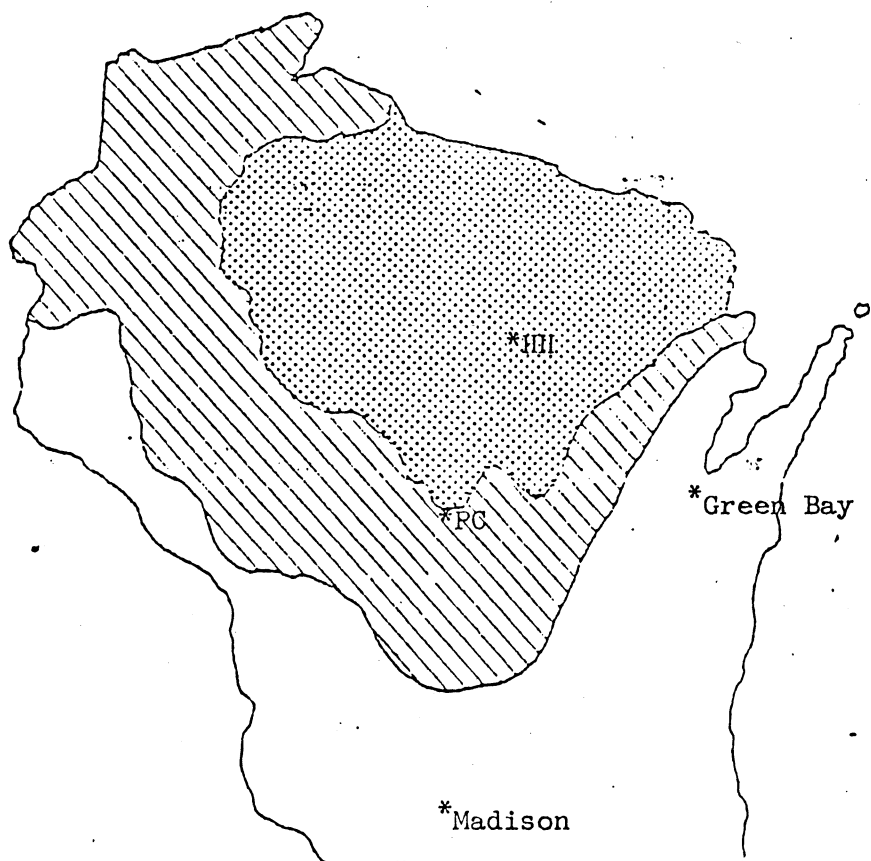


Figure 1. Map of Wisconsin showing location of northern Harrison Hills lakes(HH), and the Portage County lakes(PC) including generalized bedrock geology of Wisconsin; igneous[stippled], sandstone [diagonal hatching], limestone [plain white].

value of greater than 3 is considered susceptible to acid deposition. The average depth of the lakes is approximately 4.2 meters, and all have high watershed to lake area ratios (Table 2). The shoreline development factor varies considerably, with Turtle lake having the highest value (3.99) for a shoreline development factor (SDF). Shoreline development values for Otter, Bass, Buteau, and Clara lakes are 1.32, 2.11, 1.93, and 1.77, respectively. University and Jacqueline lakes are located in central Wisconsin's Portage County (Fig. 1). This area receives more acid loading but is more buffered than the Harrison Hills area. Jacqueline is a 40.3 acre, low alkaline, bog influenced lake, situated in a farming area in northern Portage County (Table 3). The SDF for Jacqueline lake is 2.12. University is a 22.74 acre man-made lake located in the University of Wisconsin-Stevens Point's Schmeckle Reserve. University is a hardwater, oligotrophic lake (Table 3).

Table 1. Alkalinity and Nutrient Data, Northern Lakes. (J. Eilers, WI DNR 1982).

	BASS	BUTEAU	CLARA	OTTER	TURTLE
Alkalinity (mg/l)	1.75	2.00	2.35	2.50	2.10
pH	6.66	5.79	5.93	6.16	6.28
CSI	4.03	6.14	4.94	4.32	4.56
Total P. (mg/l)	0.009	0.011	0.025	0.021	0.029
Rea. P. (mg/l)	<.002	<.002	<.002	<.002	<.002
TKN-Nitrogen(mg/l)	0.26	0.55	0.32	0.84	1.00
NO2/NO3 (mg/l)	<.01	<.01	<.01	<.01	<.01
Ammonia (mg/l)	0.10	0.16	0.30	0.14	0.21
Seechi Disk (m)	6.0	8.7	5.7	2.4	2.6
Color (PCU)	0.0	10.0	0.0	30.0	30.0
Turbidity	0.0	0.0	0.0	1.0	1.0

Table 2. Physical Description of Northern Lakes, ( J.Eilers Wisconsin DNR 1982)

	BASS	BUTEAU	CLARA	OTTER	TURTLE
Total watershed area (ha)	87.0	37.0	77.0	99.0	183.0
Lake area (ha)	38.3	21.0	34.1	14.1	12.5
Lake perimeter(km)	4.63	3.13	3.66	1.75	3.99
Maximum depth(m)	13.1	15.2	9.75	4.87	3.35
Mean depth(m)	5.67	5.15	4.55	2.92	2.42
Volume (m3/1000)	2169	1082	1551	412	302
Shoreline development factor(SDF)	2.11	1.93	1.77	7.02	14.60
Watershed:Lake Area (ratio)	2.27	1.76	2.26	7.02	14.60

Table 3. Alkalinity and Nutrient Data for the Portage County  
Lakes, Summer 1983. (Environmental Task Force, UW/SP)

	Jacqueline	University
Alkalinity (mg/l)	8.00	57.0
pH	6.55	7.94
Total P. (mg/l)	0.008	0.018
Reactive P. (mg/l)	<.002	<.002
TKN-Nitrogen (mg/l)	0.52	0.20
Nitrate/Nitrite (mg/l)	<.01	<.01
Ammonia (mg/l)	0.01	0.01

## Experimental Procedures

Sampling, handling, and analytical procedures for water and snow samples

Water samples were collected using a Van Dorn sampler in winter, during spring thaw, and in late summer. Four sampling sites were used for each lake: two deep and two shallow sites. The samples were stored in aged one liter polyethylene bottles. These bottles were pre-washed with an acid solution and rinsed three times in double distilled water. Two one-liter samples were collected from each sampler throw. One of these was left unpreserved and the other received 0.5 ml of 6 N HCl. This lowered the pH to approximately three and reduced the chance of metal sorption, precipitation, and biological uptake. Samples were transported, packed in ice, and stored in refrigerators at the lab. Alkalinity, and pH analyses were conducted both in the field and immediately upon returning to the lab. There was no significant difference between the field and lab results; therefore, field measurements were eliminated from the sampling program, (Appendix 1).

Snow samples were collected and analyzed three separate periods throughout the winter. Three sampling locations were selected around each lake and samples were collected using a PVC core sampler. Volume of sample varied according to depth of

snow at each site. Samples were placed into pre-cleaned plastic bags, sealed, and packed in ice during transportation back to the lab. At the lab each sample was divided into subsamples; one was preserved with 6 N HCL for metal analysis.

For trace metal analysis (Al, Cd, Cu, Fe, Ni, and Zn), a 50 ml portion of preserved sample was placed into a clean, acid-washed beaker with 3.0 mls of concentrated nitric acid (HNO<sub>3</sub>), placed on a hot plate, and evaporated to near dryness. Once near dryness was achieved, the beaker was removed from the hot plate and allowed to cool. Another 3.0 mls of HNO<sub>3</sub> was then added and the sample was refluxed until the solution became colorless. When refluxing was completed, water that had collected on the watch glass was rinsed back into the beaker with double distilled water and the sample was again evaporated to near dryness. After this second evaporation the sample was allowed to cool and an additional 5.0 ml of HNO<sub>3</sub> was added. The sample was heated to redissolve any precipitation or residue formed during the evaporation process. The sides of the beaker were rinsed with double distilled water and the solution was transferred to a 50 ml volumetric flask and brought up to volume. All metals, except iron, were analyzed by graphite furnace on a Varian atomic absorption instrument. Iron analyses were done using the units flame absorption mode.

Nitrogen analyses were done, using a Technicon Auto Analyzer II according to manufacturer recommendations. Anion

analyses for chloride and sulfate were conducted with a Dionex Ion chromatograph. Analytical procedures involving conductivity, hardness, pH, dissolved oxygen, and alkalinity, were done according to Franson, M. H., ed. 1980. Standard Methods for the Examination of Water and Wastewater, 15th ed. American Public Health Association.

Sampling, handling, and analytical procedures for sediment samples

Shallow water and deep water sediment samples were collected from all lakes. Samples were collected, using a home-made sediment core sampler, consisting of a 5 cm diameter PVC pipe, approximately 1 m long, connected to a series of pipe extensions through a one-way valve. Depth into sediments ranged from 15 to 25 cm, depending on sediment type. Once brought up to the surface, the sediment cores were pushed out, intact, onto a plastic dish. Only the upper 5 to 7 cm of sediment were taken and placed into pre-cleaned plastic bags. The samples were transported packed in ice, and stored in a freezer at the lab.

In preparing the samples for analysis, 0.5 g of sediment and 24 ml of 0.25 N HCL were placed in a centrifuge tube. The sample was mixed thoroughly and centrifuged for 30 min at 10,000 rpm. The centrifugate was then decanted and analyzed by flame atomic absorption.

## Procedures for the sediment leaching

Sediments from two lakes, Otter and Turtle, were used in the sediment leaching study. Forty grams of wet sediment from each lake were placed into two liter beakers, into which one liter of lake water was added. The pH was then lowered with 0.1 N HNO<sub>3</sub>, while gently stirring, until equilibrium was reached at pH 4.00. This took approximately 48 hours. After this time the mixture was allowed to settle, and triplicate samples of water were taken for metal analysis. The same procedure was followed, using 0.1 N H<sub>2</sub>SO<sub>4</sub> and 0.1 N HCL.

In addition to these acids, CO<sub>2</sub> was also used in the leaching study. The apparatus used for the CO<sub>2</sub> consisted of a two liter erlenmeyer flask fitted with a two hole stopper. A piece of tygon tubing with an air stone attached allowed CO<sub>2</sub> to be bubbled into the flask. The other hole held a glass tube to vent the system. With this system, the equilibrium pH was 4.60.

## Statistical Methods of Analysis

The quality control/quality assurance methods in this study were developed using the Environmental Protection Agency's Handbook for Analytical Quality Control in Water and Wastewater Laboratories (EPA-60014-79-019) and the 15th edition of Standard Methods. Three sites were designated as quality control (QC) sites: east turtle deep; west buteau shallow; and

west otter deep. This method uses the Shewhart theory of control charts to evaluate the accuracy and precision of analysis which was developed by Dr. Walter A. Shewhart in Bell Telephone Laboratories. Control charts were constructed for each chemical variable for each of the QC lakes. In this technique, an accuracy estimator (percent recovery) and a precision estimator (range) are used.

## RESULTS AND DISCUSSION

### Chemical Characteristics of Snow Cores

#### Northern Site

Snow cores were collected and analyzed for three separate periods throughout the winter. The acidity and hydrogen ion concentration in the snowpack was lower than data from previous years (Table 4).

There was no evidence that any of the chemical species were lost from the snowpack prior to the spring thaw period. Snow cores were not sectioned, thus migration of the chemical components within the snowpack are unknown. Johannessen and Henriksen (1978) found that there was no significant loss of water or of H, SO<sub>4</sub>, NO<sub>3</sub>, or NH<sub>4</sub> ions prior to snowmelt. Cadle, et al. (1984), working with a snowpack in northern Michigan also found a high degree of overall stability in the snowpack. However, through

sectioning the snow cores, they found that the NO<sub>3</sub> concentrations were continually displaced from the top of the snowpack to the bottom.

Table 4. Analysis of Snow Core Samples, mg/l, Northern Lakes.

	Turtle	Bass	Buteau	Otter	Clara
NH4-N	0.16	0.17	0.16	0.15	0.16
NO2/NO3-N	0.15	0.50	0.43	0.47	0.41
SO4	0.81	0.76	0.81	0.81	0.77
Cl	0.51	0.61	0.54	0.51	0.47
pH	5.09	5.11	6.01	5.07	5.00
Acidity	4.15	4.14	4.21	4.15	3.99
Alkalinity	0.49	0.46	0.41	0.49	0.39
Ca hardness	0.17	0.17	0.20	0.16	0.11
Copper, ug/l	40.0	36.0	37.0	35.0	36.0
Zinc, ug/l	156.0	154.0	155.0	156.0	155.0
Nickel, ug/l	5.0	5.0	5.0	6.0	6.0
Cadmium, ug/l	3.0	3.0	3.0	3.0	4.0
Iron, ug/l	88.0	84.0	88.0	82.0	92.0

The pH, SO<sub>4</sub>, and NO<sub>3</sub> concentrations in the snowpack in this study were lower than those found in snowfall occurring in the northeastern United States. Over the Hubbard Brook Experimental Forest, New England, SO<sub>4</sub> concentrations in precipitation ranged from 1.4 mg/l to almost 7.0 mg/l for a two year study. Sulfate was low during the fall and winter, with a winter average of 3.0 mg/l. This lower winter concentration may be due to inefficiencies of snowflakes to capture sulfur compounds (Fisher 1968). Average pH and NO<sub>3</sub> values for snow in the New England area were 4.1 and 1.0 mg/l, respectively (Fisher 1968).

#### Central Site

Snow cores collected at the central site (Table 5) showed a high degree of stability through the winter. The pH values were expectedly lower than that of the northern sites. The concentration of chemical variables in snow cores collected from both central and northern sites were similar, with the exception of SO<sub>4</sub> and Cl concentrations surrounding University lake. The higher values of SO<sub>4</sub> and Cl in snow cores taken from University lake are probably due to local sources.

#### Chemical Characteristics of Lake Sediment

##### Sediment Analysis for Trace Metals

Sediment cores were collected and analyzed from three

Table 5. Analysis of Snow Core Samples, mg/l, Central Site.

	University			Jacqueline		
	1/4/83	2/4/83	3/4/83	1/4/83	2/4/83	3/4/83
NH4-N	0.04	0.51	0.53	0.05	0.50	0.52
NO2/NO3-N	0.40	0.54	0.54	0.40	0.54	0.54
SO4	2.31	3.12	3.21	0.31	0.31	0.33
Cl	1.02	1.00	1.03	0.13	1.29	1.27
pH	4.58	4.61	4.63	4.55	4.47	4.45
Acidity	4.28	4.11	4.21	4.34	4.18	4.78
Alkalinity	0.48	0.52	0.52	0.51	0.45	0.43
Ca hardness	0.11	0.12	0.13	0.14	0.08	0.10
Copper, ug/l	34.0	31.0	32.0	31.0	32.0	34.0
Zinc, ug/l	136.0	140.0	142.0	135.0	144.0	141.0
Nickel, ug/l	2.0	2.0	2.0	2.0	1.0	1.0
Cadmium, ug/l	1.0	1.0	1.0	1.0	1.0	1.0
Iron, ug/l	75	71.0	72.0	78.0	83.0	79.0

Table 6. Trace Metal Concentrations of Sediment Cores, mg/kg  
(3/1/83).

	Copper	Zinc	Cadmium	Nickel	Iron
Turtle	134.9	126.6	2.30	4.30	2334.0
Bass	131.4	128.1	1.80	4.30	2432.3
Buteau	132.3	73.1	3.20	4.10	2307.8
Otter	125.1	42.8	2.10	4.50	2728.7
Clara	135.1	81.3	2.42	4.70	2401.5
University	123.8	42.4	1.10	1.90	1616.1
Jacqueline	75.2	101.8	2.83	2.72	2318.0

locations within each lake (Table 6). Concentrations varied considerably, both within individual lakes and between lakes. The variations are likely the result of local influences. These concentrations and variations are similar to values found in unpolluted lakes in upper New York state (Galloway and likens 1979).

#### Sediment Leaching Study

Lake sediments from two lakes, Otter and Turtle, were exposed to a decreased pH in the laboratory. Zinc, iron, and aluminum were released readily from the lake sediments. Copper showed only a slight release (Table 7). Schindler (1980) found increases in Zn, Mn, Al, and Fe, after acidifying (pH 5.1 to 5.7) enclosures within a lake, while concentrations of Cu and Cd were usually below detection. These data suggest that pH values well above the level used in this study are capable of mobilizing traces metals from lake sediments. The pH values found in the snowpacks were at or below levels used by Schindler (1980), indicating that the hydrogen ion concentrations in the meltwater were more than adequate to mobilize metals from the watershed of these lakes.

#### Chemical Characteristics of the Lake Water

##### Changes in Water Chemistry During Snowmelt

Data from the 25 northern lake sites were combined for

Table 7. Results from Leachate Study. Final pH values for HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and HCL was 4.00; and 4.60 for CO<sub>2</sub>.

	Trace metal concentration, ug/L, in water			
	At pH 4.00			At pH 4.60
	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCL	CO <sub>2</sub>
Otter Lake sediment/ water initial pH 6.29 initial conc. (ug/l).				
Copper (2.00)	5.00	3.00	5.00	5.00
Zinc (22.0)	210.0	265.0	250.0	210.0
Iron (122.0)	520.0	510.0	553.0	520.0
Aluminum (25.0)	520.0	360.0	300.0	520.0
Turtle Lake sediment/ water initial pH 5.84 initial conc. (ug/l).				
Copper (2.0)	5.00	4.00	5.00	5.00
Zinc (13.0)	210.0	240.0	256.0	210.0
Iron (134.0)	590.0	513.0	550.0	590.0
Aluminum (20.0)	470.0	325.0	273.0	470.0

statistical review of changes occurring in alkalinity, hardness, pH, NO<sub>2</sub>/NO<sub>3</sub>, SO<sub>4</sub>, Cl, and trace metals during snowmelt. The statistical review of the data was conducted using analysis of variance with a 95% confidence interval for means based on pooled standard deviations. Changes occurring for the individual lakes appear in Appendix 3.

### Alkalinity, Hardness, and pH

#### Northern and Lake Jacqueline Sites

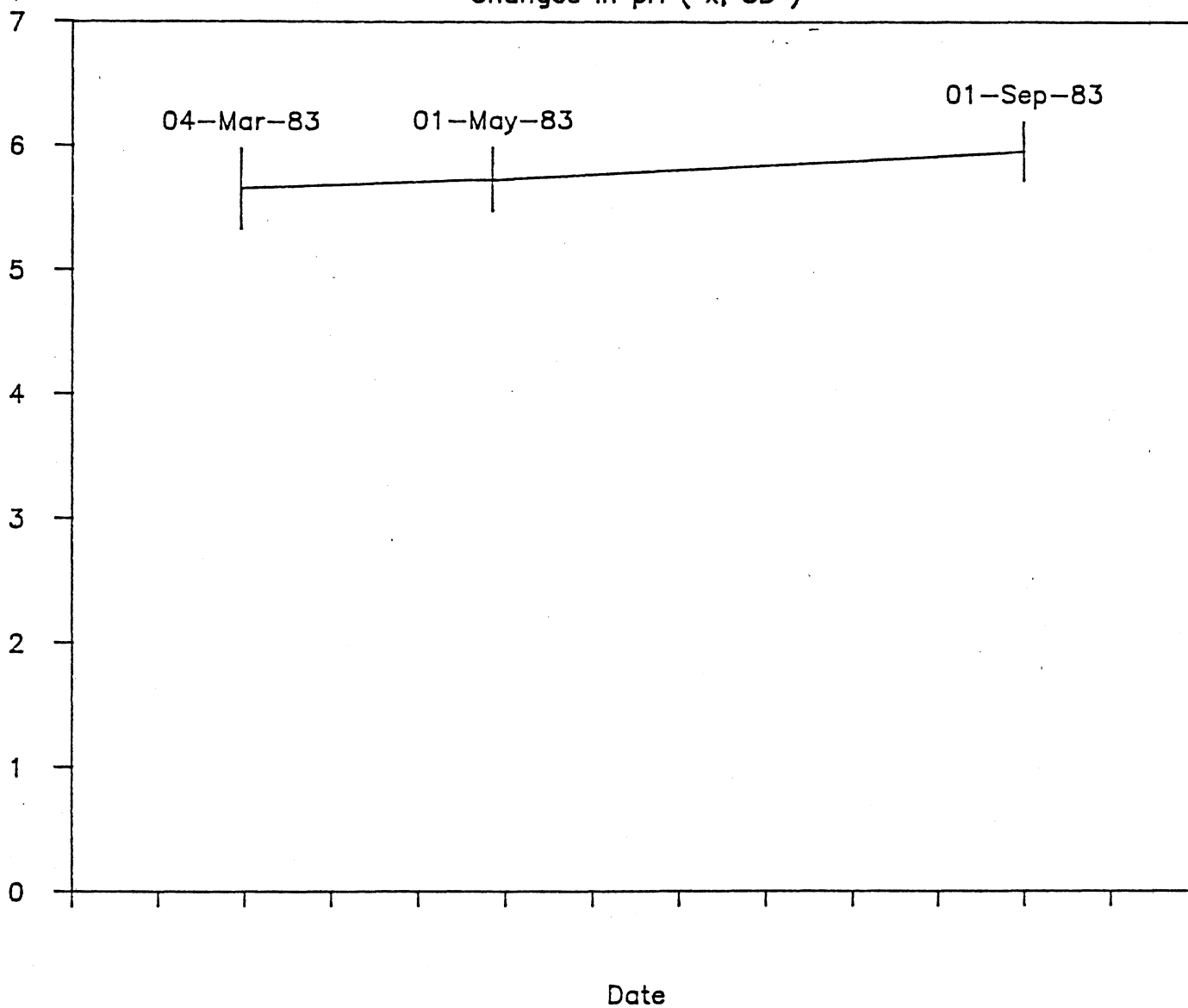
The most striking changes in chemical characteristics were the increases in pH, alkalinity, and hardness following snowmelt. The average pH of the northern lakes prior to snowmelt was 5.65. After snowmelt the pH increased to 5.73, a decrease of 16.9% in hydrogen ion concentration (Fig. 2). Jacqueline Lake had a decrease of 22.5%, from pH 6.37 to a pH of 6.48.

The average alkalinity of the northern lakes increased 49.2% following snowmelt, from 1.97 mg/l to 2.94 mg/l (Fig. 3). Alkalinity within Jacqueline Lake increased from 14.2 mg/l to 19.1 mg/l, an increase of 34.5%. Calcium hardness concentrations prior to snowmelt were 7.77 mg/l, and increased 6.82% to 8.30 mg/l in the northern lakes (Fig. 4). The calcium hardness increased 53.1% in Jacqueline Lake following snowmelt, from 7.12 mg/l to 10.9 mg/l.

The most likely cause for these increases is

Fig.2 Snow Melt Affects on Northern Lakes

Changes in pH (  $\bar{x}$ , SD )



Units

Fig. 3 Snow Melt Affects on Northern Lakes

Changes in Alk conc. (  $\bar{x}$ , SD )

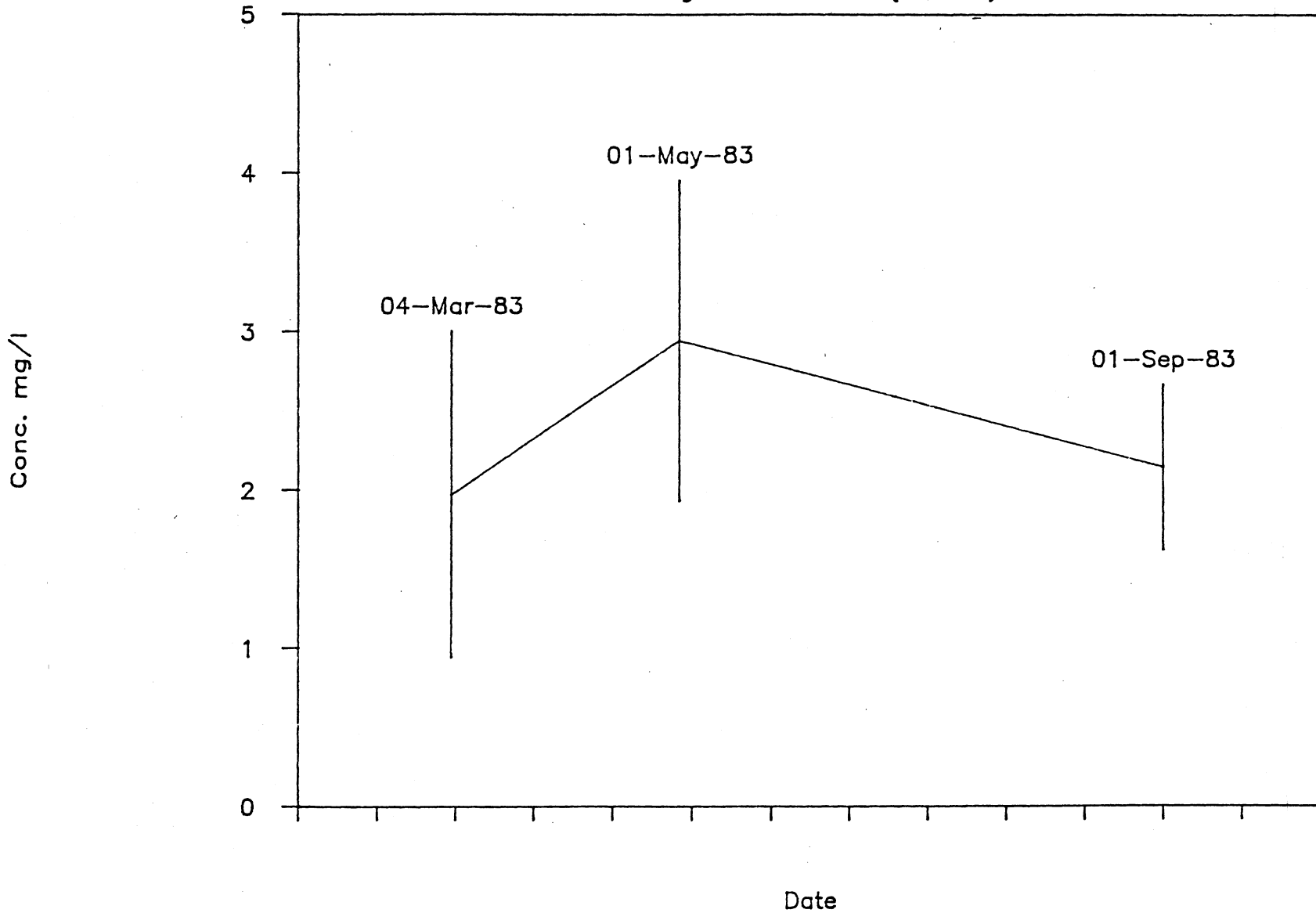
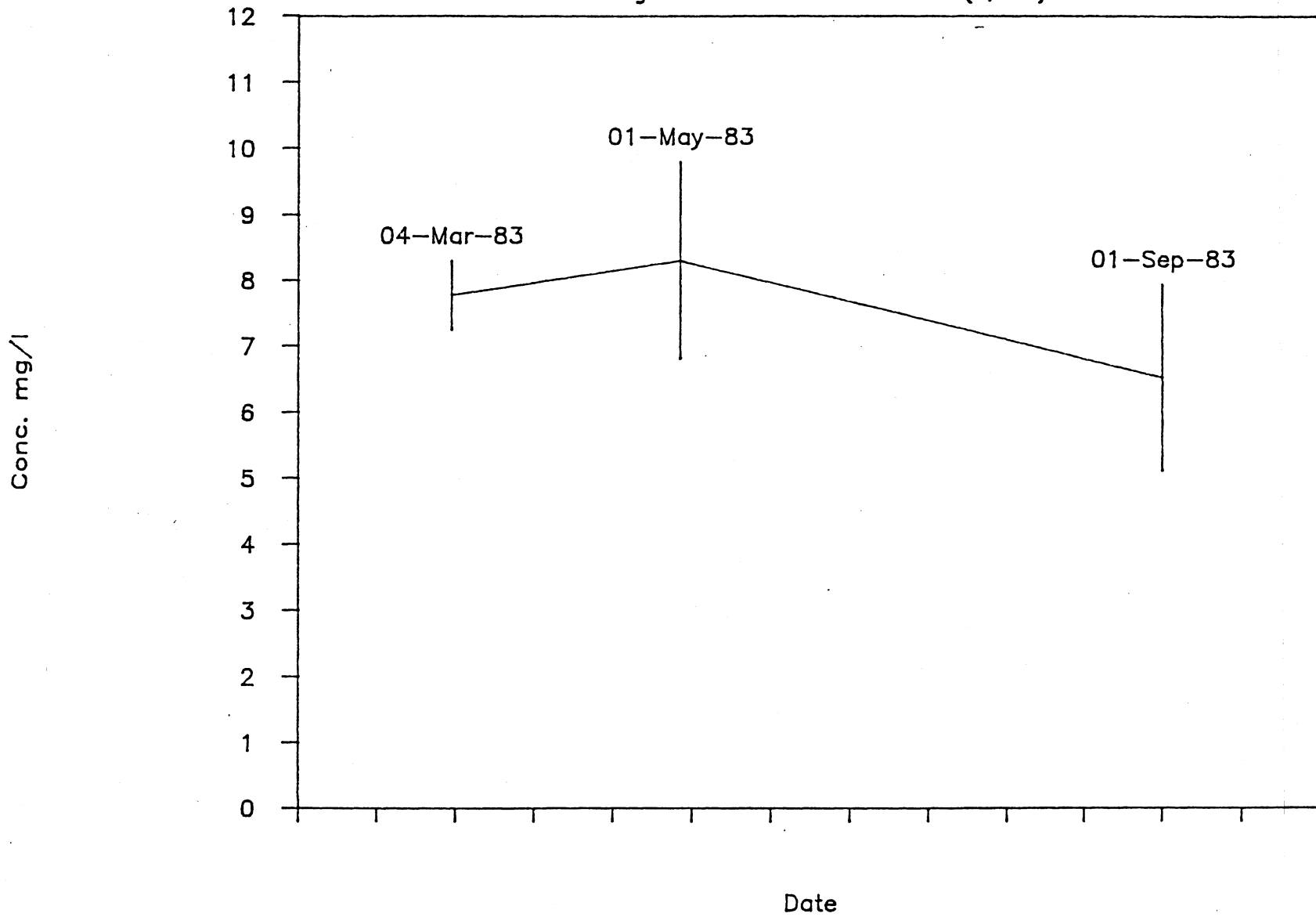


Fig. 4 Snow Melt Affects on Northern Lakes

Changes in Ca Hardness conc. (x, SD)



exchanges between the hydrogen ions in the meltwater and cations associated with the soil as this meltwater percolates through, along with the resulting bicarbonate ion production.

It is clear from data collected in the northeast that the hydrogen ion is one of the principal constituents of rain and snow in affected areas (Fisher 1968). During acid precipitation a net loss of calcium and magnesium occurs from the lake's watershed, while there is a net gain of hydrogen ions to that watershed. The net gain of hydrogen ions in the watershed is directly related to net losses of other cations. The loss of calcium and magnesium from the lake's watershed to the lake is due to inputs of acidic precipitation, possibly through cation exchange reactions in the soils (Henriksen and Wright 1977).

Fisher (1968) noted that the incorporation of hydrogen ions from percolating meltwater into non-ionized silicic acid increased the pH of the meltwater solution. Dickson (1978) found that lakes undergoing acidification have higher concentrations of non-marine calcium and magnesium.

#### University Lake Site

University lake was the only hardwater lake included in this study, and the only lake that showed a decrease in pH, alkalinity, and hardness following snowmelt. Alkalinity decreased 10.3%, from 65.3 mg/l to 58.6 mg/l; total hardness dropped 18.4%, from 101.0 mg/l to 82.4 mg/l; calcium hardness declined 14.7%, from

58.6 mg/l to 50.0 mg/l; and pH decreased from 7.92 to 7.83.

Since the concentration of these chemical variables are naturally high in this lake, it would take a correspondingly high input of these variables to produce a significant change. The small decreases shown here may be the result of dilution. If the meltwater entered the lake without being neutralized, due to frost depth or the nature of the soil/sediment, it would express itself within the water column. The result would be a decrease in pH, alkalinity, and hardness values.

Hulberg (1977) stated that snowmelt in Sweden and Norway caused pH drops in hardwater lakes and streams. Seasonal variations in pH were small in acidic lakes, while variations in lakes with pH values of 5.2-5.5 were great.

NO<sub>2</sub>/NO<sub>3</sub>, Cl, and SO<sub>4</sub>

Northern and Jacqueline Lake Sites

In the northern lakes NO<sub>2</sub>/NO<sub>3</sub> concentrations decreased from .184 mg/l to .037 mg/l following snowmelt, a decrease of 79.9% (Fig. 5). The SO<sub>4</sub> concentrations increased slightly, but this increase was not statistically significant (Fig. 6). Concentrations of Cl showed no significant change (Fig. 7).

The NO<sub>2</sub>/NO<sub>3</sub> concentrations decreased from 0.02 mg/l to below detection following snowmelt in Jacqueline Lake. Concentrations of SO<sub>4</sub> showed no significant change. Chloride concentrations decreased from 1.05 mg/l to below detection.

Fig. 5 Snow Melt Affects on Northern Lakes

Changes in NO<sub>3</sub> conc. ( x, SD )

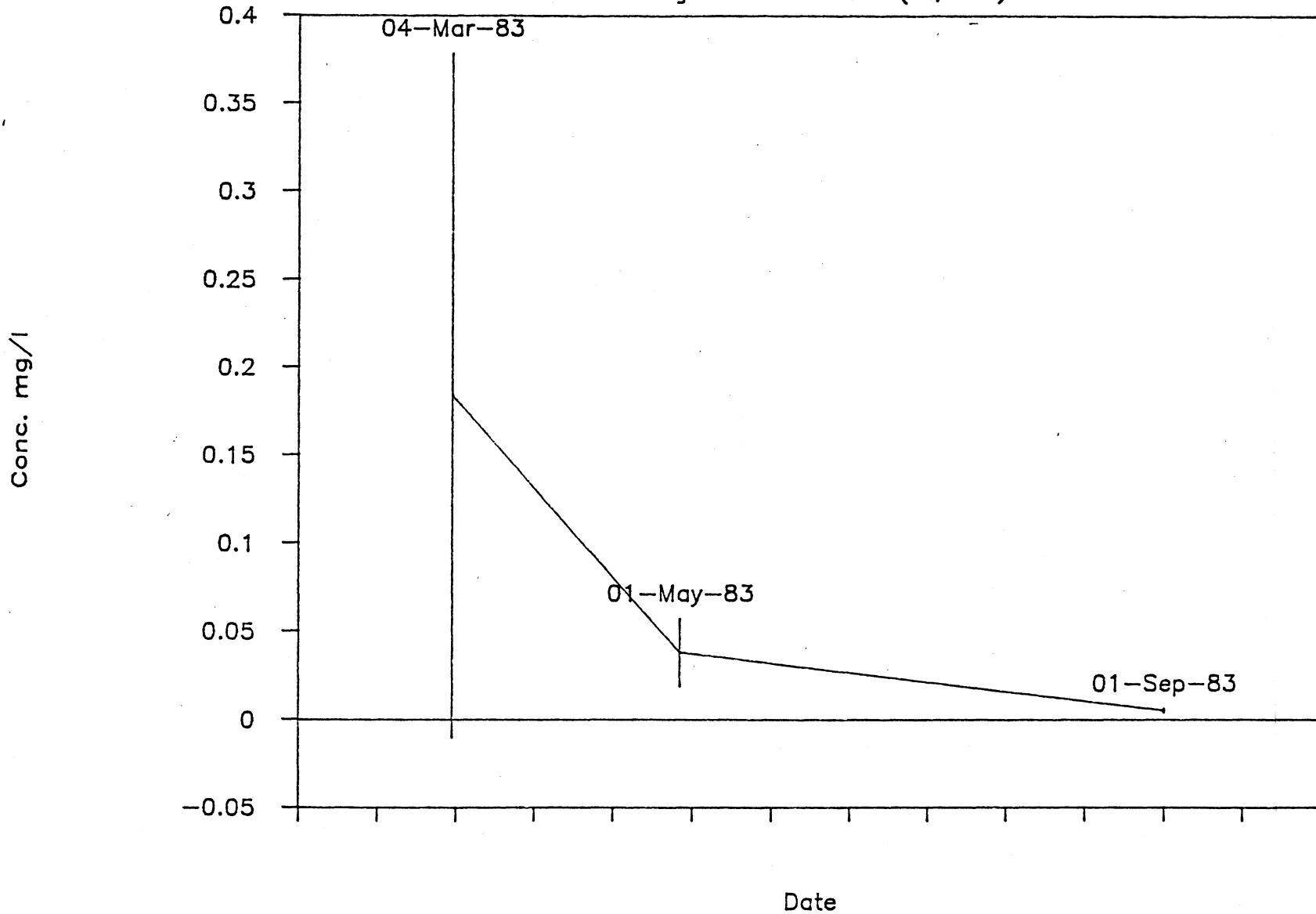


Fig. 6 Snow Melt Affects on Northern Lakes

Changes in SO4 conc. (  $\bar{x}$ , SD )

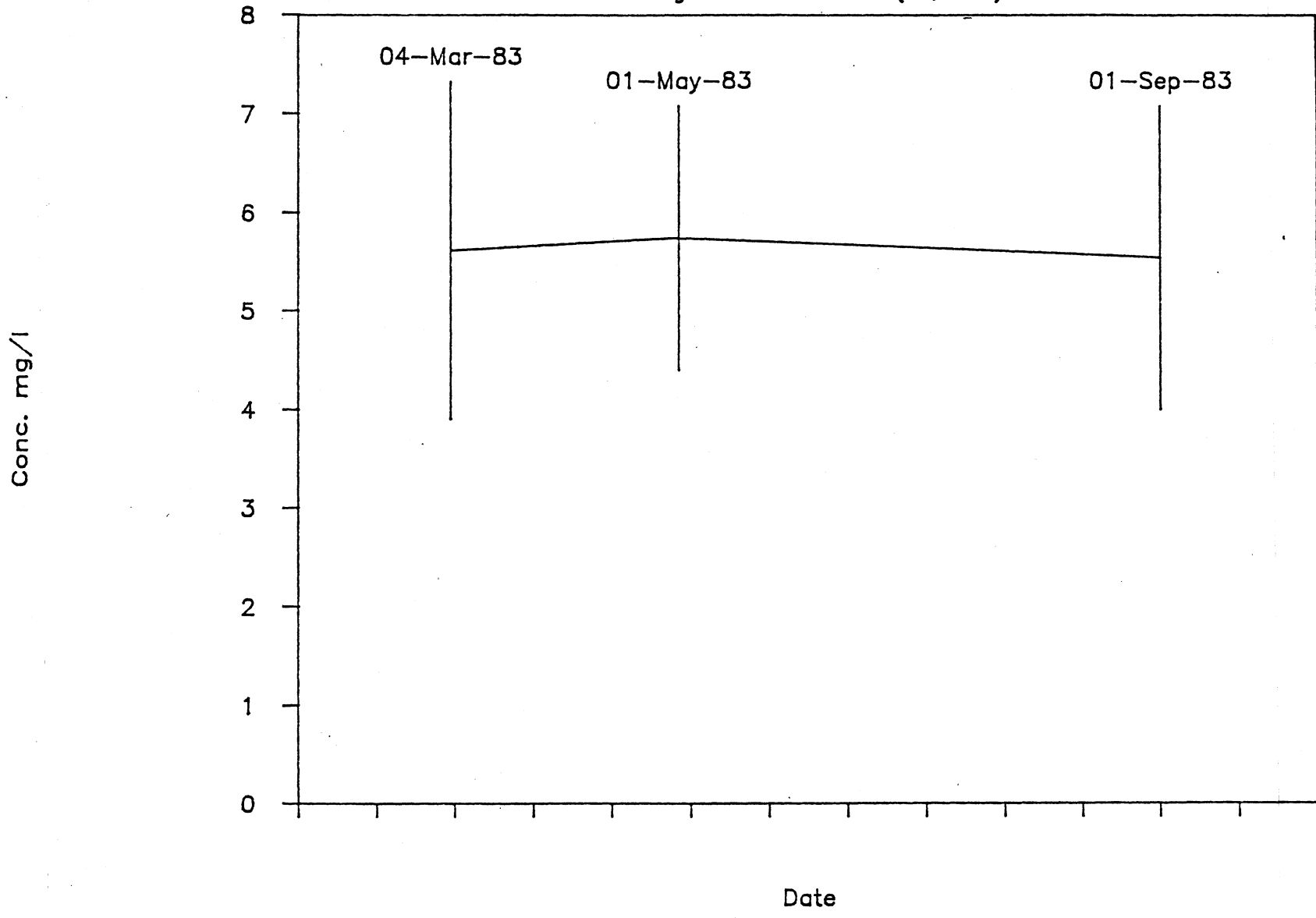
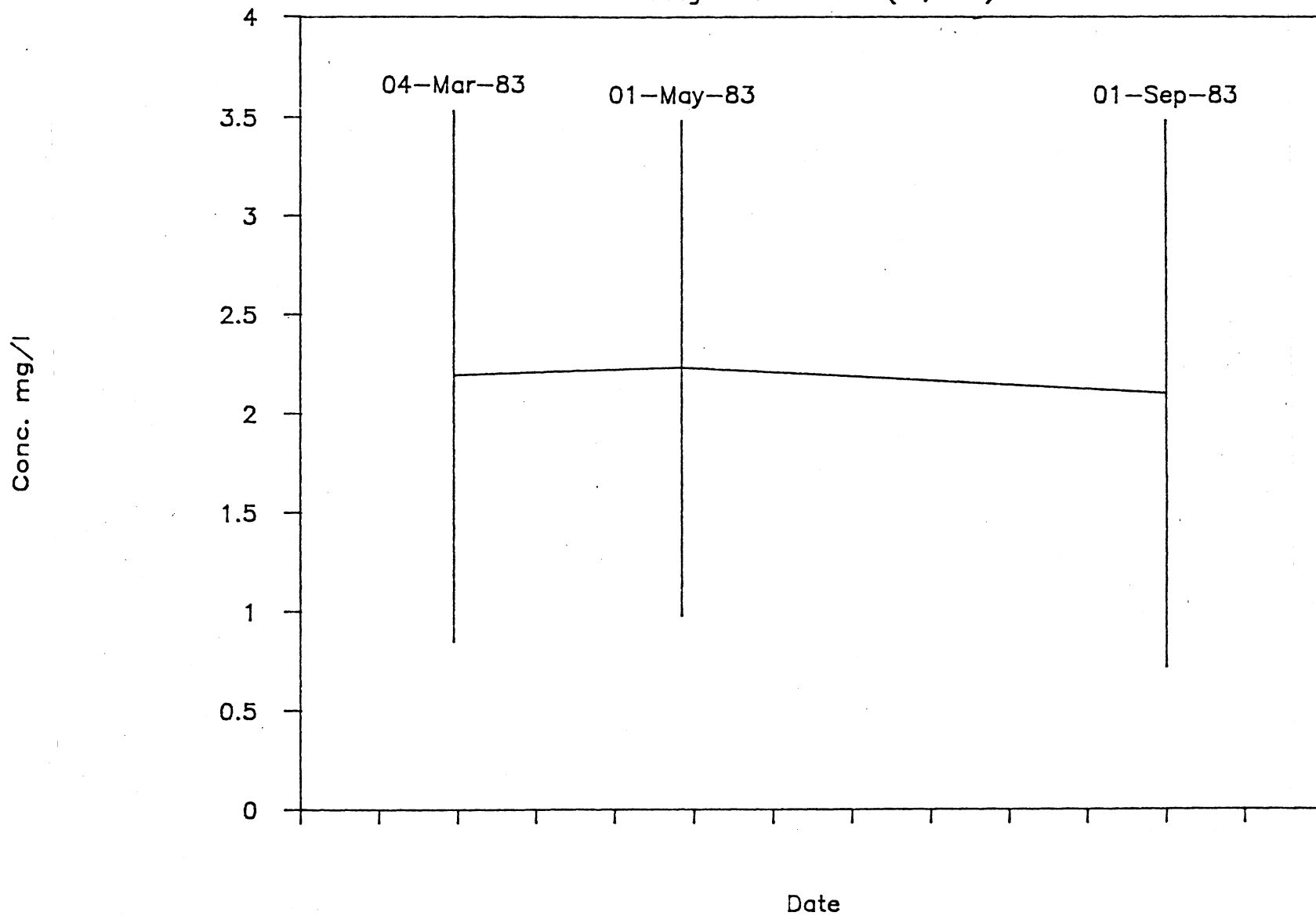


Fig. 7 Snow Melt Affects on Northern Lakes

Changes in Cl conc. (  $\bar{x}$ , SD )



Chloride is a conservative chemical variable and any changes in its concentration are most likely due to concentration in the water column during winter freezing and subsequent dilution from the spring thaw.

At the Hubbard Brook Experimental Forest aquatic  $\text{NO}_3$  concentrations begin to increase in November and remained high until the spring thaw. This increase was due to leaching of nitrogenous byproducts from decaying vegetation. Concentrations decreased following spring thaw, due to biological utilization (Fisher 1968). Martin (1984) and Johannessen and Henriksen (1978) found that  $\text{HNO}_3$  is utilized rapidly during the springmelt period, consequently reducing the concentration of  $\text{NO}_2/\text{NO}_3$  entering the aquatic system. Cadle, et al., (1968) stated from work in northern Michigan that  $\text{NO}_3$  is either biologically utilized or retained in the soil during snowmelt. The net uptake of  $\text{NO}_3$  and  $\text{NH}_4$  from the meltwater is likely due to biological uptake, such as denitrification and assimilation (Henriksen and Wright 1977).

Henriksen and Wright (1977) found that there was a net uptake of  $\text{SO}_4$  within the watershed of a small acid lake in Norway in response to acid precipitation. Cadle, et al., (1968) stated that  $\text{SO}_4$  concentrations showed large peak values during the melt period. The  $\text{SO}_4$  concentrations were higher in the discharge than predicted from meltwater and rain concentrations,

suggesting that there might be a release of  $\text{SO}_4$  from the soil during snowmelt.

#### University Lake Site

Nitrate/nitrite concentrations decreased following snowmelt, and remained low through the summer. Chloride concentrations decreased 42.3%, from 6.50 mg/l to 3.75 mg/l after snowmelt. Although  $\text{SO}_4$  concentrations were high in the snowpack (3.12 mg/l) there was no significant change following snowmelt in the lake water.

The concentration of Cl within the lake is likely the result of contamination from urban sources such as road salt. The large change in Cl is probably due to winter concentration and subsequent dilution from the spring thaw. Since the concentration of  $\text{SO}_4$  is high within the lake, it would require a large input to the lake to show a significant change. Sulfate has been shown to be taken up by watersheds, thus reducing the concentration entering the lake through snowmelt (Henriksen and Wright 1977). Decreases in  $\text{NO}_2/\text{NO}_3$  are likely the result of biological uptake, both within the water column, and as the meltwater percolates through the soil (Fisher 1968; Henriksen and Wright 1977).

#### Trace Metal Concentrations

##### Northern and Jacqueline Lake Sites

Zinc and copper concentrations in the northern

lakes increased from 15.1 ug/l and 1.65 ug/l to 22.6 ug/l and 3.65 ug/l respectively. This represents a 89.1% increase in Zn and a 83.8% increase in Cu. Aluminum and iron concentrations showed only slight changes. These changes were not significant (Figs. 8-11 ).

Jacqueline Lake showed significant increases in Cu, Fe, and Al following snowmelt: 1900%, 12.6%, and 53.3%, respectively.

Previous researchers have found that hydrogen ions from precipitation replace base metal ions, so that the base metal ions are leached from the watershed minerals. Hydrogen ion inputs to the watershed are approximately equal to the total cation increases found in the lake water. Therefore, the loss of trace metals from the watershed is due to inputs of acidic precipitation, through cation exchange reactions between the meltwater and the soil-sediment (Fisher 1968; Henriksen and Wright 1977). Norton (1981) found that considerable amounts of Zn can be accumulated in the watershed, and released upon acidification. Zinc concentrations in lakes in the Adirondack Mountains show increasing Zn concentrations with decreasing pH (Cronan 1979). Zinc is mobilized from sediments when the pH of lake water becomes lower than 5.3 (Hanson 1980). In artificial acidification experiments, Schindler (1980), found that Zn, Mn, Al, and Fe are readily released from lake sediments with decreasing pH of lake water. Cronan (1979) stated that under acidification, soil derived Al

Fig. 8 Snow Melt Affects on Northern Lakes

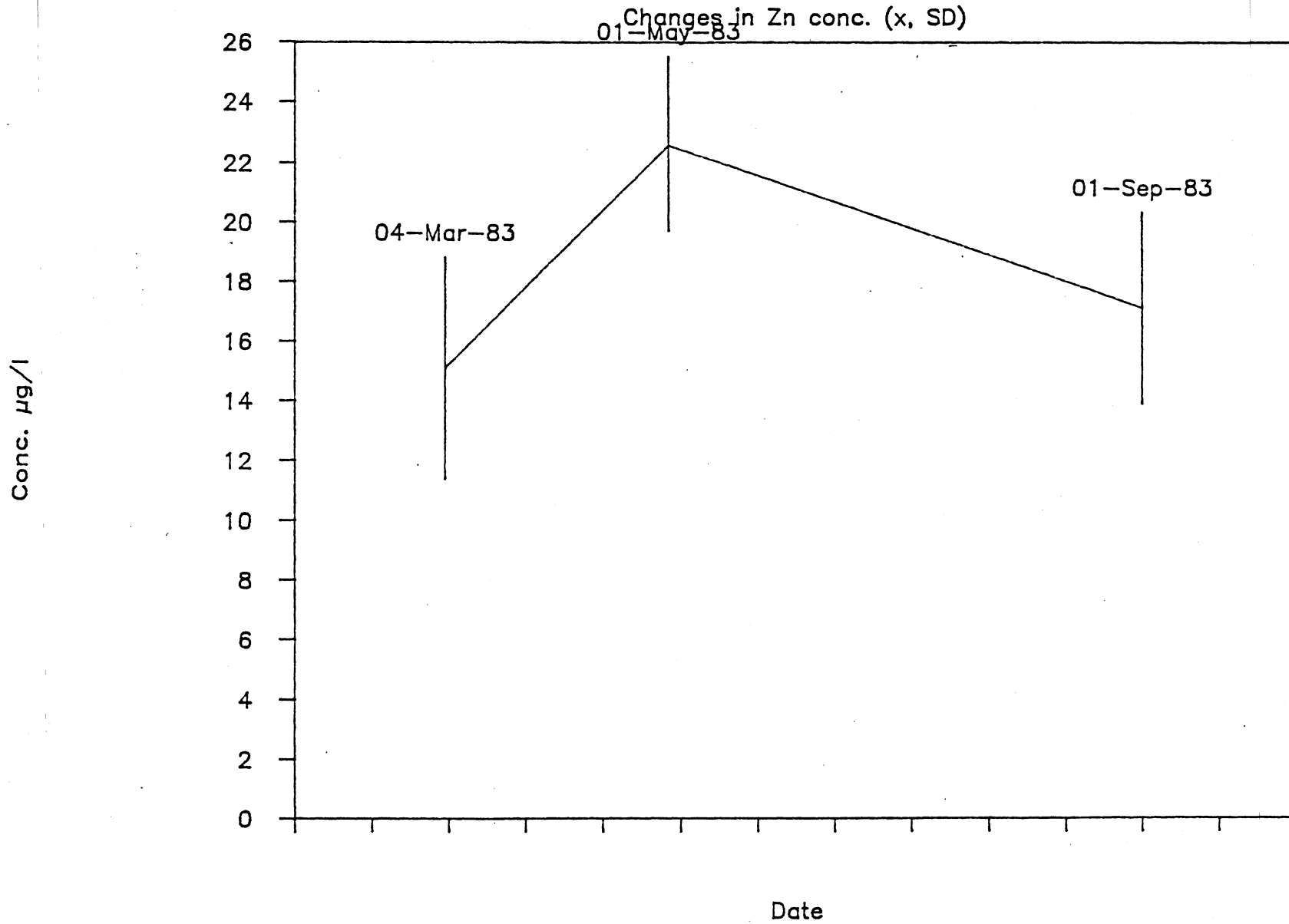


Fig. 9 Snow Melt Affects on Northern Lakes

Changes in Cu conc. (x, SD)

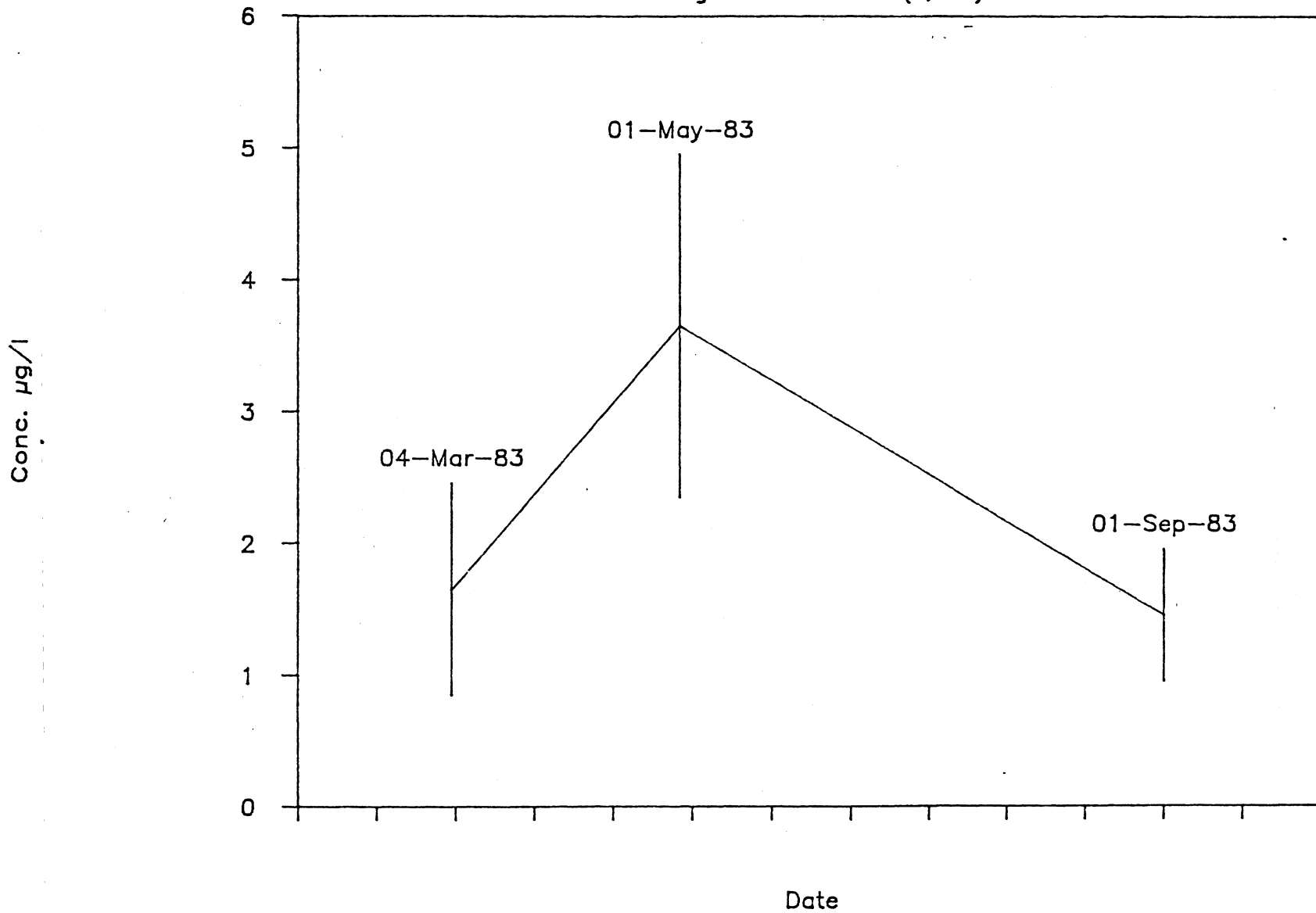


Fig. 10 Snow Melt Affects on Northern Lakes

Changes in Al conc. (x, SD)

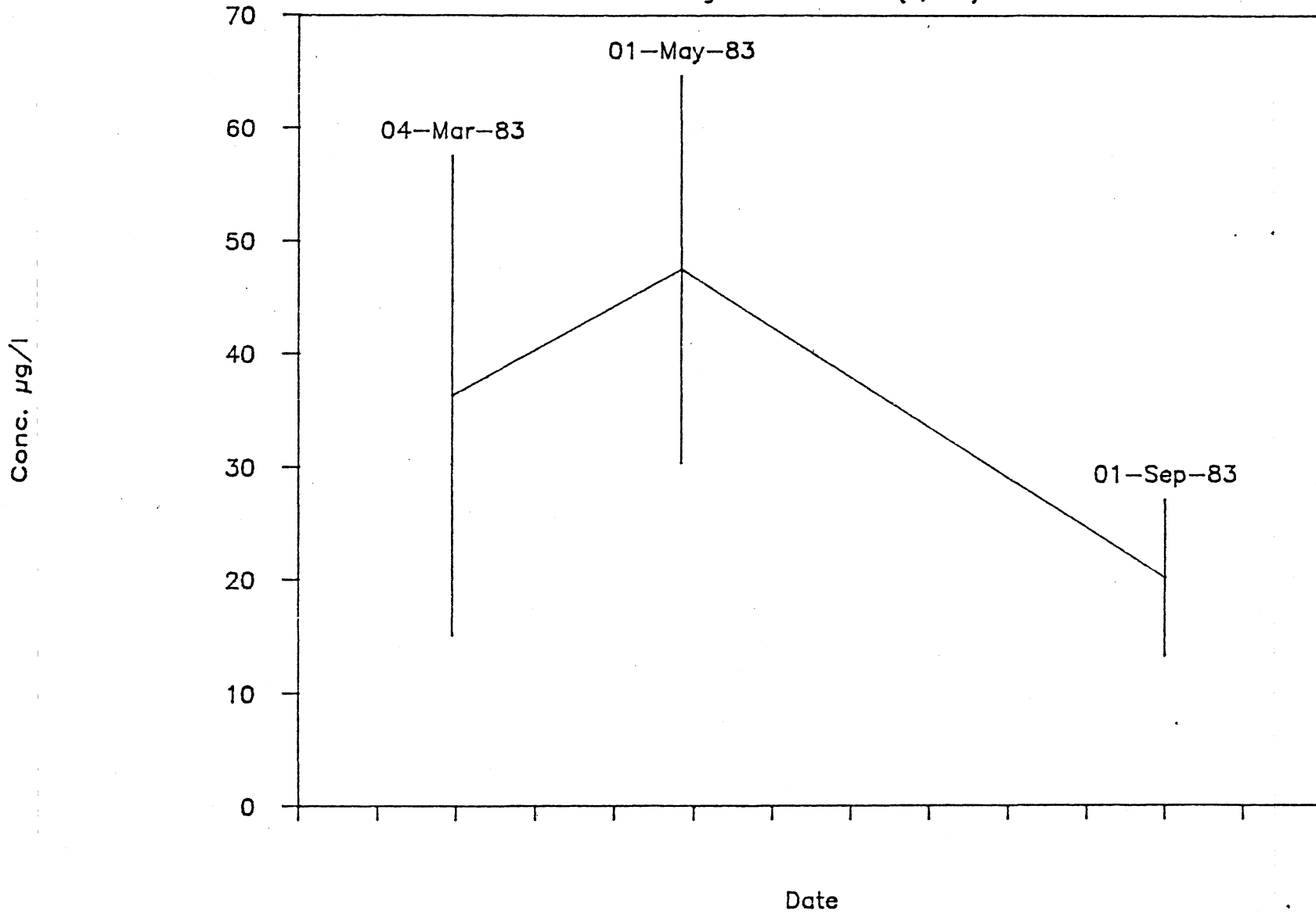
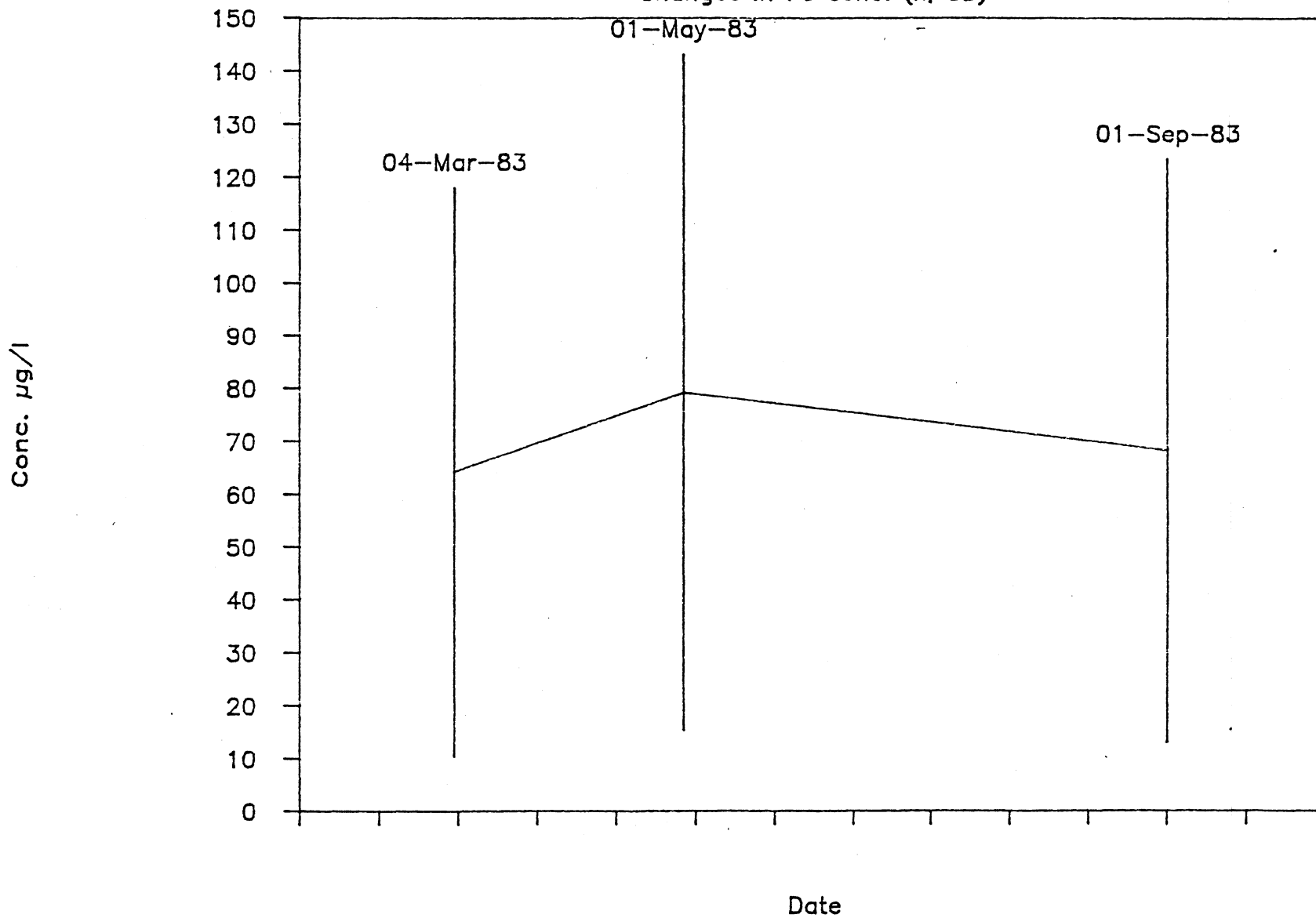


Fig. 11 Snow Melt Affects on Northern Lakes

Changes in Fe conc. (x, SD)



may be transported to lakes.

Another source for the increases in trace metals following snowmelt may be the snow itself. The concentration of copper and zinc within the snowpack surrounding the lakes was several times higher than that found within the lake prior to snowmelt. The concentration of copper and zinc in the lakes following snowmelt correspondingly showed significantly higher concentrations. The concentration of iron within the snowpack was approximately equivalent to the concentrations found within the lakes prior to snowmelt. Following snowmelt, iron concentrations within the lakes showed a slight increase. This suggests that addition to the lake of trace metals through such processes as cation exchange are minimal.

#### University Lake Site

University Lake increased in Cu, Zn, Fe, and Al concentrations following the snowmelt period. Copper concentrations increased from 20.0 ug/l to 41.0 ug/l, Zn from 13.0 ug/l to 21.8 ug/l, Fe from 140.0 ug/l to 165.0 ug/l, and Al from 10.0 ug/l to 40.0 ug/l. Percent increases were 105%, 67.7%, 17.9%, and 300%, respectively. Concentration of copper and zinc were lower in the lake water than in the snow prior to snowmelt. Iron concentrations were higher in the lake than in the snow pack. This indicates that the snow itself may be the source of these increases. Additional increases may be the result

of displacement of base metal ions from the soil/sediment by the hydrogen ions contained in the meltwater (Fisher 1968; Cronan 1979; Henriksen and Wright 1977).

Nickel and cadmium concentrations did not show a significant change throughout the study. Since their values were at or below detection, some changes may have gone unnoticed.

In all cases the concentration of trace metals returned to pre-snowmelt values by late summer. This is probably the result of adsorption and precipitation reactions, along with biological uptake within the lake.

#### CONCLUSION

Trace metals increased in all seven lakes included in this study. There appears to be two major sources of these increases: the displacement of trace metal ions from the soil-sediment by hydrogen ions contained within the percolating meltwater, and the snowpack itself. It is beyond the design of this project to evaluate which of the above factors, as individual events, has the primary role responsible for these increases. Further studies using speciation techniques, separating and measuring the various forms of trace metals present (dissolved, exchangeable, bound to organics, bound to oxides, residual) may indicate their sources and mechanisms of release, and define the portion of these increases available for biological uptake. The importance of measuring the

forms of the trace metals lies in determining whether or not the chemically and biologically active forms and concentrations that make up the total dose are sufficiently comparable when interpreting cause-effect relationships.

Whether the increases are the result of cation exchange or directly from trace metals contained within the snow, there is an increase of trace metals, approaching toxic levels, occurring during the spring thaw in these Wisconsin lakes. Maximum concentrations of aluminum and zinc found in the lakes were 47.5 ug/l, and 22.6 ug/l, respectively. Concentrations of 50.0 ug Al/l have been known to kill brook trout, while 18 ug Zn/l has caused death in the fathead minnow (Benoit and Holcomb 1978, 1979; Brungs, et al 1976; Burton, et al 1972; Mckim, et al 1975; Mount 1973; Benoit 1975). Considering the number of Wisconsin lakes with similar geology and acid loadings, the potential ecological damage is great. Glass (1980) reported that approximately 3/4 of the lakes sampled in northern Minnesota and Wisconsin are potentially susceptible to acid deposition, and estimates 2,600 Wisconsin lakes have little or no alkalinity.

Increases in alkalinity, and hardness are the result of cation exchange between the H ion contained within the percolating meltwater and cations associated with the soil/sediment. This may be indicative of a loss of this area's limited buffering capacity through leaching processes.

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Appendix 1. Comparison Between Field and Laboratory Analysis  
of pH and Alkalinity, (3/4/83).

	pH		alkalinity(mg/l)	
	field	lab.	field	lab.
E. Turtle deep	5.65	5.63	3.38	3.35
E. Turtle shallow	5.71	5.70	2.52	2.52
W. Turtle deep	5.63	5.65	3.53	3.54
W. Turtle shallow	5.74	5.75	2.50	2.50
E. Bass deep	5.97	5.96	2.52	2.52
E. Bass shallow	5.88	5.85	1.90	1.90
W. Bass deep	5.94	5.95	2.50	2.50
W. Bass shallow	5.90	5.90	2.00	2.05
E. Buteau deep	5.36	5.35	1.08	1.06
E. Buteau shallow	5.36	5.36	1.30	1.30
W. Buteau deep	5.40	5.40	1.10	1.11
W. Buteau shallow	5.33	5.35	1.50	1.50
E. Otter deep	5.96	5.98	0.30	0.31
E. Otter shallow	4.93	4.95	0.72	0.72
W. Otter deep	5.65	5.64	0.32	0.32
W. Otter shallow	5.00	5.01	0.72	0.71
E. Clara deep	5.93	5.93	2.34	2.35
E. Clara shallow	5.83	5.84	3.26	3.25
W. Clara deep	5.95	5.93	2.80	2.81
W. Clara shallow	5.88	5.85	3.12	3.12

## APPENDIX 2. Changes in Chemical Variables for the Northern Lakes

Average anion concentrations of lake water for the three sampling periods, northern lakes. (mg/l).

	Ice Covered (March 4, 1983)			Ice Out (May 1, 1983)			Late Summer (Sept. 1, 1983)		
	SO4	Cl	NO2/NO3	SO4	Cl	NO2/NO3	SO4	Cl	NO2/NO3
Turtle	4.97	2.23	0.15	5.06	2.07	<.01	4.92	2.19	<.01
Bass	5.49	4.57	0.10	5.55	4.57	0.05	5.43	4.55	<.01
Buteau	6.10	1.35	0.03	6.17	1.30	0.04	6.04	1.30	<.01
Otter	7.30	1.40	0.42	7.14	1.64	0.04	7.04	0.96	<.01
Clara	4.26	1.42	0.22	4.78	1.61	0.06	4.29	1.41	<.01

Average alkalinity, total hardness, calcium hardness, (mg/l), and pH of lake water for the northern lakes during the three sampling periods.

Ice Covered (March 4, 1983)

	Alkalinity	T. hardness	Ca. hardness	pH
Turtle	2.98	8.68	7.50	5.67
Bass	2.23	9.23	8.00	5.42
Buteau	1.25	10.13	7.88	5.38
Otter	0.51	9.75	7.95	5.38
Clara	2.88	9.89	7.50	5.95

Ice Out (May 1, 1983)

	Alkalinity	T. hardness	Ca. hardness	pH
Turtle	3.04	8.50	7.50	5.66
Bass	3.58	9.00	8.10	6.11
Buteau	1.37	9.50	7.50	5.38
Otter	4.04	11.02	8.52	5.73
Clara	2.68	10.14	10.05	5.78

Late Summer (Sept. 1, 1983)

	Alkalinity	T. hardness	Ca. hardness	pH
Turtle	2.08	11.55	6.75	5.91
Bass	1.75	6.00	5.95	5.53
Buteau	2.00	8.03	4.51	6.12
Otter	5.00	10.51	7.50	6.03
Clara	2.38	9.89	7.90	5.90

Average Trace Metal Concentrations for the Northern  
Lakes During the Three Sampling Periods, ug/l.

Ice Covered (March 4, 1983)

	Copper	Zinc	Nickel	Cadmium	Iron	Aluminum
Turtle	2.0	13.0	1.0	1.0	134.0	20.0
Bass	2.0	13.0	1.0	1.0	31.0	16.0
Buteau	1.0	13.0	1.0	1.0	15.0	9.0
Otter	2.0	22.0	1.0	1.0	122.0	25.0
Clara	2.0	15.0	1.0	1.0	20.0	25.0

Ice Out (May 1, 1983)

	Copper	Zinc	Nickel	Cadmium	Iron	Aluminum
Turtle	5.0	18.0	1.0	1.0	175.0	50.0
Bass	4.0	20.0	1.0	1.0	42.0	30.0
Buteau	2.0	24.0	1.0	1.0	22.0	30.0
Otter	3.0	24.0	1.0	1.0	130.0	73.0
Clara	4.0	25.0	1.0	1.0	26.0	53.0

Late Summer (Sept. 1, 1983)

	Copper	Zinc	Nickel	Cadmium	Iron	Aluminum
Turtle	2.0	14.0	1.0	1.0	144.0	25.0
Bass	2.0	16.0	1.0	1.0	35.0	10.0
Buteau	< 2.0	20.0	1.0	1.0	17.0	20.0
Otter	< 2.0	20.0	1.0	1.0	122.0	20.0
Clara	2.0	14.0	1.0	1.0	22.0	35.0