

**Chemical and Biotic Characteristics of Two
Low-Alkalinity Lakes in Northern Wisconsin:
Relation to Atmospheric Deposition**

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ABSTRACT

In the late 1970s, concern arose regarding the impact of acid deposition on lakes in Wisconsin. Initial research focused on determining the problem extent and on quantifying the resource at risk. Synoptic surveys of water chemistry in north-central Wisconsin documented the presence of many low alkalinity lakes potentially sensitive to acid deposition (Eilers et al. 1983). Furthermore, lake hydrologic type proved to be a key factor in determining lake sensitivity: the low alkalinity systems were predominately seepage lakes. Eilers et al. (1983) hypothesized that sensitive seepage lakes received a majority of their water from direct precipitation—they were dilute, low in acid neutralizing capacity (ANC) and anions were dominated by sulfate. To test this hypothesis and identify the controls on the chemistry of these low alkalinity systems, we initiated hydrologic, chemical, biological and limnological studies at Lakes Clara and Vandercook in 1980. Lake Clara is in northern Lincoln County and Vandercook Lake is in central Vilas County in north-central Wisconsin.

This report summarizes the results of those studies (including previously published hydrologic results) conducted between 1981 and 1983. The major goals are to assess the sensitivity of the study lakes to acid deposition and to identify key processes controlling the acid-base chemistry of these softwater seepage lakes.

The biological species assemblages found in the two lakes were typical of softwater lakes in the region, especially for the zooplankton, macrophytes, and fish—the communities studied most extensively. None of the biological communities studied showed signs of stress due to acidic conditions. Lakewater pH measured during the study period averaged 6.1-6.2. Many biological effects of acidification occur when pH declines below 6.0. Many of the common fish and zooplankton species in the lakes are considered fairly tolerant of low pH. One surprising finding from the fish studies was the high mercury concentration measured in walleyes collected from Lake Clara. They exceeded recommended health standards in 12 of 13 fish tested.

Evaluation of the lakes' chemistry showed both had clear water, with pHs above 6.0, and positive, but low, alkalinity (18 and 36 $\mu\text{eq L}^{-1}$ at Vandercook and Clara, respectively). Sulfate and calcium were the dominant anion and cation, respectively in Vandercook Lake. At Lake Clara, the impact of road salt application to a neighboring highway resulted in Cl^- and Na^+ dominating their respective anion and cation sums in both lakewater and groundwater. Without the ionic contributions from road salt, the major ion chemistry of Lake Clara would have been similar to Vandercook. Based on indices of trophic state, Lakes Clara and Vandercook were classified as unproductive to moderately productive systems (oligo- to mesotrophic).

The concentrations of major ions in groundwater were enriched compared with lake water due to silicate hydrolysis reactions within the soil. Major ion and silica concentrations increased with well depth, due to the greater contact time between water and minerals in the soil. Groundwater from wells located downgradient from the lake generally had lower ionic strength than those located upgradient, due to lakewater recharge into the local aquifer. Groundwater near Lake Clara showed the impact of road salt in the extremely high concentrations of Cl^- and Na^+ .

Bulk deposition collected at the two study lakes and at the nearby Trout Lake National Atmospheric Deposition Program (NADP) site suggested that Lake Clara received higher loadings of mineral acids, most likely due to point sources of SO_2 in the cities of Rhinelander and Tomahawk. Problems with the efficiency of the bulk collectors were related to the monthly collection period, which allowed chemical transformations in such constituents as NO_3^- , NH_4^+ , and SO_4^{2-} . More conservative variables, such as the base cations, showed a close correspondence with NADP wet annual loads and estimated dry deposition.

Lake Clara receives intermittent surface inflow from four inlets constructed to conduct storm water runoff from a nearby highway to the lake. Chemical analysis of inlet water during the spring snowmelt period found it enriched with base cations and Cl^- compared to snow cores collected just before the snowmelt. Corroborating conclusions from other Wisconsin studies, contact between snowmelt waters and exposed soil in spring neutralizes the high mineral acidity of snow, preventing the occurrence of episodic acidification, a phenomenon observed in drainage lakes situated in impervious bedrock (e.g. in the Adirondack region of New York).

Ion enrichment analysis suggested that the ANC of Vandercook Lake was largely controlled by base cation enrichment, primarily related to groundwater inputs. The loss of SO_4^{2-} (supplied primarily from atmospheric sources) from the lake also contributed to ANC production, with SO_4^{2-} reduction and sedimentation the probable key processes. Reactions involving NO_3^- and NH_4^+ were not significant net producers of alkalinity because the H^+ produced by assimilatory/reduction reactions involving NO_3^- was balanced by H^+ uptake during assimilatory processes or oxidation of NH_4^+ . Based on the chemical data and assuming that deposition rates of mineral acids continue their downward trend and that groundwater inputs continue to supply base cations and ANC, there is little reason to suspect these lakes will become more acidic.

The study results support the original hypothesis that softwater seepage lakes in northern Wisconsin have a dilute chemistry and are thus sensitive to atmospheric deposition because their water budgets are dominated by direct precipitation. However, even a small influx of groundwater (< 10%) was sufficient in Vandercook Lake to adequately buffer the mineral acids deposited by precipitation. In seepage lakes with water residence times of about 5 years and low groundwater inflow rates, in-lake processes become a significant source of ANC. Thus, at current or lower rates of mineral acid deposition, seepage lakes with alkalinities as low as 20 $\mu\text{eq L}^{-1}$ may be less sensitive than initially believed and may possess a greater capacity to internally counteract acid additions.

The hydrologic characteristics of seepage lakes which receive localized inputs of groundwater suggest that special care should be taken in siting lake shore developments. Land use alterations in groundwater discharge areas would impact in-lake chemistry more than would development in downgradient groundwater recharge zones. The relatively closed nature of seepage lakes with hydrologic inputs dominated by direct precipitation suggests they are suitable sites to study the biological uptake of mercury and other atmospheric contaminants that accumulate in aquatic organisms.

Chemical and Biotic Characteristics of Two Low-Alkalinity Lakes in Northern Wisconsin: Relation to Atmospheric Deposition

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INTRODUCTION

The Upper Midwest states of Minnesota, Wisconsin and Michigan contain tens of thousands of glacially-formed lakes, comprising one of North America's most significant lake districts. For example, more than 3,000 lakes occur in just three north-central Wisconsin counties: Vilas, Oneida, and Lincoln (Lillie and Mason 1983). These lakes, major attractions for a growing tourist industry, provide a variety of recreational benefits of major economic importance to the area.

Water quality surveys in north-central Wisconsin, from the pioneering studies of E.A. Birge and C. Juday between 1920 and 1940 (Frey 1963) to the present, have consistently shown that many of the area's lakes have low productivity and low ionic content (Eilers et al. 1983; Nichols and Verry 1985; Linthurst et al. 1986; Schnoor et al. 1986; Cook et al. 1987). Many northern Wisconsin lakes have low acid neutralizing capacity (ANC) and are thus vulnerable to acidification from atmospheric deposition. The National Surface Water Survey showed that lakes in north-central Wisconsin had lower median ANC than lakes in most regions surveyed in the eastern United States, including the Adirondacks and New England (Linthurst et al. 1986). About 8.7% of the lakes in north-central Wisconsin were acidic (defined as having $ANC \leq 0$), and 43% had $ANC \leq 40 \mu\text{eq L}^{-1}$ and were considered potentially sensitive to acidification (Eilers 1990).

Low-ANC lakes in north-central Wisconsin have several features in common. Most are seepage lakes, lacking inflowing and outflowing streams (Eilers et al. 1983). These glacially formed lakes are located well above Precambrian granitic bedrock, in the pitted outwash and morainal drift deposited during the Wisconsin glaciation, 25,000 to 12,500 years ago. Glacial material in the region is generally low in carbonates, accounting, in part, for the low concentrations of base cations (e.g. calcium and magnesium) in many of the region's lakes.

The acid-base chemistry of lakes in northern Wisconsin can further be differentiated by hydrologic type. This relationship between hydrologic type and lake chemistry was first discussed by Juday and Birge (1933) and Juday and Meloche (1944). Eilers et al. (1983), in a survey of 275 lakes in the region, identified hydrologic type as a key factor determining lake ANC and thus sensitivity to acidification. They hypothesized that because seepage lakes, which lack surface water inflows and outflows, receive a majority of their hydrologic inputs from direct precipitation, their chemistry was more vulnerable to alteration by anthropogenic pollutants in deposition. In contrast, drainage lakes receive a higher proportion of their hydrologic input from inflows of surface water and groundwater, both of which are relatively ANC-rich compared to precipitation.

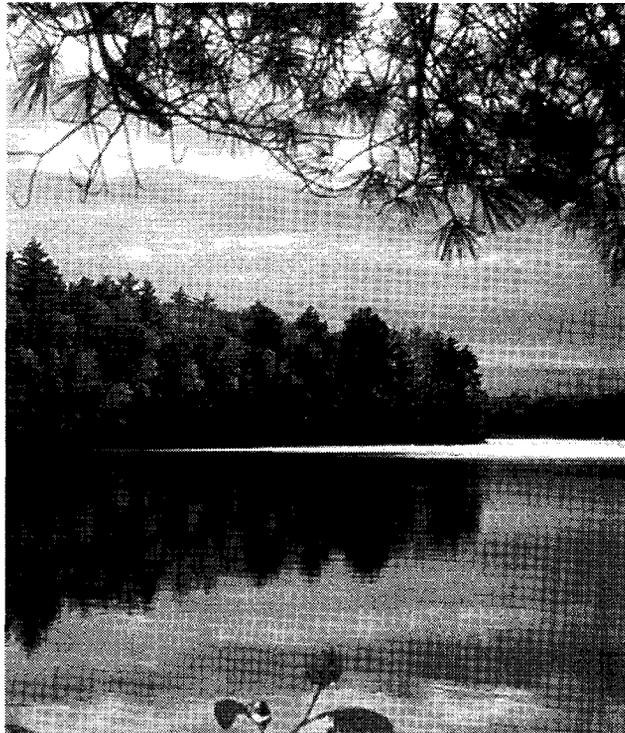


PHOTO: K.E. WEBSTER

Vandercook Lake

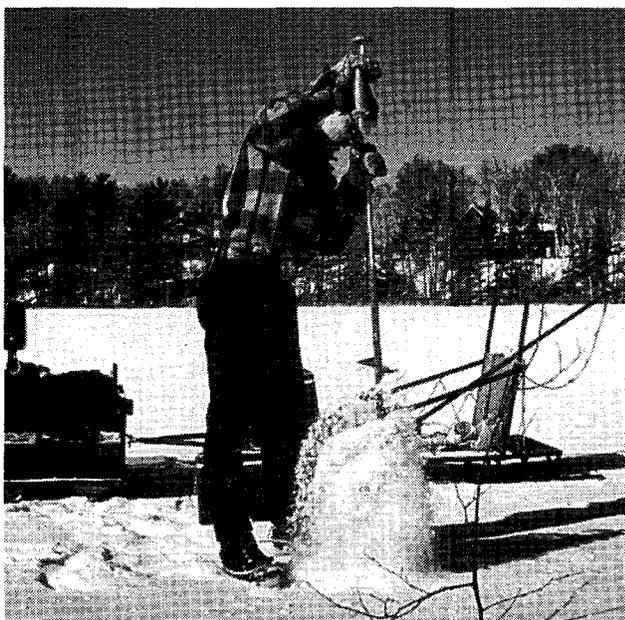
The Lakes Clara and Vandercook project was initiated in 1980 to evaluate the role of hydrology in determining the acid neutralizing capacity (ANC) of softwater seepage lakes in Wisconsin and their resultant sensitivity to acidification. The study, a cooperative effort between the Wisconsin Department of Natural Resources (DNR), the U.S. Geological Survey (USGS), and the U.S. Environmental Protection Agency (USEPA), focused on data collection in three main areas—water chemistry, hydrology, and biology. At the time the study was conducted, there was little information available on the hydrologic characteristics of softwater seepage lakes. The hydrologic results published by Wentz and Rose (1987, 1991) and Wentz et al. (in review) support our hypothesis that hydrology is a key factor determining the acid base status of these seepage lakes.

In this report we focus on the chemical, biological and limnological characterization of Lakes Clara and Vandercook and include results from a separate U.S. Fish and Wildlife Service (USFWS) study on mercury concentrations in the walleye of Lake Clara. These data set a valuable baseline for future investigations not limited to the acid deposition issue. The results are discussed in the context of the published hydrologic information to address the following questions:

1. Is there evidence that the two lakes are currently acid stressed and what is the potential for future acidification?
2. In addition to hydrology, what are the key processes controlling the ANC and acid-base chemistry of these softwater seepage lakes?

SITE DESCRIPTION

The two study sites were selected from the 275 lakes in the Upper Wisconsin River Basin sampled by Eilers et al. (1983) in a random survey of lakes larger than 8 ha in surface area. The study sites were selected using the following criteria, listed in order of decreasing importance: (1) ANC in the range of 10-40 $\mu\text{eq L}^{-1}$; (2) relatively simple lake-perimeter shape; (3) absence of adjacent lakes that might strongly influence the hydrologic regime; and (4) accessibility of the entire watershed for installing and



DNR field assistant Stuart Schueler drilling a hole in the ice at Lake Clara to collect water samples.



DNR field assistants Nan Eckert and Lisa Huberty determining water table depths in a groundwater piezometer at Lake Clara.

maintaining instruments. Although it was desirable to have minimal anthropogenic disturbance in the watershed, this factor was weighed against the need for easy access and the other criteria.

The ANC selection criterion was based on the perceived sensitivity to acidification; a low-ANC lake would best represent those lakes most sensitive to acidification. Later publications supported our ANC criterion. Based on a simple titration model, Galloway et al. (1984) predicted that lakes with an ANC between 10 and 40 $\mu\text{eq L}^{-1}$ should show the largest change in pH per unit change in ANC and thus, their acid-base chemistry would respond more quickly to changes in acid loading. Garrison et al. (1987) proposed an ANC of 40 $\mu\text{eq L}^{-1}$ as the upper limit for extreme sensitivity for lakes in Wisconsin. The ANC range of 10-40 $\mu\text{eq L}^{-1}$ represented about 20% of the lakes in the study area (Eilers et al. 1983; Linthurst et al. 1986).

After the ANC criterion was satisfied, we identified watersheds and lakes that provided few complications for measuring hydrologic inputs and outputs. The uncertainties associated with measuring hydrologic budgets are large, especially for estimates of ground-water inflow, which has often been calculated as the difference between other inputs and outputs (Winter 1978). Consequently, we selected lakes that appeared to have simplified groundwater flow patterns based on lake basin shape, proximity to other lakes, and watershed topography.

The requirement for ready access to the entire watershed precluded satisfying our criterion of minimal anthropogenic disturbance. Thus, both study watersheds had some land use development as do most of the lakes in north-central Wisconsin. Indeed, we selected Lake Clara, which was known to receive de-icing salt (NaCl and CaCl_2) in runoff from a nearby road, with the expectation that the resulting chloride inputs could be used as a tracer of surface water contributions (e.g., Hemond 1980; Kilham 1982).

Both Lake Clara and Vandercook Lake (Fig. 1) are located in the Northern Highland region of the Upper Wisconsin River Basin (Oakes and Cotter 1975). The local topography is characterized by gently rolling hills of relatively low relief, which rarely exceeds 50 m (Attig 1985). The Northern Highland region is underlain by Precambrian crystalline bedrock, a southern extension of the Canadian Shield. This bedrock material is relatively impervious to erosion and consists mainly of granite and gneiss, gabbro, diorite, basalt, quartzite, sandstone, shale, and associated metamorphic rocks (Hole 1976). Bedrock outcroppings in northern Wisconsin are rare (Attig 1985), and thickness of drift ranges from zero m to 70 m (Oakes and Cotter 1975). With seismic refraction, Okwueze (1983) estimated the thickness of glacial material at Vandercook Lake to be 50-55 m. The drift is about 30 m thick in the Lake Clara watershed (Oakes and Cotter 1975).

Glacial material was deposited in the Northern Highland during the Pleistocene Epoch. Many of the present

land features resulted from the fourth and final advance of the Woodfordian glacier during the Wisconsin glaciation (Hadley 1976). Lakes Clara and Vandercook lie in the Wisconsin Valley Lobe of this glacier, which covered the area between 25,000 and 12,500 years ago (Attig 1985). The drift deposits are mostly noncalcareous sand and gravel outwash; carbonate deposits are rare (Broughton 1941; Attig 1985). Vandercook Lake is located just south of the Muskellunge end moraine in stream-deposited sand and gravel (Attig 1985). Lake Clara lies in the southern part of the Wisconsin Valley Lobe in outwash deposits of sorted and stratified material, chiefly sand and gravel (Hadley 1976).

Soils are generally thin, sandy and acidic with high hydraulic conductivities. The dominant soil types in the two watersheds (Append. A.1), such as the Padus sandy loam and Vilas loamy sand, have low organic content (<5%), low cation exchange capacity (10-15 meq 100g⁻¹ or less), moderate base saturation (around 50%), and low pH (4.5-5.0) (Hole 1976). Peat deposits having high organic content (50%) and cation exchange capacity (200 meq 100g⁻¹), but low pH (3.5), occur in small bogs within each watershed.

Climate in the region is characterized as humid continental with cool summers. Mean July and January temperatures are 19 and -11°C, respectively (Burley 1964). Precipitation averages near 80 cm yr⁻¹ with mean evaporation of 50 cm yr⁻¹ (Oakes and Cotter 1975). A majority of precipitation falls during the summer, with June the wettest month, while winter is generally the driest season (Finley 1975). Roughly 20-25% of the annual precipitation falls as snow, which averages 150 cm yr⁻¹ at Lake Clara and 200 cm yr⁻¹ at Vandercook Lake (Hole 1976). Due to the early onset of snowfall in November and the insulating effect of the snowpack, forest soils in northern Wisconsin seldom freeze deeper than a few centimeters and much of the spring snowmelt (late March to early April) percolates into the sandy soils (Bockheim et al. 1988). The lakes are ice-covered from mid-November until mid-April with ice thickness reaching ~45 cm. A National Atmospheric Deposition Program (NADP) monitoring site has been operating since 1980 at Trout Lake, 5 km from Vandercook Lake (Fig. 1), providing weekly data on the chemistry of wet deposition. Annual wet deposition of sulfate and nitrate between 1981 and 1982 averaged 310 and 170 eq ha⁻¹, respectively; mean volume-weighted pH was 4.7 (Glass and Loucks 1986).

Vegetation in the Northern Highlands was dominated by white pine, hemlock, and mixed hardwoods until about 1900 when extensive logging cleared most of the area. Regrowth consists of aspen, birch, mixed hardwoods, and some conifers (Curtis 1959). In the Vandercook Lake watershed, the dominant white pine is interspersed with aspen, birch, and mixed hardwoods (Append. A.2). The extreme northeastern portion of the watershed, about 200 m from the lakeshore, was clear-cut in 1980 along

with other small plots comprising <1 ha of the total 250 ha watershed. Thirty-six dwellings are along the southern shoreline. Only a few are used as year-round residences, the rest are primarily seasonal cottages. The northern half of the watershed is within the boundaries of the state forest and is undeveloped except for a few unpaved roads.

In the Lake Clara watershed, land use is primarily mixed hardwoods and red pine plantation, with some agricultural activity on the western margin of the watershed (Append. A.2; Table 1). Lake Clara is bordered by seven permanent residences, two summer cottages, and a paved road (county highway A) along the north-west shore.

The two lakes have similar topographic watershed characteristics with relatively small lake and watershed areas (Table 1; Append. A.3). Topographic watershed areas generally do not accurately reflect groundwater contributing areas for these small seepage lakes (Garrison

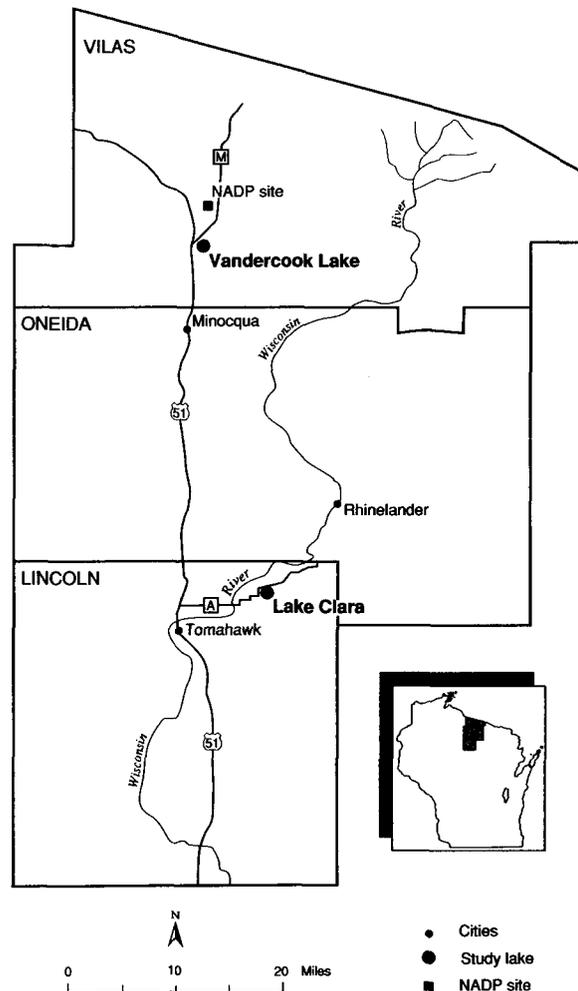


Figure 1. Location of Lake Clara and Vandercook Lake.

et al. 1987). The major morphometric difference between the two lakes is in maximum depth. Lake Clara at 11.3 m is nearly 5 m deeper than Vandercook. Thus, Lake Clara is dimictic, whereas Vandercook Lake rarely stratifies. The second major distinguishing feature relates to surface drainage. Due to the lack of inflowing and outflowing streams, Vandercook Lake is classified as a seepage lake. In contrast, Lake Clara receives some channelized runoff, primarily during spring snowmelt and major precipitation events, through three culverts under county

highway A (northwest edge of the lake) and a fourth culvert at its northeast corner. Even though Lake Clara is classified as a drained lake following the definition in Eilers et al. (1983), surface discharge was intermittent and contributions from surface water inflow were minimal and generally restricted to a short time period in the spring. The relatively low contribution of surface inflows and the low-ANC status suggest that Lake Clara is hydrologically more similar to low ANC seepage lakes than to drainage lakes in the region.

Table 1. *Physical features of the study lakes.*

Parameter	Lake Clara	Vandercook Lake
Location		
County	Lincoln	Vilas
Town-Range-Section	35N-07E-14	41N-06E-36
Latitude	45-30'44"N	45-58'55"N
Longitude	89-34'15"W	89-41'13"W
Site elevation (m above sea level)	462	496
Morphometry		
Lake area (ha)	32	40
Shoreline length (km)	3.5	3.2
Maximum depth (m)	11.3	6.7
Mean depth (m)	4.6	3.5
Volume (m ³ /10 ⁶)	1.58	1.94
Contributing topographic watershed area) (ha)*	88	250
Land use		
% Upland coniferous	17	24
% Upland deciduous	28	40
% Open bog	1	1
% Swamp conifer	7	0
% Agriculture	12	0
% Old field/pasture	6	0
% Cultural (dwellings, roads, etc.)	4	5
% Lake water	25	30
Number of shoreline dwellings	9	36
Surficial geology	Pitted outwash	End moraine
Depth to bedrock (m)	30	53
Dominant soil types	Vilas loamy sand Greenwood and Dawson peat Rubicon sand	Padus sandy loam Pence sandy loam

* Excludes lake area.

METHODS

Biological Sampling

Phytoplankton Collection and Enumeration

Between December 1982 and July 1983, 1-L samples for phytoplankton analysis were collected at 1 m depth with a Kemmerer¹ bottle and preserved with merthiolate (APHA 1975). Prior to counting, algal cells were concentrated during two consecutive 48 hour periods. After the first settling period in a 1-L graduated cylinder (height 34.5 cm), the top 900 ml of water was siphoned off and the remaining concentrate transferred to a 100 ml graduated cylinder (height 18.7 cm). A final concentrate of 5.0 or 10.0 ml, depending on phytoplankton abundance, was transferred to a culture tube for storage. For identification and counting, 0.1 ml of well-mixed concentrate was placed in a Palmer counting chamber and covered with a #1 coverslip. At least 20 fields were counted at a magnification of 450X with an American Optical-Fifty¹ microscope. Two chambers were counted from each sample. Phytoplankton identifications were based on keys by Prescott (1962, 1970). We defined ultraplankton as unidentified phytoplankton cells less than 7 μ in diameter. Wetzel (1983) gives a size range of 0.5 to 10 μ for ultraplankton.

Macrophyte Surveys

Macrophyte surveys were conducted in August 1982 using the method in Jessen and Lound (1962). Sampling stations, stratified by depth, were established using a grid overlaid on bathymetric maps (Fig. 2). Littoral sites in Lakes Clara and Vandercook were selected from the 0-4 m and the 0-3 m depth intervals, respectively. SCUBA divers recorded the occurrence of each macrophyte species within the four quadrants of a 1.8 m diameter circle. A relative density rating of 0-4 was assigned based on the number of quadrants in which the species was present. A relative density rating of 5 was assigned if a species was densely distributed throughout all four quadrants. The distribution and location of monotypic stands of emergent and floating-leaved macrophytes were mapped in the littoral zones of both lakes. At deeper sites, macrophytes were collected with an Ekman dredge. Water depth and sediment texture (e.g. organic, sand) were noted at all sites. Specimens were collected and pressed for later identification and to prepare a reference collection. Macrophyte taxonomy was determined using keys by Fassett (1957) and Voss (1967).

Zooplankton Collection and Enumeration

Zooplankton were collected concurrent with water chemistry sampling using a 20 cm diameter, 153 μ mesh conical tow net. At each of the three lake water quality sampling sites (see Fig. 2), three vertical tows (from 1 m above the bottom to the surface) were pooled and

preserved in 5% formalin buffered with Borax. After March 1982, when we discontinued routine water quality sampling at the two secondary lake stations, zooplankton samples were collected only at the primary lake station. (Lake stations are described later in this section.)

Cladocera and Copepoda species were counted in 1.0 ml Sedgwick-Rafter cells. For samples collected between March 1981 and July 1982, counts were made until 100 individuals were tallied or three 1.0 ml subsamples were analyzed. For the remaining samples, three 1.0 ml subsamples were counted. Because immature stages of copepods are difficult to speciate, we classified copepodites to order (Calanoida or Cyclopoida) and did not separate nauplii. Rotifers were identified and counted in three 1-drop subsamples (0.08 ml per drop) until 100 individuals were tallied or until 30 drops were analyzed. As the vertical tow net mesh size was too large to quantitatively collect most rotifers, no counts were made on this group after July 1982 and only a species list is presented. The counting efficiency and taxonomic classifications were verified by Torke of Ball State University for 10 samples which were also split between the two institutions responsible for the zooplankton analysis.

Benthic Macroinvertebrate Survey

Qualitative surveys of benthic macroinvertebrates were made at Lakes Clara and Vandercook on June 23, 1983. Using an Ekman dredge, sediments were collected at depths of 1, 3, and 7 meters at Vandercook along a transect from station 1 (Fig. 2) west to shore. Lake Clara samples were collected at 1 m and 10 m from station 1 to the west shore, as well as within the southwestern lobe (near station 4; Fig. 2). Contents of the grabs were washed in a 0.5 mm mesh screen-bottomed bucket to remove fine particles and preserved in 70% ethanol. Individuals were identified to family. Additional taxa were collected by visually surveying much of the perimeter of both lakes and netting with a sweep net in littoral areas.

Fishery Assessment

Early Surveys and Fish Stocking Records

Records of fish populations and fish stocking in Lakes Clara and Vandercook were retrieved from files of the Wisconsin Department of Natural Resources in Antigo, Rhinelander, and Woodruff. The Department had conducted two surveys in Lake Clara (July 1953 and June 1969) and one in Vandercook (June 1951). Each of these surveys used a single type of sampling gear (Append. C.2).

¹Reference to trade names does not imply government endorsement of commercial products.

These records are presented as a base for comparing more recent survey results. An index of common and scientific names is given in Appendix C.1.

Recent Surveys

A fishery survey, employing four sampling gears (Append. C.2), was conducted on Lake Clara in August 1980 by the U.S. Fish and Wildlife Service (Wiener 1983). Minnow traps were placed near fyke nets. All fish were measured (total length) to the nearest millimeter. About 50 fish of each species, or the total number caught if less than 50, were weighed to the nearest 0.1 gram. Additional sampling with fyke nets (Append. C.2) was done by the Fish and Wildlife Service in June 1981 to obtain bluegills for serum calcium analyses (Wiener et al. 1985). No quantitative data on other species were collected during the June 1981 sampling, but their presence in the catch was recorded (Wiener 1983).

Vandercook Lake fish were surveyed during summer 1981 by J. Lyons (University of Wisconsin-Madison, Trout Lake Research Station). Three gears—bag seine, trammel net, and fyke net—were used (Append. C.2). All adult fish were measured (total length) and many were weighed. Many young-of-the-year fishes were collected in seines. All young-of-the-year were enumerated but only a sub-sample of the catch of each species was measured.

Length-weight data for fish are not summarized here. However, these data as well as documentation of sampling sites have been archived by the Wisconsin Department of Natural Resources, Bureau of Research, in Madison.

Analysis of Mercury in Fish

We analyzed 13 walleyes from Lake Clara for total mercury—12 collected on 5-6 August 1980, and 1 collected on 29 June 1982. The fish were held in polyethylene bags on ice until frozen (within 12 hours after capture) and stored at -4C. Each fish was later thawed, weighed and measured (total length). Scales were taken for age determinations, and scale impressions were examined under magnification on a scale reader. The age assigned to each fish was equal to the total number of completed scale annuli, according to criteria described by Tesch (1971). Skinless axial muscle samples were dissected from the area lateral and ventral to the dorsal fin of each fish with stainless steel implements on an acid-washed, polyethylene work surface. Polyethylene gloves were worn during dissection. Muscle tissue samples were placed in acid-washed polyethylene vials and stored at -4C until digestion.

Fish samples were individually acid-digested and analyzed for total mercury by cold vapor atomic absorption spectrophotometry. Samples collected in 1980 were digested and analyzed at the National Fisheries Contaminant Research Center, Columbia, Mo., by methods described by Wiener (1983). The fish collected in 1982 was digested and analyzed at the State Laboratory of Hygiene, Madison, by methods described by Sullivan and Delfino (1982). Sample preparation and analytical procedures for mercury were verified by analyses of spiked fish samples, replicate fish samples, procedural blanks, and U.S. National Bureau of Standards reference materials (Wiener 1983).

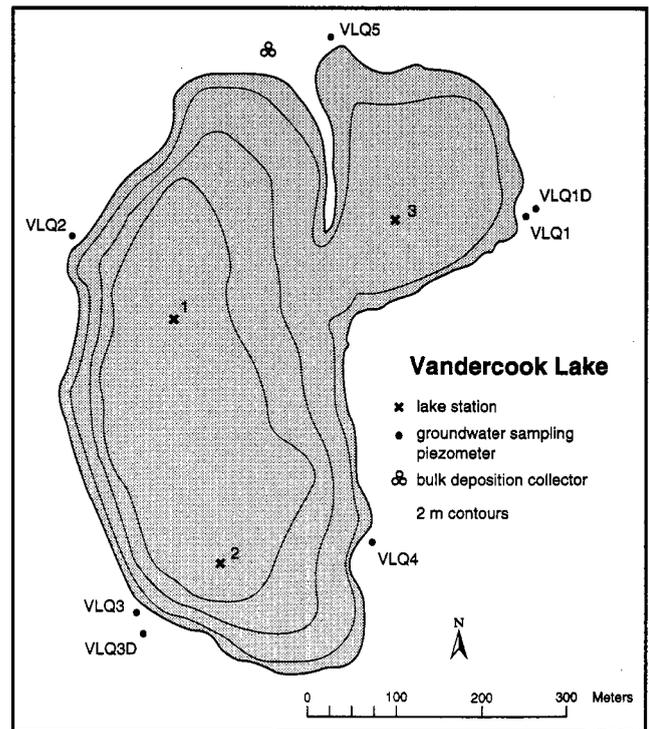
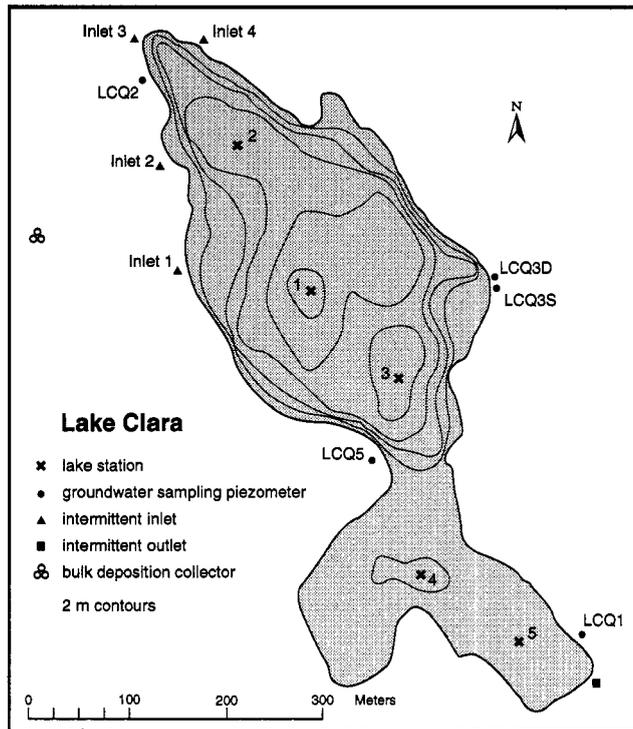


Figure 2. Location of lake and groundwater sampling stations and bulk-deposition collectors at Lake Clara and Vandercook Lake; also shown are inlets and outlets to Lake Clara.

Water Chemistry

Lake sampling

Lake sampling station locations are shown in Figure 2. The primary stations (1), located near the deepest point of each lake basin, were monitored on a monthly basis with bi-weekly visits during the summers of 1981 and 1982. Intervals between trips often extended to 6-8 weeks during the winter. Two secondary stations (2 and 3) were sampled until June 1982 to evaluate within-lake variability. Occasionally, water quality samples were collected from sites in the southernmost lobe of Lake Clara (stations 4 and 5).

Field observations included water column profile measurements of conductance, temperature (YSI model 33 S-C-T meter) and dissolved oxygen (DO) (YSI model 54 meter) at 1 m (primary stations) or 2 m (secondary stations) intervals below lake surface. In addition, we determined Secchi disk transparency (20-cm black and white disk), surface-water and air temperature, and recorded descriptions of weather and lake conditions.

Lake samples were collected with a 3.2-L acrylic Kemmerer sampling bottle (Wildco model 1540-C25) at 1 m depth and at either mid-depth (if isothermal) or 1 m above the bottom (if thermally stratified). The water column was considered stratified if there was at least a 1C change in temperature in a 1 m interval and a minimum 3C difference between surface and bottom temperatures. The 1-L linear polyethylene Nalgene sample bottles were rinsed twice with deionized water and twice with site water before collecting the sample. Additional site water from primary lake stations was transported to shore in 8-L polyethylene containers for filtration.

Twenty-four hour surveys of lake pH were conducted at Vandercook Lake on 29-30 July 1981 and at Lake Clara on 1-2 August 1993. Water samples were collected at 1 m depth with a Kemmerer sampling bottle and returned to the lake shore where they were analyzed using an Orion pH meter (model 407a) and a combination glass electrode.

Groundwater Sampling

Five piezometers for groundwater sampling were installed around each lake (Fig. 2). These were constructed of 38-mm PVC pipe and finished just below the water table. Two nested piezometers at Lake Clara, LCQ3S and LCQ3D, were finished at the water table and 6.7 m below the water table, respectively. Water samples were collected monthly, generally in conjunction with lake sampling. Two deep wells (VLQ1D and VLQ3D), finished at 22 meters below the water table at Vandercook Lake, were occasionally sampled for chemical analysis.

Three sampling devices for groundwater were used over the course of the study: a 2.3-cm diameter PVC bailer (Jun-Jul 1981), a Black and Decker Jack Rabbit (R) plastic hand pump with 4-mm silicon tubing (Sep 1981-Feb 1982), and a Masterflex peristaltic pump (Horizon Ecology model 7573-80) with 4-mm silicon tubing (Aug

1981, Mar 1982, and thereafter). In all cases, more than one volume of standing water was removed before sample collection proceeded. The calculated removal volumes were verified in July 1981 by monitoring temperature and conductance of groundwater during the bailing/pumping process (K.E. Webster, unpublished data). In all wells tested, groundwater temperature and conductance stabilized before samples were collected, indicating standing water had been removed. Water samples were stored in 8-L polyethylene jugs until processed.

Runoff Monitoring

Water samples were collected from four channelized inlets at Lake Clara (Fig. 3) during peak flows, usually during the spring snowmelt period or following a major precipitation event. The two intense sampling periods fell during March and April of 1982 and 1983 when major thaws melted much of the accumulated snowpack. Samples were collected manually or with a peristaltic pump at points upstream of the three culverts channelizing flow under county trunk highway A (CTH-A) toward the lake. A fourth inlet flowed under a driveway at the northeast corner of the lake. Most of the runoff samples were collected at inlet 1 where a Parshall flume and stage recorder provided the best estimates of flow rates. Flow at inlets 2-4 was more diffuse and thus water samples were

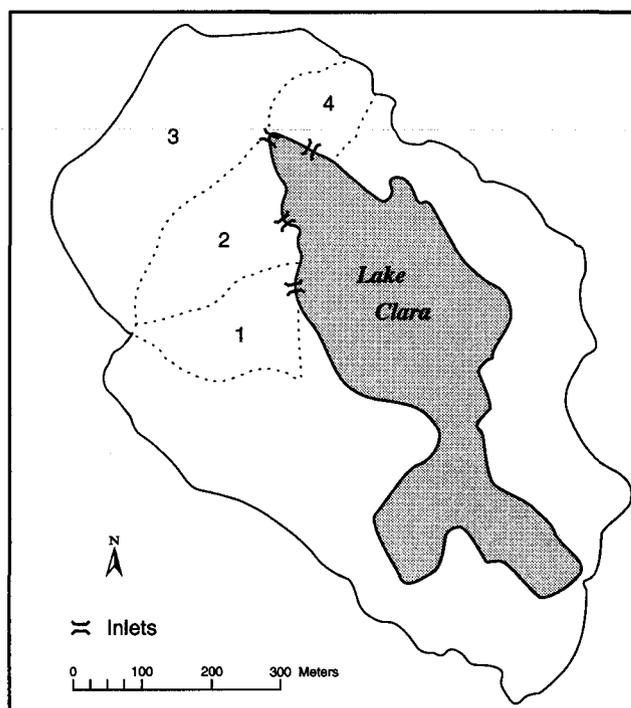


Figure 3. Surface water contributing areas (outlined in ...) of 4 channelized inlets into Lake Clara. The solid outer boundary represents the entire topographic contributing watershed.

collected at a lower frequency. At these two inlets flow rates were estimated manually by measuring the volume of stream flow collected within a known time interval.

We concentrated our water quality sampling efforts at inlet 1 where continuous flow rates were available from spring snowmelt until late fall. The sampling location was established upstream of the recording V-notch weir. Water was collected either with a peristaltic pump or as a manual grab sample. Culverts at inlets 2, 3 and 4 were often blocked with snow and ice making flow measurements and sample collection difficult. When flow rates were sufficient, water samples were collected at the outlet of Lake Clara in conjunction with the routine lake monitoring.

Bulk Deposition

Bulk deposition was collected at one station within the watershed of each lake (Fig. 2). The bulk deposition collector consisted of three metal tubes 1.5 m high and 0.25 m in diameter placed adjacent to each other on a wooden platform. A wind shield surrounded the three tubes near the top. Plastic poly-bags, 1.65 m long, 0.25 m in diameter, and 0.001-mm gage were set in each tube and retrieved at the end of the month. During the snow-free period, fiberglass screening was clamped over the top of each tube to prevent insects and large debris from contaminating the samples.

Bulk deposition was collected on a monthly basis. All bags were shipped to the EPA Environmental Research Laboratory-Duluth, MN (ERL-D), where precipitation volume was determined and a composite made using aliquots from each of the three bags. Only samples with minimal leakage and lacking contamination by large particles were included in the final composite.

Snow Samples

Ten snow courses were established in a variety of cover types (open, coniferous, deciduous, and mixed) throughout the watersheds of the two lakes and sampled in early



PHOTO: K.E. WEBSTER

Co-author Joe Eilers changing collection bags at the bulk deposition collector at Lake Clara.

March 1982. Each course consisted of two perpendicular 150-m lines set along north-south and east-west axes. Ten sampling sites were located along each line at 15-m intervals. At each site, snow depth was recorded and a snow core was collected with a 6.5-cm diameter plexiglas tube; cores from all 20 sites per snow course were pooled in the same type of plastic bags used to collect bulk deposition.

Water Sample Processing

In addition to the unfiltered samples collected from the lake, inlets, outlets, and bulk deposition, we prepared filtered samples from the groundwater piezometers and the primary lake sampling stations on site as soon as possible after collection. Samples were filtered through a 0.45 μm Millipore membrane filter into a 1-L bottle pre-rinsed with de-ionized water (DIW). The filtration apparatus consisted of a 142-mm backwash attached with silicon tubing to a Geofilter Series 1 Peristaltic Pump equipped with a Masterflex 7015 pumphead. Water samples were kept on ice in coolers and shipped the night of collection to ERL-D. Snow samples and bulk deposition samples were shipped intact to ERL-D where they were kept frozen until fall 1982 when they were processed. Aliquots for chemical analysis were prepared at ERL-D as follows:

1. metals: acidified to pH of ~ 1 with HNO_3
2. anions: filtered through 0.45 μm Millipore membrane filters and frozen
3. nutrients: chilled

Based on ANOVA (SAS 1985), we detected no significant difference in Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , and Cl^- concentrations between field-filtered and unfiltered samples. There was a significant, but small (i.e. $< 3 \mu\text{eq L}^{-1}$) difference for NO_3^- . As a result, we present data only for samples which were not field-filtered.

Laboratory Analyses

ANC (Gran alkalinity titration), pH, true color, turbidity, and conductance were analyzed by ERL-D within 48 hours of sample collection (analytical methods appear in Append. D.1). Anion concentrations were determined at ERL-D and the USEPA Region X Laboratory at Manchester, WA, by ion chromatograph (Dionex model 12). Metals (defined as total acid exchangeable) were analyzed at the EPA Environmental Research Laboratory at Corvallis, OR, by atomic absorption (Perkin Elmer model 5000) and inductively coupled plasma emission spectrometry (Bausch and Lomb model QA-137). Nutrients were analyzed by the US Fish and Wildlife Service laboratory in Winton, MN.

Analyses for chlorophyll *a* were performed on ten samples collected between April 1981 and October 1982. Lake water was collected at 1 m depth with a Kemmerer sampling bottle, filtered through a glass fiber filter, and frozen until analysis (APHA 1980). A 50:50 mixture of dimethyl sulfoxide and 90% acetone was used to extract the pigments (Shoaf and Lium 1976). Reported values were corrected for phaeophytin (Lorenzen 1967).

Quality Control

The chemistry database was checked for outliers and systematic errors in measurement or manipulation through examination of charge balance, comparison of measured versus calculated conductance, and visual inspection of interparameter plots. Incomplete analyses where cation or anion values were missing made it difficult to completely verify the database. Outliers were flagged and eliminated from further analysis. Changes in analytical detection limits over the course of the study resulted in many flagged values for Mg^{2+} in Vandercook Lake; a large portion of the record is reported as $< 0.50 \text{ mg L}^{-1}$ ($41.1 \mu\text{eq L}^{-1}$).

Precision and accuracy data for the water quality variables in the database are summarized in Appendix D.2.

These summaries were based on values determined for a larger database assembled by ERL-D at the same time as data from Lakes Clara and Vandercook were being analyzed. Precision was determined by analyzing field replicates and laboratory duplicates.

$$\text{Precision} = [(d_i^2) / 2n],$$

where d_i is the difference between each replicate or duplicate and n is the number of replicates or duplicates.

Accuracy was calculated based on standard additions and analysis of USEPA and National Bureau of Standards (NBS) standard samples.

RESULTS AND DISCUSSION

Phytoplankton, Zooplankton, Macrophyte and Benthic Macroinvertebrate Community Structure

Phytoplankton

Thirty-eight phytoplankton genera from 6 phyla were identified in the Lake Clara samples collected between December and July (Append. B.1). The Chlorophyta was the most diverse group with 18 genera; chrysophytes and cyanophytes each had 7 genera. Highest densities (cells ml^{-1}) were recorded in December, mainly due to a large population of ultraplankton (Fig. 4). Excluding the ultraplankton, the dominant taxa in December included *Chroomonas*, *Dinobryon* and *Cryptomonas* (Fig. 5). By February, abundance and species richness was much reduced (Fig. 4) and the cryptophytes *Chroomonas* and *Cryptomonas* numerically dominated the phytoplankton community (Fig. 5). By late March, the cyanophyte

Chroococcus was the dominant taxa. The May sample, collected after ice-out, was largely dominated by diatoms (Chrysophyta) especially *Fragilaria*. The summer samples showed greater phytoplankton diversity, with a switch to dominance by blue-green algae, first by *Merismopedia tenuissima* followed by *Rhabdoderma* in July. The ultraplankton, which were numerically dominant in winter, declined thereafter and were absent in the July samples (Fig. 4).

In Vandercook Lake, we identified 40 genera of phytoplankton representing 6 phyla (Append. B.1). Over half (22) were chlorophytes, 8 were cyanophytes, and 5 were chrysophytes. Highest cell densities were recorded in January, largely due to ultraplankton (algae $< 7\mu$) (Fig. 6). *Dinobryon* was the most abundant genus, followed by *Cryptomonas* and *Oocystis* (Fig. 7). During February and March when total phytoplankton densities were lowest, chrysophytes (mainly *Asterionella* and *Dinobryon*) were the most important group. Following ice-out in May, the assemblage was mixed, with *Asterionella*, *Tabellaria*, *Oocystis*, and *Chroococcus* co-dominant. Similar to the successional pattern observed in Lake Clara, diatom densities declined by June. Abundances of the green alga, *Oocystis*, were highest in June, then declined by July when the blue-greens *Merismopedia* and *Chroococcus* became dominant. Despite this mid-summer numerical dominance by cyanophytes, the Chlorophyta showed the highest species diversity (Fig. 6).



Co-author Mark Johnson conducting a macrophyte survey at Lake Clara.

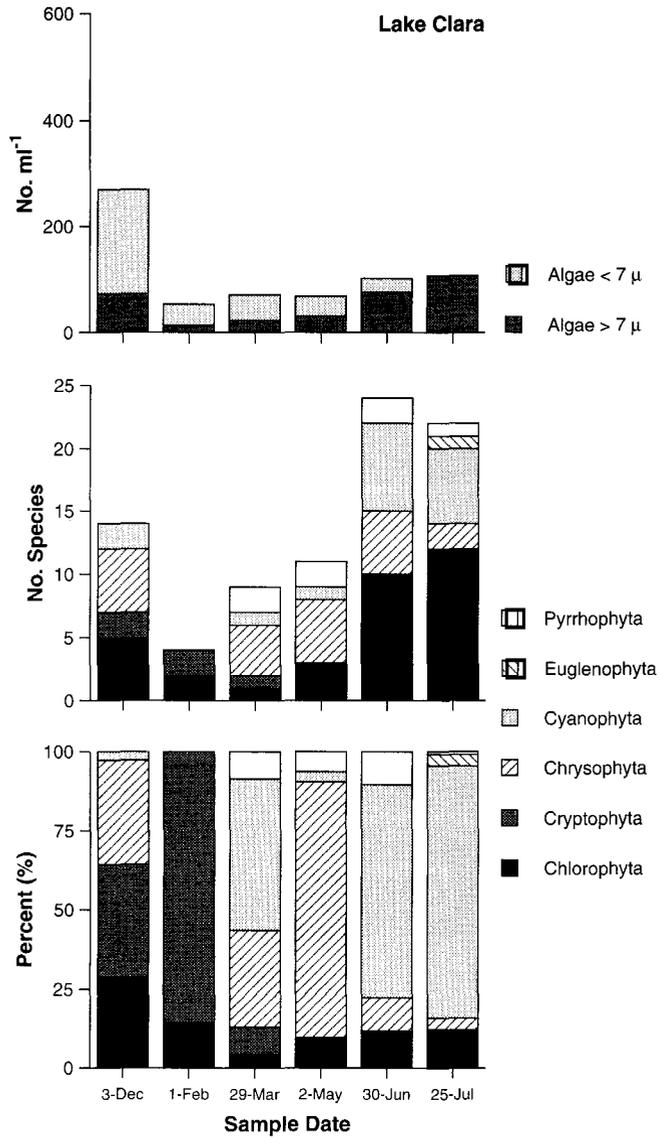


Figure 4. Phytoplankton total abundance and percent numerical composition and number of species by phylum in samples collected at 1.0 m depth from Lake Clara, December 1982-July 1983.

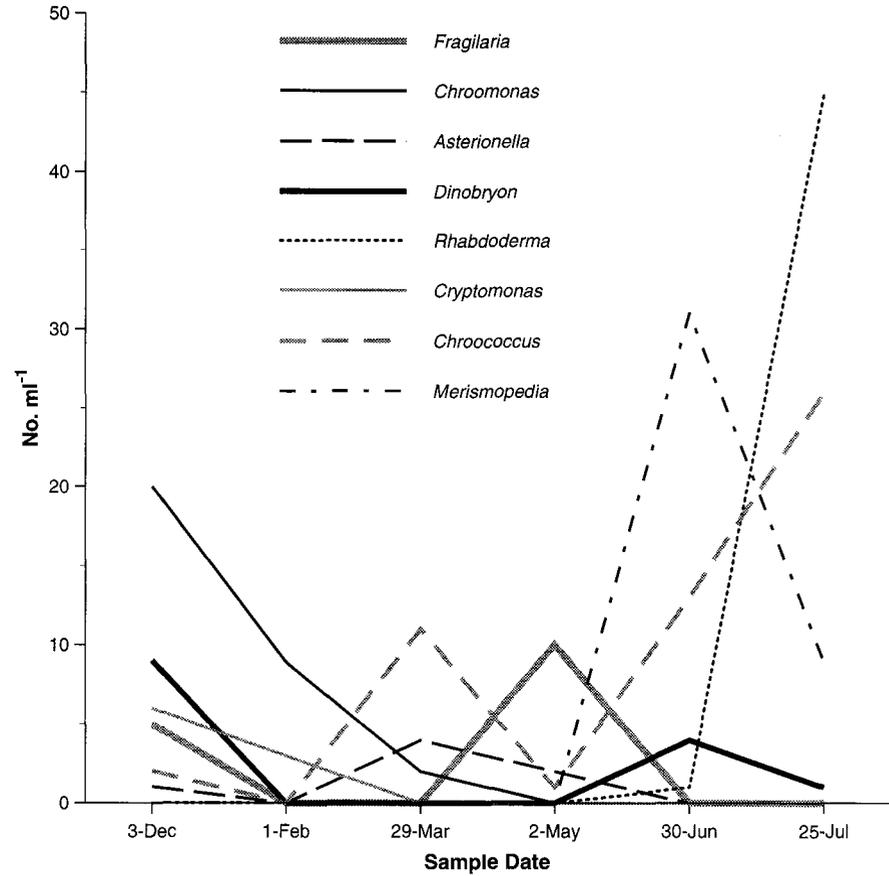


Figure 5. Abundance of dominant phytoplankton species in Lake Clara.

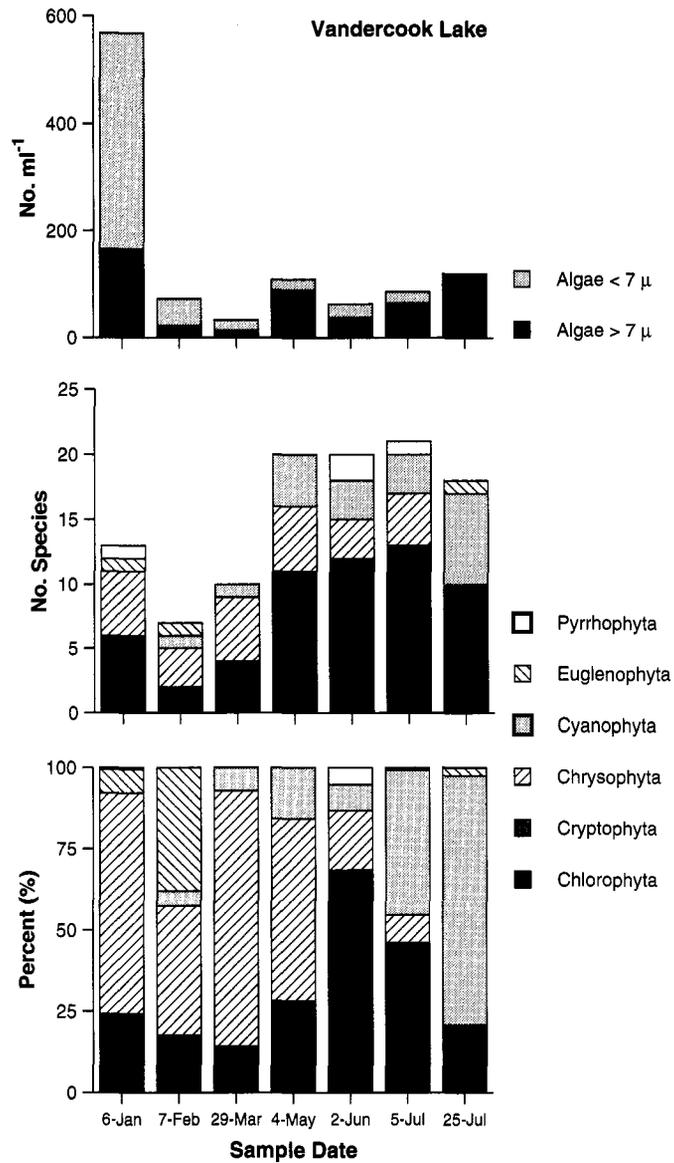


Figure 6. Phytoplankton total abundance and percent numerical composition and number of species by phylum in samples collected at 1.0 m depth from Vandercook Lake, January-July 1983.

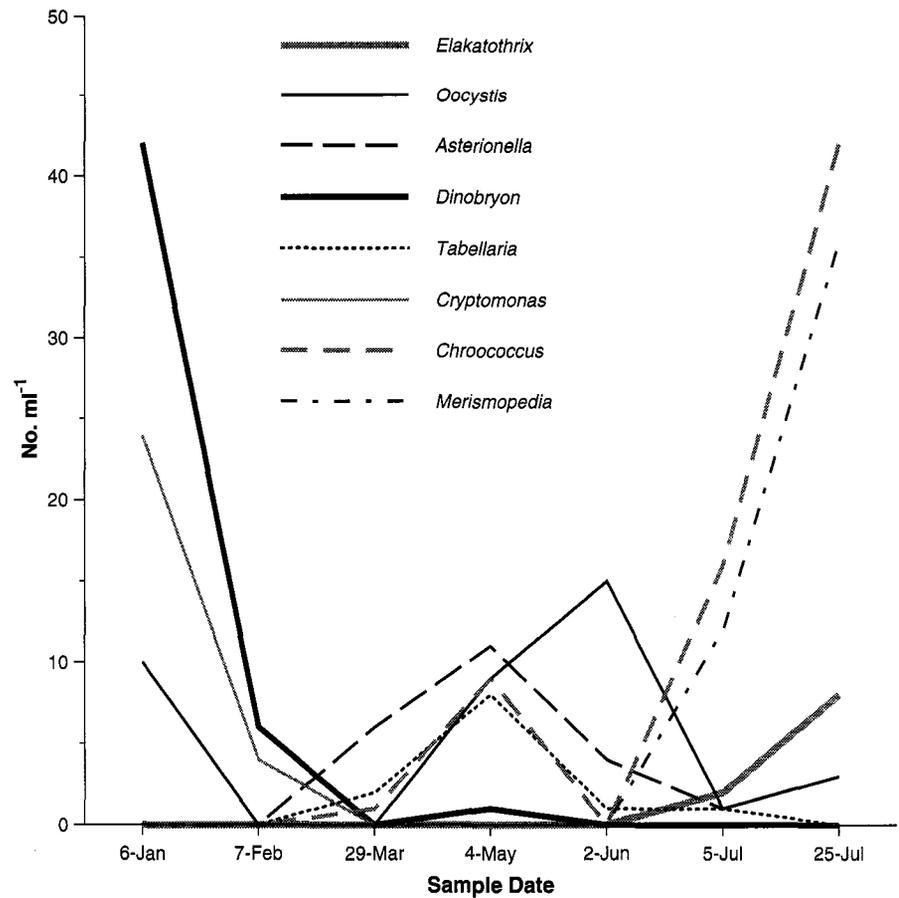


Figure 7. Abundance of dominant phytoplankton species in Vandercook Lake.

Macrophytes

Forty macrophyte species were collected from Lake Clara (Append. B.2). In the main basin, the emergent vegetation was primarily *Pontederia cordata* with some *Dulichium arundinaceum*; sedges were more commonly observed along the shoreline of the southern lobe (Figs. 8, 9). The floating-leaved macrophytes formed intergrading stands of *Sparganium angustifolium*, *Brasenia schreberi*, *Nymphaea odorata*, and some *Potamogeton natans*. The sediments underlying these stands were typically organic and very flocculent. Except in a few deeper areas, the shallow southern lobe was almost entirely covered by mats of *Nymphaea odorata*. The submergent vegetation in the main basin consisted primarily of rosette or "isoetid" species and mats of sterile forms.

In nearshore areas of Lake Clara, *Lobelia dortmanna* was the most common submergent macrophyte species. *Isoetes macrospora* densities increased with depth, peaking between 1.9 and 4.5 m (Fig. 9; Table 2). *Myriophyllum tenellum* was actually a complex of sterile macrophytes representing a gradation of three species (including some *E. submersa* and *U. resupinata*) which were not differentiated at the time of the survey. At sites deeper than 2.8 m, only 3 taxa were present: *Isoetes macrospora*, the alga *Nitella flexilis*, and the moss *Drepanocladus* sp. *Nitella* was distributed across the depth range 2.8-8.2 m. However, *Isoetes* appeared restricted to depths less than 4.6 m and *Drepanocladus* only occurred at depths of 4.6 and greater. No macrophytes were collected at sites with depths exceeding 8.2 m.

Twenty-seven macrophyte species were collected at Vandercook Lake (Append. B.2). Emergents were not important, limited to a single stand of *Nuphar variegatum* and three areas of concentrated *Sparganium angustifolium* growth (Figs. 10, 11). Substantial areas of mineral sediment were exposed, which in places appeared disturbed by benthic organisms. The only thick littoral organic sediments found in Vandercook Lake occurred under the *N. variegatum* stand northeast of the peninsula,

where a floating bog mat extended into the lake. Except in areas fronting cottages, nearly the entire shoreline was surrounded by *Myrica gale* and *Chamaedaphne calyculata*. *J. pelocarpus* f. *submersus* was most abundant at the shallow sites (Fig. 11; Table 2); *E. septangulare* and *I. macrospora* occurred at shallow and deeper littoral sites, respectively. The deep-water stratum of 18 survey sites produced only one observation of *I. macrospora* and *Nitella* at 3.1 m; other sites, generally composed only of muck or fine organic sediments overlaying sand, were lacking macrophyte growth.

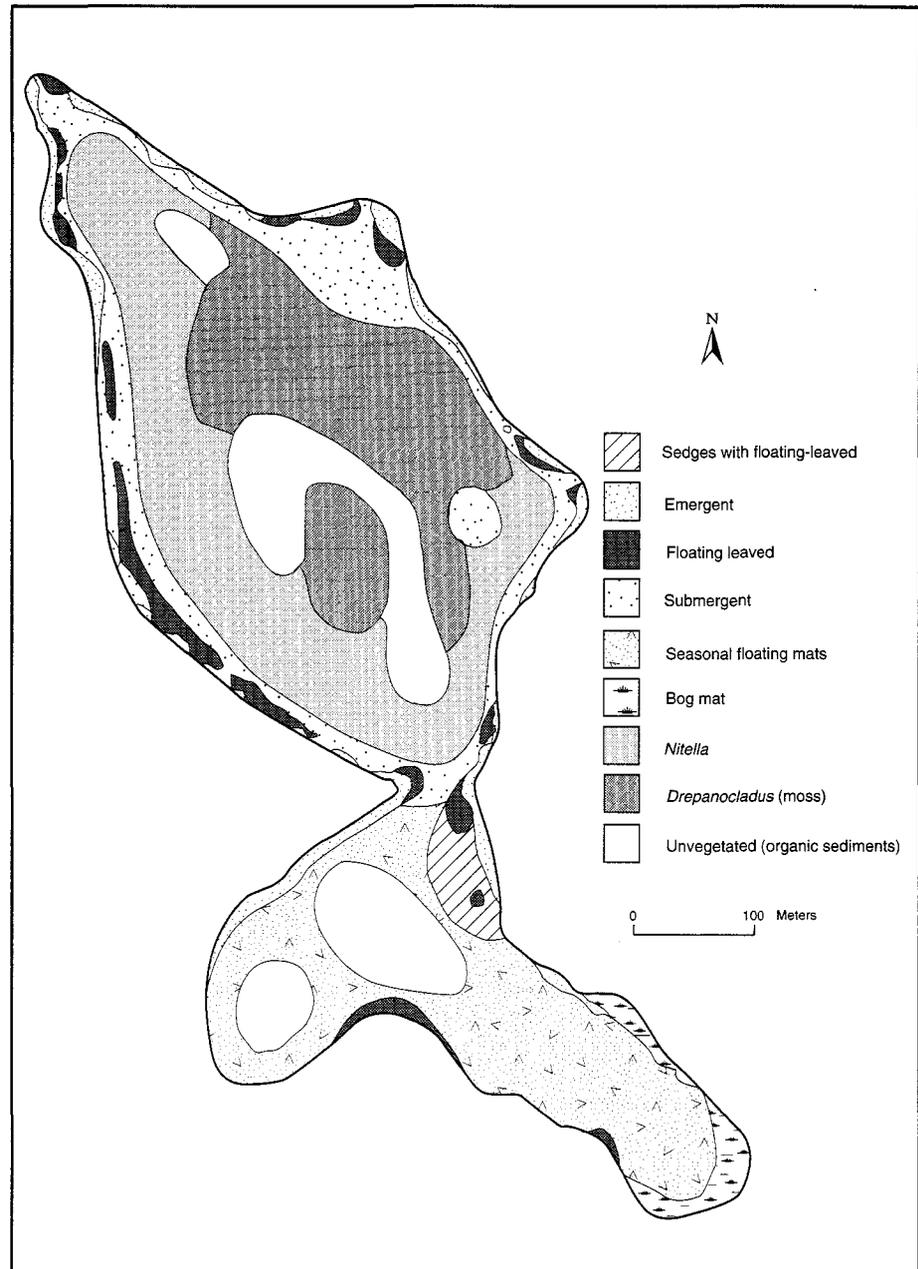


Figure 8. Macrophyte map for Lake Clara.

Zooplankton

We found 9 cladoceran, 5 copepod and 8 rotifer species in Lake Clara (Append. B.3). Cladocerans and cyclopoids numerically dominated the zooplankton community of Lake Clara while cladocerans tended to be the most species rich group (Figs. 12, 13). Total abundances generally peaked during mid-summer to early fall (Fig. 13). The dominant cyclopoid in Lake Clara, *Tropocyclops prasinus*, was most common from early fall until mid-summer, reaching peak densities during the ice-covered period (Fig. 13). Two other cyclopoid species were collected in low numbers—*Diacyclops bicuspidatus thomasi* throughout the year except in mid-summer, and *Mesocyclops edax*, during the summer. The only calanoid species present in significant numbers, *Leptodiatomus minutus*, experienced one annual reproductive cycle with females carrying eggs through late spring (Fig. 13). Following egg hatch in early spring, the numbers of copepodites (the immature stage) increased greatly through late spring and early summer, when the copepodites became adults. Adult numbers usually declined until the following spring.

Cladoceran abundances were generally much higher in Lake Clara during the first half of the study period (Fig. 13). Although this density decline occurred at approximately the same time that there was the switch in analysts, recounts of earlier samples provided no evidence that the apparent decline in numbers was related to differences in counting procedure (P. J. Garrison, unpublished data). The dominant cladoceran in Lake Clara during the cool water period was *Eubosmina tubicen*/*Bosmina longirostris*. Only a limited attempt was made to distinguish between

Table 2. Percent occurrence and average density ratings for most common macrophytes in Lake Clara (41 littoral sites) and Vandercook Lake (43 littoral sites).

Species	Percent (%) Occurrence	Average Density Rating
Lake Clara		
<i>Elatine minima</i> *	46	3.1
<i>Lobelia dortmanna</i>	46	2.5
<i>Juncus pelocarpus</i> f. <i>submersus</i>	39	2.9
<i>Isoetes macrospora</i>	37	3.1
<i>Myriophyllum tenellum</i> **	29	4.4
<i>Pontederia cordata</i> (immature seedlings)	24	2.1
<i>Eriocaulon septangulare</i>	22	3.1
<i>Brasenia schreberi</i>	15	3.3
<i>Nymphaea odorata</i>	10	2.5
<i>Pontederia cordata</i> (mature stands)	5	5.0
Vandercook Lake		
<i>Juncus pelocarpus</i> f. <i>submersus</i>	48	3.0
<i>Myriophyllum tenellum</i> ^a	34	3.7
<i>Isoetes macrospora</i>	30	3.4
<i>Sparganium angustifolium</i>	25	2.7
<i>Lobelia dortmanna</i>	23	3.0
<i>Elatine minima</i>	20	3.2
<i>Eriocaulon septangulare</i>	9	3.0
<i>Myrica gale</i>	7	2.0

* Observations included some *Gratiola area* forma *pusilla*.

** Observations included some *Eleocharis acicularis* var. *submersa* and *Utricularia resupinata*.

^a Observations included *Utricularia resupinata* and some *Eleocharis acicularis* var. *submersa*.

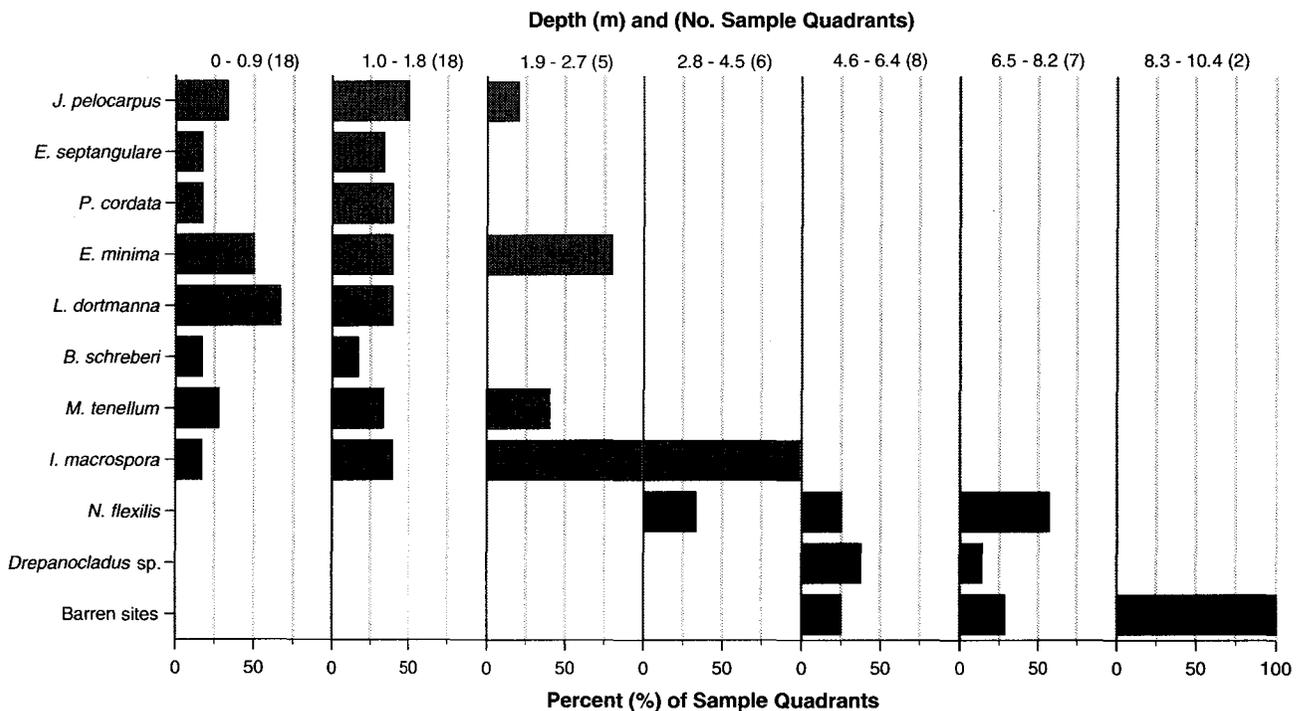


Figure 9. Depth distribution of macrophytes in Lake Clara. Bars represent the percentage of sample quadrants containing the species. Observations of *M. tenellum* included some *Eleocharis submersa* and *Utricularia resupinata*.

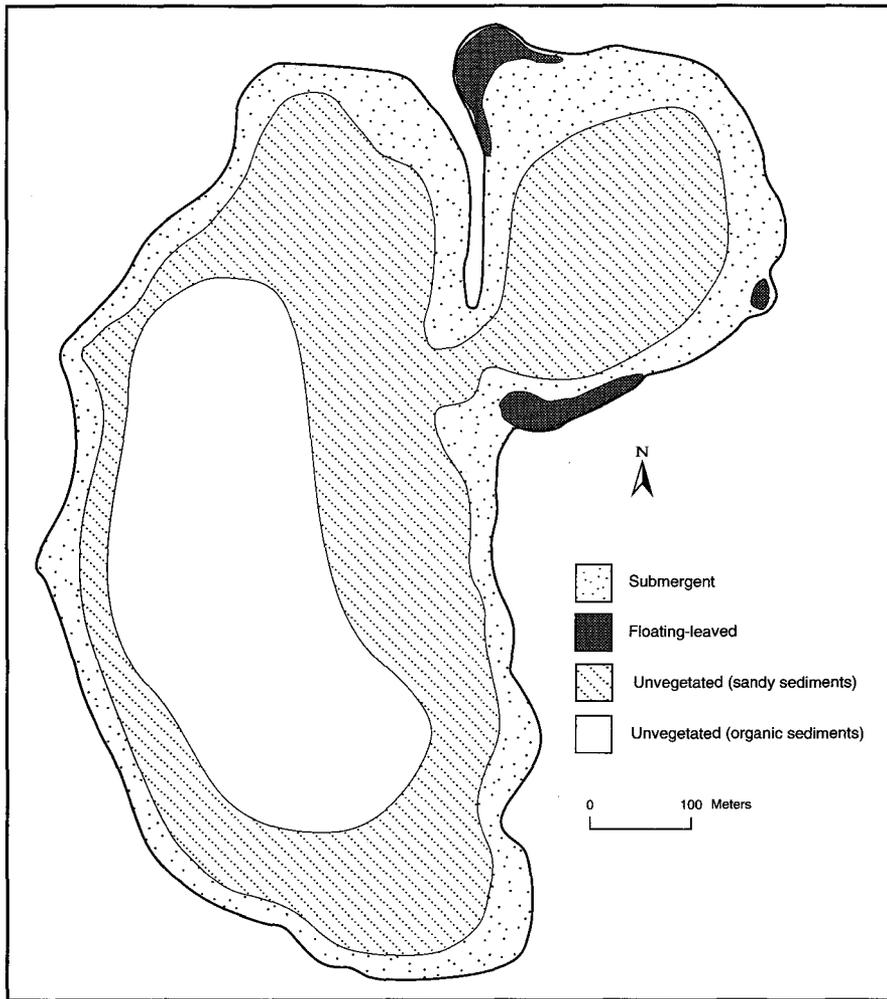


Figure 10. Macrophyte map for Vandercook Lake.

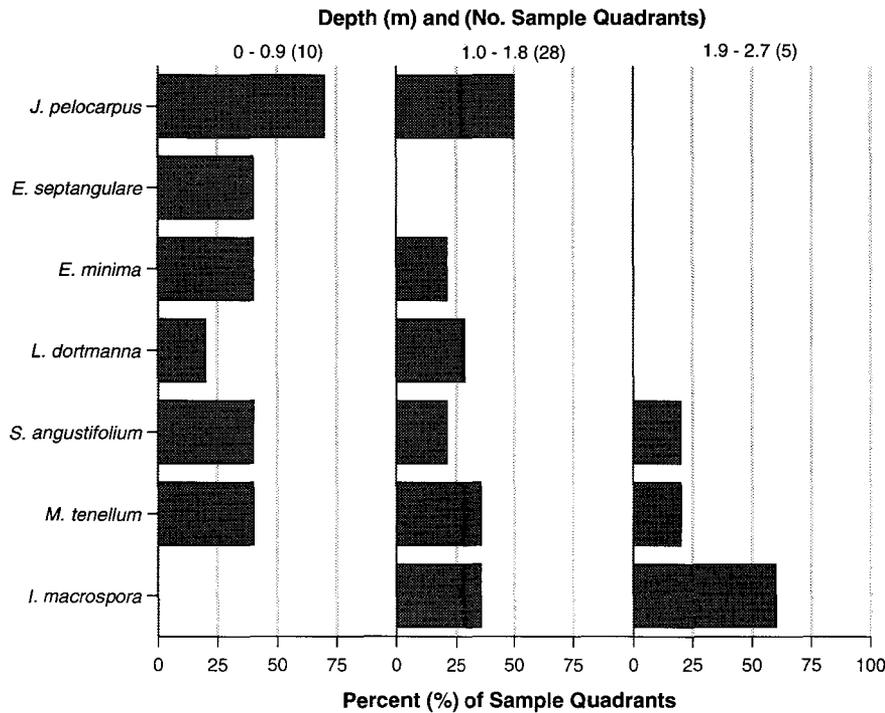


Figure 11. Depth distribution of macrophytes in Vandercook Lake. Bars represent the percentage of sample quadrants containing the species.

the two species, but it appears that *Eubosmina* is a cold water form whereas *Bosmina* is more common in warm water (P. J. Garrison, unpublished data). The density of bosminids greatly increased in late fall, peaked in early winter and declined thereafter to very low densities by late winter. The bosminid peak in late summer 1981 was likely composed of *B. longirostris*, not *E. tubicen*. The composition of the cladoceran assemblage during the summer varied during the three years. The assemblage in 1981 was dominated by *E. tubicen*, *Diaphanosoma birgei*, *Daphnia parvula*, and *Daphnia dubia*.

In 1982, the dominant cladocerans were *Holopedium gibberum*, *D. parvula*, and *D. dubia*. In 1983, there were almost no *Daphnia*; instead *E. tubicen*, *H. gibberum*, and *Diaphanosoma birgei* were the important species. A third daphnid, *Daphnia galeata mendotae*, was collected in low numbers in Lake Clara during the winter.

In Vandercook Lake, 7 cladoceran, 5 copepod and 9 rotifer species were collected. Numerically, cladocerans were the dominant microcrustaceans followed by cyclopoid and calanoid copepods (Fig. 12). Densities generally peaked in the summer and reached lowest values in March. Exceptions to this pattern occurred in the spring of 1981, when cyclopoid copepodites dominated, and in the early summer of 1983, when *L. minutus* copepodites were important.

The dominant cyclopoid, *D. b. thomasi*, was usually present from fall through spring, primarily as copepodites (Fig. 14). Copepodites of *D. b. thomasi* frequently encyst during the summer months (Elgmork 1980). Adult forms co-occurred with the copepodites, but at lower densities. *M. edax* and *T. prasinus* were present in low abundance during the summer and winter to spring, respectively. *Leptodiptomus minutus*, the dominant calanoid copepod, experienced one annual reproductive cycle (Fig. 14). In contrast to *L. minutus* in Lake Clara, in Vandercook Lake females began carrying eggs earlier, during the ice-covered period. Following egg hatch in early spring, copepodite numbers dramatically increased through early summer, reaching adult stages during the summer.

Thereafter, adult numbers slowly declined or remained the same until the following spring.

Except for midsummer, *Eubosmina tubicen* / *Bosmina longirostris* was the most abundant cladoceran (Fig. 14). *E. tubicen* (most likely) first appeared in significant numbers in October, increased in number and remained at elevated abundance until early June. During the summer, there was a shift towards *Diaphanosoma birgei* and *Chydorus sphaericus* along with lesser numbers of *Daphnia retrocurva* and *H. gibberum*.

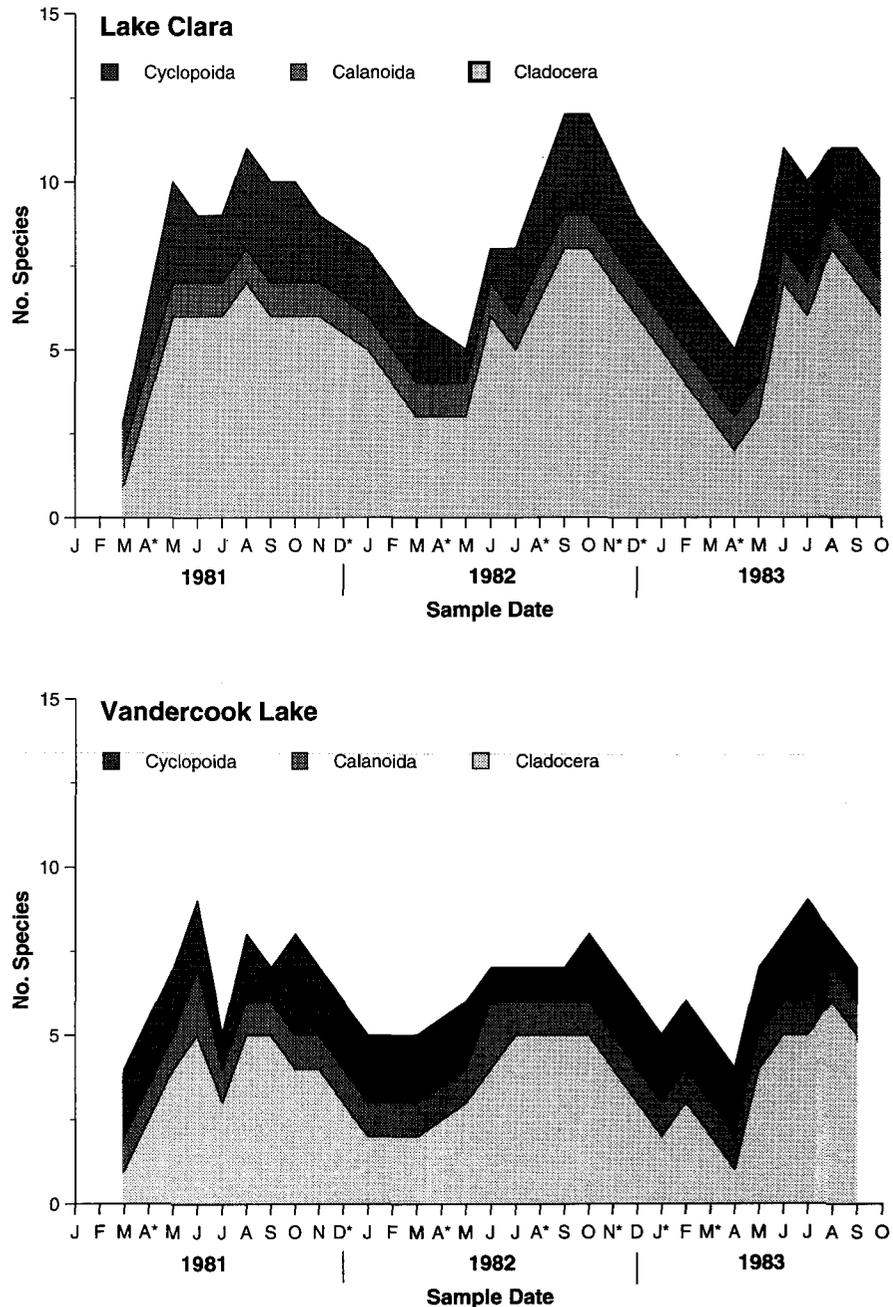


Figure 12. Cumulative species richness for Cyclopoida, Calanoida, and Cladocera in Lake Clara and Vandercook Lake. Asterisks (*) indicate interpolated data for months with no samples.

Benthic Macroinvertebrates

A list of the taxa collected during the June 1983 benthic survey is in Table 3. Although the list is by no means complete, it suggests that the community in Vandercook Lake was noticeably less rich than that of Lake Clara. Lake Clara contained a wide variety of benthic macroinvertebrates, including snails, fingernail clams, amphipods, and representatives from several insect orders. In contrast, the shoreline survey at Vandercook Lake yielded no snails or fingernail clams, and the fauna collected by shoreline netting and sediment grabs were limited to flies and midges, aquatic worms, caddisflies, and mayflies.

Evaluation of Acid-Stress

Much public concern about the biological effects of lake acidification has focused on fishery resources. However, adult fishes, and game fish in particular, are generally more tolerant of low pH and, thus, have not been reliable biological indicators of the early stages of lake acidification (Schindler 1988). Many species in lower trophic levels appear to be most sensitive to acid stress in the pH range 6.0 to 5.0 (Eilers et al. 1984; Schindler 1988). In particular, changes in phytoplankton (e.g. loss of diatoms), loss of sensitive benthic macroinvertebrates (e.g., amphipods, molluscs, leeches and crayfish), the formation of filamentous algal mats in littoral areas, and alterations in zooplankton community structure and life history characteristics, have been suggested as early biological indicators of acidification (Schindler 1987, 1988; Mills and Schindler 1986). Because the life cycles of these organisms are on the order of days to a year, it is not surprising that they respond more quickly than fish to pH stress. Moreover, the species redundancy in lower trophic levels provides a pool of taxa able to fill niches vacated by less tolerant forms. This is believed to be one reason for the lack of response to increased acidity by functional ecosystem-level

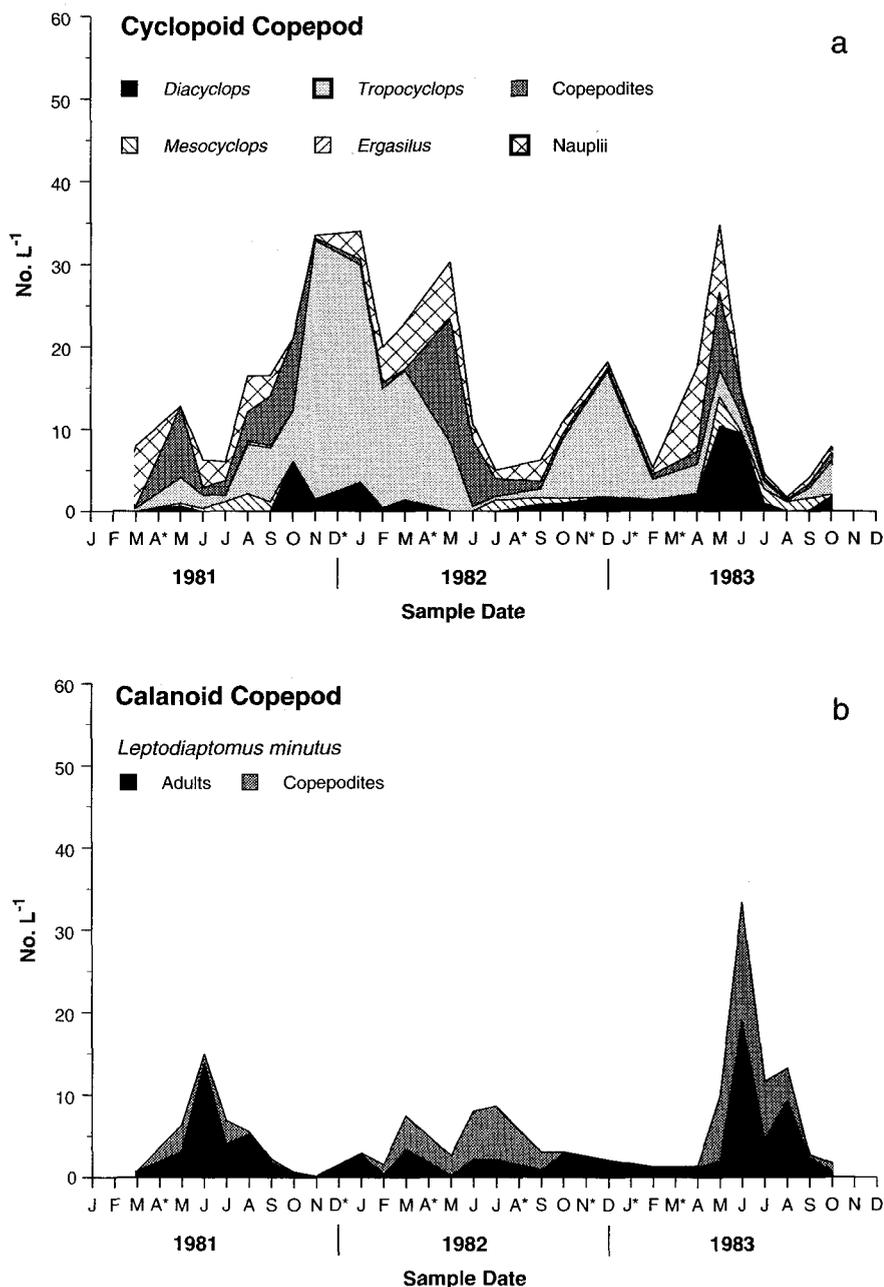


Figure 13. Cumulative abundance, by genera, of cycloids (a), the calanoid *Leptodiatomus minutus* (b), cladocerans (c) and *Daphnia* species (d) in Lake Clara. Asterisks (*) indicate interpolated data for months with no samples. Nauplii in panel a include both calanoids and cycloids.

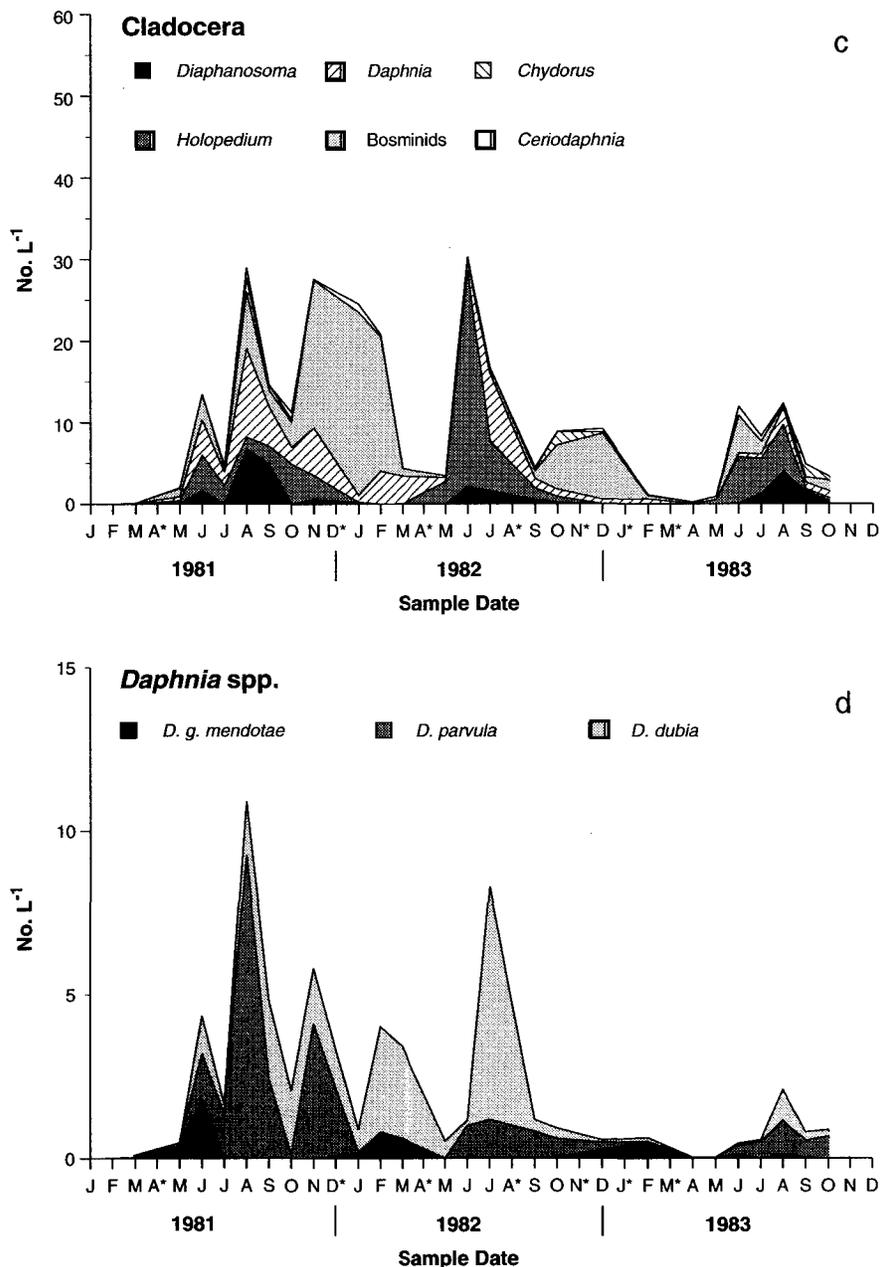


Figure 13. Continued.

parameters in lakes, such as production, decomposition, and nutrient cycling, (Schindler 1988).

The zooplankton assemblage observed in Lakes Clara and Vandercook was not similar to that typically observed in acidified systems. Studies in Ontario (Sprules 1975; Malley and Chang 1986) and the Adirondack region of New York (Confer et al. 1983; Sutherland et al. 1984; Siegfried et al. 1987) have shown that taxa such as *D. birgei*, the daphnids, and *T. prasinus*, which are common in Lakes Clara and Vandercook, are not found in acidified lakes. Morgan Lake, a shallow, acidic (pH 4.7, alkalinity -23 $\mu\text{eq L}^{-1}$) seepage lake in north-east Wisconsin, contains a zooplankton assemblage dominated almost exclusively by *Leptodiatomus minutus* (Hodgson et al. 1987). The experimental acidification of Little Rock Lake, located about 3 km west of Vandercook Lake, provided a view of species shifts over the pH range 6.1 to 4.7. There, the zooplankton community shifted to dominance by *Daphnia catawba* and *Bosmina longirostris* while species such as *D. dubia*, *Holopedium gibberum*, *Leptodiatomus minutus*, *Mesocyclops edax*, and *Tropocyclops prasinus* declined (Brezonik et al. 1993). Those latter acid-sensitive taxa maintained substantial populations in Lakes Clara and Vandercook.

The zooplankton community of both Lakes Clara and Vandercook was similar to that found in other softwater, non-acidic lakes in northern Wisconsin. Round Lake in the northwestern part of the state, with a slightly higher pH of 6.7 and ANC of 120 $\mu\text{eq L}^{-1}$, was dominated by a similar species assemblage of *L. minutus*, *B. longirostris*, *D. birgei*, *D. galeata mendotae*, and *D. b. thomasi* (P. Garrison, unpublished data). Little Rock Lake, with a similar pH (6.1) and ANC (20 $\mu\text{eq L}^{-1}$) to our study lakes prior to experimental acidification, had a zooplankton community dominated by *L. minutus*, *D. b. thomasi*, *H. gibberum*, and *Daphnia* spp. (Frost and Montz 1988).

The benthic macroinvertebrate survey suggested that diversity of benthic macroinvertebrates was lower in Vandercook Lake than in Lake Clara. In addition, some of the acid-sensitive groups (gastropods, fingernail clams, and amphipods) were not collected at Vandercook Lake, although acid-sensitive mayflies were found. There are two possible explanations for the poorer benthic fauna at Vandercook Lake which are independent of an acidification effect. First, the relatively open sandy substrates and low macrophyte densities do not provide as diverse a habitat for benthic invertebrates at Vandercook Lake as at Lake Clara. Second, the low calcium concentrations at Vandercook Lake (average of $65 \mu\text{eq L}^{-1}$) are close to limiting values for molluscs and other sensitive macroinvertebrates (Økland and Økland 1986).

The isoetid species of macrophytes common in the two study lakes often dominate the vascular vegetation of soft-water lakes in North America and Europe (Hutchinson 1975; Moeller 1975; Wile and Miller 1983; Roberts et al. 1985; Jackson and Charles 1988). Examining overall macrophyte diversity, Jackson and Charles (1988) observed a decline in species richness with pH in a set of lower elevation Adirondack lakes ranging in pH from 4.5 to 7.8, suggesting that a loss of macrophyte species and simplification of the community are possible results of lake acidification. However, Yan et al. (1985) found no correlation between pH and macrophyte species richness in 30 Ontario lakes. Invasion of acidic lakes by the moss *Sphagnum* described for Swedish lakes (Grahn 1977) has rarely been observed in North America (Stokes 1986).

The macrophyte, plankton, and zoobenthic communities in Lakes Clara and Vandercook demonstrated a fair degree of similarity in species composition, although overall biological diversity appeared slightly higher in Lake Clara. The zooplankton assemblages in Lakes Clara and Vandercook showed the most overlap in

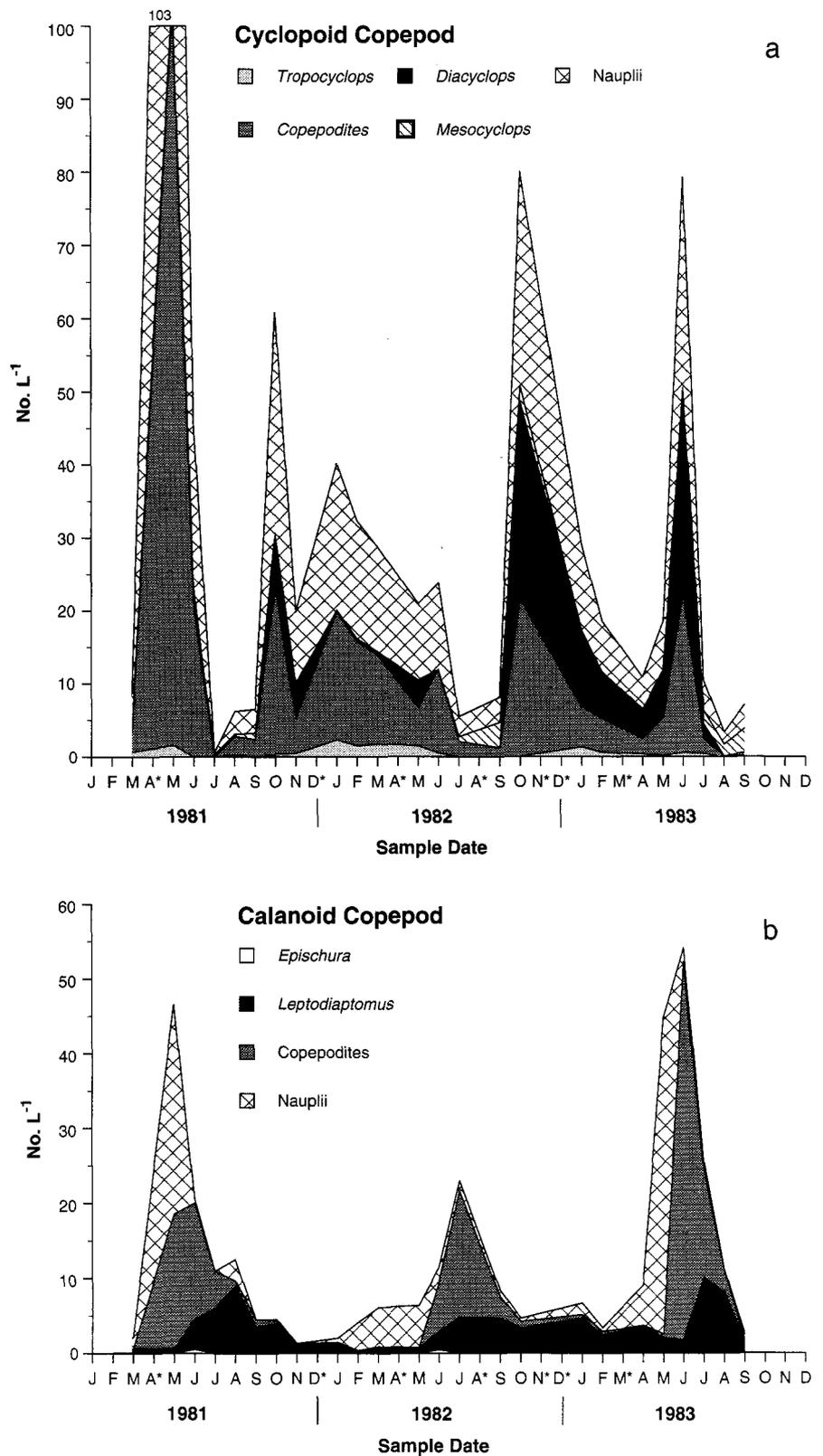


Figure 14. Cumulative abundance, by genera, of cycloids (a), calanoids (b), and cladocerans (c) in Vandercook Lake. Asterisks (*) indicate interpolated data for months with no samples. Nauplii in panel a include both calanoids and cycloids.

Table 3. Benthic macroinvertebrates collected from Vandercook Lake and Lake Clara on 23 June 1983.

Taxa	Vandercook Lake			Lake Clara	
	0-2m*	3m	7m	0-2m*	10m
Gastropoda (snails)				X	
Sphaeriidae (fingernail clams)				X	
Isopoda (aquatic sowbugs)				X	
Amphipoda (scuds)				X	
Oligochaeta (aquatic worms)	X	X		X	X
Diptera (flies and midges)					
Chironomidae	X	X	X	X	X
Chaoboridae			X		X
Trichoptera (caddisflies)					
Polycentropodidae				X	
Limnephilidae	X	X		X	
Leptoceridae		X		X	
Phryganeidae				X	
Odonata					
Zygoptera (damselflies)					X
Ephemeroptera (mayflies)					
Ephemerellidae		X			
Ephemeridae		X			

* Present in sediment samples and shoreline surveys.

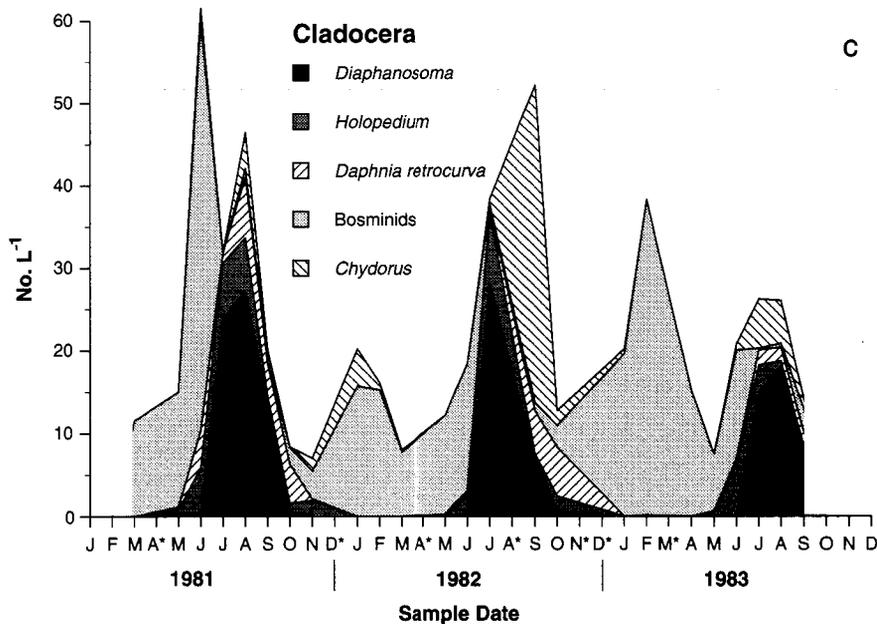


Figure 14. Continued.

species composition (Append. B.3). Both lakes contained one dominant calanoid copepod, *Leptodiaptomus minutus*, and from one to three cyclopoid species at any one time. A major difference was in the *Daphnia* species: three species, *D. dubia*, *D. parvula* and *D. g. mendotae* were abundant in Lake Clara (Fig. 13), while in Vandercook only *D. retrocurva* was common (Fig. 14). The cladocerans in both lakes were the most species rich group among the microcrustaceans, with Lake Clara showing slightly higher overall diversity than Vandercook Lake (Fig. 12). Some researchers have observed a decline in the number of zooplankton species with decreasing pH (Confer et al. 1983; Mills and Schindler 1986; Sutherland et al. 1987), however, the lower species richness in Vandercook Lake compared to Lake Clara was probably a result of morphometric differences. Lake Clara is deeper and stratifies more strongly, and the development of a hypolimnion provides more niches for the zooplankton community. This could explain the absence from Vandercook Lake of *Daphnia dubia*, a species more commonly found in the metalimnion of lakes than in the epilimnion (Brooks 1957).

Differences in productivity may account for some of the other small differences between the two lakes in zooplankton species composition. Gliwicz (1969) reported that in eutrophic lakes small cladocerans were more successful than larger species during periods when relatively high concentrations of larger phytoplankton are present. In Vandercook Lake, cladoceran assemblages were dominated in the summer by *Diaphanosoma birgei* and *Chydorus sphaericus*, smaller species which are often indicative of a more productive system. In contrast, the dominant cladocerans in Lake Clara were *Daphnia* spp. and *Holopedium gibberum*, taxa which are often found in less productive lakes.

The most striking biological difference between the two study lakes was in the macrophyte and benthic

macroinvertebrate communities. Lake Clara had a much more extensive and diverse macrophyte community composed of several stands of floating-leaved and emergent macrophytes in the littoral zone and intergrading stands of submerged forms extending to about 8 meters. In contrast, submerged macrophytes dominated in Vandercook Lake and little growth was observed at sites deeper than 3 meters. Areas of extensive growths of emergent and floating-leaved species were rare. Sandy sediments, which are more widespread in Vandercook Lake, may be more limiting to macrophyte distributions than the more organic sediments at Lake Clara (Barko and Smart 1986).

The biota of the two study lakes were, in general, characteristic of softwater, unproductive systems. Although the macrophyte and zoobenthic communities in Vandercook were dominated by taxa considered acid-tolerant, zooplankton community structure was moderately diverse. Lake Clara, on the other hand, showed high diversity in nearly all biotic groups studied. As described later, the pH of both Clara and Vandercook averaged around 6.1-6.3, values above the range where loss of many acid sensitive species is expected to occur (Eilers et al. 1984). Experimental lake acidification studies at the Experimental Lakes Area of Ontario (Schindler et al. 1985) and at the nearby Little Rock Lake site in northern Wisconsin (Brezonik et al. 1993), have demonstrated biological responses in lower trophic levels as pH values decline below 6.0.

Fishery Resources

Fish Community Composition: Past and Present

Records of the Wisconsin Department of Natural Resources showed that both lakes had been extensively stocked with fish (Append. C.3). The species most commonly stocked were game fishes, primarily northern pike and largemouth bass. During the early 1940s, fish were commonly collected from other drainage systems, transported, and stocked into northern Wisconsin lakes (L. M. Andrews, DNR, Woodruff, pers. comm.). At that time, the fish stocked were commonly recorded as "shiners," "chubs," and "suckers;" the actual taxa of fish included in such groupings are unknown. Such stocking was done into Lake Clara during 1941-42.

Eight species of fish, primarily centrarchids (sunfishes), were collected during the two early surveys on Lake Clara (Table 4). Bluegills represented 94% of the catch in 1953 and 89% in 1969. Four species of fish were collected during the 1951 survey of Vandercook Lake (Table 5); 92% of the 638 fish collected were stunted yellow perch, mostly less than 15 cm (6 inches) long (Burdick 1952).

Based on more recent surveys, fish communities in the two lakes were dominated largely by sunfishes (Centrarchidae) and perches (Percidae). A total of 1,342 fish, representing six species and four families, was collected during the 1980 survey of Lake Clara (Table 4). The most abundant species were bluegills (59% of the

Table 4. Number or presence of fish collected during fishery surveys in Lake Clara.

Species	Early Surveys		Recent Surveys	
	1953	1969	1980	1981*
Northern pike	1	4	20	+
White sucker	0	1	0	0
Yellow bullhead	0	70	178	+
Pumpkinseed	0	4	0	***
Bluegill	237	644	792	+
Largemouth bass	11	2	44	+
Black crappie	3	1	0	***
Yellow perch	0	1	285	+
Walleye	0	0	23	+
Total number of fish	252	727	1,342	—
Total number of species	4	8	6	8

* A plus sign (+) indicates presence and a zero (0) indicates absence in the catch.

** Only one individual present in catch.

Table 5. Number of fish collected during fishery surveys in Vandercook Lake.

Species	Early survey (1951)	Recent survey (1981)			
		Seine	Trammel Net	Fyke Net	Total Catch
Northern pike	8	3	5	3	11
Golden shiner	0	1	0	11	12
White sucker	26*	0	7	5	12
Rock bass	0	20	3	235	258
Pumpkinseed	0	18	1	100	119
Bluegill	0	19	0	110	129
Largemouth bass	16	174**	1	5	180*
Yellow perch	588	2,711**	0	8	2,719**
Total number of fish	638	2,946	17	477	3,440
Total number of species	4	7	5	8	8

* Listed as "suckers" in the file of the Wisconsin Department of Natural Resources; assumed to be white sucker.

** Catch composed largely of young-of-the-year fish.

total number caught), yellow perch (21%), and yellow bullhead (13%). Three piscivorous species—northern pike, largemouth bass, and walleye—were also present. Several large northern pike and walleyes were taken in gill nets and fyke nets during the 1980 survey (Wiener 1983). Sampling with fyke nets during June 1981 in Lake Clara yielded eight species, including one specimen each of two species (pumpkinseed and black crappie) not collected in the 1980 survey (Table 4).

The species composition of the fish community in Lake Clara has seemingly changed little during recent

decades. Except for the white sucker, a species represented by one individual caught in 1969, all species present in Lake Clara during the early surveys were also found in 1980 or 1981 (Table 4). Although 400 adult fathead minnows were stocked into Lake Clara in 1942, none was found in subsequent surveys. The other known species stocked into the lake (northern pike, largemouth bass, and walleye) were caught in 1980 and 1981. The abundance of yellow perch in Lake Clara seems to have increased between 1953 and 1981 (Table 4). Additional information on the status of fish populations in Lake Clara is available elsewhere (Wiener and Hanneman 1982; Wiener 1983; Wiener et al. 1984; Wiener et al. 1985; Wiener and Rago 1987).

A total of 3,440 fish, representing eight species and five families, was collected in the 1981 survey of Vandercook Lake (Table 5). The most abundant taxa were yellow perch (79% of total number caught) and members of the sunfish family (four species totaling 20% of the catch). All four species recorded during the 1951 survey were present in 1981. Two of the four species stocked into the lake—largemouth bass and northern pike—were also present. Vandercook Lake was stocked with walleyes in 1934 and with muskellunge in 1940 and 1963, but neither species was caught in the fishery surveys of 1951 and 1981.

Differences in sampling gear and methods precluded quantitative comparisons of the relative abundance of fish species between Lakes Clara and Vandercook. However, the species richness and composition of the fish assemblages in the two lakes were similar. Eight species were found in recent surveys of each lake, and five (northern pike, pumpkinseed, bluegill, largemouth bass, and yellow perch) occurred in both. Yellow perch and centrarchids seemed to be numerically dominant in both lakes.

The fish assemblages in Lakes Clara and Vandercook are fairly typical of those in non-winterkill, low-alkalinity seepage lakes in northern Wisconsin. They are mostly dominated by yellow perch, largemouth bass, sunfishes (*Lepomis* spp.), bullheads *Ameiurus* spp.), and white suckers (Rahel and Magnuson 1983; Wiener 1983; Wiener et al. 1984; Rahel 1986). Each of the two lakes contained four of these taxa during recent surveys. Northern pike, rock bass, smallmouth bass, black crappies, golden shiners, and walleyes also occur in more than 20% of such lakes (Rahel 1986). Each of the two lakes contained three of these species during recent surveys.

Acid Sensitivity

The acidification of low-alkalinity lakes in the northeastern United States (Haines and Baker 1986), eastern Canada (Kelso et al. 1986), and Scandinavia (Muniz 1984; Henriksen et al. 1989) has caused declines or losses of fishery resources. It is known that the species composition and richness of fish assemblages in clear-water lakes in northern Wisconsin are influenced by natural gradients in pH and associated chemical factors, such as calcium concentration (Rahel and Magnuson 1983; Wiener 1983; Rago and Wiener 1986; Rahel 1986). However, Wiener and Eilers (1987), who assessed the status of fishery

resources in the Upper Midwest in relation to lake chemistry, reported that existing data were insufficient to permit general conclusions about the impact or lack of impact of cultural acidification on Wisconsin's fishery resources.

The relative acid-sensitivity of fishes can be partly inferred by examining pH minima, defined as the lowest pH at which self-sustaining populations are found (Magnuson et al. 1984). Wiener and Eilers (1987) compiled information on fish species distribution relative to the pH of 150 northern Wisconsin lakes that had been previously surveyed. Of the 29 species examined, 10 had pH minima of 6.0 or greater and were judged to be highly acid sensitive. None of these highly acid-sensitive species, which included four cyprinids, two darters (*Etheostoma* spp.), logperch, cisco, trout-perch, and burbot, were present in either Lake Clara or Vandercook Lake. However, such acid-sensitive fishes are considered to be *naturally* absent or rare in low-alkalinity lakes in northern Wisconsin (Wiener and Eilers 1987).

Judging from pH minima observed in other lakes, most of the fish species in Lakes Clara and Vandercook are fairly tolerant of low pH (Table 6). Six of the 11 species had pH minima below 5.0, and three species had pH minima of 5.1 or 5.2. Two moderately acid-sensitive fishes, the black crappie (pH minimum 5.6) and walleye (pH minimum 5.5), were present in Lake Clara. The yellow perch is probably the most acid-tolerant fish species in the two lakes (Table 6). The lowest pH values measured during this study (5.7 in Clara and 5.6 in Vandercook) exceeded the pH minima of all resident fish species in each lake.

Our assessment of acid sensitivity of fishes has focused thus far on one variable, pH. However, the observation

Table 6. Minimum pH at which occurrence of fish species present in Lake Clara and Vandercook Lake has been documented in northern Wisconsin lakes.

Species	Presence in Recent Surveys*		Minimum** pH
	Clara	Vandercook	
Northern pike	+	+	5.1
Golden shiner	0	+	5.2
White sucker	0	+	4.9
Yellow bullhead	+	0	4.9
Rock bass	0	+	5.2
Pumpkinseed	+	+	4.9
Bluegill	+	+	4.5
Largemouth bass	+	+	4.6
Black crappie	+	0	5.6
Yellow perch	+	+	4.4
Walleye	+	0	5.5

* A plus sign (+) indicates presence and a zero (0) indicates absence in the catch during recent (1980s) surveys.

** Minimum pH at which occurrence of the species was documented in 150 northern Wisconsin lakes (source: Wiener and Eilers 1987).

of high aluminum concentrations in waters of a few acidic lakes in northern Wisconsin and the Upper Peninsula of Michigan suggests that adverse biotic effects of acidification in some lakes in the Upper Midwest region could result from toxic aluminum as well as low pH (Wiener and Eilers 1987). Yet, aqueous concentrations of extractable aluminum are low in most clear-water acidic lakes in the region (Linthurst et al. 1986). During the present study, total concentrations of aqueous aluminum in Lakes Clara and Vandercook (Schmidt 1985) were below values considered toxic to fish.

Mercury Concentration in Fish

The contamination of fish by mercury (Hg), a highly toxic metal, is also a probable consequence of acidification (Wiener et al. 1990a; Spry and Wiener 1991). Fish in low-pH or low-alkalinity waters frequently contain elevated concentrations of mercury, even in watersheds distant from anthropogenic sources of the metal. Survey data for lakes in the United States, Canada, Sweden, Finland, and the Soviet Union have indicated that mercury concentration in fish (of a given species and age) is often inversely related to lake pH or alkalinity (Spry and Wiener 1991), a pattern observed in at least eight species of fish. Mercury concentrations in piscivorous fishes from low-pH or low-alkalinity waters often exceed 0.5 or 1.0 g (g wet weight)⁻¹—values widely used as criteria for fish-consumption advisories. The acidification of low-alkalinity surface waters may further increase the rate of mercury accumulation by fish (Xun et al. 1987; Wiener et al. 1990a).

Mercury concentrations in walleyes of Lake Clara were surprisingly high given the rural location of the lake and the absence of direct anthropogenic inputs of the metal. Total concentrations in axial muscle tissue of walleyes, which ranged from 40 to 54 cm long and from 0.65 to 1.67 kg in weight, varied from 0.49 to 1.74 g (g wet weight)⁻¹. Concentrations exceeded 0.50 in 12 of the 13 fish and 1.0 in 3. Raw data for the 12 walleyes collected in 1980 were tabulated by Wiener (1983, p. 107). Measurements for the one walleye collected in 1982 were total length, 49 cm; wet weight, 1.20 kg; age, 8 years; and mercury concentration, 0.71 g (g wet weight)⁻¹.

Mercury concentrations were positively correlated with fish size—a commonly observed pattern (Huckabee et al. 1979). The simple regression equation for the relation between mercury concentration (Hg, in g (g wet weight)⁻¹) and total length (TL, in centimeters) for Lake Clara walleyes was

$$\text{Hg} = 0.058 \text{ TL} - 1.80$$

The coefficient of determination (r^2) for the regression equation was 0.44.

These and other findings suggest that mercury is highly available to fish in Lake Clara. In comparison, the upper Wisconsin River downstream from Rhinelander is contaminated with mercury from point sources (Rada et al. 1986); however, mercury concentrations in axial muscle tissue of walleyes from Lake Clara (and other low-alkalinity seepage lakes in the area) were at least double those in walleyes of the same age from mercury-contaminated reaches of the upper Wisconsin River (Table 7; Wiener et al. 1990b).

In north-central Wisconsin, walleyes inhabiting lakes with pH less than 7.0 typically have higher mercury concentrations than walleyes in lakes with higher pH (Lathrop et al. 1989; Wiener et al. 1990b). The increased bioaccumulation of mercury in low-alkalinity waters seems to result partly from the following mechanisms: greater microbial production of methylmercury at low pH (Winfrey and Rudd 1990), increased permeability of biological membranes at low aqueous calcium concentration (Wiener 1987), and greater concentrations of methylmercury in the diet of piscivores in low-alkalinity lakes (Cope et al. 1990).

Earlier data on the mercury content of fish from Lake Clara are not available. However, the deposition of mercury to sediments of Clara and other lakes in north-central Wisconsin (including Vandercook) has increased substantially in recent decades, perhaps as a result of atmospheric deposition of anthropogenic mercury (Rada et al. 1989). It is therefore possible that a significant fraction of the mercury burdens in walleyes in northern Wisconsin lakes is anthropogenic in origin. The recent enrichment of lake sediments with mercury, widely attributed to anthropogenic mobilization of the metal, is evident across North America and other parts of the northern hemisphere (Wiener 1987; Norton et al. 1990; Spry and Wiener 1991).

The Wisconsin Division of Health and the Wisconsin Department of Natural Resources have jointly issued a health advisory concerning consumption of fish from Lake Clara because of mercury contamination (Wis. Dep. Nat. Res. and Wis. Div. Health 1990).

Table 7. Mean mercury concentrations in axial muscle tissue of walleyes from Lake Clara and from mercury-contaminated reaches of the upper Wisconsin River.

Age (years)	Mean Mercury Concentration* and (Sample Size)	
	Lake Clara Walleyes	Wisconsin River Walleyes
4	0.57 (5)	0.28 (13)
5	0.92 (4)	0.31 (2)
7	1.34 (3)	0.50 (5)

* Grams mercury per gram wet weight of muscle tissue. Data for the upper Wisconsin River are for fish collected in July and August 1981 (source: Rada et al. 1986).

Limnologic and Chemical Characterization

Lake Chemistry and Limnology

Stratification patterns. Lake Clara, with a maximum depth of 11.3 m, exhibited strong summer stratification in temperature and oxygen throughout the study period (Fig. 15). The lake was commonly stratified from early June until late September, with midsummer oxygen concentrations depleted below 6 m in 1981 and 8 m in 1982-83. In the winter, oxygen concentrations in the hypolimnion approached zero.

In contrast, Vandercook Lake, with a maximum depth of 6.7 m, did not exhibit as strong a summer thermal stratification (Fig. 16) as Lake Clara and the extent of anoxic water was limited to about 0.5 m above the sediment surface. Metalimnetic oxygen increases were detected in June and early July in 1982 and 1983 but not in 1981. Winter oxygen stratification patterns were similar to those of summer with oxygen again becoming depleted only near the sediment surface.

Chlorophyll *a* and Secchi disk transparency. Chlorophyll *a* ranged from 2.0 to 4.6 $\mu\text{g L}^{-1}$ (median 3.2) in four surface samples collected from Lake Clara between November 1981 and June 1982. Eight surface samples from Vandercook Lake (Apr 1981-Jul 1983) contained chlorophyll *a* concentrations ranging from 0.8 to 5.3 $\mu\text{g L}^{-1}$ (median 3.9). Secchi disk transparency averaged 3.8 m (range 2.3-5.6 m) in Vandercook Lake (Fig. 17). Despite seasonal variability, Secchi disk transparency was consistently higher at Lake Clara (mean 4.9 m; range 4.0-5.9 m) than at Vandercook Lake.

Based on Secchi disk transparency (4.9 and 3.9 m), chlorophyll *a* (3.2 and 3.4 $\mu\text{g L}^{-1}$), and spring total phosphorus (TP) concentrations (0.010 and 0.013 mg L^{-1}), Lakes Clara and Vandercook can be classified as moderately productive. Trophic state index (TSI) values calculated using the above measures of productivity place Clara and Vandercook lakes in the oligo-mesotrophic range (Carlson 1979). The lower mean summer Secchi disk transparency of 3.9 m and slightly higher TP and chlorophyll *a* for Vandercook compared to Clara, suggest that the algal standing crop was slightly higher at Vandercook.

Chemical composition. Lakes Clara and Vandercook were both characterized by clear water (color of 11 and 8 PCU) (Tables 8, 9). With an average surface pH above 6.0, the lakes were only slightly acidic (defined as pH < 7.0), but ANC was low, averaging 30 and 18 $\mu\text{eq L}^{-1}$ at Clara and Vandercook, respectively. Low conductance values (17 μS) at Vandercook reflect the dilute nature of this lake. Conductance values for Lake Clara (mean of 35 μS) were elevated above that expected for a lake of its ANC.

The ionic composition of the two study lakes differed only slightly in Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} , and NO_3^- (Fig. 18). There were, however, major differences in the concentrations of Na^+ and Cl^- . At Vandercook Lake, these were

minor ions with SO_4^{2-} and Ca^{2+} as the dominant anion and cation, respectively. In contrast, the ion composition for Lake Clara was dominated by Na^+ and Cl^- at concentrations averaging 7 and 16 times higher, respectively than those in Vandercook Lake. This enrichment of Na^+ and Cl^- was a likely result of road-salt application to CTH A which runs near the north end of Lake Clara.

Spatial Patterns. We evaluated spatial variability in the pelagic zone by sampling three stations per lake between January 1981 and July 1982. Differences between stations for a series of chemical parameters were examined using a general linear model ANOVA procedure (SAS 1985). Station differences were not significant (at $p < 0.05$) for ANC, SO_4^{2-} , specific conductance, color, or anion sums for both lakes, and for pH, base cations, and Cl^- for Lake Clara. Significant differences were detected for pH, Ca^{2+} , base cation sums, and Cl^- in Vandercook, and for Ca^{2+} in Clara. However, the absolute differences were quite small (1 $\mu\text{eq L}^{-1}$ for Cl^- , 5 $\mu\text{eq L}^{-1}$ for Ca^{2+} , and 0.1 unit for pH) and close to precision estimates (Append. D.2). As the observed intra-basin differences were minor, water chemistry data from the primary sampling stations (station 1) were used in later discussions.

In contrast to the low variability shown for the pelagic zone, samples collected from station 4, located in the southern lobe of Lake Clara, showed elevated ANC (74 $\mu\text{eq L}^{-1}$), conductance (40 μS), color (17 PCU), and turbidity (1.1 NTU) compared to surface values for the main basin given in Table 8. This lobe is shallow (generally less than 2 meters), densely vegetated, and drains through the outlet exiting the southeast corner of the lake.

Temporal Patterns. Seasonal patterns were exhibited by several chemical variables in the epilimnion of the two

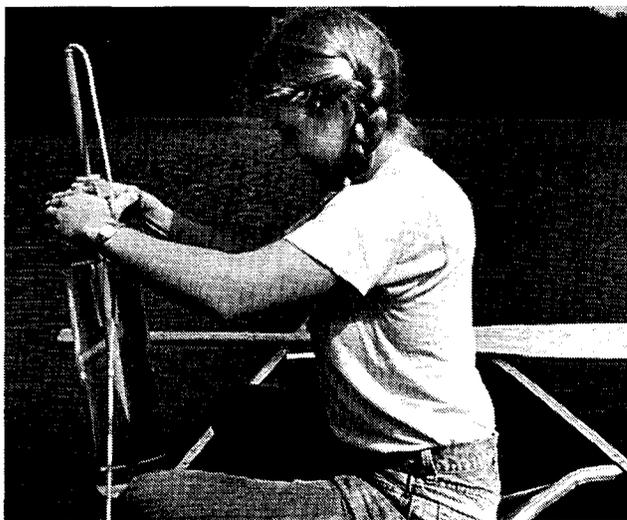


PHOTO: K.E. WEBSTER

DNR field assistant Lisa Huberty using a Kemmerer sampling bottle to collect water samples.

lakes (Figs. 19, 20). In many cases (e.g. SO_4^{2-} , NO_3^- , Ca^{2+} , and Na^+) ion concentrations were characterized by winter maxima and summer minima. In Lake Clara, the more pronounced shifts in Ca^{2+} and Na^+ were associated with winter increases in Cl^- confirming the influence of road salt contamination. The pH of the study lakes varied seasonally in a pattern of winter lows and summer highs with annual pH shifts on the order of 0.5 units (Fig. 21). Diurnal shifts in pH were also documented during 24 hour surveys (Fig. 22). During the day, pH increased then sharply declined after dark. The diurnal pH shifts were on the order of 0.2 units.

Although there was no strong seasonal pattern, ANC did increase in Vandercook Lake during the winter of 1982 to a maximum of $42 \mu\text{eq L}^{-1}$, followed by a sharp

decrease after ice-out (Fig. 20). As there were no measurable decreases in acid anions or increases in base cations of similar magnitude, the cause of the ANC increase is unknown and may be attributable to unmeasured constituents such as NH_4^+ .

The magnitude of change in ionic composition of hypolimnetic waters during the summer exceeded the seasonal fluctuations observed in the epilimnion in the strongly stratifying Lake Clara (Fig. 23). In Lake Clara, the increases in ANC were balanced by equivalent increases in Ca^{2+} , Fe^{2+} , and Mn^{2+} and decreases in SO_4^{2-} . A similar pattern of hypolimnetic ANC generation was observed in Vandercook Lake only in the summer of 1983 when thermal stratification was strongest.

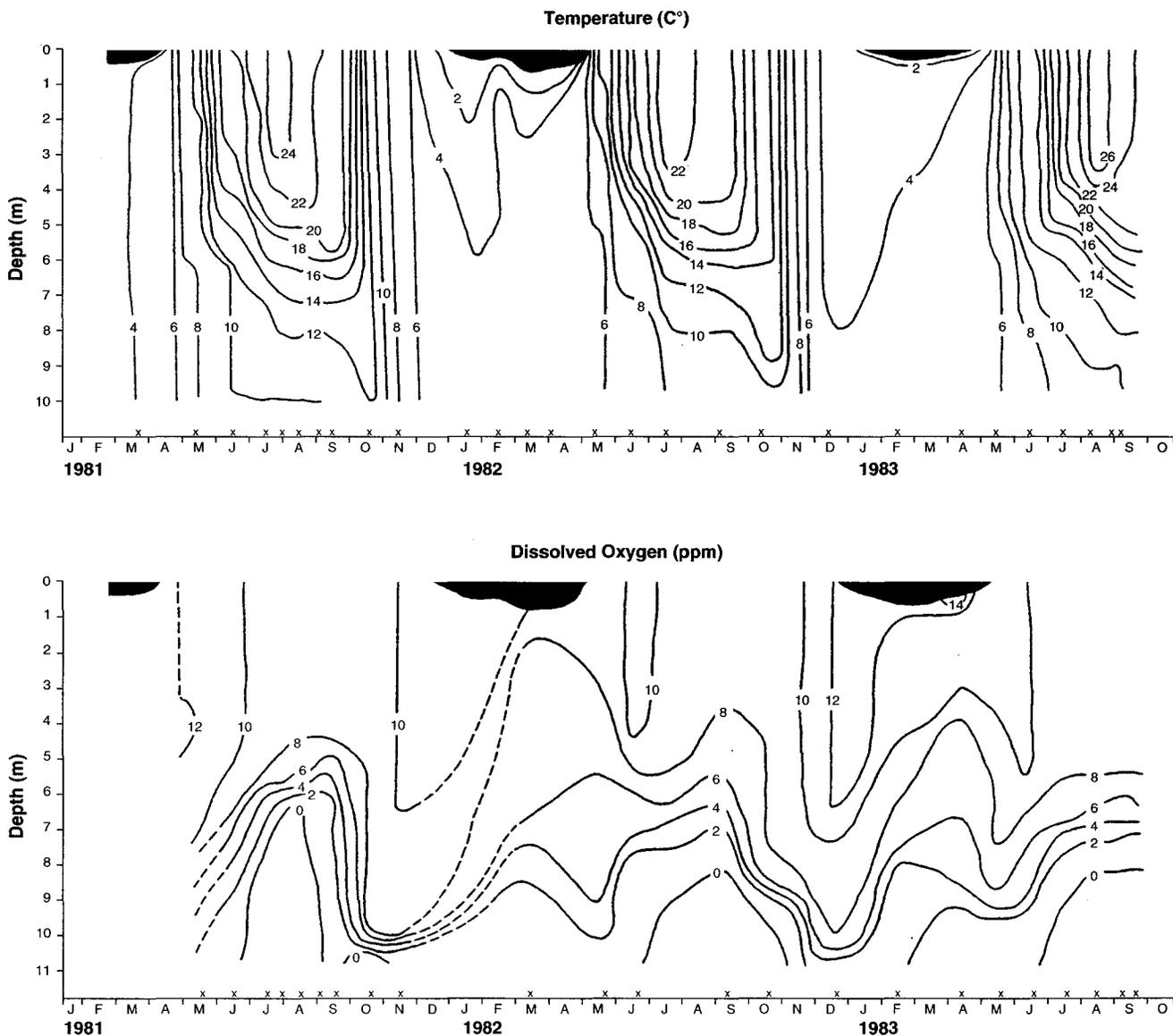


Figure 15. Temperature and dissolved oxygen isopleths for Lake Clara. Sampling dates are indicated by 'x'. Dotted lines indicate interpolated values.

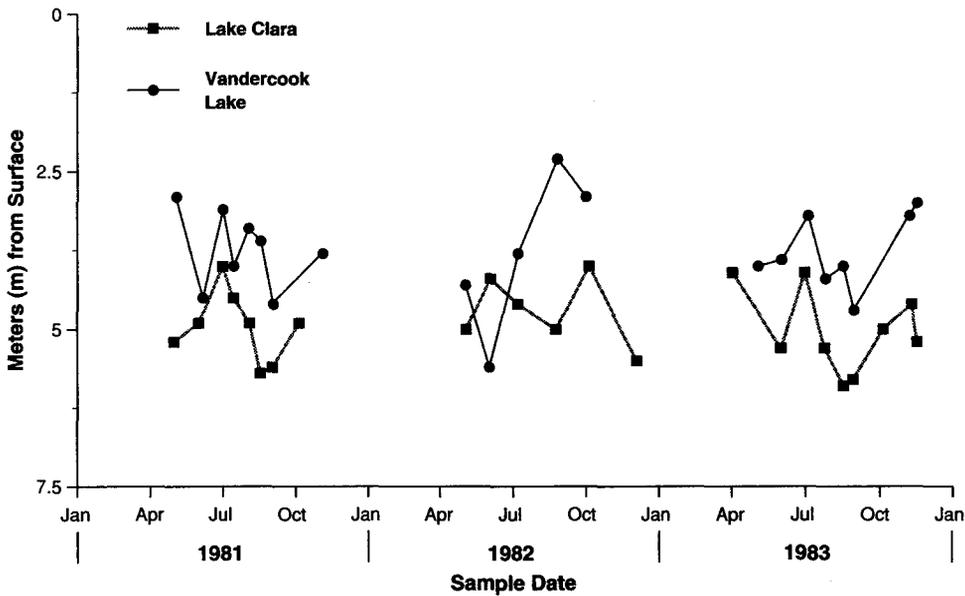


Figure 17. Secchi disk transparency (m) in Lake Clara and Vandercook Lake.

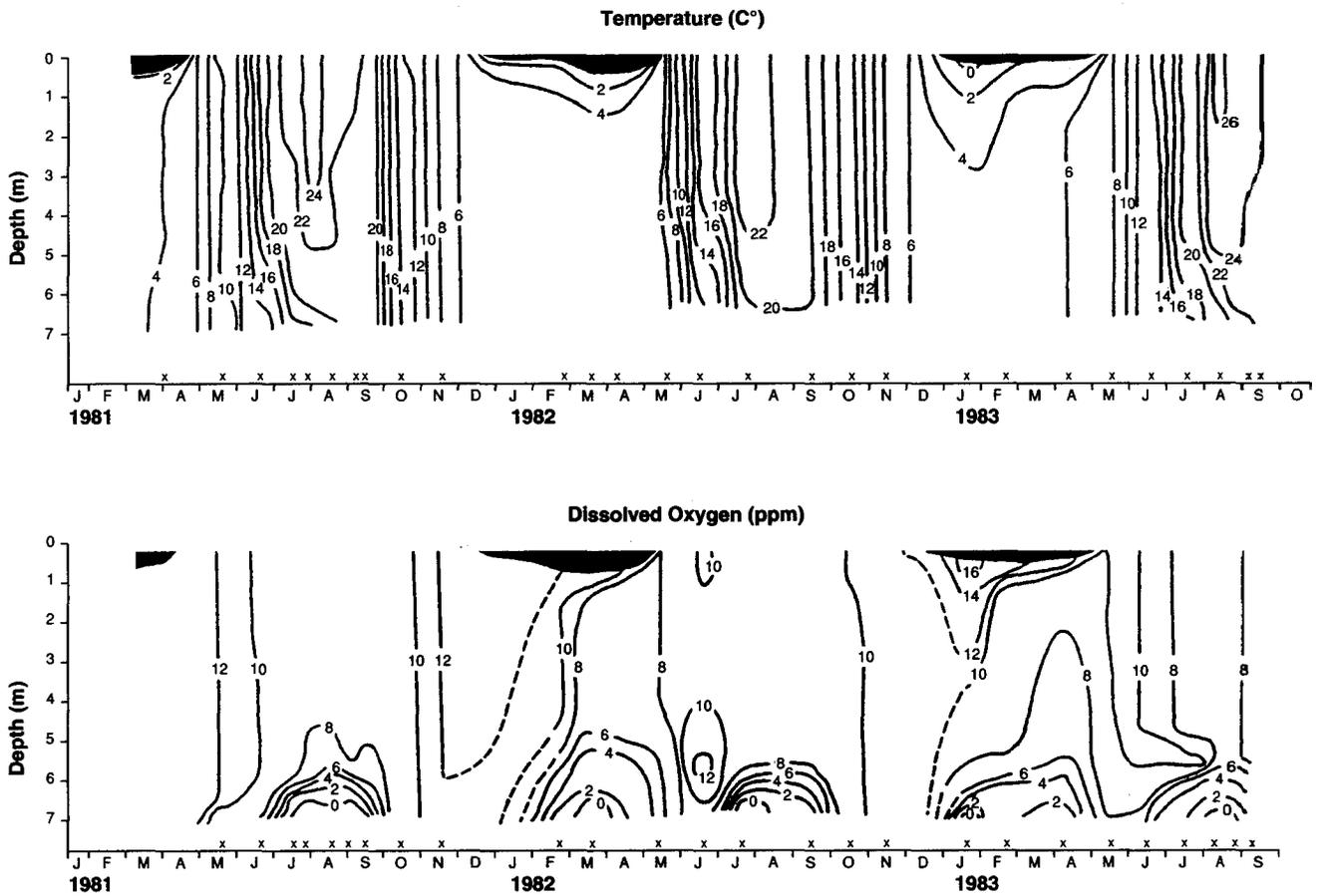


Figure 16. Temperature and dissolved oxygen isopleths for Vandercook Lake. Sampling dates are indicated by 'x'. Dotted lines indicate interpolated values.

Table 8. Summary of core chemical parameters and major ions measured in samples collected at three depths in Lake Clara, June 1981-October 1983.

Parameter*	Surface		Mid-depth		Bottom	
	Mean	Range	Mean	Range	Mean	Range
pH	6.2	5.9 - 6.5	6.0	5.7 - 6.3	6.0	5.7 - 6.4
Conductance (μS)	35	31 - 41	37	34 - 44	36	33 - 47
Color (PCU)	11	0 - 20	10	5 - 15	40	5 - 140
Turbidity (NTU)	0.6	0.3 - 0.8	0.5	0.3 - 0.8	3.1	0.3 - 10.0
ANC	30	22 - 51	35	27 - 45	73	28 - 175
SO_4^{2-}	93	87 - 106	95	87 - 110	90	56 - 100
Cl^-	123	107 - 141	130	124 - 149	118	101 - 135
NO_3^-	2	0 - 15	5	0 - 9	3	0 - 16
Ca^{2+}	92	80 - 109	96	85 - 114	114	81 - 170
Mg^{2+}	48	41 - 58	47	41 - 60	54	41 - 66
K^+	20	18 - 25	22	18 - 25	21	18 - 26
Na^+	112	106 - 126	113	105 - 127	111	104 - 116
NH_4^+	2	1 - 4		—	4	—
Fe (mg L^{-1})	0.06	0.00 - 0.22	0.07	0.04 - 0.22	0.95	0.36 - 5.31
Mn (mg L^{-1})	0.00	0.00 - 0.03	0.03	0.00 - 0.03	0.14	0.00 - 0.47
TP (mg L^{-1} as P)	0.010	0.033 - 0.016	0.013	0.010 - 0.016	0.013	0.010 - 0.016
SiO_2 (mg L^{-1})	0.14	0.06 - 0.35	0.19	0.17 - 0.21	0.15	0.06 - 0.40
TOC (mg L^{-1})	3.9	3.4 - 4.7		—	4.0	—
Total samples collected**		31		9		20

* Units are $\mu\text{eq L}^{-1}$ unless specified.

** Most samples were analyzed for core parameters and major ions; other parameters were analyzed for less than half of the samples.

Table 9. Summary of core chemical parameters and major ions measured in samples collected at three depths in Vandercook Lake, June 1981-October 1983.

Parameter*	Surface		Mid-depth		Bottom	
	Mean	Range	Mean	Range	Mean	Range
pH	6.1	5.6 - 6.4	6.0	5.7 - 6.5	6.2	5.9 - 6.4
Conductance (μS)	17	14 - 30	20	15 - 40	16	13 - 19
Color (PCU)	8	0 - 15	7	0 - 12	11	0 - 20
Turbidity (NTU)	0.9	0.3 - 1.6	0.8	0.3 - 1.8	1.5	0.6 - 2.5
ANC	18	2 - 41	22	8 - 50	22	10 - 55
SO_4^{2-}	88	75 - 104	85	77 - 92	82	60 - 94
Cl^-	8	6 - 14	7	6 - 8	7	6 - 8
NO_3^-	5	0 - 16	5	0 - 13	3	0 - 13
Ca^{2+}	66	55 - 87	67	60 - 76	66	55 - 88
Mg^{2+}	26	21 - 40	26	21 - 38	26	21 - 39
K^+	9	5 - 15	9	8 - 12	9	7 - 14
Na^+	16	14 - 22	18	14 - 29	15	13 - 17
NH_4^+	5	1 - 10		—	4	2 - 6
Fe (mg L^{-1})	0.04	0.00 - 0.74	0.04	0.00 - 0.56	0.08	0.00 - 0.25
Mn (mg L^{-1})	0.00	0.00 - 0.03	0.00	0.00 - 0.03	0.03	0.00 - 0.05
TP (mg L^{-1} as P)	0.013	0.007 - 0.023	0.016	0.010 - 0.046	0.020	0.010 - 0.026
SiO_2 (mg L^{-1})	0.07	0.06 - .12	0.08	0.06 - 0.12	0.09	0.06 - 0.14
TOC (mg L^{-1})	3.2	2.7 - 3.7		—		—
Total samples collected**		35		14		14

* Units are $\mu\text{eq L}^{-1}$ unless specified.

** Most samples were analyzed for core parameters and major ions; other parameters analyzed for less than half of the samples.

Groundwater Chemistry

Major Ion Composition. Groundwater chemistry was influenced by the position of the water table sampling well with respect to gradients of local flow and lake recharge. The upgradient piezometers, LCQ2 at Lake Clara and VLQ1 at Vandercook Lake, tended to have higher concentrations of major ions and SiO_2 compared to their counterpart downgradient piezometers and to in-lake values (Tables 10, 11). The extremely high Cl^- in LCQ2 suggests substantial contamination by road salt. LCQ2 is located between CTH A and Lake Clara.

The major ion composition of groundwater in downgradient piezometers showed the influence of lake water recharge (Table 10). The piezometers LCQ3S, LCQ3D, and LCQ5, located away from the direct influence of CTH A, had similar Cl^- concentrations to that of Lake Clara (Table 8). Although base cation concentrations in these wells were higher than the lake, they were less than those in the upgradient well LCQ2. LCQ5, located near the lake shore in a sandy zone, differed from the other downgradient piezometers in its higher SO_4^{2-} concentrations. LCQ1, located in a *Sphagnum* bog near the outlet at the tip of the southern lobe, had low concentrations of most parameters, including Cl^- , suggesting that this groundwater was isolated from the local aquifer.

Similar ion concentrations characterized three of the four downgradient piezometers around Vandercook Lake, VLQ2, VLQ3, and VLQ4; SO_4^{2-} concentrations were lower and base cation concentrations and ANC were higher compared to the lake water (Table 11). VLQ5, a downgradient piezometer located in a small *Sphagnum* bog, was similar to piezometers VLQ2, VLQ3, and VLQ4 in base cations and Cl^- , but was distinguished by higher color and Fe, and lower SO_4^{2-} and pH, likely caused by the presence of organics. SiO_2 was also higher in VLQ5.

A vertical gradient in ionic strength was apparent from the few samples collected from VLQ1D and VLQ3D, nested piezometers finished 22 m below the water table. High concentrations of major ions, alkaline pH, and high SiO_2 characterized these wells (Table 11). VLQ1D and VLQ3D probably intercept a more regional flow system than do the shallower piezometers which are influenced by local surface water discharge and recharge. A longer contact time between water and till materials allowed greater contributions of SiO_2 and calcium from silicate hydrolysis (Wentz et al., in review).

Temporal patterns. In general, the water chemistry of representative downgradient piezometers (LCQ3S and VLQ2) varied little either seasonally or annually (Append. D.3, D.4). Potassium declined during the winter in both wells, whereas pH and SO_4^{2-} increased in VLQ2 during the winter. A slight increase in Ca^{2+} and ANC occurred in VLQ2 late in the study period. The small decline in conductance in LCQ3S during the study period may be associated with a similar steady decline in Cl^- .

In contrast to the modest chemical fluctuations observed in the downgradient piezometers, the upgradient piezometers LCQ2 at Lake Clara and VLQ1 at

Vandercook Lake, showed large fluctuations which, for the most part, were not readily associated with any seasonal pattern. In LCQ2, conductance, Cl^- , Ca^{2+} , Mg^{2+} , and, to a lesser extent Na^{2+} followed the same sinusoidal temporal pattern (Append. D.5). Opposing trends were shown by ANC and SO_4^{2-} which increased between February and December 1982 and declined thereafter. VLQ1 showed a smaller increase in Ca^{2+} and Mg^{2+} from 1982 to 1983 (Append. D.6). Subtle seasonal fluctuations were observed for K^+ in both LCQ2 and VLQ1, and for pH in VLQ1, similar to the patterns described above for the downgradient wells.

Lake Clara Inlets and Outlets

Samples collected from the outlet of Lake Clara (Table 12) contained higher ANC and base cation concentrations compared to the main basin of the lake. Ion composition of the outlet was more similar to that of lake station 4, located in the shallow southern basin drained by the outlet.

The chemical composition of water from the four intermittent inlets to Lake Clara (Table 12) was characterized

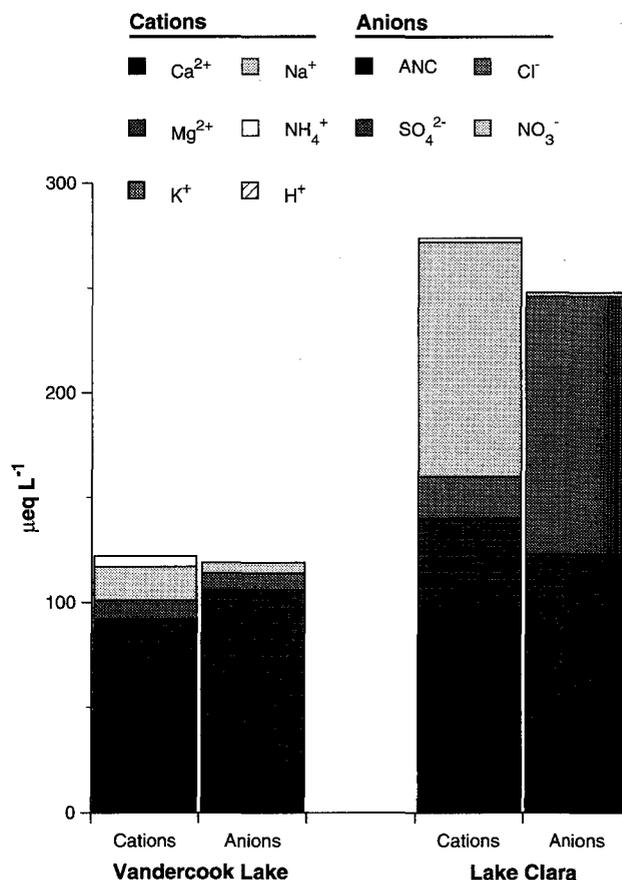


Figure 18. Bar diagrams comparing major ion chemistry of Vandercook Lake and Lake Clara.

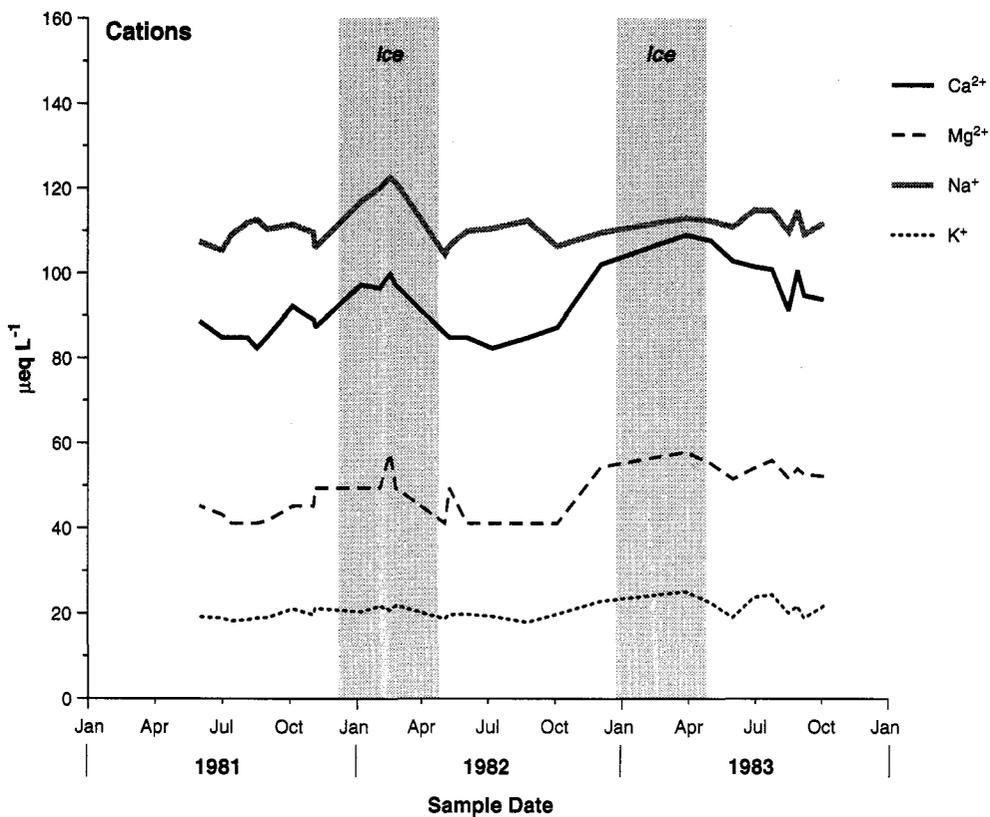
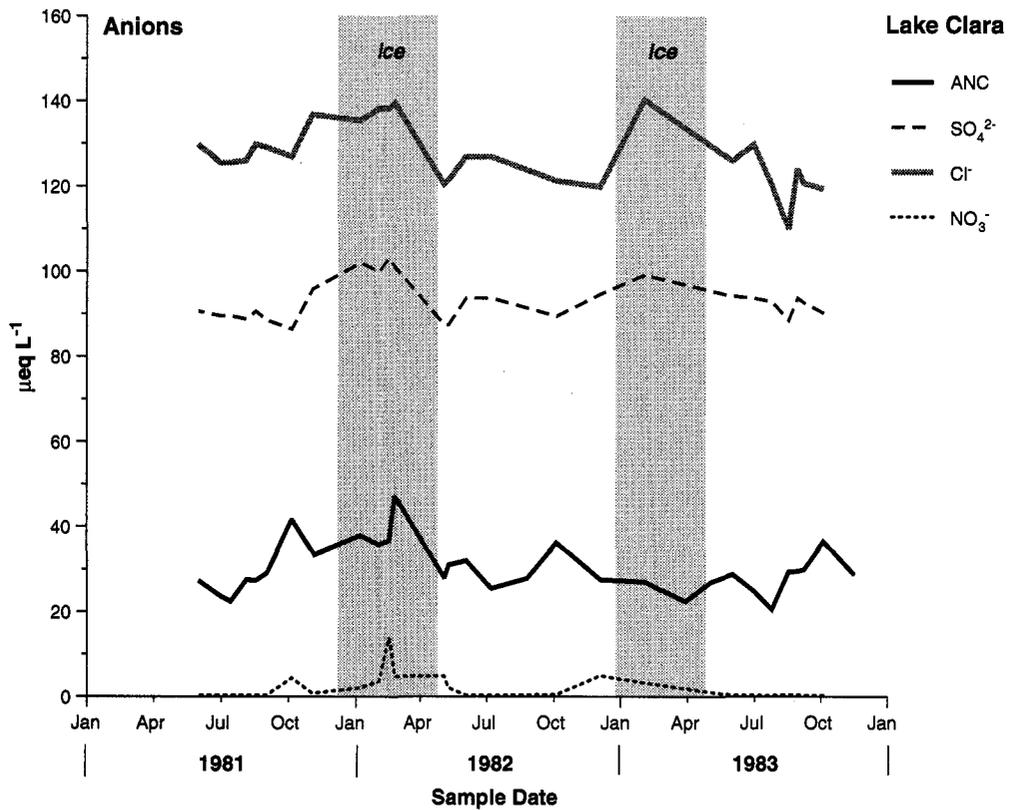


Figure 19. Time series plots for anions and base cations in surface samples from Lake Clara.

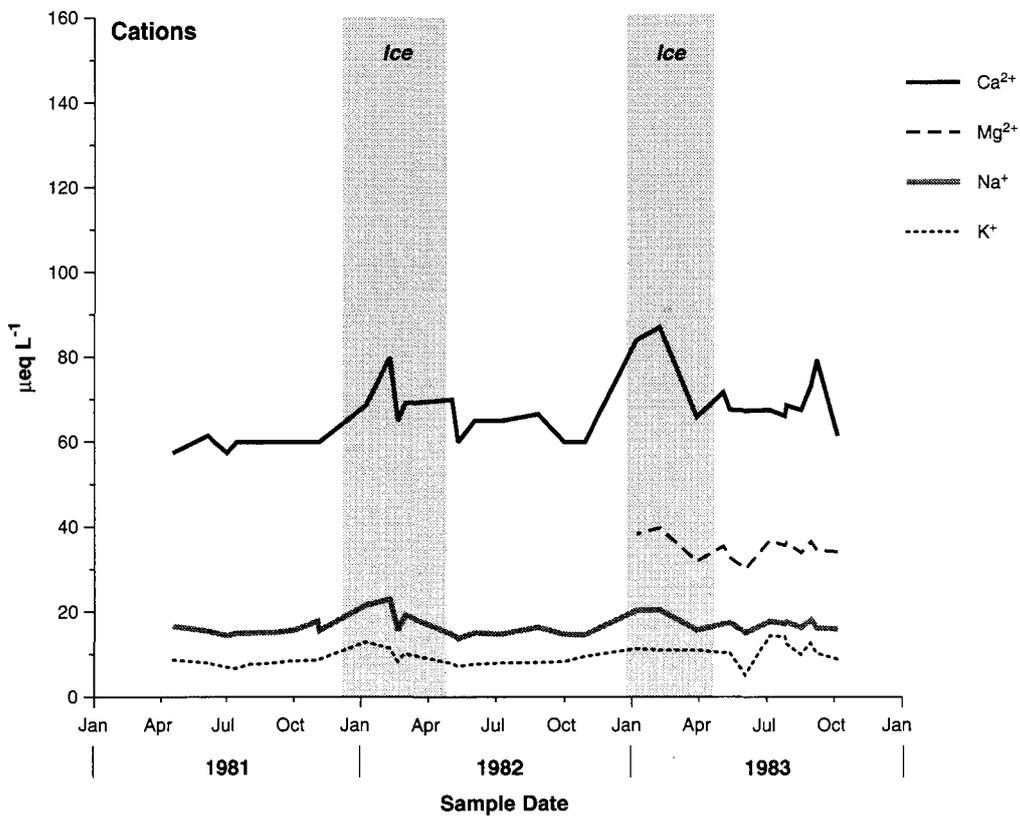
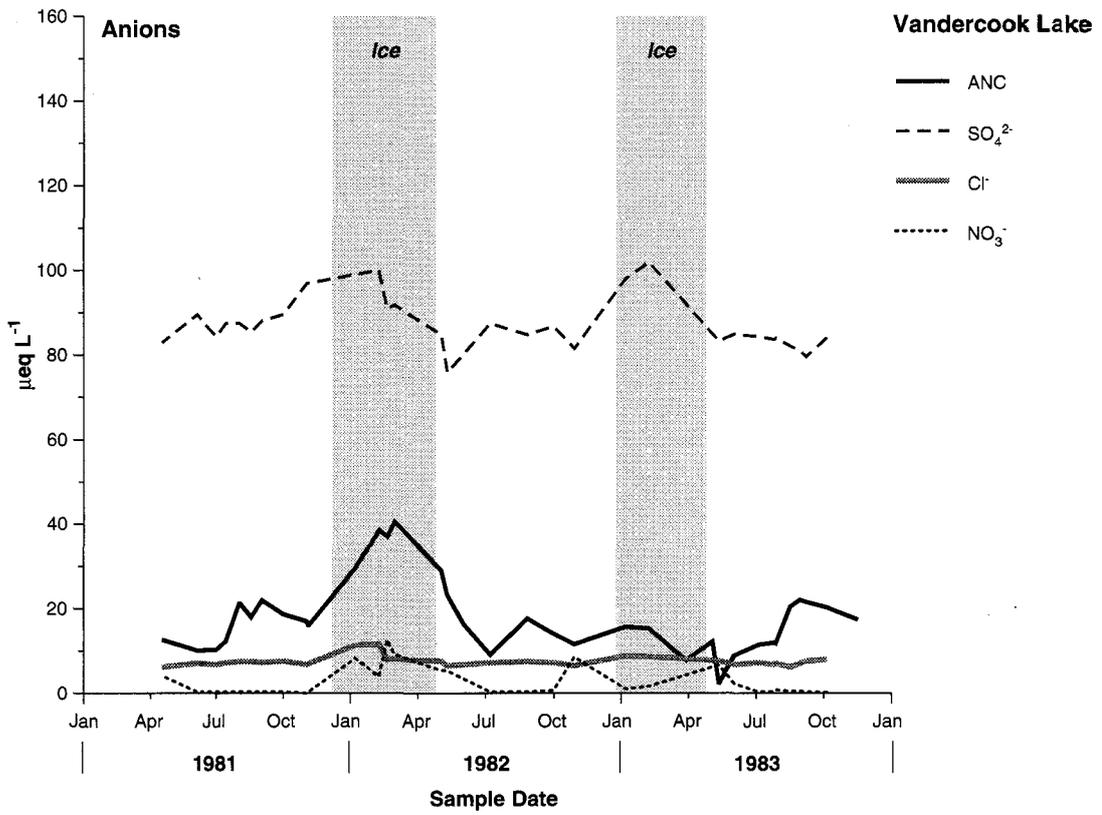


Figure 20. Time series plots for anions and base cations in surface samples from Vandercook Lake.

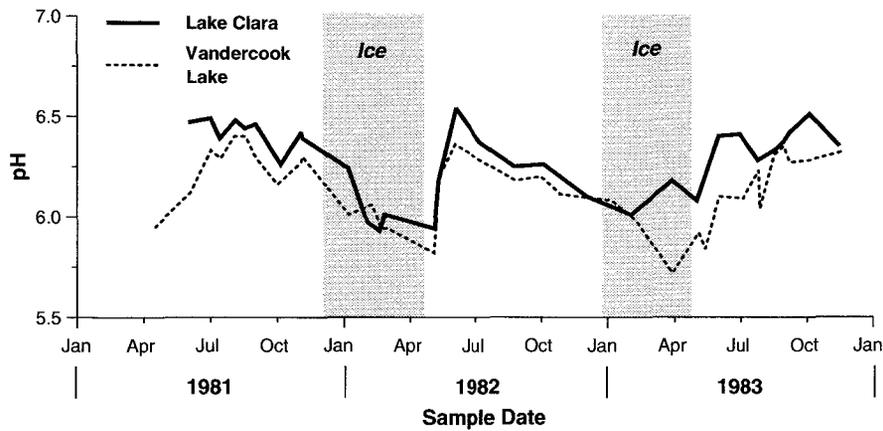


Figure 21. Epilimnetic pH in Lake Clara and Vandercook Lake.

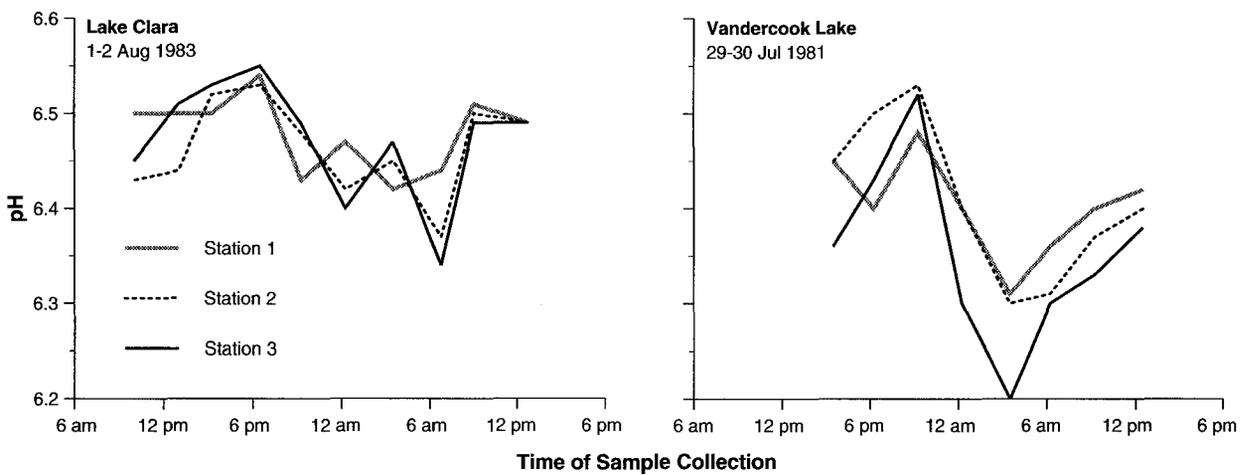


Figure 22. Diurnal shifts in epilimnetic pH in surface samples collected at three sites each in Lake Clara and Vandercook Lake.

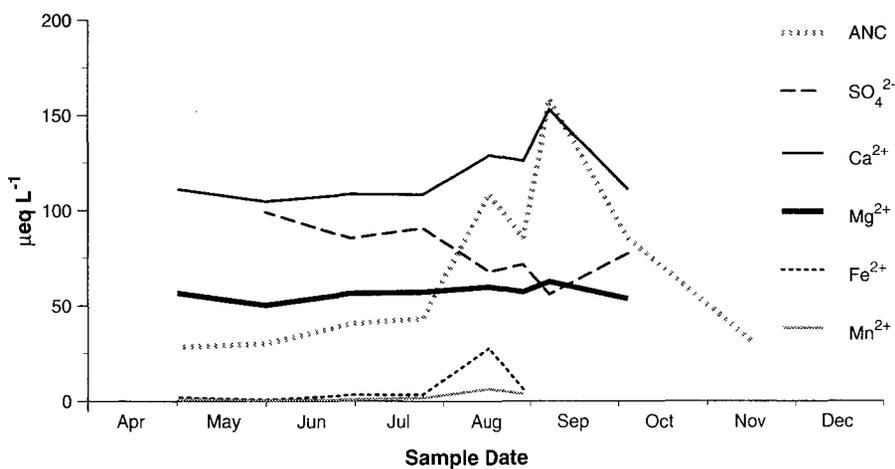


Figure 23. Hypolimnetic concentrations of major ions (ANC, SO_4^{2-} , Ca^{2+} , and Mg^{2+}), Fe^{2+} , and Mn^{2+} in Lake Clara during 1982.

Table 10. Summary of core chemical parameters and major ions measured in groundwater samples at Lake Clara June 1981-October 1983.

Parameter*	LCQ1		LCQ2		LCQ3S		LCQ3D		LCQ5	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
pH	5.7	5.6-6.3	6.1	5.9-6.3	6.0	5.9-6.2	5.9	5.8-6.1	6.0	5.8-6.1
Conductance (μS)	47	36-49	168	136-197	53	46-66	48	42-62	40	34-59
Color (PCU)	10	2-15	4	0-10	16	2-25	12	2-30	5	0-10
Turbidity (NTU)	0.2	0.0-0.8	0.2	0.0-1.0	0.8	0.0-2.9	1.0	0.0-7.0	0.1	0.0-0.3
ANC	330	282-398	283	241-347	327	278-266	298	223-416	60	48-81
SO_4^{2-}	4	2-17	280	229-333	14	2-27	10	2-69	100	77-125
Cl^-	48	39-56	766	378-1043	131	102-152	126	96-214	132	110-155
NO_3^-	0	0-1	16	11-21	1	0-2	1	0-2	1	0-2
Ca^{2+}	104	87-113	699	599-813	171	145-190	152	120-201	111	100-122
Mg^{2+}	35	21-43	268	229-312	107	90-120	50	41-67	53	41-62
K^+	17	14-21	30	24-36	34	26-42	10	7-14	24	20-28
Na^+	50	41-55	446	387-538	120	107-130	85	76-103	117	104-130
Fe (mg L^{-1})	0.63	0.41-0.86	0.00	0.00-0.06	1.23	0.34-2.09	4.10	0.04-5.62	0.34	0-4.62
Mn (mg L^{-1})	0.03	0.03	0.00	0.00	0.08	0.05-0.11	0.03	0.03-0.05	0.00	0.00-0.03
SiO_2 (mg L^{-1})	5.3	2.1-10.2	19.4	18.2-21.0	2.1	0.6-3.5	9.4	3.4-14.4	0.5	0.2-0.7
Total samples collected**		23		25		23		23		25

* Units are $\mu\text{eq L}^{-1}$ unless specified. TOC and NH_4 measurements were not available.

** Sample sizes are slightly smaller for major ions, trace metals and SiO_2 .

by high variability both within and between sites and was substantially different from the in-lake concentrations (Table 8) The four inlets could be separated into two groups based on their chemical characteristics. Inlets 1 and 2 were roughly similar in chemical composition with an average pH of around 6.0 and high concentrations of most ions. Spring snowmelt waters entering these inlets became enriched with ions (especially Na^+ and Cl^- from road salt) before reaching the lake. Inlets 3 and 4 were also contaminated by road salt, and, in contrast to inlets 1 and 2, were extremely acidic, most likely due to organic acids contributed by drainage from nearby small bogs and low-lying areas (see Append. A.2).

In 1982, the first snow runoff period lasted from 31 March to 4 April. The earliest water quality samples collected from inlet 1 (where we collected the majority of runoff samples) contained high concentrations of Cl^- , ANC, and Ca^{2+} , which varied substantially even over the course of a day (Append. D.7). Toward the end of the runoff period, concentrations of Cl^- , ANC, and Ca^{2+} had declined while SO_4^{2-} had increased. In contrast, pH remained relatively constant. The final set of runoff samples collected on 6 May, at the peak of spring flow, were higher in ANC and SO_4^{2-} but lower in Cl^- . In 1983, samples collected from inlet 1 were much less variable in chemistry than those collected in 1982. The lower concentrations of Na^+ and Cl^- in 1982 compared to 1981 suggest that road salt applications were reduced or that initial runoff was not sampled.



Recording V-notch weir at the outlet of Lake Clara.

PHOTO: J.M. EILERS

Bulk Deposition

No consistent differences in ionic concentrations among the three bulk deposition sites were apparent, although there was a tendency for the concentration of many ions to decrease in the order Clara > Vandercook > Trout (Table 13). This pattern held true for annual loads in 1981 and 1983, but not in 1982 when totals for Ca^{2+} , H^+ , SO_4^{2-} and NO_3^- were fairly similar across the three sites (Table 14). It would be expected that Lake Clara would receive higher inputs of base cations from local agricultural activities and higher inputs of mineral acidity because of its proximity to major point sources of sulfur in Rhinelander and Tomahawk. Vandercook Lake and Trout Lake, in contrast, are more remote sites in a predominantly forested area. The differences between the Trout Lake and Vandercook Lake sites in annual loads for many of the ions shown in Table 14 were unexpected as these sites are only 5 km apart. However, even over this small distance, total precipitation amounts differed (Table 14), particularly in 1983 when chemical differences were most apparent.

Several problems were inherent in the interpretation of chemical analyses from these bulk precipitation samples. Contamination from pollen, dead insects, and a variety of items falling into the collector was an obvious problem, although samples with gross contamination were not included in composites. Precipitation accumulated for up to a month before collection, allowing a substantial period for evaporative concentration and chemical transformation of unstable constituents (e.g. NO_3^- , NH_4^+ , SO_4^{2-}), especially during the summer. The efficiency of bulk collectors may decline with high winds or as a result of the fiberglass screen cover attached during the summer months to limit contamination.

Estimates of dry deposition as a percentage of total for the region have been made using data from the "dry buckets" collected as part of the NADP program (Cook and Jager 1991, Table 15). Comparisons

Table 11. Summary of core chemical parameters and major ions measured in groundwater wells at Vandercook Lake June 1981-October 1983.

Parameter*	VLQ1		VLQ2		VLQ3		VLQ4		VLQ5		VLQID		VLQ3D	
	Mean	Range	Mean	Range	Mean	Range								
pH	6.6	6.4-6.9	6.0	5.8-6.1	6.1	5.8-6.3	6.0	5.8-6.2	5.5	5.0-5.8	7.8	7.6-7.9	7.7	7.4-8.0
Conductance (μS)	62	56-74	22	16-30	21	14-46	25	16-80	32	26-39	133	108-197	116	100-142
Color (PCU)	13	5-22	15	8-20	11	0-30	16	5-35	237	165-300	9	8-10	11	10-12
Turbidity (NTU)	1.4	0.1-3.3	0.4	0.0-2.0	1.0	0.0-7.3	1.1	0.0-8.0	4.5	0.2-33.0	0.2	0.1-0.2	0.6	0.3-1.0
ANC	413	300-641	137	85-187	123	79-165	145	32-251	177	66-354	1,30	1,046	1,12	1,023
SO_4^{2-}	154	131-169	33	12-75	32	19-50	43	17-200	6	2-27	116	94-152	99	146-181
Cl^-	11	8-14	8	6-17	8	6-8	9	6-11	8	6-11	11	8-20	21	11-25
NO_3^-	3	0-5	3	0-24	3	0-36	3	0-34	11	0-96	1	0-2	1	0-2
Ca^{2+}	291	238-372	74	55-122	72	55-90	76	55-90	79	52-101	924	641-1,447	822	718-983
Mg^{2+}	169	124-205	29	21-50	30	21-42	37	21-74	44	21-72	372	329-492	323	297-353
K^+	11	8-20	12	8-18	14	8-20	14	10-21	10	5-13	32	30-34	36	33-38
Na^+	88	63-96	22	15-31	23	20-28	27	19-35	32	17-56	108	99-129	12	113-133
Fe (mg L^{-1})	0.60	0.04-2.08	0.89	0.61-1.12	0.67	0.37-0.97	1.42	0.04-5.88	3.87	2.64-4.92	0.01	—	0.03	—
Mn (mg L^{-1})	0.03	0.00-0.08	0.03	0.03	0.03	0.00-0.03	0.03	0.03-0.05	0.03	0.00-0.03	0.04	0.00-0.11	0.04	0.02-0.06
SiO_2 (mg L^{-1})	19.4	18.3-20.0	1.0	0.7-2.1	1.3	0.6-2.5	1.7	0.7-3.9	12.0	4.4-20.1	17.3	16.4-18.6	13.9	13.6-14.3
Total samples collected**		22		23		23		23		23		4		3

* Units are $\mu\text{eq L}^{-1}$ unless specified. TOC and NH_4^+ measurements were not available.

** Sample sizes are slightly smaller for major ions, trace metals, and SiO_2 .

Table 12. Summary of core chemical parameters and major ions in outlet and inlets at Lake Clara June 1981–October 1983.

Parameter*	Outlet		Inlet 1		Inlet 2		Inlet 3		Inlet 4	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
pH	5.7	5.6-6.0	6.2	5.9-6.6	6.0	5.8-6.3	4.3	4.1-5.3	3.9	3.8-4.0
Conductance (µS)	35	27-52	93	32-416	97	31-503	47	11-77	114	97-149
Color (PCU)	29	8-120	35	11-100	35	15-60	131	55-275	231	200-260
Turbidity (NTU)	0.9	0.4-2.5	5.2	0.8-22.0	4.7	1.2-12.0	2.8	1.3-7.4	2.0	1.6-2.6
ANC	52	15-178	110	56-536	72	43-105	-57	(-114)-32	-177	(-217)-136
SO ₄ ²⁻	78	67-94	144	100-200	186	154-210	149	133-171	175	119-341
Cl ⁻	113	85-152	505	6-3,158	561	11-3,722	98	65-164	273	149-392
NO ₃ ⁻	4	0-14	16	0-104	22	1-100	6	0-22	27	5-102
Ca ²⁺	106	83-190	234	138-500	276	149-927	476	74-1164	136	116-194
Mg ²⁺	51	41-80	84	60-156	99	62-268	142	46-291	85	65-135
K ⁺	23	16-39	40	16-177	30	13-75	55	22-118	47	31-85
Na ⁺	100	78-146	478	52-2,911	465	51-3,135	1,150	40-3,268	256	171-318
Fe (mg L ⁻¹)	0.19	0.06-0.39	0.48	0.04-5.64	0.50	0.08-3.09	0.48	0.11-1.38	0.39	0.30-0.45
Mn (mg L ⁻¹)	0.03	0.00-0.03	0.14	0.00-1.15	0.05	0.00-0.33	0.38	0.05-1.62	0.08	0.05-0.11
SiO ₂ (mg L ⁻¹)	0.3	0.1-0.5	5.3	0.6-7.0	7.8	1.3-10.1	6.6	1.3-7.1	5.9	1.5-6.5
Total samples collected**	19		17		9		5		6	

* Units are µeq L⁻¹ unless specified. TOC and NH₄⁺ measurements were not available.

** Sample sizes are slightly smaller for major ions, trace metals, and SiO₂.

Table 13. Annual volume-weighted mean concentrations of major ions (µeq L⁻¹) in wet deposition collected at the NADP Trout Lake site (weekly)* and in bulk deposition collected at the Trout Lake site and at the two study lakes (monthly).

Year	Site	Sample Size	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	H ⁺ **	NH ₄ ⁺	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
1981	Trout Lake NADP	44	11	4	1	2	17	20	35	3	18
	Trout Lake bulk	12	27	8	5	4	16	10 ^a	44	3	23
	Vandercook bulk	8	24	8	9	8	15	25	58	7	24
	Clara bulk	9	31	8	6	6	14	28	60	5	28
1982	Trout Lake NADP	48	10	3	1	2	21	20	38	2	20
	Trout Lake bulk	9	15	4	2	2	24	21	45	2	22
	Vandercook bulk	10	16	5	2	2	22	20	43	3	21
	Clara bulk	12	19	6	2	2	25	11	50	3	22
1983 ^b	Trout Lake NADP	45	10	3	1	2	22	15	32	2	18
	Trout Lake bulk	5	14	3	1	1	25	29	43	2	28
	Vandercook bulk	6	15	4	2	3	26	40	55	4	31
	Clara bulk	5	18	4	1	2	31	31	52	3	32

* National Atmos. Deposition Prog. 1985

** H⁺ calculated from pH.

^a NH₄⁺ concentrations were not measured in the bulk deposition samples; values were estimated as the difference between the sum of the cations minus the sum of the anions.

^b Bulk deposition in 1983 analyzed only from Jan-Jun by ERL-D; NADP results are for the entire year.

Table 14. Annual loads of major ions ($\text{eq ha}^{-1} \text{yr}^{-1}$) for constituents of wet deposition collected at the NADP Trout Lake site (weekly) and in bulk deposition collected at the Trout Lake site and at the two study lakes (monthly).

Year	Site	Annual Precip. (mm)	Sample Size	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	H ⁺	NH ₄ ⁺	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
1981	Trout Lake NADP	720	44	74	27	6	16	122	139	253	18	134
	Trout Lake bulk		12	178	50	31	24	103	na**	290	23	153
	Vandercook bulk	741	8	163	51	62	53	102	na	382	46	156
	Clara bulk	770	9	226	61	40	44	99	na	435	34	204
1982	Trout Lake NADP	1,017	48	105	32	7	17	223	216	396	23	203
	Trout Lake bulk		9	134	37	21	16	213	na	397	19	195
	Vandercook bulk	1,107	10	136	45	21	14	194	na	375	25	182
	Clara bulk	990	12	149	43	12	13	192	na	383	26	171
1983 ^a	Trout Lake NADP	746	45	80	25	6	18	187	128	273	20	152
	Trout Lake bulk		11	117	36	11	42	145	na	251	24	156
	Vandercook bulk	959	12	140	41	91 ^b	59	162	na	314	26	180
	Clara bulk	967	12	148	41	10	46	198	na	342	23	224

* H⁺ calculated from pH.

** na = not analyzed

^a Annual loads for bulk deposition in 1983 include monthly samples collected between Jul-Dec analyzed by the USGS laboratory.

^b Suspect contamination in sample collected 28 Oct-29 Nov 1983.

Table 15. Percent of total annual deposition comprised of dry deposition for major ions determined from a comparison of bulk vs. wet-only samples from Trout Lake 1981-83 (this study) and estimates for the Upper Midwest based on NADP dry bucket data (Cook and Jager 1991).

Location	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
Trout Lake	37	30	65	28	1	6	4
Upper Midwest estimate	35	40	60	20	27	16	23

Table 16. Summary statistics for chemical constituents and major ions analyzed in snow cores collected from Lake Clara and Vandercook Lake in March 1982.

Parameter*	Lake Clara			Vandercook Lake		
	Mean	Sample Size	Standard Deviation	Mean	Sample Size	Standard Deviation
pH	5.12	9	0.43	4.74	10	0.07
Conductance (μS)	14.00	10	2.00	13.70	10	1.30
NO ₃ ⁻	34.40	10	5.30	30.80	10	2.20
SO ₄ ²⁻	27.20	10	6.20	19.30	10	2.70
Cl ⁻	7.90	10	3.40	5.40	10	1.40
Ca ²⁺	25.40	9	6.90	15.90	10	2.60
Mg ²⁺	11.80	9	4.30	6.30	10	1.60
Na ⁺	9.60	9	7.80	4.60	10	2.20
K ⁺	15.50	9	12.10	5.60	10	2.30
NH ₄ ⁺	30.90	10	9.10	17.80	10	6.10
Anion deficit**	35.40	8	24.90	13.30	10	7.10
Total acidity	24.20	10	11.80	30.00	10	7.60
Strong acidity (%) ^a	29.50	7	20.30	51.00	9	8.80

* Units are $\mu\text{eq L}^{-1}$ except for pH and conductance.

**Difference between sum of cations (including H⁺) and sum of the anions.

^a Strong acidity values were negative for 3 cores from Lake Clara and 1 core from Vandercook Lake.

between these estimates and the percent dry deposition derived from this study and NADP wet loads, suggest that bulk collectors were fairly efficient at collecting base cations and Cl^- , but not SO_4^{2-} and NO_3^- . The NO_3^- underestimate was expected due to the instability of this ion. Because NH_4^+ was not measured in bulk samples we cannot fully evaluate nitrogen concentrations.

Snow Cores

The chemical composition of snow cores collected at 10 sites in each lake watershed is summarized in Table 16. Concentrations of all ions except H^+ (as indicated by pH) were higher in samples from the Lake Clara watershed than in samples from the Vandercook Lake watershed. Total acidity was higher at Vandercook; and, on average, a greater proportion of the total acidity was comprised of strong versus weak acids. The anion deficits for the snow cores were quite high, especially at Lake Clara (mean of $35.4 \mu\text{eq L}^{-1}$). Either there was a significant contribution of organic anions in the snow samples, or there was some degradation in the samples due to the long holding time (frozen for 6 months).

Chemical Sensitivity to Acidification

A lake's chemical composition is determined by a complex series of factors including local geologic setting, the sources and sinks of chemical constituents to the system, and anthropogenic disturbances. In the Northern Highland region of Wisconsin there is a large population of lakes with low acid-neutralizing capacity, due in part to the low-carbonate glacial till characterizing the region. Much of the variability in chemical composition between the region's lakes can be explained by hydrology, which plays an important role in determining lake ANC (Broughton 1941; Eilers et al. 1983; Anderson and Bowser 1986; Kenoyer and Anderson 1989). Low ANC lakes in the region are typically seepage lakes which receive most of their water from direct precipitation, which contains high concentrations of the mineral acids SO_4^{2-} and NO_3^- . Even small inputs of ion-rich groundwater to such lakes (on the order of 5% or less) can be important in neutralizing incoming precipitation and maintaining a positive ANC (Anderson and Bowser 1986; Garrison et al. 1987; Kenoyer and Anderson 1989; Webster et al. 1990).

The chemical composition of Vandercook Lake was typical of softwater seepage lakes in northern Wisconsin of concern with respect to the potential effects of acidic deposition (Eilers et al. 1983; Linthurst et al. 1986; Cook et al. 1987; Garrison et al. 1987). These potentially sensitive lakes have $\text{ANC} < 40 \mu\text{eq L}^{-1}$, low base cation concentrations, and the dominant anion is SO_4^{2-} .

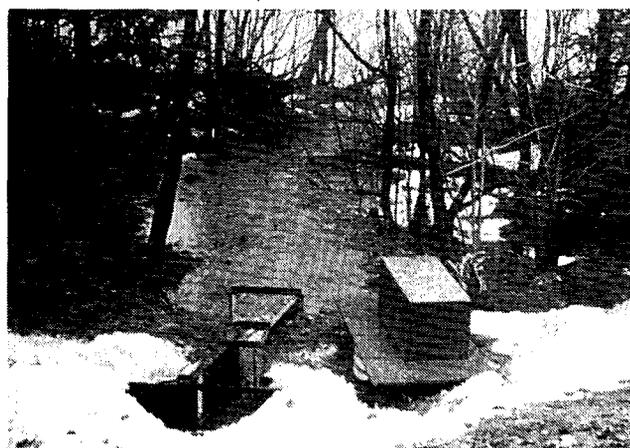
The ANC of Lake Clara was also less than $40 \mu\text{eq L}^{-1}$ and SO_4^{2-} , detected in concentrations similar to those in Vandercook Lake, would have been the dominant anion without the anthropogenic additions of Cl^- . However, the application of salt to CTH A during the winter altered the ionic composition of the lake to the extent that Na^+

and Cl^- were the dominant cation and anion, respectively. These road salt applications have contaminated the lake, as well as the local groundwater and the surface water flowing into Lake Clara during the spring melt period.

The chemical characteristics of snowmelt runoff flowing into Lake Clara differed substantially from regions where release of mineral acids from the snowpack in spring can cause large pH depressions in lakes (Jeffries et al. 1979; Driscoll et al. 1991). These pH depressions can adversely impact intolerant species as well as those whose more sensitive early life stages coincide with the spring snowmelt period (France and LaZerte 1987). Despite the moderately high concentrations of mineral acidity measured in snow cores at Lake Clara, spring runoff from two inlets, 1 and 2, (Table 12) was not acidic, but, in fact, contained higher ANC and base cation concentrations than did the lake. In northern Wisconsin, soils do not freeze deeply during the winter due to the insulating effect of snow cover (Garrison et al. 1987; Kratz et al. 1987), allowing sufficient contact time for neutralization



Parshall Flume and stage recorder at inlet 1 of Lake Clara during snowmelt runoff — view upstream of the lake.



Parshall Flume and stage recorder at inlet 1 of Lake Clara during snowmelt runoff — view downstream from County Highway A.

PHOTOS: J.M. EILERS

of acidic meltwater. Although high acidity levels were measured in the other inlets (3 and 4), the corresponding high color suggests this acidity was due to organic rather than mineral acids.

The runoff data (Append. D.7) show that snowmelt was not responsible for the depression in surface water pH of roughly 0.5 units that we observed during the winter at both lakes (Fig. 21). Kratz et al. (1987) reported similar pH depressions during the winter and early spring in nearby lakes in northern Wisconsin. They attributed the pH declines to the buildup of CO₂ produced by decomposition under the ice rather than to increases in strong mineral acids or weak organic acids. We did not observe decreased ANC or increased SO₄²⁻ concurrent with the pH depression in either of our study lakes, and the slight increase in NO₃⁻ concentrations during the winter was not large enough to explain the pH pattern. Following ice-out and spring overturn, CO₂ is degassed into the atmosphere and pH values quickly rebound.

Increased algal activity was likely responsible for the higher pH observed in surface waters during the summer months and for the diurnal shifts we observed (Wetzel 1983). Photosynthesis causes CO₂ uptake and increased pH, while respiration has the opposite effect, decreasing pH. The diurnal cycling of pH that we observed during 24 hour periods in both lakes during the summer can thus be related to the respiration and photosynthesis cycles of phytoplankton.

Similar to pH, NO₃⁻ concentrations were influenced by biological uptake, and thus showed distinct seasonal patterns. NO₃⁻ was only detected in Lakes Clara and Vandercook in winter when biological activity and uptake rates were low. Upon ice-out, algal uptake quickly reduced NO₃⁻ concentrations to below analytical detection limits.

The changes in ionic composition detected during summer stratification in the anoxic hypolimnion of Lake Clara demonstrate the ability of lakes to internally generate ANC. Under anoxic conditions, ANC was generated by reduction reactions of ions such as Fe²⁺, Mn²⁺ and SO₄²⁻. By comparing the changes in equivalents for these parameters at the beginning and end of the summer stratification period, the contributions by each process to ANC can be calculated. As shown in Table 17, SO₄²⁻ reduction and transformation of Fe(III) to Fe(II) were the major sources of ANC produced in the hypolimnion of Lake Clara. The 10 µeq L⁻¹ difference between measured and predicted ANC in Table 17 was at least partially due to

reactions involving NH₄⁺ which could not be evaluated due to lack of data. Because these reactions are redox sensitive, the ANC generated during anoxic periods is not permanent, but is mostly consumed at fall turnover when oxygen levels increase. Processes such as SO₄²⁻ reduction and cation exchange occurring at the sediment-water interface can generate permanent ANC under oxic conditions in the littoral zone (Kelly and Rudd 1986) and can be important internal sources of permanent ANC, especially in these softwater seepage lakes with relatively long residence times (Baker and Brezonik 1988; Cook et al. 1986).

Processes Controlling ANC

If Clara and Vandercook were "teflon" lakes, receiving all their water from precipitation and lacking internal sources and sinks, their ionic composition would reflect that of deposition. Not unexpectedly, this was not the case. We found striking differences in the ionic composition of deposition and lake water. Bulk deposition was dominated by the cations NH₄⁺ and H⁺ and the anion SO₄²⁻ (Figs. 24, 25). Vandercook Lake water samples were similar to deposition in the large contribution of SO₄²⁻ to the anion total (74%), but had low NO₃⁻ and higher ANC (Fig. 25). Major differences were apparent in cation composition. Ca²⁺ and Mg²⁺ dominated the cations in Vandercook, with only minor contributions of NH₄⁺ and virtually no H⁺ (Fig. 25). The base cation composition of Vandercook Lake was more similar to that of groundwater from the adjacent shallow aquifer. The upgradient and down gradient groundwater, however, tended to have much higher ANC and lower SO₄²⁻ compared to both the lake and deposition. Contamination of the Lake Clara watershed by road salt was evident from the dominance of Na⁺ and Cl⁻ in the lake, inlet, and groundwater samples (Fig. 24).

Ion enrichment analysis uses the differences between the concentrations of major ions expected from the "teflon" model, which assumes that evapo-transpiration is the only influence on lake ion concentrations, and measured values to indicate the biogeochemical and watershed processes which determine lake chemistry, and specifically ANC (Lee and Schnoor 1988). Important processes in seepage lakes include weathering/groundwater contributions, cation exchange at the sediment-

Table 17. Changes in concentrations of major ions (µeq L⁻¹) contributing to ANC production in the hypolimnion of Lake Clara during summer stratification.

Time Interval	ANC			Fe ²⁺ **	Mn ²⁺	NH ₄ ⁺	SO ₄ ²⁻	NO ₃ ⁻
	Predicted	Measured						
4 May-8 Jul 1982	52	42	=	19	+	4	+	na** - (-14) - (-5)
1 Jun-29 Aug 1983	55	43	=	8	+	8	+	na - (-28) - (-4)

* Due to anoxic conditions, Fe and Mn were assumed to be valence 2+.

** Not analyzed.

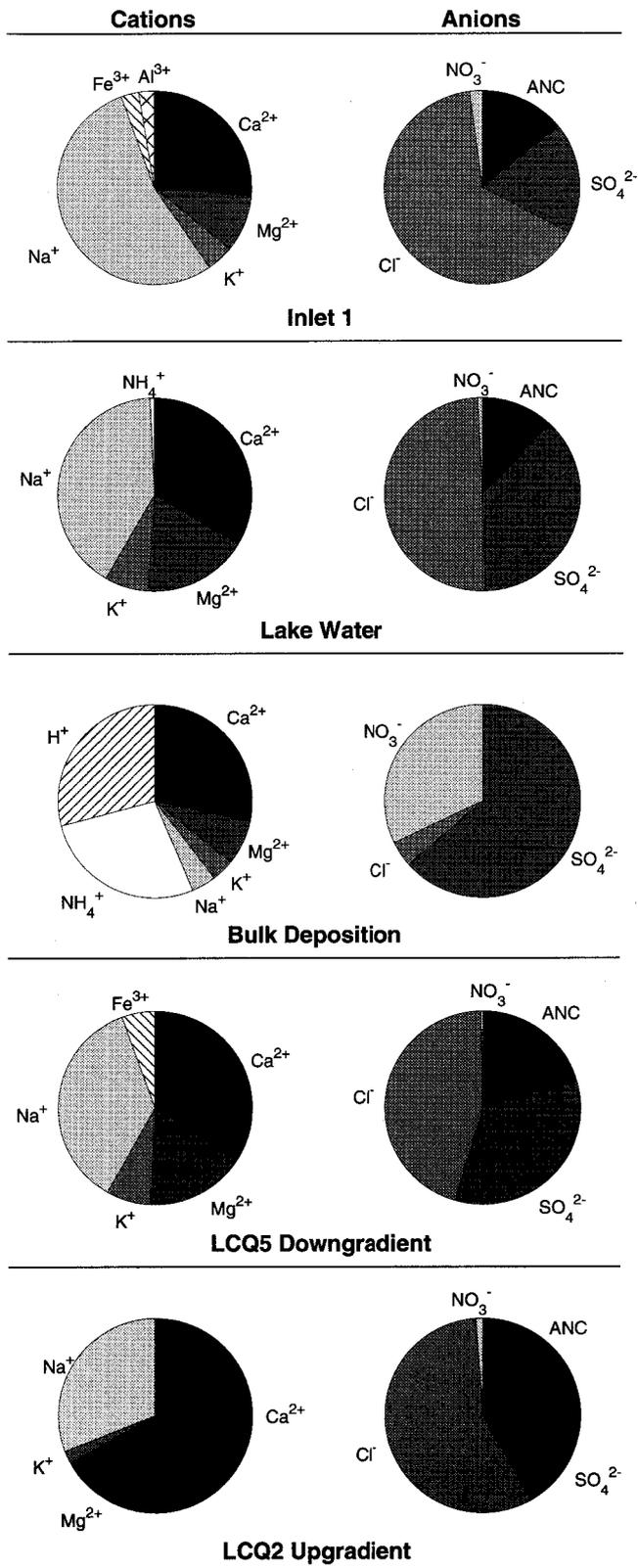


Figure 24. Percent ionic composition of water at inlet 1, lake water, bulk deposition, and downgradient (LCQ5) and upgradient (LCQ2) groundwater at Lake Clara.

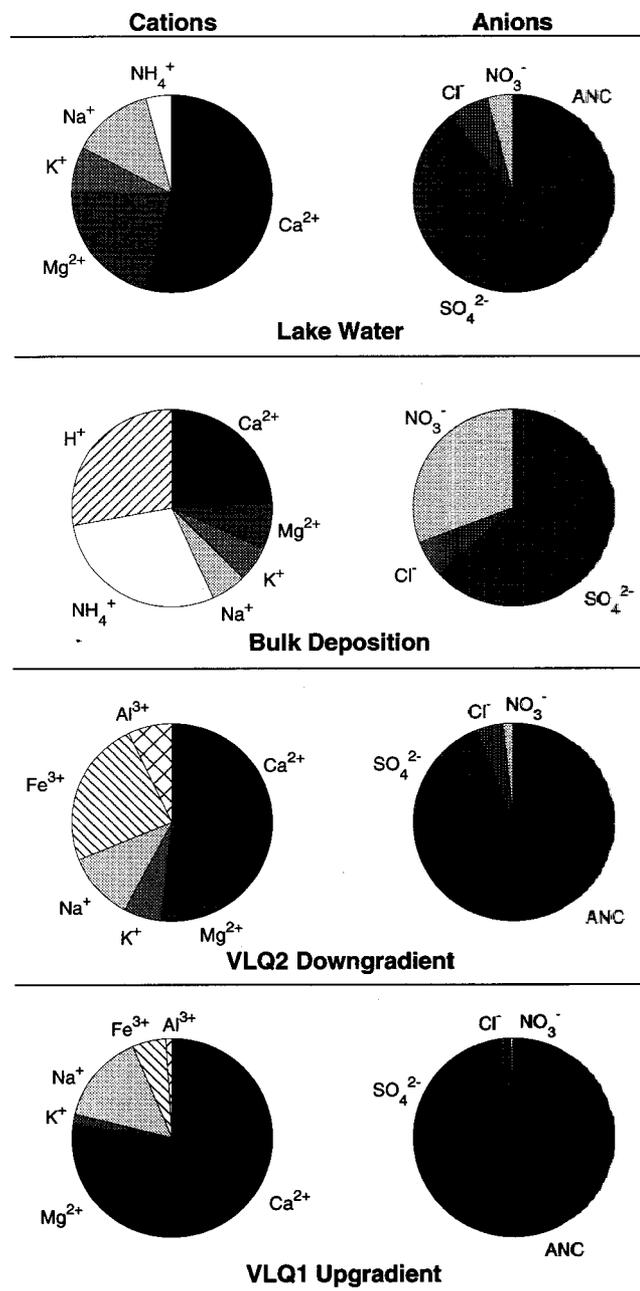


Figure 25. Percent ionic composition of lake water, bulk deposition, and downgradient (VLQ2) and upgradient (VLQ1) groundwater at Vandercook Lake.

water interface, and in-lake processes such as sulfate reduction, sedimentation, and algal uptake. Expected lake water concentrations were estimated by multiplying the ion concentration in bulk deposition by the evapo-concentration factor, calculated as the ratio between Cl^- in the lake and Cl^- in deposition (Baker et al. 1991). This approach assumes that Cl^- is conservative and not supplied by external sources, a condition which prevented a similar analysis of the roadsalt-contaminated Lake Clara. The difference between expected and measured concentrations, or R_i , is an estimate of the net contribution to lake ANC. $\text{ANC}_{\text{Cb-Ca}}$ is the sum of the reaction terms (R_i) for the base cations minus the strong acid anions (Cook and Jager 1991). Note that a negative R_i for an anion corresponds to a gain of ANC to the system.

The calculated evapo-concentration factor for Vandercook Lake was 1.6, close to the mean determined in a similar analysis of clear water, groundwater recharge lakes in north-central Wisconsin (Cook and Jager 1991). Expected in-lake concentrations of major ions were calculated as the product of 1.6 times the concentration in bulk deposition. The differences between lake concentrations and expected values suggest that enrichment by base cations was the major contributor to the ANC of Vandercook Lake (Fig. 26). Cook and Jager (1991) also concluded that the acid-base chemistry of lakes in the Upper Midwest was controlled primarily by base cations supplied primarily by groundwater influx, with minor contributions from cation exchange at the sediment surface. In lakes which are more isolated from the groundwater system and thus receive a lower influx of base cations, in-lake processes such as SO_4^{2-} reduction increase in importance as contributors of ANC.

Nitrogen deposition had a negligible net effect on ANC in Vandercook Lake. R_i values for NO_3^- and NH_4^+ were nearly equal in magnitude but opposite in their effect on ANC. The low concentration of these ions in the lake demonstrates the fairly rapid biological assimilation and nitrification/denitrification processes which consume nitrogen species supplied by deposition.

SO_4^{2-} showed a net loss and corresponding contribution to lake ANC. In general, two processes have been identified as important in-lake sinks for sulfur: sedimentation and sulfate reduction. In nearby Little Rock Lake, sedimentation accounted for 70% of the SO_4^{2-} retained in the system (Baker et al. 1989). Sulfate reduction, a microbially-mediated process occurring in the sediments, can be a significant ANC generating process in low ANC seepage lakes with relatively long residence times (Kelly et al. 1986, Baker and Brezonik 1988). Applying the Trickle-Down Model to the Vandercook Lake chemistry data, Lin and Schnoor (1986) estimated that sulfate reduction accounted for 54% of the ANC production in Vandercook Lake, a higher contribution than that calculated by the ion enrichment analysis presented here (15%).

The ion enrichment analysis for Vandercook Lake indicates that there is sufficient ANC produced within the watershed to neutralize current loading of acidic deposition. The amount of ANC required to neutralize

the acid inputs from deposition ($32.8 \mu\text{eq L}^{-1}$) and produce $18 \mu\text{eq L}^{-1}$ of lake ANC was $51.8 \mu\text{eq L}^{-1}$ (ANC_{gran} in Fig. 26). The contributions from biogeochemical processes ($\text{ANC}_{\text{Cb-Ca}}$) totalled $80.6 \mu\text{eq L}^{-1}$, an amount more than sufficient to account for the ANC of Vandercook Lake.

Relationship Between Hydrology and Lake Acid-Base Chemistry

Hydrologic budgets for the two study lakes have been reported by Wentz and Rose (1989; 1991). These earlier water budgets for Vandercook Lake were later adjusted through refinements in estimating hydraulic conductivity

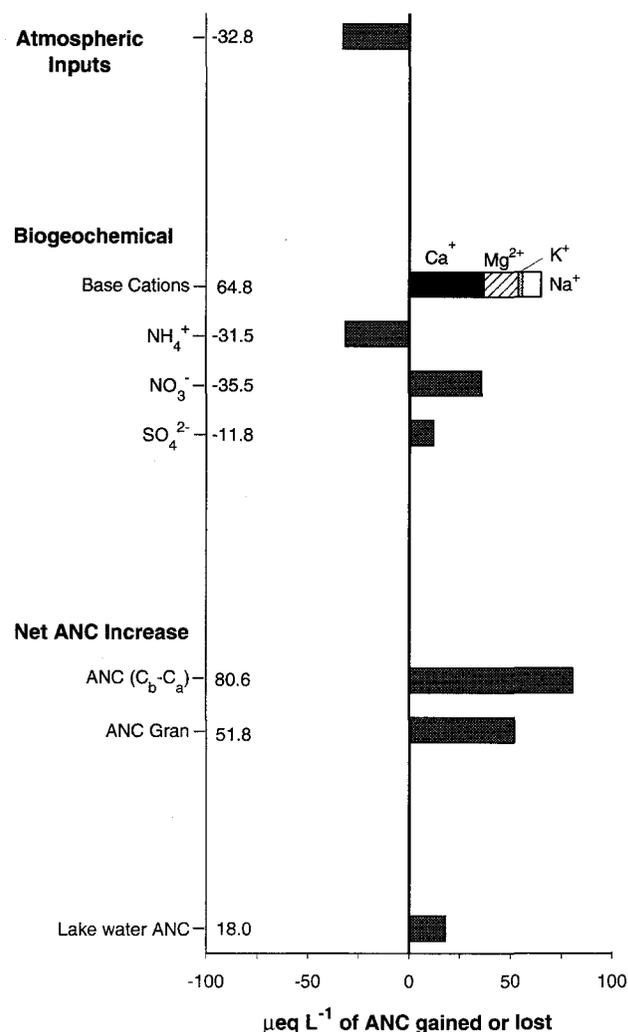


Figure 26. Ion enrichment estimates for Vandercook Lake. Bulk deposition concentrations were taken from Table 14. NH_4^+ was estimated by combining wet deposition from NADP with an estimate of 16% of total NH_4^+ as dry (Cook and Jager 1991). Due to the underestimation of SO_4^{2-} in bulk deposition (Table 15), we increased measured bulk deposition by 20%.

and calculating groundwater outflow (Wentz et al. in review). In the initial interpretation of the hydrologic flowpaths to these low ANC lakes, it became apparent that techniques for quantifying hydrologic and chemical inputs and outputs were untested and in the developmental stage for seepage systems. Furthermore, evaporation and groundwater inputs, which are important in seepage systems, are notoriously difficult to measure and were often estimated by difference (Winter 1978). Low ANC lakes posed additional challenges because relatively small absolute errors in either the chemical or the hydrologic components can obscure important fluxes due to the large uncertainty around many of the chemical and hydrologic terms.

Hydrologic budgets reported by Wentz and Rose (1991) for Lake Clara and Wentz et al. (in review) for Vandercook Lake confirm the hypothesis that precipitation was the dominant hydrologic input to these two lakes (Fig. 27). During the 3-year study period, Vandercook received an average of 93% of its water by direct precipitation while groundwater inflow provided the remaining 7%. Groundwater inputs accounted for 9% of the hydrologic inputs to Lake Clara. However, direct precipitation comprised a slightly lower percentage at 84%. The difference was due to an estimated 7% input of surface discharge contributed by the channelized inlets to Lake Clara.

The 5-9% groundwater input calculated by Wentz et al. (in review) for Vandercook Lake for the period 1981-83, was similar to the 4% value determined by Lin et al. (1987) who applied the Trickle Down Model (TDM) to the same database. The TDM used an ANC-based mass balance approach to calibrate the hydrologic budgets rather than independent measurement of each hydrologic component. The relatively long water residence time of Vandercook Lake, 5 to 6 years, may dampen

chemical responses to short-term fluctuations in groundwater inputs. Thus the TDM may not be sensitive to short-term fluctuations in groundwater inputs, but may better represent the long-term mean groundwater input. Hydrologic budgets calculated for the years 1981 through 1988 by Wentz et al. (in review) demonstrated the dynamic nature of groundwater inputs to Vandercook Lake. Groundwater inputs declined from the 5-9% range in the wet years of 1981-83 to 3-0% as the region entered a persistent drought period (1986-89).

Compared to lake-water and precipitation chemistry, groundwater is enriched in base cations and ANC due to silicate weathering reactions occurring in the soil and till (Fig. 28). Small inputs of groundwater are sufficient to counteract the acids deposited from acid deposition (Anderson and Bowser 1986; Garrison et al. 1987; Kenoyer and Anderson 1989). Data from Lakes Clara and Vandercook, combined with results from hydrologic studies of other seepage lakes in the Upper Midwest, show a positive relationship between ANC and the percentage of groundwater input (Fig. 29). Further evidence of the strong linkage between groundwater inputs and lake acid-base chemistry was demonstrated by the rapid acidification of Nevins Lake, a seepage lake in the Upper Peninsula of Michigan (Webster et al. 1990). There, a



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Evaporation pan being monitored by Mr. Hugh Rutherford, the local observer at Vandercook Lake.

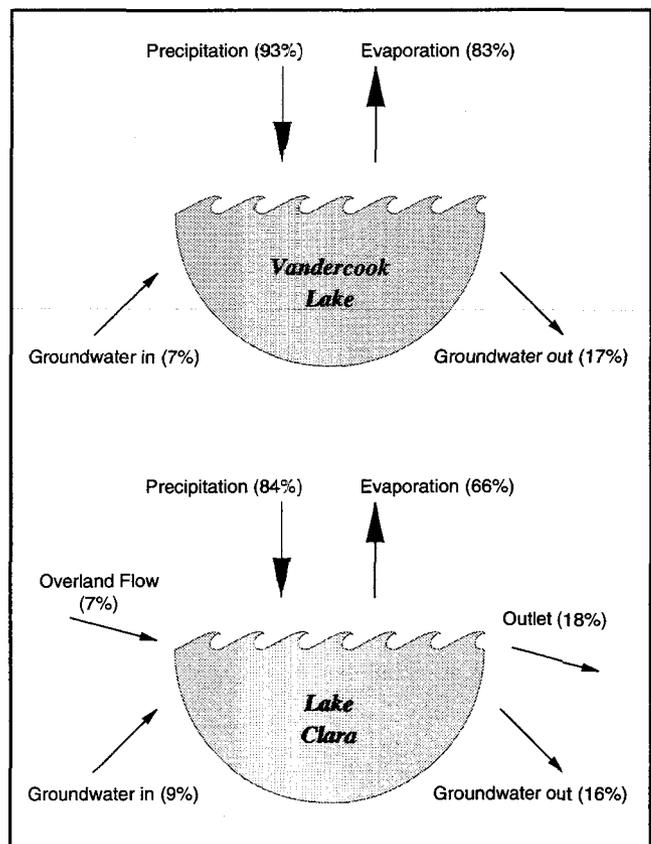


Figure 27. Hydrologic budget diagrams for Vandercook Lake (Wentz et al. in review) and Lake Clara (Wentz and Rose 1991).

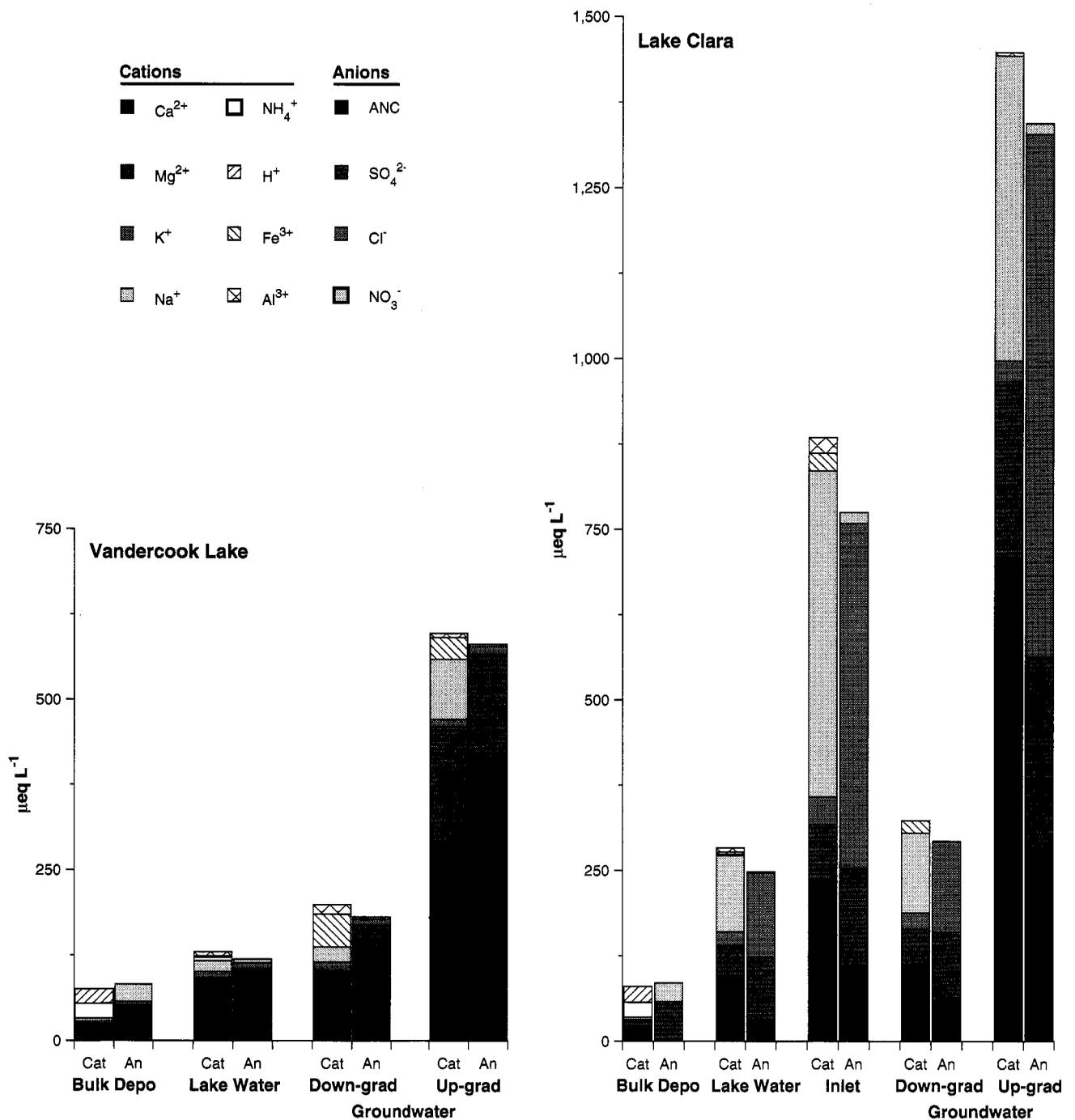


Figure 28. Bar diagrams of the major ion composition of bulk deposition, lake water, groundwater (downgradient and upgradient), and inlets at Vandercook Lake and Lake Clara.

drought-induced decline in groundwater inputs between 1983 and 1989 caused a $150 \mu\text{eq L}^{-1}$ loss of ANC due to cessation of inputs of base cations.

Using the ILWAS model, Garrison et al. (1987) simulated the effect of SO_4^{2-} reduction and groundwater inputs on controlling the ANC of Vandercook Lake. Eliminating only sulfate reduction would have a larger impact on ANC (decrease of $46 \mu\text{eq L}^{-1}$) than would eliminating only groundwater input (ANC decrease of $28 \mu\text{eq L}^{-1}$). The chemical budgets published by Lin et al. (1987) also suggest that in-lake processes supply more ANC to Vandercook Lake than does groundwater input.

Seepage lakes such as Vandercook are weakly coupled with their surrounding watersheds in that in-lake processes, atmospheric deposition, and weathering are the important controls on lake chemistry. Watershed processes are important only near the immediate shoreline and in the groundwater contributing area, defined as the land area overlaying the region of groundwater flow to the lake. For seepage lakes, topographic watersheds are of less importance (Garrison et al. 1987). Such characteristics contrast with those of drainage lakes which have shorter water residence times and a closer connection with the topographic watershed, and whose chemistry is thus controlled more by watershed processes than by internal processes.

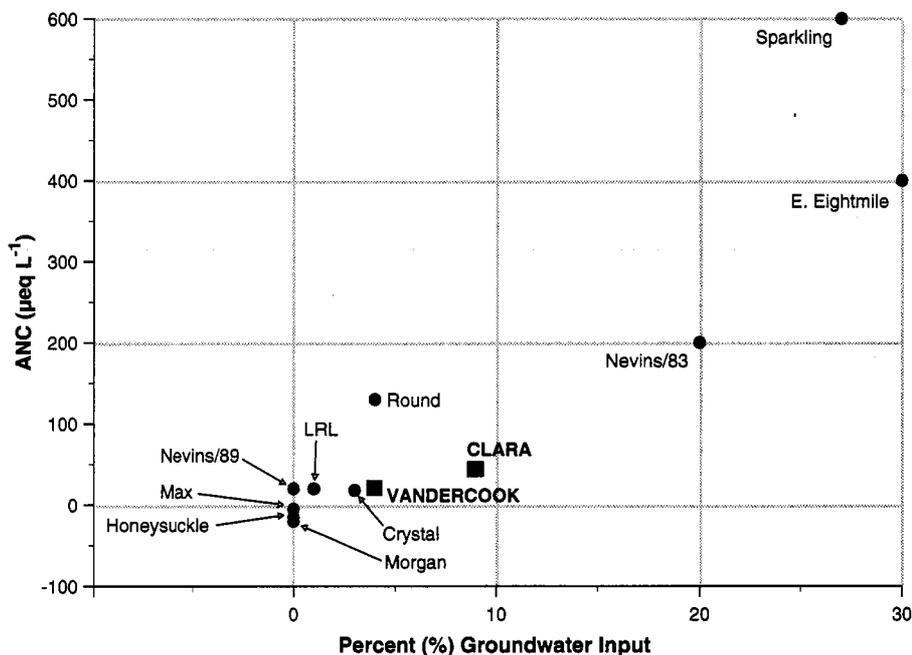


Figure 29. Percent groundwater input plotted against lake ANC for a set of seepage lakes in north-central Wisconsin. References: Crystal Lake (Kenoyer and Anderson 1989); Round Lake and East Eightmile Lake (D. Wentz, U.S. Geol. Surv., pers. comm.); Sparkling Lake (Krabbenhof et al. 1990); Nevins Lake (D. Krabbenhof, pers. comm.); Honeysuckle, Morgan, and Little Rock Lakes (W.J. Rose, pers. comm.).



PHOTO: K. E. WEBSTER

Vandercook Lake

CONCLUSIONS AND MANAGEMENT RECOMMENDATIONS

Potential for Acidification

Based on the chemistry data for Lakes Clara and Vandercook, there is little cause for concern regarding their potential to become more acidic. This conclusion assumes that current loadings of acids from atmospheric deposition do not increase and that groundwater inputs are maintained. Although results from the TDM (Schnoor et al. 1986) suggested the lakes were not at steady state with respect to current loading rates of mineral acids, application of the ILWAS model to Vandercook Lake by Greb et al. (1987), suggested this was not the case. During 1981-83 both lakes maintained positive ANC, averaging $18 \mu\text{eq L}^{-1}$ at Vandercook and $30 \mu\text{eq L}^{-1}$ at Lake Clara and neither lake was acidic (i.e., with $\text{ANC} \leq 0$) at any time during the study period. There was no evidence that spring snowmelt events caused episodic acidification. At Lake Clara, spring snowmelt waters were substantially enriched with base cations and ANC (Fig. 30). The high acidity levels measured in inlets 3 and 4 at Lake Clara were associated with organic acids, not strong mineral acids such as SO_4^{2-} and NO_3^- . Eilers and Bernert (1989) found little evidence that pulses of mineral acids during snowmelt caused episodic acidification of 37 streams in Wisconsin.

There is little information upon which to assess the historical ANC of the study lakes. A limited amount of historical data on the chemistry of Vandercook Lake was collected by Birge and Juday in the 1930s (Eilers et al. 1989). Similar to the pattern exhibited by a majority of lakes in the Birge and Juday sample set, recent values for Ca^{2+} , pH and ANC at Vandercook Lake were higher than the historical data (Table 18). This was attributed by Eilers et al. (1989) to increasing anthropogenic development. At Vandercook, there are currently 36 (mostly seasonal) dwellings compared to 1 during the Birge and Juday era. Other factors such as forest regrowth, fish stocking, and climate changes may also have contributed to chemical changes in these lakes.

In addition, the biota of the two lakes do not suggest that these lakes have undergone substantial acidification. Community composition at all trophic levels (phytoplankton, macrophytes, zooplankton, benthic macroinvertebrates, and fisheries) revealed no obvious pH-related stress. Although the fish assemblages in these lakes were comprised mainly of relatively acid-tolerant species, available data indicate that the fishery has not changed measurably in recent decades. Characterization of the biota provides a baseline for evaluating future changes.

Deposition rates of SO_4^{2-} are expected to decline in northern Wisconsin. Emissions of SO_2 decreased substantially during the 1980s, due in part to acid rain control legislation enacted in Wisconsin. Annual SO_4^{2-} loadings at the Trout Lake NADP station appear to be declining (Webster et al. 1993). Both ILWAS and TDM forecast simulations for Vandercook Lake predicted ANC increases under scenarios of decreasing SO_4^{2-} loading. The ILWAS model predicted $\sim 10 \mu\text{eq L}^{-1}$ increase in ANC by the year 2000 should SO_4^{2-} loadings decline by 25% (Garrison et al. 1987). In contrast, the model results indicated that increasing the loading by 25% would roughly halve current ANC over the same time frame (Lin and Schnoor 1986).

Other Water Quality Issues

Lake Clara and Vandercook Lake are both high-quality waters in relatively undisturbed settings, although there are a number of shoreline dwellings around each lake. Data on chlorophyll *a*, nutrient concentrations, and Secchi disk transparency confirmed that the lakes are moderately productive and typical of mesotrophic systems. We found no evidence of nuisance algal blooms or excessive macrophyte growth.

Contamination with road salt had a major influence on the major ion composition at Lake Clara, not only in channels carrying runoff to the lake, but also in the lake and the groundwater system. It is unlikely that salt contamination in the lake water presents a serious problem biologically, but the high concentrations of chloride and sodium in groundwater and inlet samples could be of human health concern. Contamination of groundwater by road salt has been documented for other northern Wisconsin lakes including Sparkling Lake, located west of highway 51 in Vilas County 2.2 km from Vandercook Lake (C. Bowser, Univ. of Wis. and D. Krabbenhoft, U.S. Geol. Surv., Madison, Wis., pers. comm.).

The observation of high mercury concentrations in walleyes from Lake Clara was an unexpected result from the fisheries studies. These elevated mercury concentrations exceeded Wisconsin health advisories in most fish tested (Wis. Dep. Nat. Res. and Wis. Div. Health 1987). There are no known anthropogenic sources of mercury in the watershed of either lake. However, recent analyses of mercury profiles in sediment cores suggest that atmospheric transport and deposition, perhaps from anthropogenic sources, supplied much of this mercury (Rada et al. 1989). Although research at Lakes Clara and Vandercook was initiated because of concern regarding the effects of deposition of mineral acids, the fisheries data demonstrated that transport and deposition of mercury and other toxic metals, particularly lead and cadmium (Wiener 1983; Rada et al. 1989), is an important and developing research issue for the region. A comprehensive study of the biogeochemical fate of mercury in aquatic ecosystems includes Vandercook Lake as one of the study lakes (Watras et al. 1991).

Management Recommendations

After it was established that low ANC seepage lakes comprised the resource of concern in Wisconsin with respect to potential impacts of acidification, the Lakes Clara and Vandercook study was among the first detailed examinations of the hydrologic and chemical characteristics of such lakes in the region. The results have contributed to an improved understanding of the relationships between hydrology and lake ANC, helping management develop protective strategies for these potentially acid-sensitive systems. Our analysis suggests that even lakes with ANC of $\sim 20 \mu\text{eq L}^{-1}$ may not be as sensitive to current loadings of mineral acids in deposition as initially thought. These lakes are protected by having small inputs of groundwater. Also, the hydraulic residence time is sufficiently long to permit internal processes to generate a significant amount of ANC. Internal processes such as sulfate reduction and denitrification were able to neutralize a significant portion of the two major mineral acids in deposition, SO_4^{2-} and NO_3^- , producing ANC in the process. While we conclude that the likelihood of acidification of Lakes Clara and Vandercook is low, this is predicted on maintaining current or lower deposition rates.

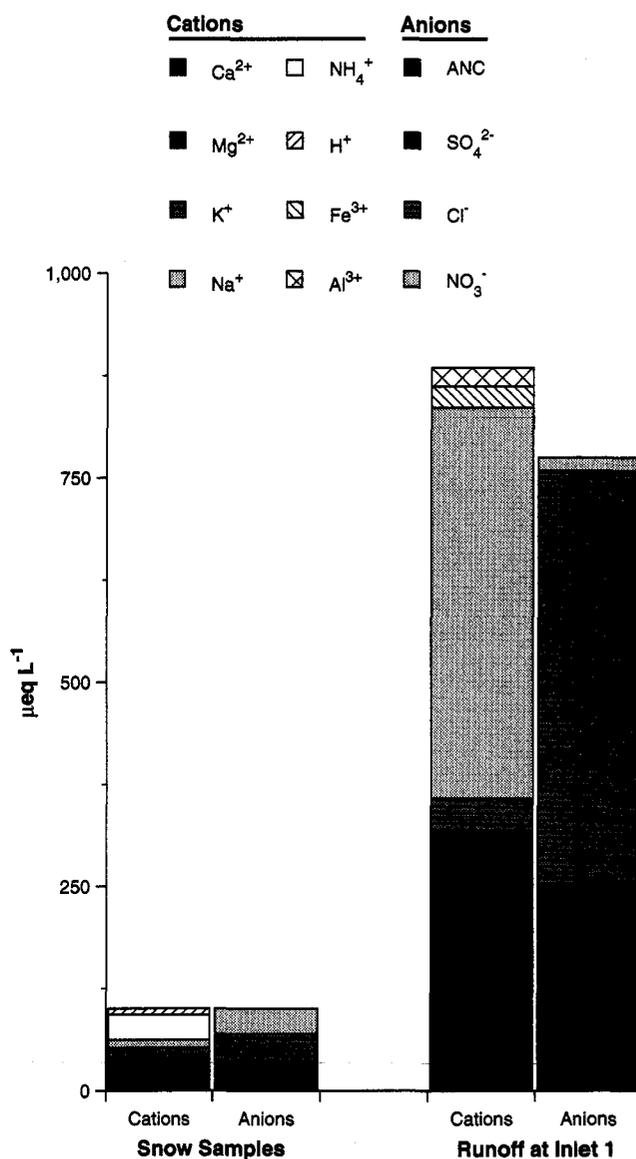


Figure 30. Bar diagrams showing the ionic composition of snow and spring runoff samples from inlet 1 at Lake Clara in 1982.

Table 18. Historic and current surface water chemistry of Vandercook Lake.

Variable	Birge & Juday*	This Study
pH	6.0	6.1
Conductance (μS)	11	17
ANC ($\mu\text{eq L}^{-1}$)	13	18
Ca^{2+} ($\mu\text{eq L}^{-1}$)	44	66
SO_4^{2-} ($\mu\text{eq L}^{-1}$)	21	88
Color (PCU)	6	8
Number of dwellings	1	36

* Eilers et al. (1989).



Vandercook Lake

Internal processes would not be able to counteract significantly increased loadings of acid from deposition. Any persistent decline in lake pH below 6.0 would harm the biological communities of the two lakes.

Low ANC seepage lakes, with hydrologic inputs dominated by precipitation, have proven to be suitable sites for studying the biological uptake of mercury and other atmospheric contaminants that accumulate in aquatic organisms. Most low ANC lakes in northern Wisconsin are weakly coupled, in a hydrologic sense, to their terrestrial catchments. Therefore, terrestrial influxes of mercury to such lakes may be small relative to direct atmospheric inputs. Moreover, chemical conditions in such lakes (e.g., low Ca^{2+}) enhance the direct uptake of dissolved metal ions across biological membranes (Wiener 1987). Elevated mercury concentrations in walleyes in north-central Wisconsin, for example, are most prevalent in low-ANC seepage and drained lakes (Wiener et al. 1990b). Lastly, the aquatic communities and trophic systems of seepage lakes are confined by the absence of inflowing and outflowing streams and are exposed to atmospherically deposited contaminants cycling through the water column and surficial sediments.

Thus, the exposure history of organisms in seepage systems can be more accurately described.

Although not the focus of the research at the two lakes, contamination of Lake Clara by road-salt runoff provides a cautionary note for the ecological disturbances caused by lakeshore development. It is likely that Lake Clara did not receive channelized input of water prior to the construction of county highway A and associated drainage ditches. The resulting storm-water runoff has contaminated not only the lake water, but also the local groundwater. A better practice would be to divert runoff away from seepage lakes whose closed basins and long hydraulic residence times make them less able to assimilate such pollutants. Seepage lakes are also more sensitive to development in their groundwater contribution areas which discharge water into the lake. In these areas, land use alterations can alter both the flowpath and composition of groundwater which eventually enters the lake. In contrast, development along the downgradient reaches of the shoreline (i.e. those groundwater discharge zones) is less likely to affect lake water quality directly as the local groundwater regime carries water and pollutants away from the lake.

APPENDIXES

Appendix A. Site Description

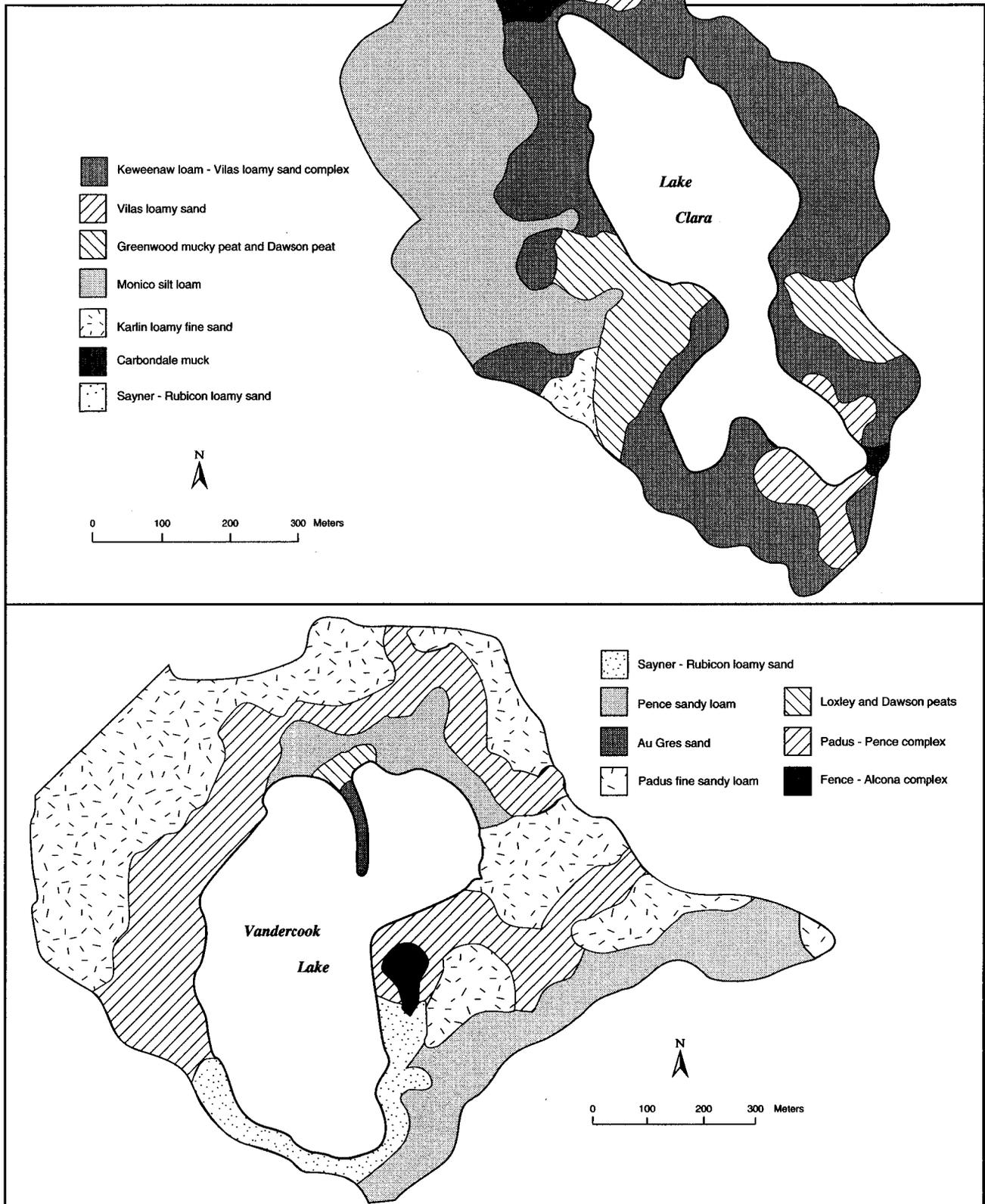


Figure A.1. Major soil types in the contributing topographic watersheds of Lake Clara and Vandercook Lake.

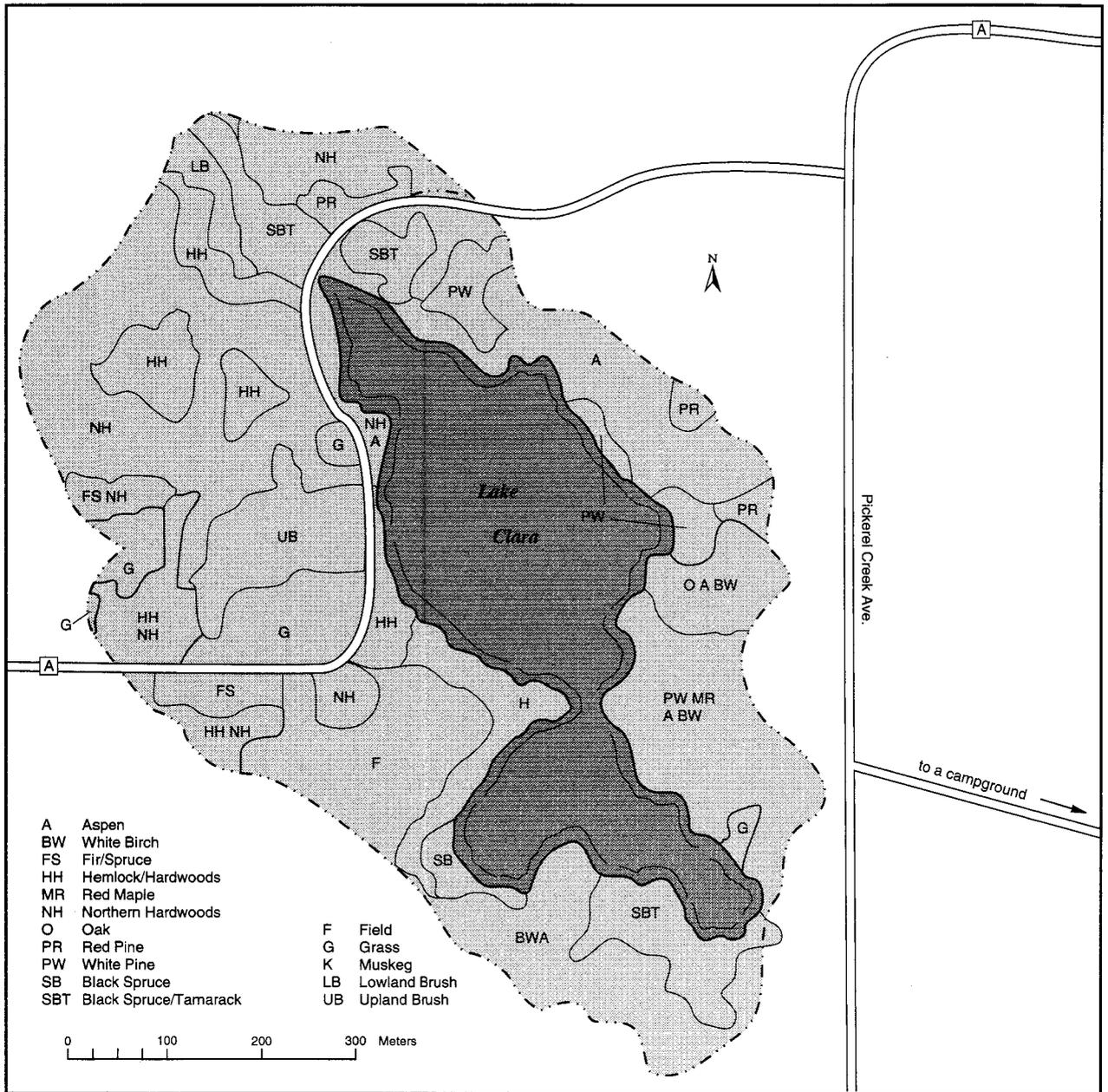


Figure A.2. Land use in the contributing topographic watersheds of Lake Clara and Vandercook Lake.

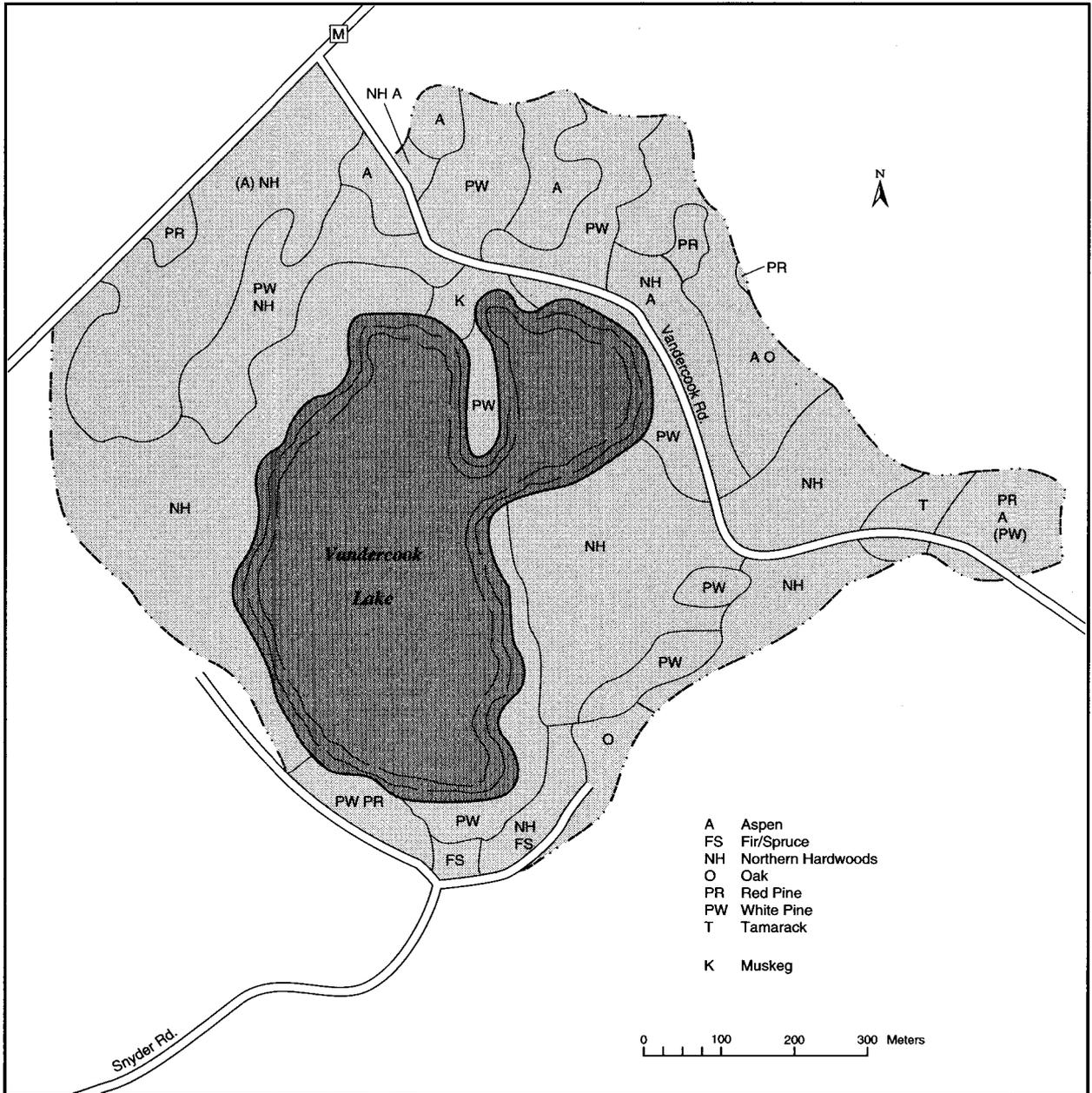


Figure A.2. Continued.

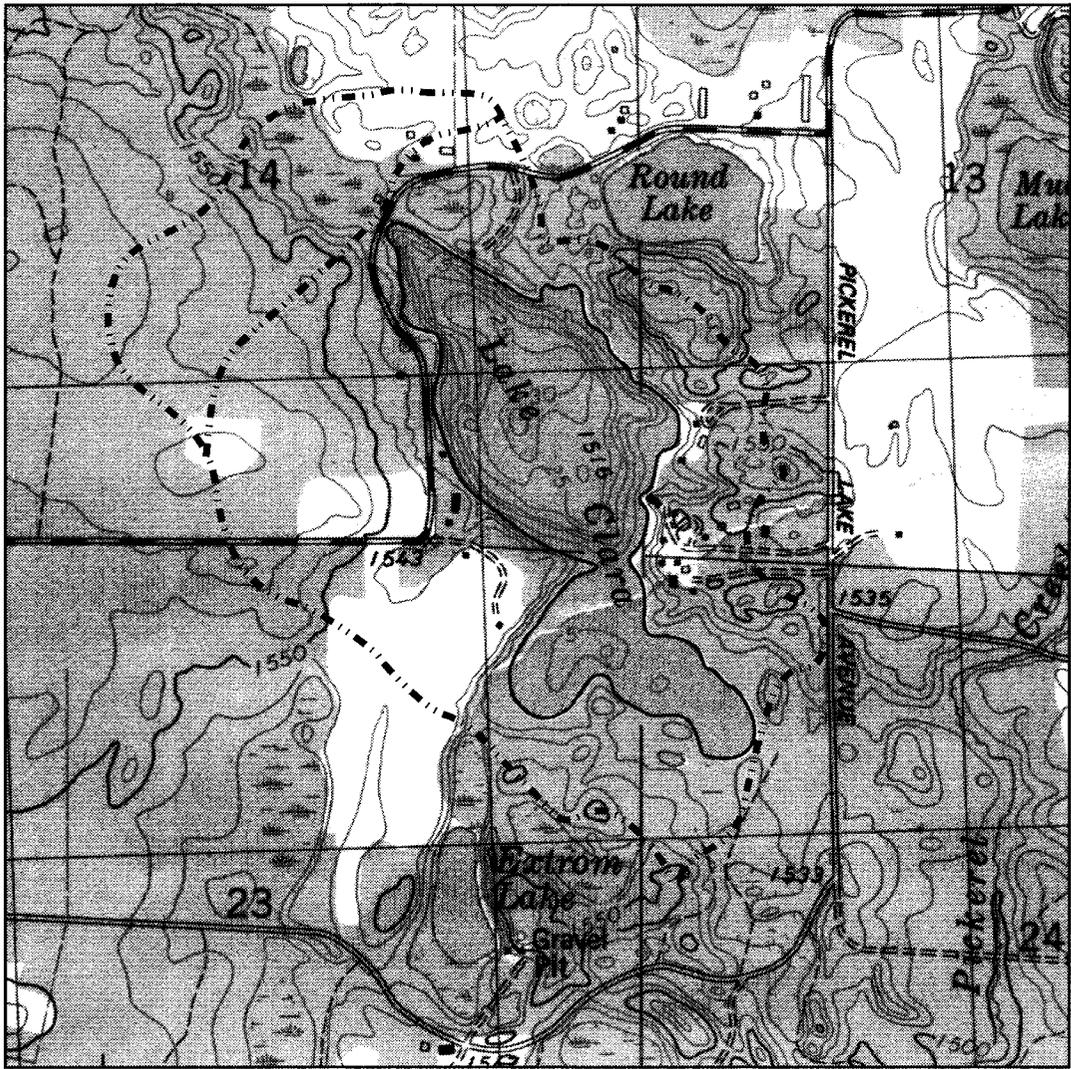
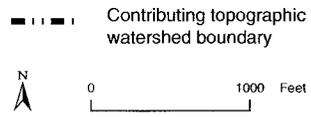


Figure A.3. Topography of the contributing topographic watersheds of Lake Clara and Vandercook Lake and surrounding areas.



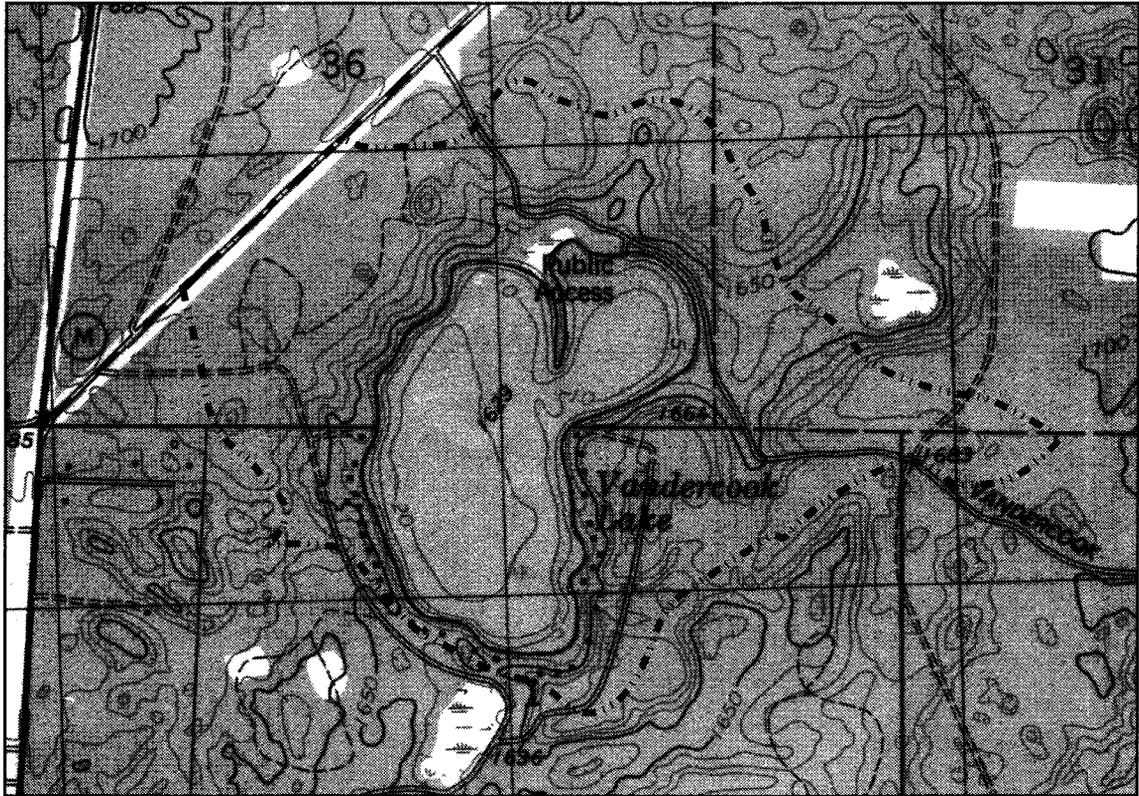
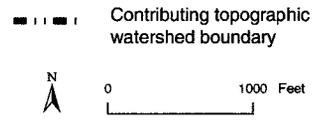


Figure A.3. Continued.



Appendix B. Biology

Table B.1. Phytoplankton species collected in Lake Clara (Dec-Jul 1983) and Vandercook Lake (Jan-Jul 1983).

Taxonomic Group	Presence		Taxonomic Group	Presence	
	Clara	Vandercook		Clara	Vandercook
CHLOROPHYTA			CHRYSOPHTA		
<i>Ankistrodesmus falcatus</i>	X	X	<i>Asterionella</i> sp.	X	X
<i>A. spiralis</i>	—	X	<i>Diceras</i> sp.	X	X
<i>Arthrodesmus</i> sp.	X	—	<i>Dinobryon bavaricum</i>	X	X
<i>Arthrodesmus</i> spp.	—	X	<i>D. cylindricum</i>	X	X
<i>A. incus</i>	X	X	<i>D. tabellarea</i>	X	—
<i>A. phimus</i>	—	X	<i>Fragilaria</i> sp.	—	X
<i>Botryococcus braunii</i>	—	X	<i>Fragilaria</i> *	X	—
<i>B. protoberans</i> v. <i>minor</i>	—	X	<i>Mallomonas</i> sp.	X	—
<i>B. sudeticus</i>	—	X	<i>Synura uvella</i> *	X	—
<i>Chlamydomonas</i> spp.	X	—	<i>Tabellaria</i> sp.	X	X
<i>Closteriopsis longissima</i>	X	—	<i>T. fenestrata</i>	X	—
<i>Coelastrum cambricum</i>	—	X	CRYPTOPHYTA		
<i>Cosmarium</i> sp.	X	—	<i>Chroomonas Nordstedtii</i> *	X	—
<i>Cosmarium</i> spp.	—	X	<i>Cryptomonas</i> sp.	—	X
<i>Crucigenia</i> sp.	X	—	<i>Cryptomonas ovata</i> *	X	—
<i>C. quadrata</i>	X	X	CYANOPHYTA		
<i>C. rectangularis</i>	—	X	<i>Anabaena</i> sp.	X	—
<i>C. tetrapedia</i>	X	X	<i>Aphanocapsa delicatissima</i>	X	X
<i>Dictyosphaerium pulchellum</i>	—	X	<i>A. elachista</i> v. <i>conferta</i>	X	X
<i>Dimorphococcus lunatus</i>	—	X	<i>Aphanothece stagnina</i>	—	X
<i>Dispora crucigenioides</i> *	—	X	<i>Chroococcus</i> sp.	X	X
<i>Elakatothrix gelatinosa</i>	X	X	<i>C. giganteus</i>	—	X
<i>Euastrum</i> sp.	—	X	<i>C. limneticus</i>	—	X
<i>Gloeocystis gigas</i>	X	X	<i>C. minimus</i> *	X	—
<i>G. planktonica</i> *	—	X	<i>Coelosphaerium kuetzingianum</i>	X	—
<i>Nephrocytium</i> sp.	X	—	<i>Gloeopcapsa</i> sp.	—	X
<i>Nephrocytium</i> spp.	—	X	<i>Gloethece rupestris</i> *	X	X
<i>Oedogonium</i> sp.	X	—	<i>Gomphosphaeria lacustris</i> v. <i>comparta</i>	X	X
<i>Oocystis</i> sp.	X	—	<i>Merismopedia tenuissima</i>	X	X
<i>Oocystis</i> spp.	—	X	<i>Rhabdoderma gorskii</i>	X	X
<i>O. borgei</i>	X	X	EUGLENOPHYTA		
<i>Pediastrum</i> sp.	X	X	<i>Trachelomonas</i> spp.	X	—
<i>P. tetras</i>	—	X	<i>T. pulcherrima</i> *	—	X
<i>Quadrigula chodatii</i>	X	—	PYRRHOPHYTA		
<i>Q.* closteroides</i>	—	X	<i>Cystodinium</i> sp.	—	X
<i>Scenedesmus bijuga</i> *	X	—	<i>Glenodinium</i> sp.	—	X
<i>S. quadricauda</i>	—	X	<i>G. armatum</i> *	X	—
<i>S. hystrix</i> *	—	X	<i>G. pulvisculus</i> *	X	—
<i>S. serratus</i>	—	X	<i>Gloeodinium</i> sp.	—	X
<i>Sphaerocystis Schroeteri</i>	—	X	<i>Gymnodinium</i> sp.	X	—
<i>Sphaerosozma excavatum</i>	X	—	<i>Peridinium</i> sp.	—	X
<i>Spinocosmarium</i> sp.	—	X	<i>P. Willei</i>	X	X
<i>Spondylosium planum</i> *	—	X	<i>P. wisconsinense</i>	X	—
<i>Staurastrum</i> spp.	—	X			
<i>S. cuspidatum</i>	X	—			
<i>S. limneticum</i>	X	—			
<i>S. natator</i>	—	X			
<i>S. paradoxum</i>	—	X			
<i>Teilingia</i> sp.*	—	X			
<i>Tetraedron</i> sp.	X	—			
<i>T. limneticum</i>	—	X			
<i>T. minimum</i>	—	X			
<i>Tetrastrum</i> sp.	X	—			

* Identification is uncertain.

Table B.2. Macrophyte* species list for Lake Clara and Vandercook Lake.

Species	Common Name	Clara	Vandercook
<i>Brasenia schreberi</i>	water shield	—	X
<i>Calamagrostis canadensis</i> **	bluejoint grass	X	X
<i>Calla palustris</i>	water arum	—	X
<i>Carex lasiocarpa</i>	sedge	X	—
<i>C. rostrata</i>	sedge	—	X
<i>C. stricta</i> **	sedge	—	X
<i>Chamaedaphne calyculata</i>	leatherleaf	X	X
<i>Drepanocladus</i> sp.	moss	—	X
<i>Drosera leucanth</i>	sundew	—	X
<i>Dulichium arundinaceum</i>	three-way sedge	X	X
<i>Elatine minima</i>	waterwort	X	X
<i>Eleocharis acicularis</i> var. <i>submersa</i>	sterile needle rush	X	X
<i>E. robbinsii</i>	triangle spike rush	—	X
<i>Eriocaulon septangulare</i>	pipewort	X	X
<i>Fontinalis</i> sp.	water moss	X	X
<i>Glyceria canadensis</i> **	rattlesnake manna grass	X	X
<i>G. Grandis</i> **	reed meadow grass	X	—
<i>Gratiola aurea</i> forma <i>pusilla</i>	dwarf hyssop	—	X
<i>Iris versicolor</i>	blue flag	—	X
<i>Isoetes macrospora</i>	quillwort	X	X
<i>Juncus canadensis</i>	rush	X	—
<i>J. effusus</i>	soft rush	X	X
<i>J. pelocarpus</i>	rush	X	—
<i>J. pelocarpus</i> forma <i>submersus</i>	sterile rush	X	X
<i>Lobelia dortmanna</i>	water lobelia	X	X
<i>Myrica gale</i>	sweet gale	X	X
<i>Myriophyllum tenellum</i>	water milfoil	X	X
<i>Nitella flexilis</i>	stonewort	—	X
<i>Nuphar variegatum</i>	yellow pond lily	X	X
<i>Nymphaea odorata</i>	white water lily	—	X
<i>Polygonum coccineum</i> var. <i>pratincta</i>	smartweed	—	X
<i>Pontederia cordata</i>	pickerelweed	—	X
<i>Potamogeton epihydrus</i>	pondweed	X	X
<i>Potamogeton natans</i>	pondweed	—	X
<i>Rotala ramosior</i> var. <i>interior</i> **	loosestrife	—	X
<i>Rynchospora fusca</i>	beak rush	—	X
<i>Scirpus cyperinus</i> *	rush	X	X
<i>S. subterminalis</i>	water bullrush	X	X
<i>Scutellaria epilobifolia</i> **	scull cap	X	—
<i>Solidago graminifolia</i> **	goldenrod	X	—
<i>Sparganium angustifolium</i>	floating-leaf bur reed	X	X
<i>Sphagnum</i> sp.**	peat moss	X	X
<i>Typha latifolia</i>	cattail	—	X
<i>Utricularia cornuta</i>	bladderwort	—	X
<i>U. geminiscapa</i> ^a	bladderwort	—	X
<i>U. resupinata</i>	bladderwort	X	X

* Includes the moss *Drepanocladus* and the alga *Nitella*.

** Observed on the shoreline.

^a Species identification is uncertain.

Appendix B. *Continued.*

Table B.3. *Limnetic zooplankton species collected in Lake Clara and Vandercook Lake.*

Species	Lake Clara	Vandercook Lake
Cladocerans		
<i>Bosmina longirostris</i>	X	X
<i>Ceriodaphnia lacustris</i>	X	X
<i>Chydorus sphaericus</i>	X	X
<i>Daphnia dubia</i>	X	X
<i>D. parvula</i>	X	—
<i>D. galeata mendotae</i>	X	—
<i>D. retrocurva</i>	X	—
<i>Diaphanosoma birgei</i>	—	X
<i>Eubosmina tubicen</i>	X	X
<i>Holopedium gibberum</i>	X	X
Cyclopoid copepods		
<i>Diacyclops bicuspidatus thomasi</i>	X	X
<i>Ergasilus</i> sp.	X	X
<i>Mesocyclops edax</i>	X	X
<i>Tropocyclops prasinus</i>	—	X
Calanoid copepods		
<i>Epischura lacustris</i>	—	X
<i>Leptodiaptomus minutus</i>	X	X
Rotifers		
<i>Asplanchna priodonta</i>	X	X
<i>Conochilus unicornis</i>	X	X
<i>Gastropus stylifer</i>	X	X
<i>Kellicottia longispina</i>	X	X
<i>K. bostoniensis</i>	—	X
<i>Keratella cochlearis</i>	X	X
<i>K. taurocephala*</i>	X	—
<i>K. quadrata</i>	X	X
<i>Polyarthra remata</i>	—	X
<i>Trichocerca cylindrica</i>	X	X

* Identification is uncertain.

Appendix C. Fish Studies

Table C.1. Common and scientific names of fishes referenced by common name in the text.*

Family	Common Name	Scientific Name
Salmonidae	Cisco	<i>Coregonus artedi</i>
Esocidae	Northern pike	<i>Esox lucius</i>
	Muskellunge	<i>Esox masquinongy</i>
Cyprinidae	Golden shiner	<i>Notemigonus crysoleucas</i>
	Fathead minnow	<i>Pimephales promelas</i>
Catostomidae	White sucker	<i>Catostomus commersoni</i>
Ictaluridae	Yellow bullhead	<i>Ameiurus natalis</i>
Percopsidae	Trout-perch	<i>Percopsis omiscomaycus</i>
Gadidae	Burbot	<i>Lota lota</i>
Centrarchidae	Rock bass	<i>Ambloplites rupestris</i>
	Pumpkinseed	<i>Lepomis gibbosus</i>
	Bluegill	<i>Lepomis macrochirus</i>
	Smallmouth bass	<i>Micropterus dolomieu</i>
	Largemouth bass	<i>Micropterus salmoides</i>
	Black crappie	<i>Pomoxis nigromaculatus</i>
Percidae	Yellow perch	<i>Perca flavescens</i>
	Logperch	<i>Percina caprodes</i>
	Walleye	<i>Stizostedion vitreum</i>

* Nomenclature follows American Fisheries Society Special Publication 20, 1991.

Table C.2. Summary of sampling gear and effort used in fishery surveys of Lake Clara and Vandercook Lake.

Lake and Date	Type of Gear	Total Effort
Clara		
23 Jul 1953	800-ft seine	Unknown
24-27 Jun 1969	Fyke net (1-inch mesh)	4 nets for 3 nights
	Fyke net (1/4-inch mesh)	2 nets for 3 nights
4-5 Aug 1980	300-ft variable mesh gill net	4 nets for 2 nights
	Fyke net (3/8-inch mesh)	7 nets for 2 nights
	Minnow trap (1/4-inch mesh)	10 traps for 2 nights
	25-ft bag seine with 3/16-inch mesh in bag	25 seine hauls
9 Jun 1981	Fyke net (1-inch mesh)	4 nets for 1 night
Vandercook		
4-8 Jun 1951	Fyke net (1-inch mesh)	2 nets for 4 nights
	Fyke net (1/4-inch mesh)	2 nets for 4 nights
29 Jun-9 Jul 1981	40-ft seine with 1/8-inch mesh in bag and 1/4-inch mesh in wings	Seine was hauled in 8 areas
	Trammel net (100 x 3.5-ft net; outer and inner nets had 7-inch and 1-inch square mesh, respectively)	2 tows
	Fyke net (14-ft long with 25-ft lead; 3/16-inch mesh throughout)	8 overnight nets

Appendix C. *Continued.*

Table C.3. *Records of fish stocking in Lake Clara and Vandercook Lake.**

Lake and Species	Year	Life Stage Stocked	Number Stocked
Lake Clara			
Northern pike	1954	adult	18
	1956	adult	172
Fathead minnow	1942	adult	400
Largemouth bass	1942	fingerling	80
	1947	fingerling	1,600
	1950	fingerling	2,600
	1952	fingerling	430
Walleye	1957	fingerling	4,700
"Chubs"***	1942	adult	150
"Suckers"***	1941	adult	950
	1942	adult	2,000
Vandercook Lake			
Northern pike	1937	fry	174,000
	1938	fry	52,000
	1939	fry	168,000
	1940	fry	100,000
	1947	adult	3
	1947	fingerling	100
	1947	fry	5,000
	1948	adult	135
	1948	fingerling	84
	1952	adult	635
	1953	adult	122
	1954	fingerling	42
	1959	adult	49
	1960	adult	122
	1960	fingerling	88
	1967	adult	368
	1968	adult	317
	1972	adult	927
	1974	adult	915
	1975	adult	900
	1976	fry	62,000
	1979	fingerling	200
	1980	adult	200
1981	adult	200	
1982	adult	261	
1983	adult	200	
1984	adult	200	
Muskellunge	1940	fry	100,000
	1963	fingerling (hybrids)	300
Largemouth bass	1937	fingerling	14,000
	1938	fry	4,000
	1940	fry	2,000
	1941	fry	2,000
	1944	fingerling	300
	1947	fingerling	900
	1950	fingerling	1,800
Walleye	1934	fry	86,000

* Compiled from records of the Wisconsin Department of Natural Resources.

** The taxa of fish included in this group are unknown.

Appendix D. Water Chemistry

Table D.1. Analytical methods for analysis of water samples.*

Parameter	Method	Instrument	Reference**
pH	Potentiometric	Radiometer pHM63	EPA 150.1
Conductance	Conductance bridge	Radiometer CDM83 YSI Model 31	EPA 120.1
ANC	Gran titration to pH 3.8	Radiometer DTS 800	EPA 310.1 Rapp et al. 1985
Acidity	Alkalometric titration	Radiometer DTS 800	Rapp et al. 1985
Chlorophyll <i>a</i>	Spectrophotometry	Beckman DU	APHA (1980)
True color	Comparative	Hellige Aqua Tester	EPA 110.2
Turbidity	Nephelometry	Hach Model 18900 Turbidimeter Hach Model 2100A Turbidimeter	EPA 180.1
Total organic carbon	Carbon analyzer	Ionics Model 1258	Rapp et al. 1985
NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻	Ion chromatograph	Dionex Model 12	EPA 300.0
Base cations and minor metals (total acid exchangeable metals)	Atomic absorption Inductively coupled plasma emission spectrometry	Perkin Elmer 5000 Bausch and Lomb Model QA-137	EPA 200.7

* Rapp et al. 1985, Eilers et al. 1989.

**EPA methods according to USEPA (1979).

Table D.2. Quality assurance data for water quality variables.*

Chemical	Variable	Reporting Units	Detection Limit	Precision		Certified Samples	
				Lab Duplicates	Field Replicates	Bias	Standard Error
Ammonium	NH ₄ ⁺	µeq L ⁻¹	3.60	0.60	1.50	-1.20	0.43
ANC		µeq L ⁻¹	—	7.2	6.1	-1.7	1.9
Calcium	Ca ²⁺	µeq L ⁻¹	0.5	8.0	18.0	-5.0	4.3
Chloride	Cl ⁻	µeq L ⁻¹	1.70	1.10	10.70	0.11	0.08
Chlorophyll <i>a</i>		µg L ⁻¹	0.10	0.76	1.37	—	—
Conductance		µS	—	1.8	1.3	-0.6	0.4
Iron	Fe	mg L ⁻¹	0.0100	0.0052	0.260	0.0037	0.0029
Magnesium	Mg ²⁺	µeq L ⁻¹	2.500**	4.50	0.094	-0.097	0.022
Manganese	Mn	mg L ⁻¹	0.0000	0.0024	0.0084	-0.0021	0.0006
Nitrate	NO ₃ ⁻	µeq L ⁻¹	3.70	1.00	2.10	0.50	0.12
pH		su	—	0.09	0.07	0.01	0.01
Total Phosphorus	TP	mg L ⁻¹ P	0.0600	0.0021	0.0150	-0.0250	0.0300
Potassium	K ⁺	µeq L ⁻¹	1.20	0.50	1.00	-1.40	0.38
Silica	SiO ₂	mg L ⁻¹	0.06	—	0.26	—	—
Sodium	Na ⁺	µeq L ⁻¹	1.30	7.80	2.50	0.65	3.30
Sulfate	SO ₄ ²⁻	µeq L ⁻¹	4.20	3.10	5.00	-0.42	0.10
Tot. Org. Carbon	TOC	mg L ⁻¹	0.10	0.75	0.74	0.28	0.12
True color		PCU	—	4.1	6.6	—	—
Turbidity		NTU	0.05	0.58	2.64	—	—

* Precision and bias data are based upon a larger data base generated by ERL-D and USEPA Manchester Lab.

**The detection limit on samples collected between 1980 and 1982 was 41 µeq L⁻¹.

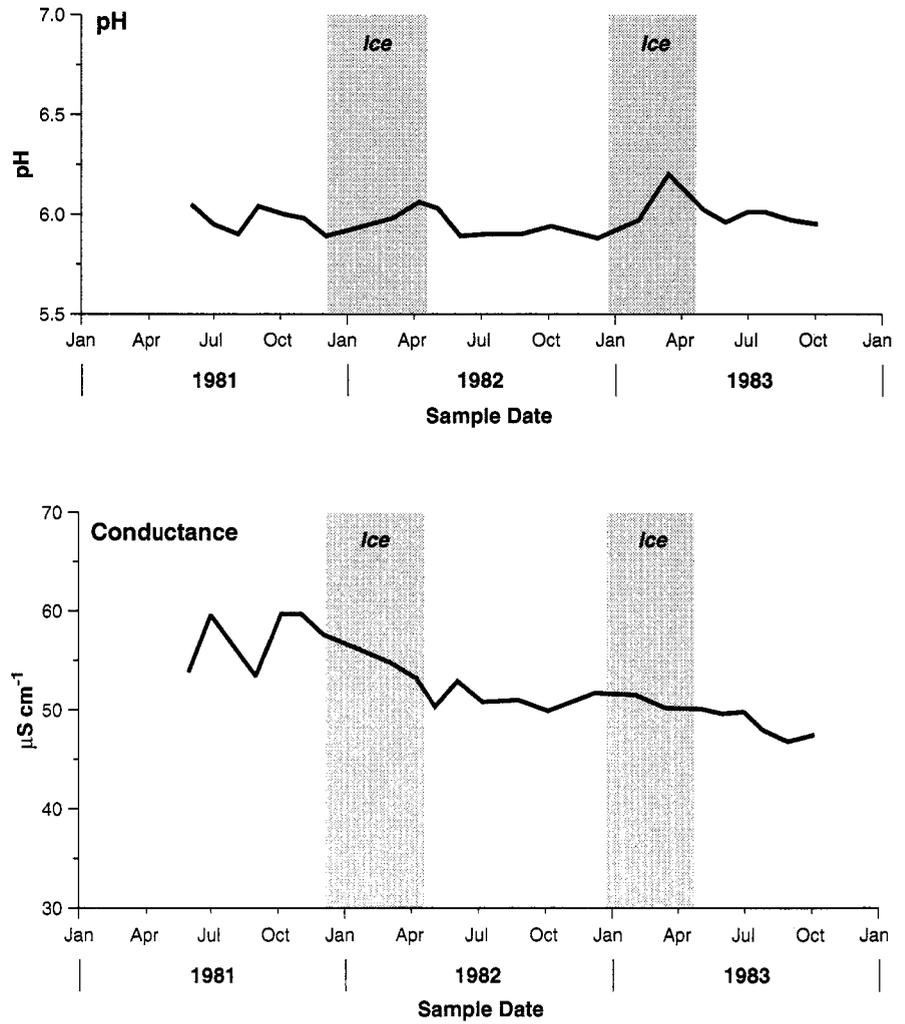
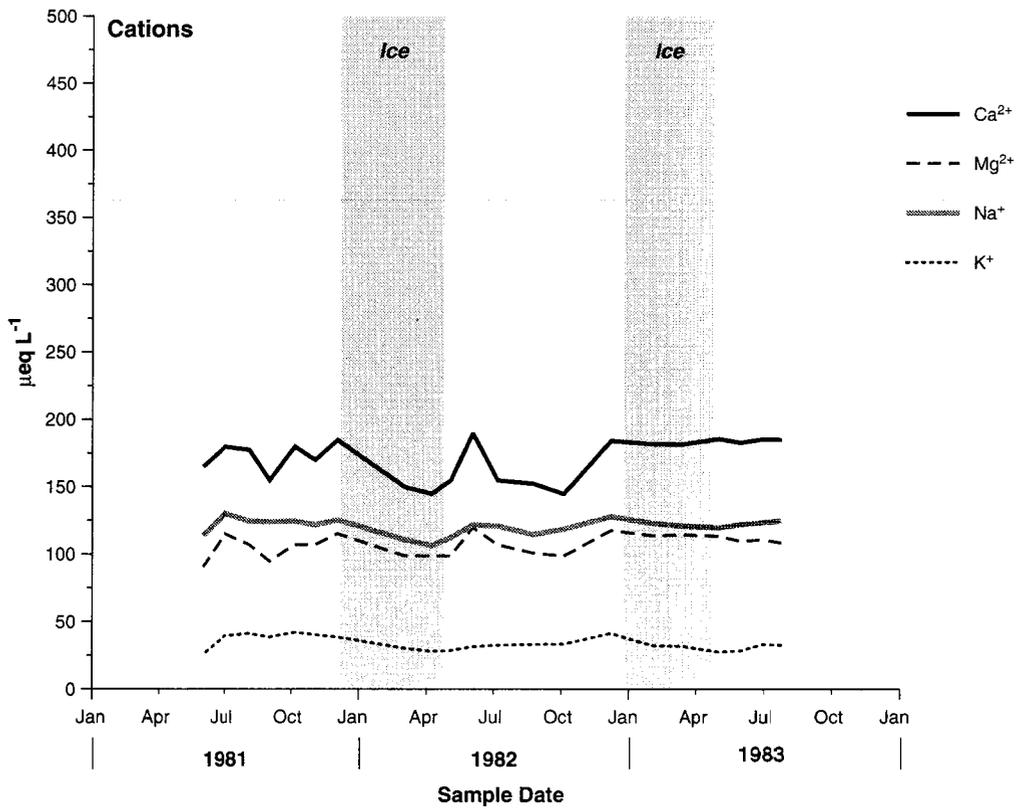
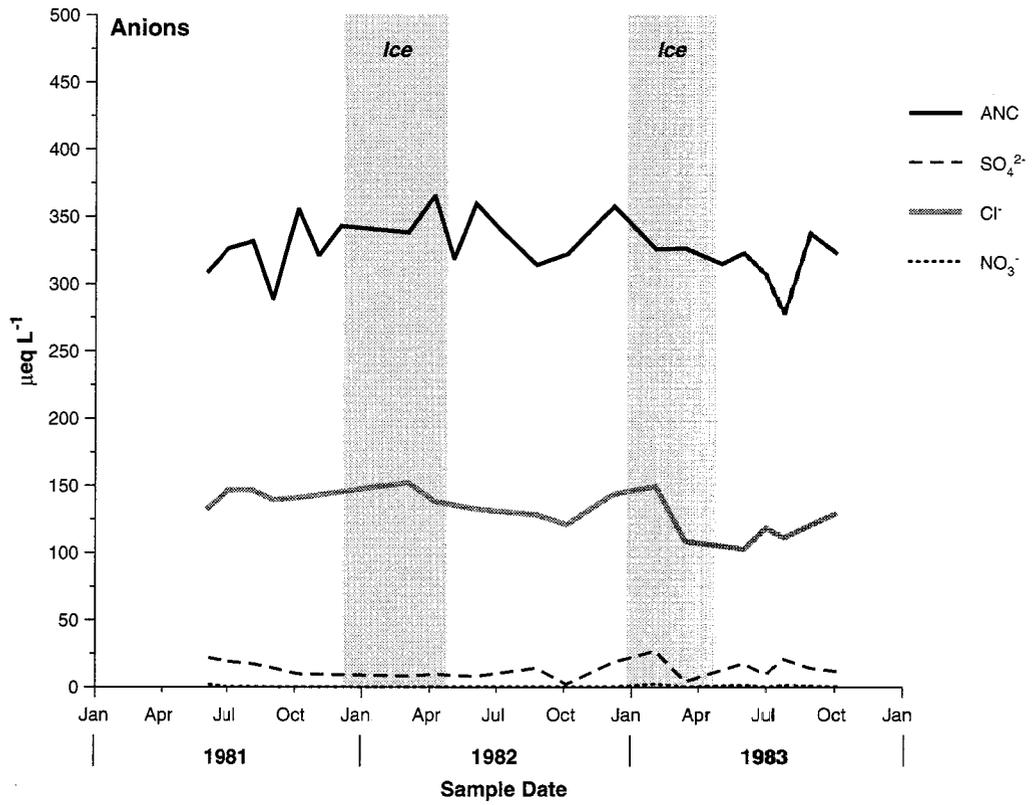


Figure D.3. Time series plots for pH, conductance, anions and base cations in LCQ3S, downgradient groundwater piezometer at Lake Clara.



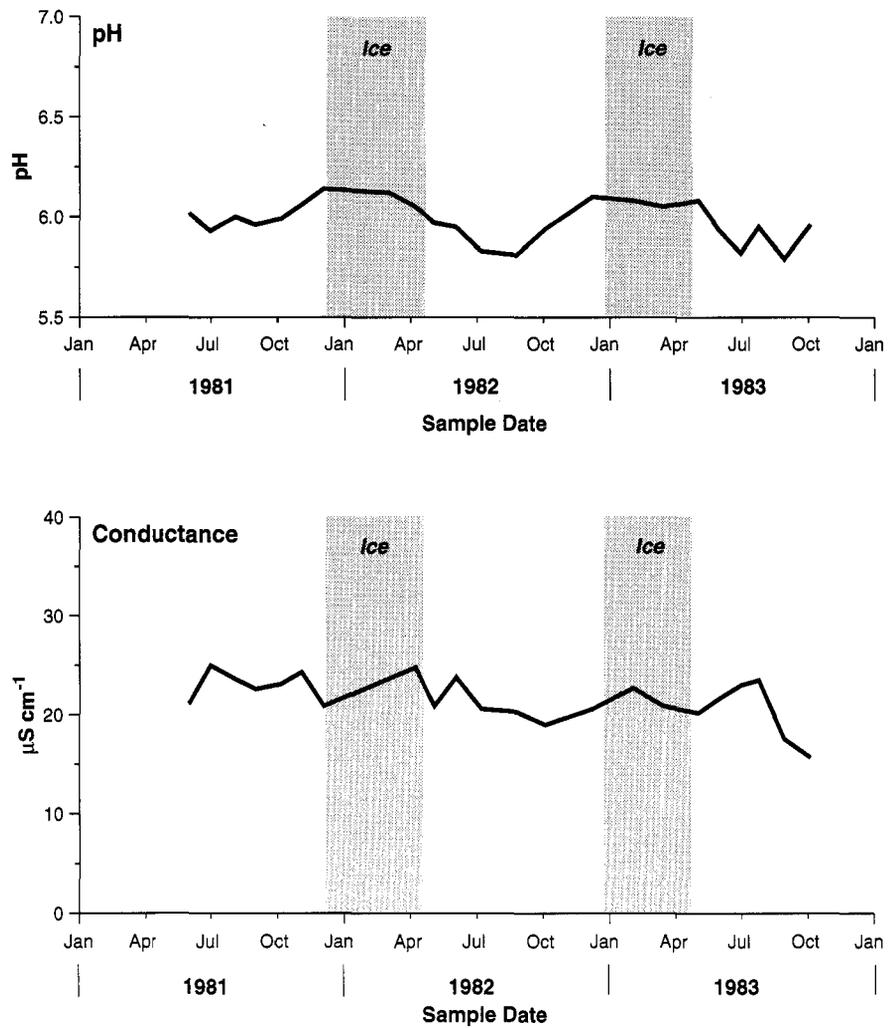
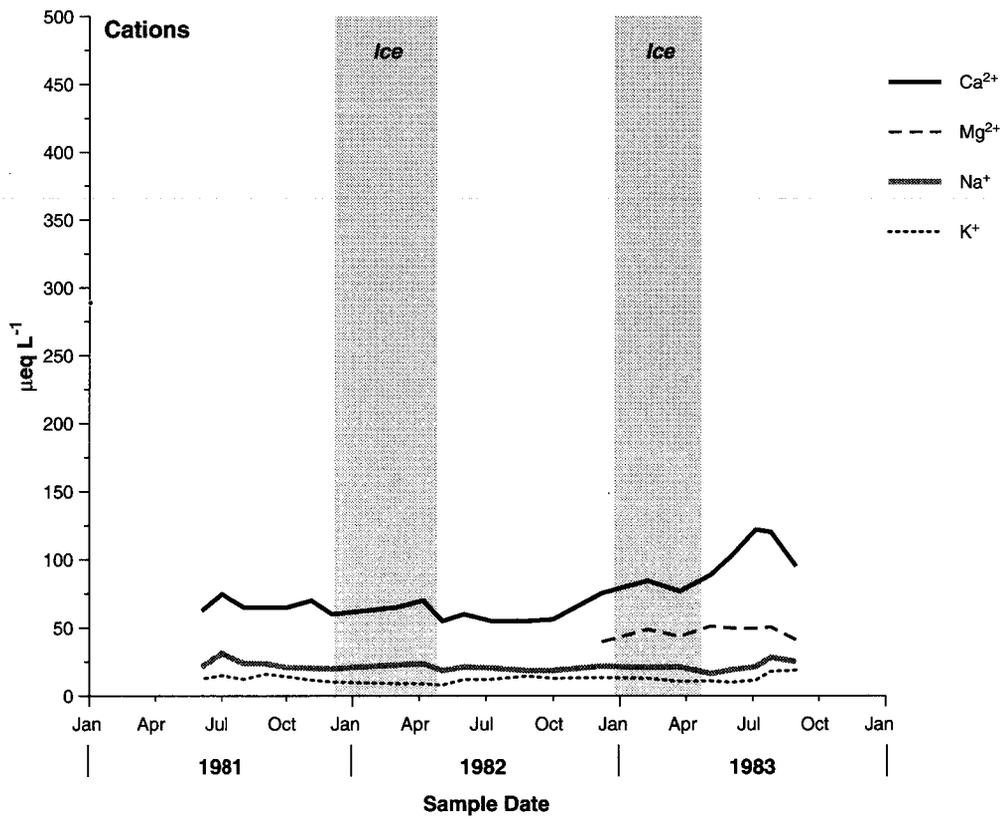
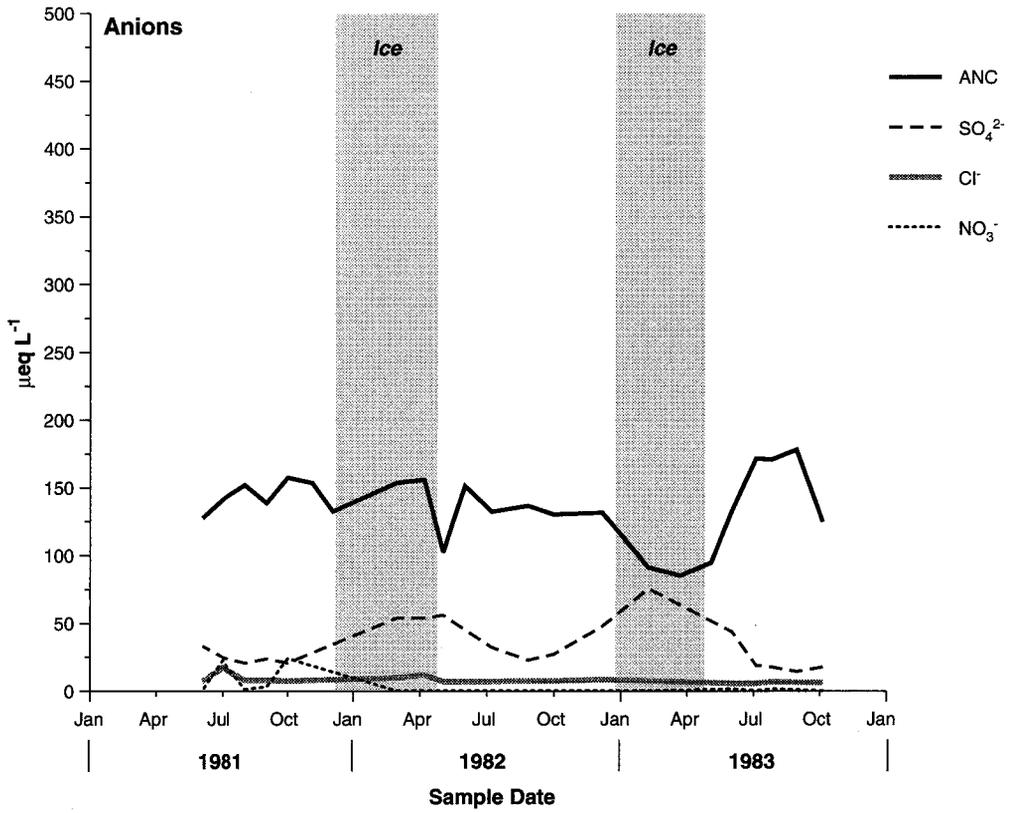


Figure D.4. Time series plots for pH, conductance, anions and base cations in VLQ2, downgradient groundwater piezometer at Vandercook Lake.



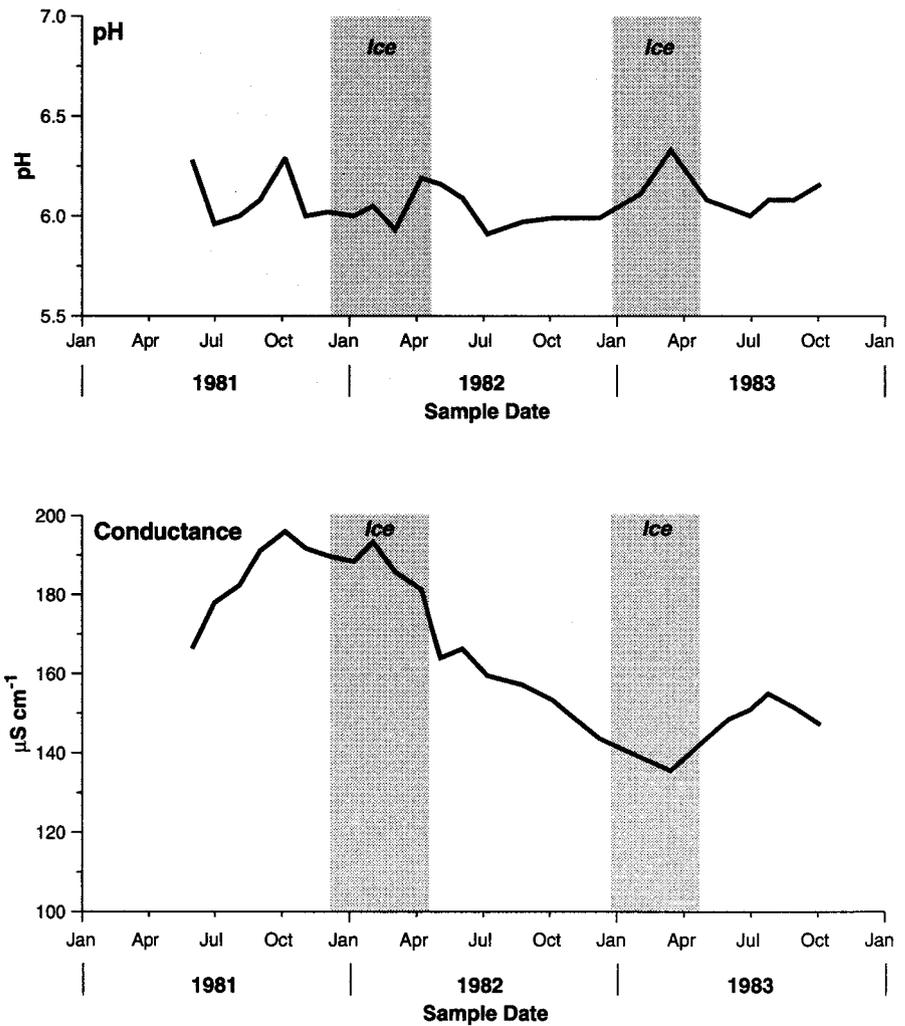
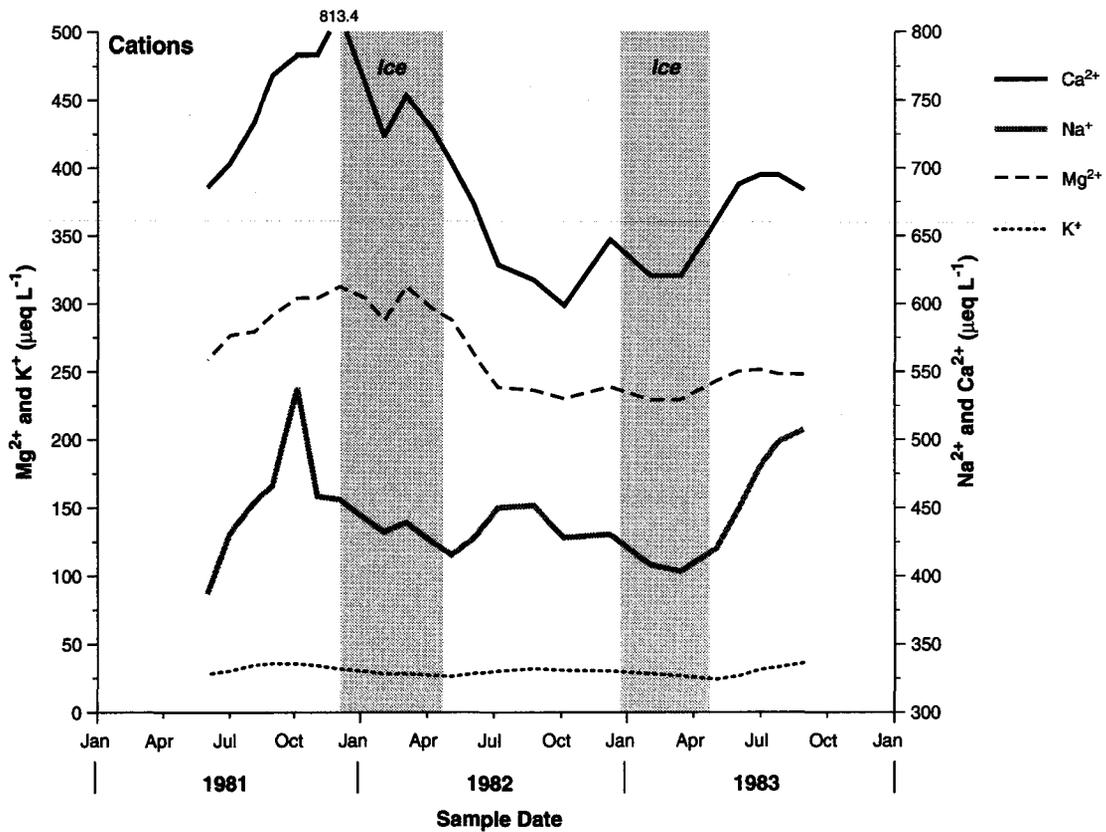
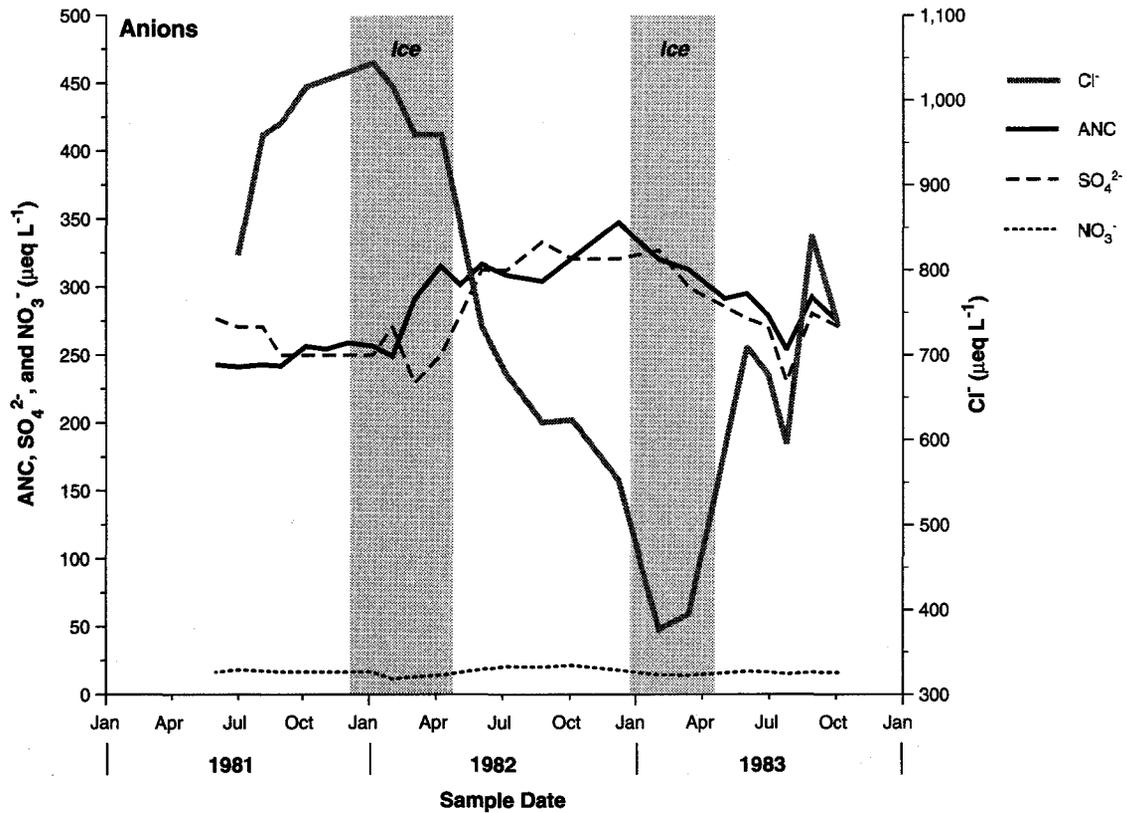


Figure D.5. Time series plots for pH, conductance, anions and base cations in LCQ2, up-gradient groundwater piezometer at Lake Clara.



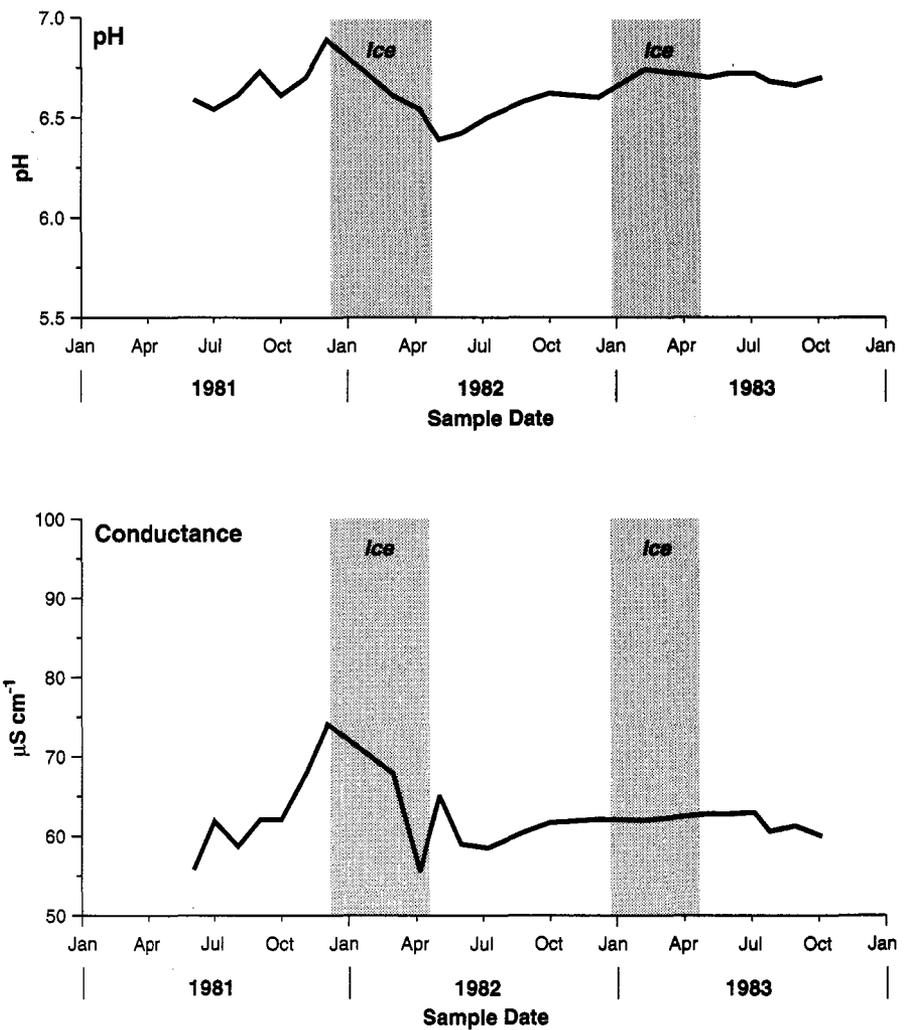
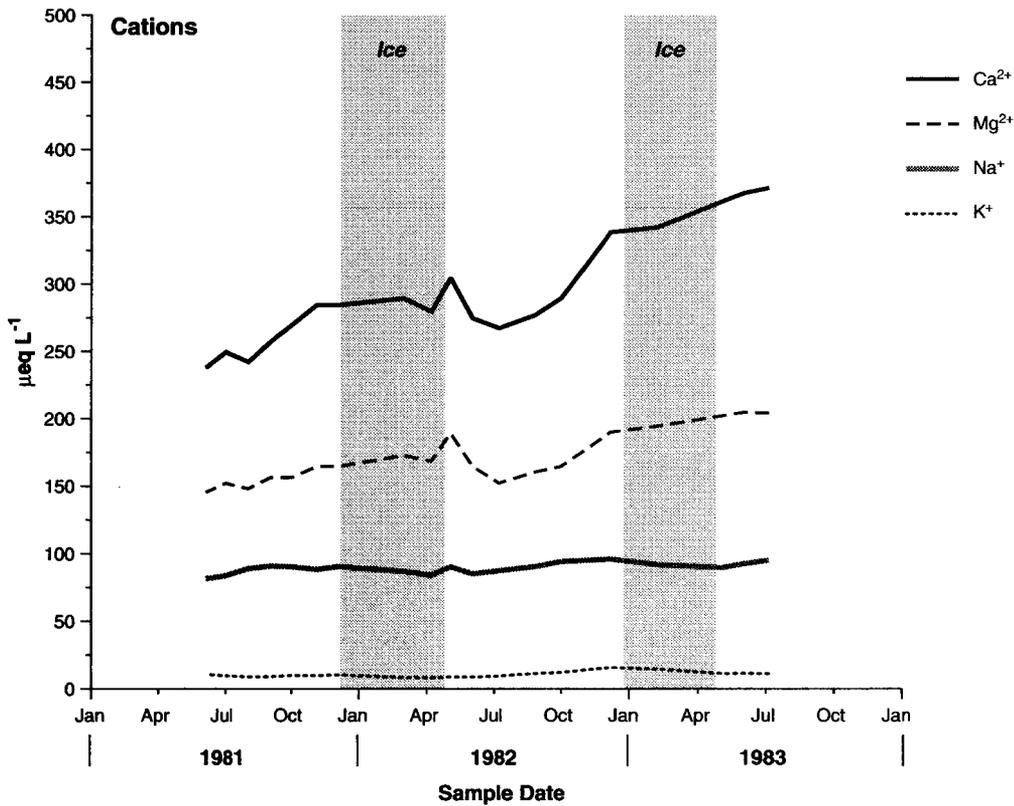
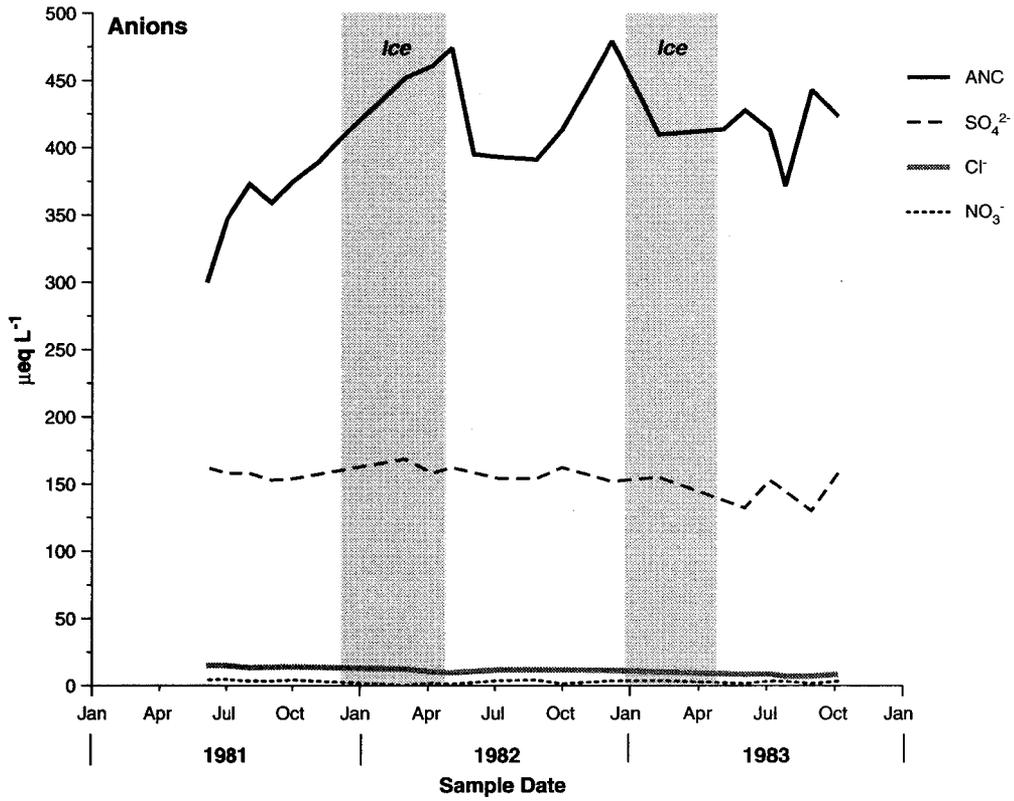


Figure D.6. Time series plots for pH, conductance, anions and base cations in VLQ1, up-gradient groundwater piezometer at Vandercook Lake.



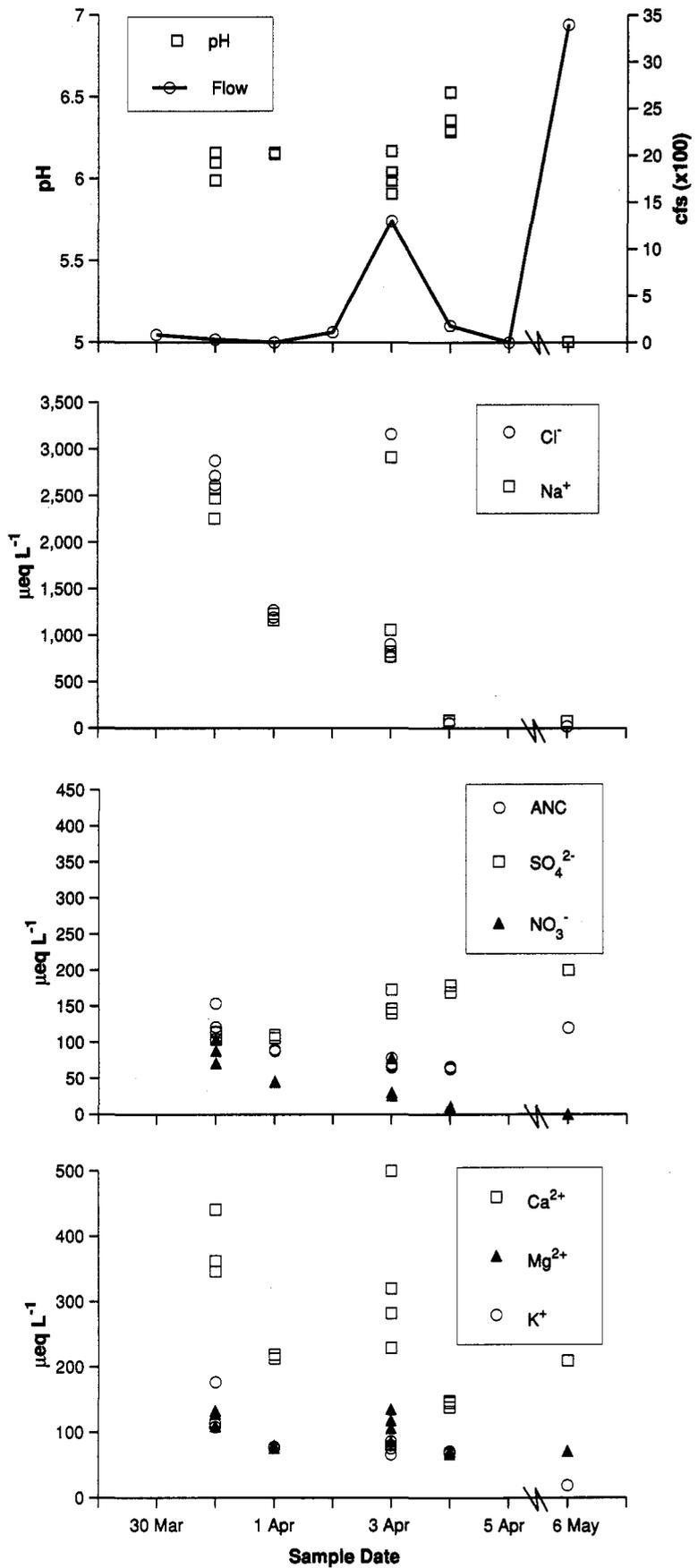
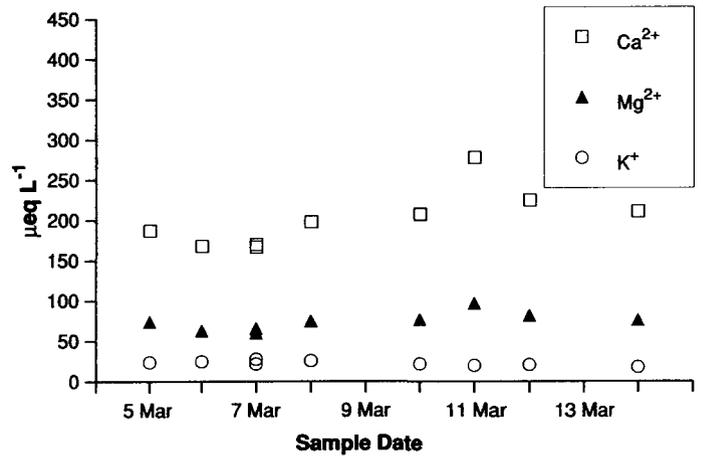
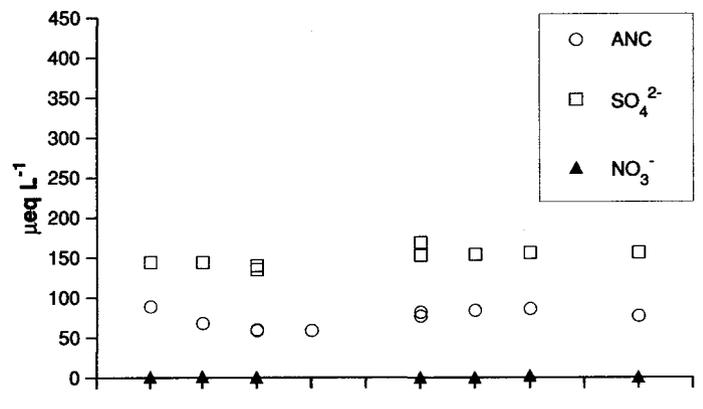
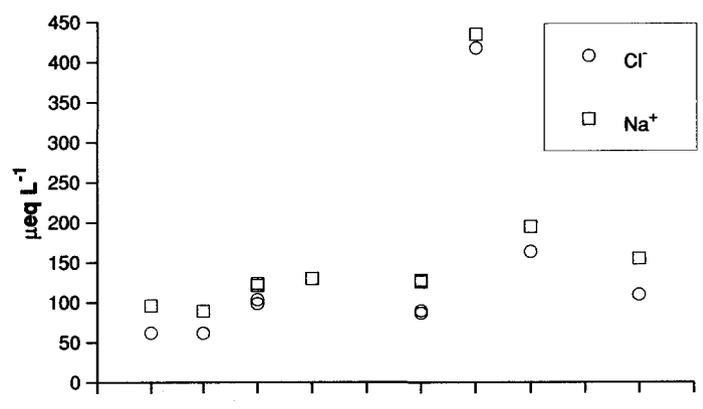
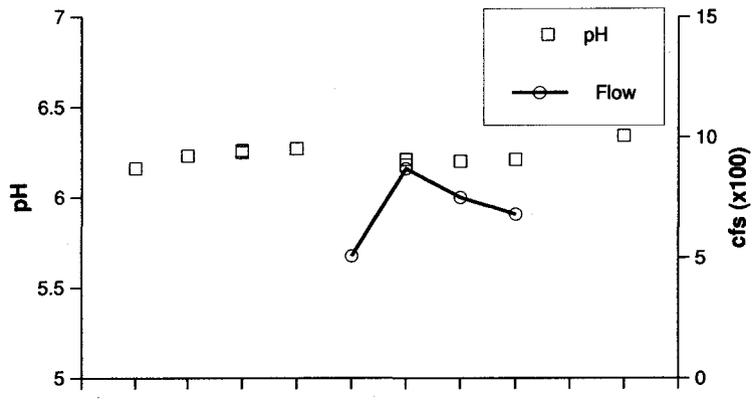


Figure D.7. Flow and major ion chemistry of spring runoff samples collected in 1982 and 1983 at inlet 1 at Lake Clara.



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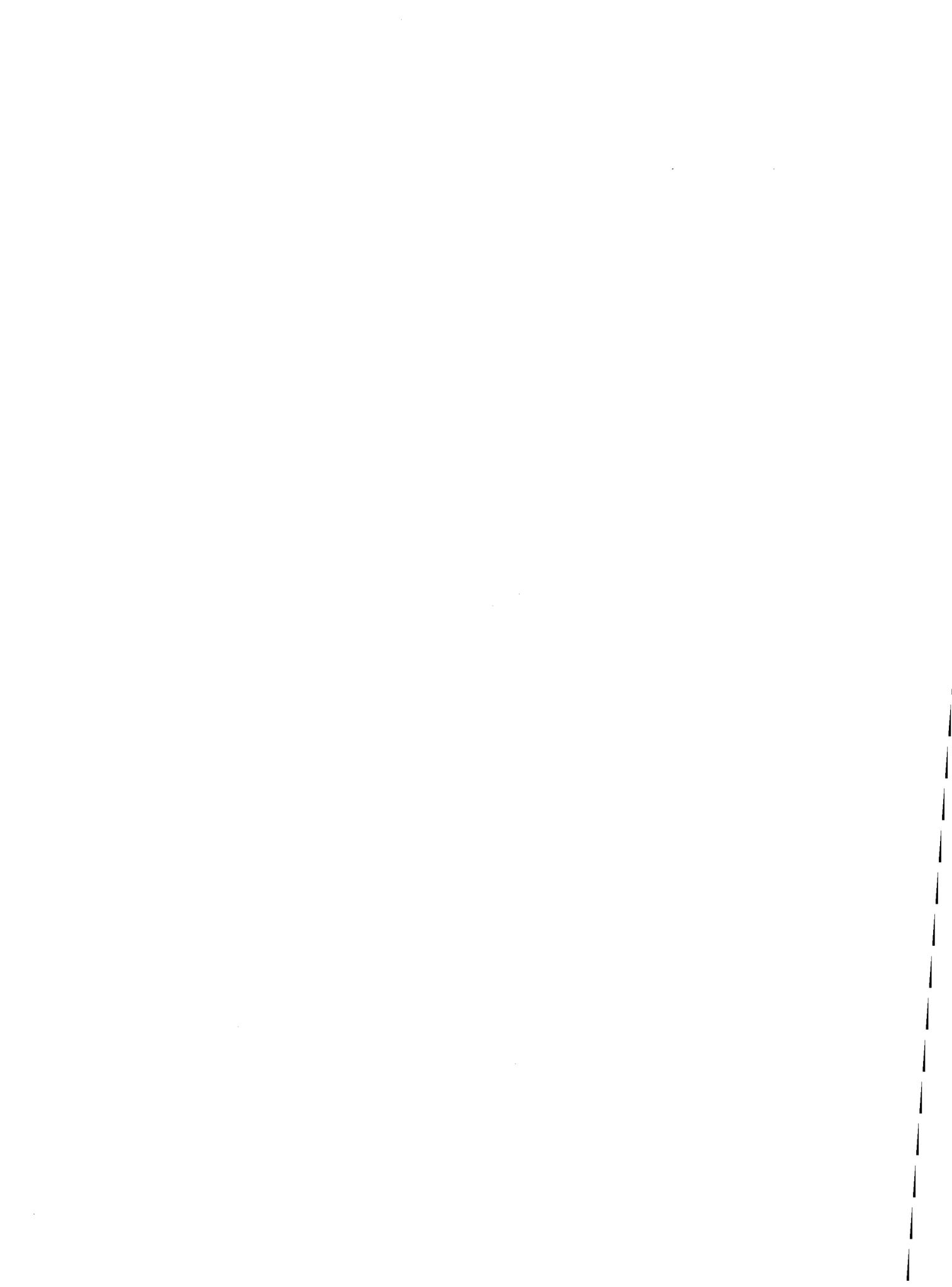
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