SOURCES AND CYCLING OF MAJOR IONS AND NUTRIENTS IN DEVILS LAKE, NORTH DAKOTA

By Robert M. Lent

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
cubic meter (m^3)	35.31	cubic foot
foot (ft)	0.3048	meter
gram (g)	0.002205	pound (avoirdupois)
gram per cubic meter (g/m^3)	0.0009989	ounce (avoirdupois) per cubic foot
gram per square centimeter per year [$(g/cm^2)/yr$]	0.00003795	ounce (avoirdupois) per square foot per year
gram per square meter per day [$(g/m^2)/d$]	0.002637	pound (avoirdupois) per square yard per day
gram per year (g/yr)	0.002205	pound per year
meter (m)	3.281	foot
micrometer (µm)	0.00003937	inch
milligram per liter per centimeter [(mg/L)/cm]	0.3937	milligram per liter per inch
milligram per square centimeter per day [$(mg/cm^2)/d$]	0.00000003795	ounce (avoirdupois) per square foot per day
milligram per square meter per day [$(mg/m^2)/d$]	0.00004218	ounce (avoirdupois) per square yard per day
milligram per square meter per hour [$(mg/m^2)/h$]	0.00004218	ounce (avoirdupois) per square yard per hour
milliliter (mL)	0.03381	ounce
millimeter (mm)	0.03937	inch
square centimeter (cm^2)	0.001076	square foot
square centimeter per second (cm^2/s)	0.001076	square foot per second
square kilometer (km^2)	0.3861	square mile
square meter per day (m^2/d)	10.76	square foot per day
square meter per year (m^2/yr)	10.76	square foot per year

To convert degrees Celsius (°C) to degrees Fahrenheit (°F), use the following formula: °F=1.8°C+32.

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Microsiemens per centimeter at 25 degrees Celsius (µS/cm) replaces micromhos per centimeter at 25 degrees Celsius used for specific conductance in older reports. The two units are equivalent.

Milligrams per liter (mg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (milligrams) of solute per unit volume (liter) of water.

Sources and Cycling of Major Ions and Nutrients in Devils Lake, North Dakota

By Robert M. Lent

ABSTRACT

Devils Lake is a saline lake in a large, closed drainage basin in northeastern North Dakota. Previous studies determined that major-ion and nutrient concentrations in Devils Lake are strongly affected by microbially mediated sulfate reduction and dissolution of sulfate and carbonate minerals in the bottom sediments. These studies documented substantial spatial variability in the magnitude of calculated benthic fluxes coincident with the horizontal salinity gradient in Devils Lake. The purpose of the present study is to evaluate seasonal variability in benthic-flux rates, and to understand the effect of these fluxes on the major-ion and nutrient chemistries in Devils Lake between May and October 1991.

During the study period, the water column was well mixed, and specific conductance, pH, and temperature did not vary with depth. Dissolved oxygen was enriched near the lake surface due to photosynthesis. Major-ion concentrations and nutrient concentrations did not vary with depth. Because the water-quality data were obtained during open-water periods, the vertical profiles reflect well-mixed conditions. However, the first and last profiles for the study period did document near-bottom maxima of major cations. Secchi-disk depth varied from 0.82 meter on May 7, 1991, to 2.13 meters on June 5, 1991. The mean Secchi-disk depth during the study period was 1.24 meters. Seasonal variations in Secchi-disk depths were attributed to variations in primary productivity and phytoplankton communities.

Nutrient cycles in Devils Lake were evaluated using gross primary productivity rate data, sediment trap data, and major-ion and nutrient benthic-flux rate data. Gross primary productivity rate was smallest in May (0.076 gram of carbon per square meter per day) and largest in September (1.8 grams of carbon per square meter per day). Average gross primary productivity for the study period was 0.87 gram of carbon per square meter per day. Average gross primary productivity is consistent with historic data from Devils Lake and with data from other eutrophic lakes.

The average flux of organic carbon for the study period was 12 grams per square meter per day. The calculated carbon to nitrogen to phosphorus ratio (317:25:1) is similar to the Redfield ratio (106:16:1); therefore, most organic matter probably is derived from lacustrine phytoplankton.

Calculated benthic-flux rates indicated that bottom sediments are important sources of major-ions and nutrients to Devils Lake. Only one of the cores collected during this study indicated a net sulfate flux from the lake into the sediments. Seasonal variations in major-ion and nutrient benthic fluxes generally were small. However, there were important differences between the calculated benthic fluxes for this study and the calculated benthic fluxes for 1990. Calculated benthic fluxes of bicarbonate, ammonia, and phosphorus for this study were smaller than calculated benthic fluxes for 1990. The large differences between fluxes for 1990 and 1991 were attributed to calm, stratified water-column conditions in 1990 and well-mixed water-column conditions in 1991.

The role of benthic fluxes in the chemical mass balances in Devils Lake was evaluated by calculating response times for major ions and nutrients in Devils Lake. The calculated response times for major ions in Devils Lake ranged from 6.7 years for bicarbonate to 34 years for sulfur (as SO_4). The response times for major ions are significantly shorter than previous estimates that did not include benthic fluxes. In addition, the relatively short response times for nitrogen (4.2 years) and phosphorus (0.95 year) indicate that nutrients are recycled rapidly between bottom sediments and the lake. During the study period, benthic fluxes were the dominant source of major ions and nutrients to Devils Lake and greatly reduced the response times of all major ions and nutrients for Devils Lake. As a result, bottom-sediment processes appear to buffer major-ion and nutrient concentrations in the lake. Any future attempt to evaluate water quality in Devils Lake should include the effects of bottom-sediment processes.

INTRODUCTION

Three and a half million lakes and six to eight million wetlands are located in the northern prairies of North America (Last, 1989). These lakes and wetlands vary from small ephemeral wetlands to large permanent lakes (Eisenlohr and others, 1972; Swanson and others, 1988; Last, 1989). They provide valuable habitat for wildlife and migratory waterfowl, and many of the larger lakes support sport fisheries. Devils Lake in northeastern North Dakota is the largest natural lake in the State and one of the largest natural lakes in the northern prairie region of North America.

Extreme drought conditions during 1988 and moderate drought conditions during 1989-91 resulted in a substantial decrease in the water level in Devils Lake. Concurrent with the decrease in water level was an increase in dissolved solids in the lake and the occurrence of esthetically unpleasant algal blooms. Changes in water level in Devils Lake may adversely affect the sport fishery, migratory waterfowl, and recreational activities associated with the lake.

Water enters Devils Lake by precipitation onto the lake surface and by inflow of surface water and ground water. The contribution by ground-water inflow, however, is small compared to the contribution by surface-water inflow and precipitation (Pusc, 1993). Water is removed from the lake only by evaporation; therefore, there are no outlets for the dissolved solids and nutrients. As a result, Devils Lake is saline and nutrient rich.

In response to numerous requests from local and national fishing, hunting, recreational, and environmental organizations, State and Federal agencies are evaluating the feasibility of importing water to stabilize the lake level and to alleviate potential water-quality problems. Recent studies in Devils Lake have documented that bottom-sediment/water-column interactions have important effects on concentrations of dissolved solids and nutrients in the lake (Lent, 1992; Komor, 1992; 1994). However, these studies did not examine seasonal variability of benthic fluxes and specific processes that are responsible for the increase in nutrient concentrations and for the algal blooms in Devils Lake that need to be addressed. The U.S. Geological Survey, in cooperation with the North Dakota State Department of Health and Consolidated Laboratories, North Dakota State Water Commission, and North Dakota Game and Fish Department, conducted an investigation to evaluate seasonal variability in benthic-flux rates and to understand the effect of these fluxes on the major-ion and nutrient chemistries in Devils Lake. The specific objectives of this study were to: (1) determine the seasonal variability of benthic fluxes of selected chemicals from the bottom sediments to the water column, (2) describe the basic nutrient cycles, (3) determine the magnitude of benthic fluxes relative to nutrient cycling, and (4) calculate chemical mass balances for major ions and nutrients. The results of the investigation are summarized in this report.

Physiography and Climate

The Devils Lake Basin is located in the Drift Prairie section of the Central Lowland Province of the Interior Plains (Fenneman, 1946). The bedrock in the area is predominantly the Pierre Shale of Cretaceous age. Major surficial deposits are of glacial origin and include ground moraines, end moraines, lacustrine deposits, and outwash deposits (Hobbs and Bluemle, 1987).

The study area has a semiarid continental climate characterized by long cold winters and short hot summers (Jensen, 1972). Generally, January is the coldest month (mean monthly temperature is about -15 °C) and July is the warmest month (mean monthly temperature is about 21 °C). Average annual precipitation in the Devils Lake area is about 44 cm. About 70 percent of the annual precipitation occurs during the warm months from May through September. Average annual evaporation in the area is about 86 cm and potential evapotranspiration exceeds precipitation throughout most of the late spring, summer, and early fall (Winter and others, 1984).

Hydrology

The Devils Lake Basin is a 9,840-km^2 closed drainage basin located in northeastern North Dakota (fig. 1). About 8,570 km^2 of the basin is tributary to Devils Lake, and the remaining 1,270 km^2 is tributary to Stump Lake. However, much of the northern part of the basin has poorly integrated drainage and probably does not contribute flow to either lake (Wiche, 1986).

Devils Lake is composed of a series of bays. The bays are, from west to east, West Bay, Main Bay, Mission Bay, East Bay, and East Devils Lake (fig. 1). Sixmile Bay and Creel Bay are connected to Main Bay. At high lake levels, the bays are connected and the movement of water in the lake generally is from west to east, and dissolved-solids concentrations generally increase from west to east. At lower lake levels, the bays are isolated.

Infrequent lake-level measurements are available for Devils Lake for 1867 to 1901 (fig. 2). Detailed lake-level measurements are available beginning in 1901. During the period of record, lake levels have fluctuated substantially. The highest recorded lake level of Devils Lake was 438.3 m (1,438 ft) above sea level in 1867. From 1867 to 1940, the lake levels generally declined to a historic minimum of 427 m (1,400.9 ft) above sea level. From 1940 to 1987, the lake level generally increased to a recent maximum of 435.5 m (1,428.8 ft) above sea level. Since 1987, the lake level generally has declined. During wet periods (large amounts of precipitation and runoff and increasing lake level), input by direct precipitation is about equal to input by surface-water runoff, and input by ground water is negligible. During dry periods (little direct precipitation, little or no tributary inflow, and decreasing lake level), input by precipitation is much greater than input by surface-water runoff. During dry periods, ground-water input may be more significant.

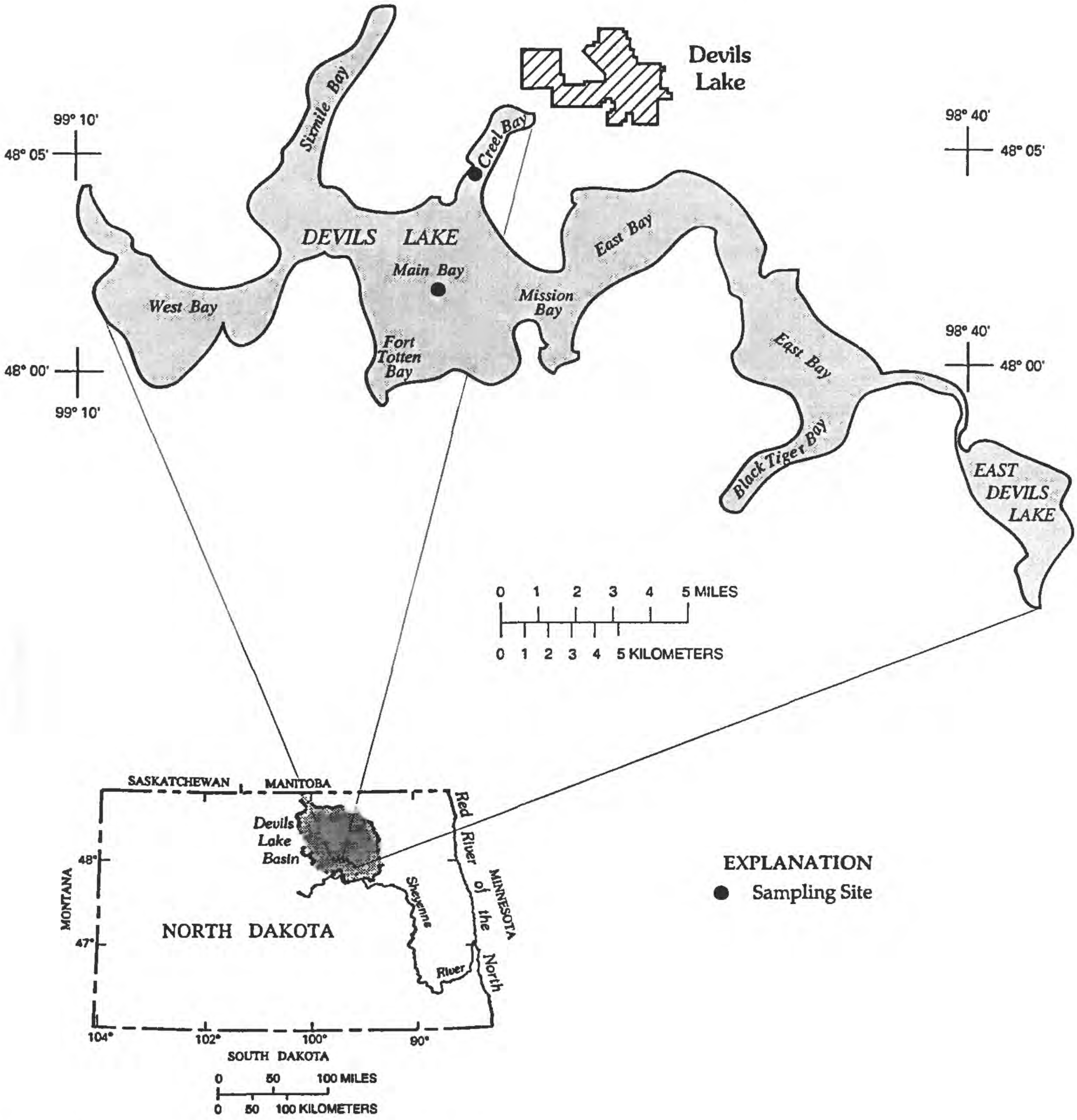

Figure 1. Location of Devils Lake Basin in North Dakota.

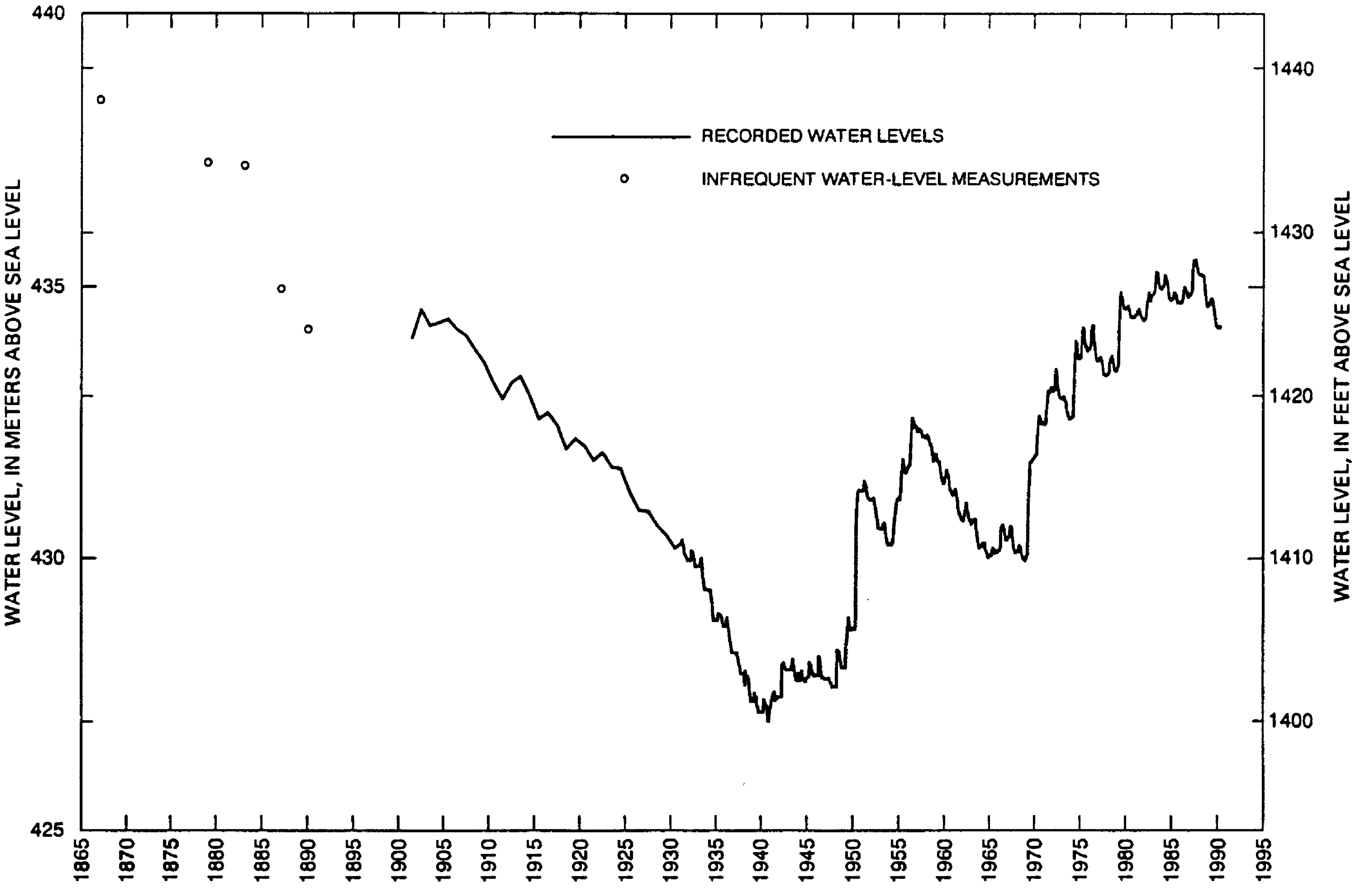

Figure 2. Water levels in Devils Lake, 1867-1991.

Previous Investigations

Devils Lake has been the focus of numerous water-quality investigations (Abbott, 1924; Swenson and Colby, 1955; Jones and Van Denburgh, 1966; Callender, 1968; Mitten and others, 1968; Anderson, 1969; Farmer, 1973; Shubert, 1976; Sether and Wiche, 1989; Komor, 1992, 1994; Lent, 1992; Sando, 1992; Sando and Sether, 1993). The U.S. Geological Survey has conducted routine water-quality monitoring of Devils Lake intermittently from the 1950's to 1992. The data from these investigations provide a wealth of information concerning the long-term variability in the water quality of the lake.

Water-quality data were collected from September 1988 through October 1990 to evaluate temporal and spatial water-quality variations in Devils Lake (Sando and Sether, 1993). The major-ion concentration data indicate that during periods of large runoff from spring snowmelt, the inflow water had calcium greater than magnesium and bicarbonate greater than sulfate. During periods of decreased runoff, the inflow water had magnesium greater than sodium and sulfate greater than bicarbonate. Generally, the water in Devils Lake was least saline near the western end (the dissolved-solids concentration in West Bay was about 3,500 mg/L) and increased to a maximum in East Devils Lake (the dissolved-solids concentration in East Devils Lake was about 10,000 mg/L). The major-ion composition of water in West Bay was similar to the inflow water. In contrast, the water in the eastern end of Devils Lake and in East Devils Lake had sodium greater than magnesium and sulfate. The relative decreases in the calcium and bicarbonate concentrations were attributed to evaporative concentration and precipitation of calcium carbonate (Sando and Lent, written commun., 1994).

On the basis of nutrient concentrations and trophic-state indices, Sando (1992) characterized Devils Lake as hypereutrophic. During 1988-90, the total nitrogen mass in Devils Lake was largest during the late spring and summer and decreased during the fall and winter (Sando, 1992). External sources of nitrogen were insignificant compared to seasonal variations in the nitrogen mass in the lake. The increase in nitrogen mass that occurred from midwinter to summer was attributed to resuspension of nutrient-rich sediments, decomposition of organic matter, and nitrogen fixation by phytoplankton (Sando, 1992; Sando and Lent; written commun., 1994). External sources of phosphorus to Devils Lake also were insignificant compared to seasonal variations in the phosphorus mass in the lake. The only significant external source of phosphorus to Devils Lake was discharge of storm water and wastewater effluent from the city of Devils Lake. In general, this discharge accounted for less than 5 percent of the measured phosphorus mass increases in the lake during the study period. The increase in phosphorus mass was attributed to resuspension of nutrient-rich sediment and decomposition of organic matter (Sando, 1992).

During periods of low lake level, such as the 1960's, Devils Lake is saline--dissolved-solids concentrations approached 30,000 mg/L in Main Bay, and the total dissolved-solids mass in Devils Lake (including West Bay, Sixmile Bay, Main Bay, Creel Bay, and East Bay) was about 2.2×10^{12} g. In contrast, when the lake level reached its recent maximum in 1987, the dissolved-solids concentration was less than 5,000 mg/L in Main Bay, and the dissolved-solids mass in Devils Lake approached 3.2×10^{12} g (Sando and Lent, written commun., 1994).

During summer 1990, Komor (1992; 1994) conducted a study to evaluate the importance of the geochemical processes that occur in Devils Lake bottom sediments on the chemistry of Devils Lake. One of the principal objectives of the study was to quantify the midsummer benthic-flux rates of dissolved chemical species from the bottom sediments to the lake water. To accomplish this objective, sediment cores were collected from two locations in Devils Lake, Main Bay and Creel Bay, and the sediments and sediment pore waters were analyzed for a variety of chemical constituents.

Results of Komor's 1990 study (Komor, 1992) indicated that bottom sediments have the potential to be significant contributors of dissolved solids and nutrients to the lake. However, because the sources of dissolved solids and nutrients could not be definitively identified, two general processes were proposed to account for the benthic fluxes. The process proposed to account for the majority of the major-ion (sodium, potassium, calcium, magnesium, sulfate, and chloride) fluxes was dissolution of evaporite minerals such as carbonate and sulfate minerals that were buried and subsequently dissolved. The process proposed to account for the large benthic-flux rates of nutrients, sulfide, and alkalinity was oxidation of sedimentary organic matter by sulfate reduction. Sulfate reduction is a microbially mediated reaction that involves the oxidation of organic matter to inorganic nutrients by the reduction of sulfate to sulfide (Martens and others, 1978; Berner, 1980; Jorgensen, 1982; Morse and others, 1987; Kuivila and others, 1989). The amount of nutrients generated by sulfate reduction is large relative to the amount of energy produced (Berner, 1980; Jorgensen, 1982; Morse and others, 1987; Kuivila and others, 1989). Therefore, "excess" nutrients that are produced during sulfate reduction accumulate in the near-surface pore water and drive the benthic flux (Martens and others, 1978; Froelich and others, 1979; Berner, 1980; Baccini, 1985; Davison, 1985).

In addition to the sediment cores collected in 1990, sediment cores were collected from Devils Lake for chemical analysis of pore-water samples during two other studies. A single sediment core was collected near the center of Main Bay in summer 1966, and pore water was analyzed from depths down to about 3 m in the sediment core (Callender, 1968). Callender's study (1968) provides valuable information concerning the chemical nature of Devils Lake bottom sediments at a time when the lake level was significantly lower and the lake's dissolved-solids concentrations were much larger than during this study.

Four short (<50 cm) sediment cores were collected along a transect from Mission Bay to the eastern extreme of Devils Lake, and pore-water samples were obtained from the cores in summer 1986 (Lent, 1992). Data from these four cores, in conjunction with the data from Main Bay and Creel Bay (Callender, 1968; Komor, 1992), are used to describe spatial variability in benthic fluxes throughout much of Devils Lake.

Lent (1992) compiled the available pore-water data from Devils Lake and calculated benthic-flux rates for major ions and nutrients in the lake. In general, calculated benthic-flux rates for sodium, potassium, magnesium, and calcium increased from west to east. In contrast, calculated benthic-flux rates of ammonia, orthophosphate, sulfate, and bicarbonate were one to two orders of magnitude greater in Main Bay and Creel Bay than in eastern Devils Lake. These differences indicate that sulfate reduction in bottom sediments is not occurring or is occurring at a slower rate in eastern Devils Lake than in Main Bay.

Three mechanisms could explain the apparent differences in sulfate-reduction rates in the different bays of Devils Lake (Lent, 1992). Variations in the source and composition of sedimentary organic matter in Main Bay and East Bay could result in different sulfate-reduction rates. Organic matter produced in the lake by biologic activity should be more labile than detrital organic matter from the drainage basin. More labile organic matter would result in faster rates of organic-matter decomposition. The faster rates of organic-matter decomposition would quickly deplete the dissolved oxygen and nitrate in the pore water and result in a change to anaerobic conditions favorable to sulfate reduction. Calculated C:N:P ratios based on pore-water concentrations of bicarbonate, ammonia, and orthophosphate indicated that the sedimentary organic matter in Main Bay is more labile than the sedimentary organic matter in East Bay.

Variations in the sedimentation rates among the bays also could be responsible for variations in sulfate-reduction rates. Lent (1992) found that the sedimentation rates in Main Bay and Creel Bay were greater than the sedimentation rates in East Bay. In areas with relatively low sedimentation rates (such as East Bay), oxygen, nitrate, and other electron acceptors can move by diffusion or mixing from the water column to the sediment surface, eliminating the potential for sulfate reduction.

Depletion of dissolved oxygen in bottom water during periods of temporary stratification of the lake could be responsible for reducing conditions in the surficial bottom sediments (Komor, 1992). This explanation would indicate that sulfate reduction in Devils Lake is an ephemeral process related to the stability of the water column. During periods of relatively slow wind velocities, Devils Lake may stratify for short periods of time. When the lake is stratified, oxygen may become depleted in deeper lake water and cause anoxic conditions near the sediment/water interface.

DATA COLLECTION

Data for this study were collected between late spring 1991 and fall 1991. Data collected include: (1) vertical water-column profiles of specific conductance, pH, water temperature, and dissolved oxygen; (2) water-column samples from three depths to identify vertical variations in major-ion and nutrient concentrations; (3) gross primary productivity (GPP) measurements to determine the rate of carbon fixation by primary producers; (4) mass and composition of organic matter from sediment traps at two depths to calculate settling rates; and (5) chemical gradients in shallow-sediment pore water from sediment cores. All data were to be collected within 3 days during each sampling period to facilitate direct comparisons of the data and development of four "instantaneous" chemical mass balances.

Water-Column Profiles

Vertical water-column profiles of specific conductance, pH, temperature, and dissolved oxygen were collected 12 times during this study, and Secchi-disk depths were collected 11 times. Specific conductance, pH, temperature, and dissolved oxygen were measured electromagnetically using a Hydrolab multimeter. Secchi-disk depth was determined by lowering and raising a 20-cm-diameter Secchi disk to determine the depth where it was no longer visible.

Water-Column Chemistry

Water-column samples for laboratory analyses were collected on May 21, July 31, September 4, and October 8, 1991. Samples were collected with a 1-m long Kemmerer bottle. Three water depths were sampled during each trip: (1) a near-surface sample at about 0- to 1-m water depth; (2) a middle sample at about 3- to 4-m water depth; and (3) a deep sample at about 6- to 7-m water depth, which was about 1 to 2 m above the bottom.

Each water sample was put into a separate churn splitter and returned to a field laboratory on shore where subsamples from the churn splitters were analyzed for specific conductance, pH, and alkalinity. One subsample was collected in a distilled-water-rinsed 250-mL polyethylene bottle for laboratory determination of physical properties (specific conductance, pH, and alkalinity). A second subsample was collected in a distilled-water-rinsed 250-mL brown polyethylene bottle, preserved with 1 mL of mercuric chloride, and chilled to 4°C for analysis of total nutrients.

Additional subsamples were taken from the churns for analysis of dissolved species. A peristaltic pump equipped with sample-rinsed Tygon tubing was used to deliver sample water from the churns through a plate filter containing a 142-mm, 0.45-µm pore-size membrane filter. Approximately 500 mL of water was passed through the filter to remove any contaminating surfactants before sample bottles were filled. A 250-mL subsample was filtered into a distilled-water-rinsed polyethylene bottle for analysis of dissolved anions. Another 250-mL subsample was filtered into an acid-rinsed polyethylene bottle and preserved with 1 mL of nitric acid for analyses of cations and trace elements. Finally, a 250-mL subsample was filtered into a distilled-water-rinsed brown polyethylene bottle, preserved with 1 mL of mercuric chloride, and chilled to 4°C for analysis of dissolved nutrients. All samples for laboratory analyses were sent to the U.S. Geological Survey National Water Quality Laboratory in Arvada, Colo.

Gross Primary Productivity

GPP was measured six times during the study. The method used to determine GPP was the oxygen light- and dark-bottle method for phytoplankton (B-8001-85) described by Britton and Greeson (1987) and Wetzel and Likens (1991). Water samples were collected from six depths with a Kemmerer bottle. The water samples were immediately transferred to clean glass biological-oxygen-demand (BOD) bottles through Tygon tubing attached to the Kemmerer bottle. During the transfer, care was taken to avoid adding dissolved oxygen to the samples. Each BOD bottle was filled from the bottom and allowed to overflow for approximately three bottle volumes. Four BOD bottles were filled with water from each depth; two clear BOD bottles (light bottles) and two BOD bottles that were covered with black tape (dark bottles). The tops of the dark bottles were covered with aluminum foil prior to deployment. The BOD bottles were placed on racks, and deployed on a rope attached to a concrete weight.

The BOD bottles were put in the water between 10:00 a.m. and 11:30 a.m and were left in place for 3 to 4 hours. After retrieval, the bottles were immediately put in a dark wooden box and transported to shore (usually less than 10 minutes). Dissolved oxygen was measured at the field laboratory using one of two methods. On May 8, May 21, and October 8, dissolved oxygen was measured using a modified Winkler titration. On June 18, July 31, and September 4, dissolved oxygen was measured using an oxygen electrode. The results obtained using the oxygen electrode may underestimate the amount of GPP due to the length of time between retrieval of the bottles and measurement of dissolved oxygen.

Sediment Traps

Sediment traps were deployed below the lake surface five times during this study to measure the amount of organic debris settling in the water column. Two depths were measured; a near-surface (top) sediment trap at 1-m depth, and a deeper (bottom) sediment trap at 3-m depth. The sediment traps were designed and deployed based on studies by Bloesch and others (1977), Bloesch and Burns (1980), and Bloomquest and Hakanson (1981). Each trap consisted of four separate cylinders supported by a rack. Each cylinder had an 18-cm^2 opening and was 50 cm in length.

The two traps were deployed using a single rope. The bottom end of the rope was connected to a concrete weight, and the top was connected to a large marine buoy. The sediment traps were deployed for periods ranging from 43 to 120 hours. After retrieval, two to four of the cylinders from each of the two traps were combined in two different churn splitters. Subsamples for total nutrient concentrations were collected in 250-mL brown polyethylene bottles, preserved with 1 mL of mercuric chloride, and chilled to 4°C. Subsamples for analysis of total organic carbon were collected in 250-mL baked-glass bottles and chilled to 4°C.

Sediment Cores and Pore Water

Sediment cores were collected four times during 1991. The cores are identified by abbreviated location (MB=Main Bay) and date. The first sediment core (MB-5-23) was collected on May 23 from an anchored raft using a 1-m section of 10.2-cm diameter polyvinyl-chloride (PVC) pipe. The PVC pipe was attached to a one-way valve to provide suction and to separate the sediment core from the column of water in the overlying pipestem. Because this sampling method may have resulted in some sediment mixing during the collection process, data from this core were not included in chemical calculations. The remaining three sediment cores (MB-7-30, MB-8-27, and MB-10-8) were collected from an anchored boat using a stainless-steel box corer. The box corer had a removable, clear acrylic core liner that was 15.2 cm on a side and 22.9 cm deep. The box corer was lowered by hand with nylon rope to near the sediment surface, and then slowly lowered into the bottom sediment. This method allowed collection of undisturbed sediment cores. After collection, the sediment cores were covered to minimize oxidation effects, placed in a cooler, and transported back to the field laboratory. Processing of the sediment cores began within 1 hour after collection.

Immediately on arrival at the field laboratory, the sediment cores were put into nitrogen-filled glove bags. All sediment sampling and subsequent pore-water processing was done in nitrogen-filled glove bags to minimize the effects of oxidation. The sediment cores were sampled from the top using clean plastic utensils. Six 2-cm-thick sections were collected from each core to a depth of 12 cm and put into clean plastic bags. The sections were homogenized and then transferred into clean 50-mL centrifuge tubes. The centrifuge tubes were capped and taken out of the glove bag. The sediment samples were centrifuged for 45 minutes at 3,000 to 4,000 revolutions per minute. The samples were put back into a nitrogen-filled glove bag and filtered through 0.45–μm filters. A 25-mL subsample was placed in a polyethylene bottle for dissolved anion analysis. Another 25-mL subsample was placed in an acid-rinsed polyethylene bottle and preserved with 1 mL of nitric acid for dissolved cation and dissolved trace-element analysis. Finally, a 25-mL subsample was placed in a brown polyethylene bottle, preserved with 1 mL of mercuric chloride, and chilled to 4°C for dissolved nutrient analysis.

Alkalinity, pH, and sulfide concentrations were determined in the field laboratory immediately after pore-water processing. Alkalinity was determined by incremental titration of 25 mL of sample with 0.16 normal sulfuric acid, and pH was determined with a standard meter. Sulfide concentrations were determined spectrophotometrically using N,N-dimethyl-p-phenylenediamine oxalate after the appropriate dilution. Sediment porosities were determined by weight loss after drying in the U.S. Geological Survey laboratory in Bismarck, N. Dak. Major dissolved ions, dissolved trace elements, and dissolved nutrients were measured at the U.S. Geological Survey National Water Quality Laboratory in Arvada, Colo.

DATA ANALYSIS

Water-Column Profiles

Specific-conductance values varied from 5,100 to 5,460 μS/cm during the study period (table 1). Specific-conductance values were smallest during the spring and early summer, increased through the summer months, and reached a maximum during September and October 1991. Vertical variations in specific-conductance values were small during the study period. Generally pH varied between 8.4 and 9.0 during the study period. Water temperature had strong seasonal variability during the study period. Water temperature varied from 4.5°C on May 7, 1991, to 24.5°C on August 12, 1991. In general vertical temperature variations were small. Dissolved-oxygen concentrations tended to be largest in the spring (May) and fall (September and October) and smaller during the summer (June through August). However, near-surface dissolved-oxygen concentrations were large on July 9, 1991, and on August 12, 1991. Depletions of dissolved oxygen in bottom water, associated with peak dissolved-oxygen concentration in near-surface water, occurred on July 9, 1991, and August 12, 1991.

Table 1. Physical properties for Main Bay, Devils Lake, May through October 1991

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; --, no data]

Date	Sampling depth (feet)	Specific conductance (µS/cm)	pH	Water temperature (°C)	Oxygen, dissolved (mg/L)
May 7, 1991	0.0	5,120	8.4	6.5	12.2
May 7, 1991	3.0	5,120	8.4	5.0	12.1
May 7, 1991	8.0	5,120	8.4	4.5	12.1
May 7, 1991	13	5,130	8.4	4.5	12.0
May 7, 1991	18	5,130	8.4	4.5	12.0
May 7, 1991	24	5,120	8.4	4.5	12.0
June 5, 1991	0	5,300	8.6	18.0	8.0
June 5, 1991	2.0	--	--	18.0	8.0
June 5, 1991	5.0	--	--	18.5	8.0
June 5, 1991	8.0	--	--	18.0	7.9
June 5, 1991	13	--	--	18.0	7.9
June 5, 1991	18	--	--	18.0	7.8
June 5, 1991	21	--	--	--	7.7
June 19, 1991	0	5,110	8.7	21.5	8.0
June 19, 1991	3.0	5,110	8.7	21.5	8.0
June 19, 1991	7.0	5,100	8.7	21.5	7.9
June 19, 1991	12	5,100	8.7	21.0	7.6
June 19, 1991	17	5,100	8.7	21.0	7.5
June 19, 1991	22	5,110	8.7	21.0	7.5
July 9, 1991	0	5,200	--	24.0	12.8
July 9, 1991	2.5	5,220	--	21.5	14.3
July 9, 1991	5.0	5,220	--	20.0	11.2
July 9, 1991	9.0	5,230	--	20.0	10.4
July 9, 1991	14	5,230	--	20.0	10.2
July 9, 1991	19	5,220	--	20.0	10.1
July 9, 1991	24	5,210	--	19.5	6.9
July 18, 1991	0	5,240	8.8	23.0	9.8
July 18, 1991	4.0	5,250	8.7	23.0	9.8
July 18, 1991	8.0	5,250	8.7	23.0	9.7
July 18, 1991	13	5,240	8.7	22.0	8.7
July 18, 1991	18	5,240	8.6	22.0	8.2
July 18, 1991	24	5,240	8.6	22.0	8.2
July 30, 1991	0	5,270	8.7	21.5	8.5
July 30, 1991	4.0	5,270	8.7	21.0	8.3
July 30, 1991	9.0	5,270	8.6	21.0	8.2
July 30, 1991	14	5,270	8.6	21.0	8.1
July 30, 1991	19	5,280	8.6	21.0	8.1
July 30, 1991	24	5,280	8.4	21.0	8.1
August 12, 1991	0	5,340	8.8	24.5	12.0
August 12, 1991	4.0	5,340	8.7	24.0	12.0
August 12, 1991	9.0	5,320	8.7	22.0	10.6
August 12, 1991	14	5,320	8.7	21.5	8.4
August 12, 1991	19	5,320	8.7	21.0	5.7
August 12, 1991	24	5,310	8.6	21.0	2.2
August 29, 1991	0	5,140	8.8	23.0	8.8
August 29, 1991	4.0	5,150	8.8	23.0	8.6
August 29, 1991	9.0	5,150	8.8	23.0	8.6
August 29, 1991	14	5,150	8.8	23.0	8.4
August 29, 1991	19	5,150	8.8	23.0	8.3
August 29, 1991	24	5,140	8.8	23.0	8.2

Table 1. Physical properties for Main Bay, Devils Lake, May through October 1991--Continued

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; --, no data]

Date	Sampling depth (feet)	Specific conductance (µS/cm)	pH	Water temperature (°C)	Oxygen, dissolved (mg/L)
Sept. 11, 1991	0.0	5,300	8.9	19.0	9.7
Sept. 11, 1991	4.0	5,300	8.9	19.0	9.7
Sept. 11, 1991	8.0	5,300	8.9	18.5	9.2
Sept. 11, 1991	13	5,300	8.9	18.5	9.0
Sept. 11, 1991	18	5,300	8.9	18.5	8.8
Sept. 11, 1991	23	5,300	8.9	18.5	8.7
Sept. 19, 1991	0	5,450	9.0	14.0	10.1
Sept. 19, 1991	5.0	5,450	8.9	14.0	10.0
Sept. 19, 1991	10	5,450	8.9	14.0	9.9
Sept. 19, 1991	15	5,450	8.9	14.0	9.9
Sept. 19, 1991	20	5,450	8.9	14.0	9.9
Sept. 19, 1991	24	5,460	8.9	14.0	10.1
October 7, 1991	0	5,420	9.0	9.0	10.5
October 7, 1991	5.0	5,420	8.9	9.0	10.4
October 7, 1991	10	5,420	9.0	9.0	10.4
October 7, 1991	15	5,420	9.0	9.0	10.5
October 7, 1991	20	5,410	8.9	9.0	10.4
October 7, 1991	23	5,410	8.8	9.0	10.4
October 21, 1991	0	5,430	9.0	6.0	11.0
October 21, 1991	5.0	5,440	9.0	6.0	10.9
October 21, 1991	10	5,440	9.0	6.0	10.9
October 21, 1991	15	5,440	9.0	6.0	11.0
October 21, 1991	20	5,450	9.0	6.0	10.9
October 21, 1991	22	5,450	9.0	6.0	10.9

Secchi-Disk Depth

Secchi-disk depth was measured to estimate light-extinction depths in Devils Lake and to provide a measure of trophic state variation (Carlson, 1977). In general, variations in measured Secchi-disk depths are the result of variations in the amount of debris in lake water. In a system like Devils Lake where there are no large sources of detrital input, it may be assumed that the Secchi-disk depth is directly related to the amount of total organic matter in the water (Wetzel, 1983).

Secchi-disk depth was measured 11 times from May through October 1991 (table 2). Secchi-disk depth varied from 0.82 m on May 7, 1991, to 2.13 m on June 5, 1991. The mean Secchi-disk depth during the study period was 1.24 m. In general, Secchi-disk depths were small during May, increased to a maximum in June, decreased in July, and remained relatively constant from July through September. The relatively small values in the spring and late summer presumably are the result of increased phytoplankton biomass. The increase in Secchi-disk depth in October reflects a decrease in biomass related to decreases in light intensity and water temperatures.

Water-Column Chemistry

Geochemical and biogeochemical processes that occur near, or just below the sediment/water interface can have substantial impact on the water quality of a lake. In lakes where bottom-sediment processes are important, vertical variations in water quality, particularly in lakes that are seasonally or permanently stratified, can be significant (Sholkovitz, 1985). Therefore, seasonal and vertical trends in water quality can be used as indicators of bottom-sediment processes (Sholkovitz, 1985).

During the summer, Devils Lake generally is well mixed by wind-driven circulation. Therefore, vertical variations in water quality generally are small. Vertical distributions of calcium, magnesium, sodium, and potassium are indicative of a well-mixed water column (tables 3, 4, 5, and 6). No overall seasonal trends are apparent in the concentrations of major cations. No variations in major-anion or nutrient concentrations are evident with depth or season (tables 3, 4, 5, and 6). More detailed profiling, including near-bottom water samples and profiles collected during ice-covered periods, is necessary to document geochemical processes that influence water-column chemistry.

Table 2. Secchi-disk depths for Main Bay, Devils Lake, May through October 1991

Date	Secchi-disk depth (meters)
May 7, 1991	0.82
June 5, 1991	2.13
June 19, 1991	1.71
July 9, 1991	.94
July 18, 1991	.88
July 30, 1991	.88
August 12, 1991	1.13
August 29, 1991	1.13
September 11, 1991	.93
September 19, 1991	1.10
October 7, 1991	2.04

Gross Primary Productivity

GPP was determined six times during the study period. The results of the field measurements are presented in table 7. The GPP data were converted to GPP rates (table 8) using the following method outlined in Britton and Greeson (1987):

$$GPP = \left(\frac{LB - DB}{t}\right)(1{,}000)\left(\frac{12}{32}\right) \qquad (1)$$

where GPP is gross primary productivity (milligrams of carbon per square meter per hour);

LB is dissolved-oxygen concentration, in milligrams per liter, in the light bottle after incubation;

DB is dissolved-oxygen concentration, in milligrams per liter, in the dark bottle after incubation;

t is incubation period, in hours;

12 is the atomic weight of carbon; and

32 is the molecular weight of oxygen.

Light intensity and, therefore, primary productivity are not constant throughout the day. Much of the total daily primary productivity occurs during the middle of the day when light intensity is usually at a maximum. Primary productivity is smaller in the morning and evening compared to the middle of the day (Wetzel and Likens, 1991). Therefore, an 8-hour day (based on the average hourly rate) was used to calculate the total primary productivity in grams of carbon per square meter per day. This simplification is necessary because the measurements were not made for an entire daylight period.

In general, GPP rates were small during the spring sampling periods (May 8 and May 21), increased during the summer sampling periods (June 18, July 31, and September 4), and decreased during the fall sampling period (October 8; table 8). This seasonal pattern in GPP rates is consistent with results from other lakes (Wetzel, 1983).

Table 3. Major-ion, nutrient, and selected trace-element concentrations in Main Bay, Devils Lake, May 21, 1991

[All concentrations are milligrams per liter except specific conductance (microsiemens per centimeter at 25 degrees Celsius), pH (standard units), and temperature (degrees Celsius); --, not analyzed]

Property or constituent	Surface	Middle	Deep
Specific conductance	5,140	5,140	5,140
pH (field)	8.7	8.7	8.7
pH (lab)	--	--	--
Temperature	14	14	14
Alkalinity (lab)	469	472	472
Dissolved calcium	50	52	55
Dissolved magnesium	180	180	200
Dissolved sodium	820	850	880
Dissolved potassium	98	100	120
Dissolved bicarbonate	439	451	512
Dissolved carbonate	48	48	24
Dissolved sulfate	1,900	1,900	2,000
Dissolved chloride	390	420	380
Dissolved fluoride	.2	.3	.4
Dissolved silica	13	14	13
Dissolved nitrite, as nitrogen	<.01	<.01	<.01
Total nitrite, as nitrogen	--	--	--
Dissolved nitrite plus nitrate, as nitrogen	.15	.15	.15
Total nitrite plus nitrate, as nitrogen	--	--	--
Dissolved ammonia, as nitrogen	.2	.2	.2
Total ammonia, as nitrogen	--	--	--
Dissolved ammonia plus organic nitrogen, as nitrogen	.15	.18	.15
Total ammonia plus organic nitrogen, as nitrogen	--	--	--
Dissolved phosphorus, as phosphorus	.1	.1	.12
Total phosphorus, as phosphorus	--	--	--
Dissolved phosphate, as phosphorus	.06	.07	.07
Total phosphate, as phosphorus	--	--	--
Dissolved boron	.76	.78	.74
Dissolved iron	<.01	<.01	.01
Dissolved manganese	.01	.01	<.01
Chlorophyll a	--	--	--
Chlorophyll b	--	--	--

Table 4. Major-ion, nutrient, and selected trace-element concentrations in Main Bay, Devils Lake, July 31, 1991

[All concentrations are milligrams per liter except specific conductance (microsiemens per centimeter at 25 degrees Celsius), pH (standard units), and temperature (degrees Celsius); --, not analyzed]

Property or constituent	Surface	Middle	Deep
Specific conductance	--	--	--
pH (field)	8.9	8.9	8.9
pH (lab)	--	--	--
Temperature	21	21	21
Alkalinity (lab)	--	--	--
Dissolved calcium	57	57	58
Dissolved magnesium	190	190	190
Dissolved sodium	890	900	900
Dissolved potassium	120	110	110
Dissolved bicarbonate	427	442	455
Dissolved carbonate	54	66	60
Dissolved sulfate	2,000	2,000	2,000
Dissolved chloride	370	340	340
Dissolved fluoride	.3	.3	.3
Dissolved silica	19	19	19
Dissolved nitrite, as nitrogen	<.01	<.01	<.01
Total nitrite, as nitrogen	<.01	<.01	<.01
Dissolved nitrite plus nitrate, as nitrogen	<.05	<.05	<.05
Total nitrite plus nitrate, as nitrogen	<.05	<.05	<.05
Dissolved ammonia, as nitrogen	<.01	<.01	<.01
Total ammonia, as nitrogen	.2	.2	.1
Dissolved ammonia plus organic nitrogen, as nitrogen	--	--	--
Total ammonia plus organic nitrogen, as nitrogen	3.1	1.9	2.1
Dissolved phosphorus, as phosphorus	.15	.15	.15
Total phosphorus, as phosphorus	.21	.21	.2
Dissolved phosphate, as phosphorus	.1	.1	.1
Total phosphate, as phosphorus	.1	.1	.1
Dissolved boron	.83	.82	.82
Dissolved iron	<.01	<.01	<.01
Dissolved manganese	<.01	.01	.01
Chlorophyll a	--	--	--
Chlorophyll b	--	--	--

Table 5. Major-ion, nutrient, and selected trace-element concentrations in Main Bay, Devils Lake, September 4, 1991

[All concentrations are milligrams per liter except specific conductance (microsiemens per centimeter at 25 degrees Celsius), pH (standard units), and temperature (degrees Celsius); --, not analyzed]

Property or constituent	Surface	Middle	Deep
Specific conductance	5,300	5,390	5,240
pH (field)	--	--	--
pH (lab)	8.9	8.9	8.9
Temperature	19	19	19
Alkalinity (lab)	467	494	486
Dissolved calcium	51	54	50
Dissolved magnesium	180	180	180
Dissolved sodium	890	920	880
Dissolved potassium	110	120	110
Dissolved bicarbonate	--	--	--
Dissolved carbonate	--	--	--
Dissolved sulfate	2,000	2,100	2,100
Dissolved chloride	400	430	410
Dissolved fluoride	.4	.2	.4
Dissolved silica	21	21	20
Dissolved nitrite, as nitrogen	<.01	<.01	<.01
Total nitrite, as nitrogen	<.01	<.01	<.01
Dissolved nitrite plus nitrate, as nitrogen	<.05	<.05	<.05
Total nitrite plus nitrate, as nitrogen	<.05	<.05	<.05
Dissolved ammonia, as nitrogen	.03	.03	.03
Total ammonia, as nitrogen	.02	.01	.02
Dissolved ammonia plus organic nitrogen, as nitrogen	--	--	--
Total ammonia plus organic nitrogen, as nitrogen	3.0	3.2	3.4
Dissolved phosphorus, as phosphorus	.10	.11	.11
Total phosphorus, as phosphorus	.17	.17	.18
Dissolved phosphate, as phosphorus	.04	.04	.04
Total phosphate, as phosphorus	.06	.06	.06
Dissolved boron	.80	.82	.80
Dissolved iron	.02	<.01	<.01
Dissolved manganese	<.01	<.01	<.01
Chlorophyll a	.016	.017	.0021
Chlorophyll b	<.0001	<.0001	<.0001

Table 6. Major-ion, nutrient, and selected trace-element concentrations in Main Bay, Devils Lake, October 8, 1991

[All concentrations are milligrams per liter except specific conductance (microsiemens per centimeter at 25 degrees Celsius), pH (standard units), and temperature (degrees Celsius); --, not analyzed]

Property or constituent	Surface	Middle	Deep
Specific conductance	5,380	5,390	5,390
pH (field)	--	--	--
pH (lab)	8.8	8.8	8.8
Temperature	9	9	9
Alkalinity (lab)	480	480	483
Dissolved calcium	50	51	52
Dissolved magnesium	190	190	190
Dissolved sodium	830	860	890
Dissolved potassium	120	120	120
Dissolved bicarbonate	--	--	--
Dissolved carbonate	--	--	--
Dissolved sulfate	2,000	2,000	2,000
Dissolved chloride	400	400	400
Dissolved fluoride	<.01	<.01	<.01
Dissolved silica	20	20	21
Dissolved nitrite, as nitrogen	<.01	<.01	<.01
Total nitrite, as nitrogen	<.01	<.01	<.01
Dissolved nitrite plus nitrate, as nitrogen	<.05	<.05	<.05
Total nitrite plus nitrate, as nitrogen	<.05	<.05	<.05
Dissolved ammonia, as nitrogen	.02	.01	.02
Total ammonia, as nitrogen	.03	.02	.03
Dissolved ammonia plus organic nitrogen, as nitrogen	--	--	--
Total ammonia plus organic nitrogen, as nitrogen	2.6	2.5	2.5
Dissolved phosphorus, as phosphorus	.06	.07	.03
Total phosphorus, as phosphorus	.09	.09	.08
Dissolved phosphate, as phosphorus	.02	.03	.03
Total phosphate, as phosphorus	.02	.02	.02
Dissolved boron	.81	.84	.82
Dissolved iron	.021	.012	.01
Dissolved manganese	<.003	<.003	<.003
Chlorophyll a	.0065	.0041	.0074
Chlorophyll b	<.0001	<.0001	<.0001

Table 7. Dissolved-oxygen concentrations in the light bottles minus dissolved-oxygen concentrations in the dark bottles for Main Bay, Devils Lake

[In milligrams per liter]

Depth (meters)	May 8, 1991	May 21, 1991	June 18, 1991	July 31, 1991	Sept. 4, 1991	Oct. 8, 1991
0.38	0.20	0.20	0.40	1.1	1.2	0.10
.53	0	.20	.40	1.2	1.2	.05
.99	0	.05	.50	1.1	1.2	.05
1.8	0	.05	.50	.80	1.1	.08
2.4	0	.10	.40	.40	0	.15
3.0	0	.20	.40	.30	0	.01

Table 8. Calculated gross primary productivity rate

[In grams of carbon per square meter per day, based on an 8-hour day]

Date	Gross primary productivity
May 8, 1991	0.076
May 21, 1991	.36
June 18, 1991	1.2
July 31, 1991	1.6
September 4, 1991	1.8
October 8, 1991	.21

Sediment-Trap Data

Documenting the settling rate of organic matter from near-surface water to the sediment/water interface is an important facet of understanding nutrient cycles in Devils lake. Organic-matter degradation that occurs near or just below the sediment/water interface may be the primary source of nutrient regeneration in Devils Lake (Sando, 1992). One of the limiting factors to the rate of nutrient regeneration is the rate of supply of organic matter.

Sediment traps were used to provide measurements of: (1) the settling rate of organic matter from near-surface water to deep water, (2) the settling rate of organic matter from deep water to the lake bottom, (3) the rate of organic-matter remineralization (conversion of organic matter to inorganic nutrients) during settling, and (4) the general composition of the settling organic matter.

Sediment-trap data are reported as the masses of ammonia, ammonia plus organic nitrogen, phosphorus, and organic carbon (table 9). Mass values were multiplied by the length of the sampling period, in hours, (table 10) to obtain settling rates (table 11). The settling rate of ammonia plus organic nitrogen was used to approximate the settling rate of organic nitrogen. This approximation is reasonable because ammonia mass was less than 1 percent of the organic nitrogen mass (table 9). On June 18, the settling rate of organic nitrogen to the top trap was greater than the settling rate to the bottom trap. During the other four sampling periods, the settling rate of organic nitrogen to the bottom trap was consistently larger. The average settling rate of organic nitrogen in the top traps was 0.81 $(g/m^2)/d$. The average settling rate of organic nitrogen in the bottom traps was 0.86 $(g/m^2)/d$. The organic nitrogen settling rate was maximum July 29 through August 1 and was minimum October 7-9. The average settling rate of organic nitrogen during the study period was 0.84 $(g/m^2)/d$.

Table 9. Ammonia, ammonia plus organic nitrogen, phosphorus, and organic carbon masses collected in Creel Bay, Devils Lake, sediment traps

[All masses in milligrams; --, no data]

Date	Trap	Mass			
		Ammonia	Ammonia plus organic nitrogen	Phosphorus	Organic carbon
June 13-18, 1991	Top	0.036	7.2	0.73	71
	Bottom	.036	5.8	.54	96
July 29-Aug. 1, 1991	Top	.024	5.3	.47	53
	Bottom	.024	5.8	.50	56
Aug. 26-28, 1991	Top	--	--	--	49
	Bottom	--	--	--	52
Sept. 17-19, 1991	Top	.024	12	1.0	120
	Bottom	.024	13	1.1	130
Oct. 7-9, 1991	Top	0	2.0	.06	46
	Bottom	.012	2.5	.06	54

Table 10. Length of sediment-trap sampling period in Creel Bay, Devils Lake

[Time in hours]

Date	Trap	Time
June 13-18, 1991	Top	120
	Bottom	120
July 29-Aug. 1, 1991	Top	68
	Bottom	68
Aug. 26-28, 1991	Top	43
	Bottom	43
Sept. 17-19, 1991	Top	52
	Bottom	52
Oct. 7-9, 1991	Top	44
	Bottom	44

In general, the seasonal variation in settling rate of phosphorus was similar to the organic nitrogen settling rate (table 11). The phosphorus settling rate was maximum July 29 through August 1 and minimum October 7-9. There were no appreciable differences in the total phosphorus settling rates to the top and bottom traps. The average settling rate of phosphorus to the top and bottom traps during the study period was 0.06 $(g/m^2)/d$. The fact that little or no difference was measured in the phosphorus settling rate between the top and bottom sediment traps is in contrast to typical conditions in lakes where significant amounts of nutrient regeneration occur during the settling of organic particles (Stabel, 1985; Fukushima and others, 1989).

The settling rate of organic carbon to the bottom trap generally was greater than the settling rate to the top trap (table 11). If the source of organic matter is mainly primary productivity in near-surface water, and significant remineralization occurs in the water column, the settling rate of organic carbon in the top trap should be greater than the settling rate in the bottom trap. The fact that the settling rate of organic carbon was greater in the bottom trap indicates that remineralization rates in the water column were small or that significant amounts of organic matter were produced at depth. The settling rate of organic carbon varied between 7.8 (g/m^2)/d on June 16-18, 1991, and 16 (g/m^2)/d on August 26-28 and October 7-9 (table 11). The settling rate of organic carbon using the entire data set (average of the top and bottom traps) was 12 (g/m^2)/d.

Table 11. Calculated settling rates of ammonia plus organic nitrogen, phosphorus, and organic carbon in Creel Bay, Devils Lake, based on sediment-trap data

[Flux in grams per square meter per day; --, no data]

Date	Trap	Flux of ammonia plus organic nitrogen	Flux of phosphorus	Flux of organic carbon
June 13-18, 1991	Top	0.80	0.08	7.8
	Bottom	.64	.06	11
July 29-Aug. 1, 1991	Top	1.00	.09	10
	Bottom	1.13	.10	11
Aug. 26-28, 1991	Top	--	--	15
	Bottom	--	--	16
Sept. 17-19, 1991	Top	.83	.07	8.1
	Bottom	.91	.07	9.1
Oct. 7-9, 1991	Top	.62	.02	14
	Bottom	.76	.02	16

The C:N:P (carbon:nitrogen:phosphorus) ratio of organic matter settling in the sediment traps is a useful indicator of the source of organic matter (Ebise and Inoue, 1991). The Redfield ratio (C:N:P = 106:16:1) for marine phytoplankton is a reasonably good approximation of the organic composition of lacustrine phytoplankton. If the majority of organic matter in the sediment traps is from lacustrine phytoplankton, the C:N:P ratio should be similar to the Redfield ratio. Organic matter with lower nitrogen and/or phosphorus concentrations relative to the carbon concentrations would indicate either degraded phytoplankton material or significant contents of detrital, refractory organic matter (Matson and Brinson, 1990; Ebise and Inoue, 1991).

The C:N:P ratios of the organic-matter samples collected in the sediment traps during the June, August, and September sampling periods are similar (table 12). The average C:N:P ratio for the top and bottom traps for these three periods was 318:25:1. The calculated C:N:P ratio of organic matter is similar to the Redfield ratio and indicates that most of the organic matter collected in the sediment traps was derived from lacustrine phytoplankton. The deviations from the Redfield ratio (higher carbon and nitrogen concentrations relative to phosphorus concentrations) for these three sampling periods may be attributed to: (1) real differences between the composition of marine phytoplankton and the lacustrine phytoplankton in Devils Lake, (2) partial degradation of organic matter derived from lacustrine sources, or (3) an additional source of detrital organic matter from the drainage basin.

Table 12. Relative compositions of organic matter in sediment traps, Creel Bay, Devils Lake

[Ratios are based on mole concentrations; --, no data]

Date	Trap	Carbon:Nitrogen:Phosphorus
June 13-18, 1991	Top	250:22:1
	Bottom	460:24:1
July 29-Aug. 1, 1991	Top	290:25:1
	Bottom	290:25:1
Aug. 26-28, 1991	Top	--
	Bottom	--
Sept. 17-19, 1991	Top	300:27:1
	Bottom	320:27:1
Oct. 7-9, 1991	Top	2,000:75:1
	Bottom	2,300:93:1

The C:N:P ratios for the October 7-9 sampling period were noticeably different than the ratios for the other sampling periods (table 12). The average C:N:P ratio from the top and bottom traps was 2,150:84:1. The difference in the C:N:P ratio of the organic matter from the October sampling period can be attributed to a large degree of organic-matter degradation or to increased detrital input. The lack of increased surface-water runoff during the October sampling period seems to preclude the second explanation.

Sediment Pore-Water Chemistry

Results of the chemical analyses of the pore-water samples are presented in tables 13, 14, 15, and 16. Redox potential, porosity, mean porosity, and pore-water temperature are presented in table 17. The pore-water samples are alkaline, with pH values between 8.0 and 8.6. There are no observable trends in pH with depth or between cores (fig. 3). Redox conditions in the pore water were calculated based on the sulfide/sulfate redox couple for two of the four cores (missing major-ion data precluded rigorous equilibrium calculations for MB-5-23 and MB-8-27). In general, the pore-water samples were reducing with oxidation-reduction potential (Eh) values near -300 mV.

Comparisons of the pore-water concentration data from the sediment cores illustrate the similarities in major-ion concentrations among cores. The major-cation composition of pore-water samples is sodium greater than magnesium greater than potassium greater than calcium. In general, major-cation concentrations for three of the cores are at a minimum in the uppermost samples and increase with depth (figs. 4, 5, 6, and 7). However, cation concentrations reach a mid-core maximum at a depth of 6 to 8 cm for core MB-7-30.

The major-anion composition of the pore-water samples is sulfate greater than bicarbonate greater than chloride. Carbonate plus bicarbonate concentrations (hereafter referred to as bicarbonate) are smallest at the top of the cores (fig. 8). For each core, bicarbonate increases with depth to a maximum concentration at either 8 to 10 cm or 10 to 12 cm. In general, bicarbonate concentrations are larger for the two cores collected during the summer (MB-7-30 and MB-8-27) and smaller for the core collected in October (MB-10-8). The difference in bicarbonate concentrations between the two cores collected in the summer and the core collected in the fall indicates that there may be a seasonal component to pore-water bicarbonate concentrations in Devils Lake sediments.

Table 13. Major-ion, nutrient, and selected trace-element concentrations in bottom water and in pore-water samples from core MB-5-23, Main Bay, Devils Lake, May 23, 1991

[All concentrations in milligrams per liter except pH (standard units); cm, centimeters; --, not analyzed]

Property or constituent	Bottom water	0-3 (cm)	3-6 (cm)	6-9 (cm)	9-12 (cm)
pH	8.4	8.2	8.0	8.2	8.2
Dissolved calcium	51	53	56	47	49
Dissolved magnesium	190	180	190	180	300
Dissolved sodium	810	820	820	770	860
Dissolved potassium	100	100	120	91	100
Dissolved bicarbonate	--	--	--	--	--
Dissolved carbonate	--	--	--	--	--
Dissolved sulfate	2,100	1,900	2,300	2,100	2,000
Dissolved chloride	350	330	380	220	330
Dissolved fluoride	.3	.3	.3	.2	.3
Dissolved silica	15	33	36	22	37
Dissolved nitrite, as nitrogen	--	--	--	--	--
Dissolved nitrite plus nitrate, as nitrogen	.13	<.05	<.05	<.05	<.05
Dissolved ammonia, as nitrogen	1.1	3.6	5.7	4.6	6.0
Dissolved ammonia plus organic nitrogen, as nitrogen	5.0	6.0	10	11	15
Dissolved phosphorus	.26	1.6	1.9	1.5	1.8
Dissolved orthophosphate, as phosphorus	.15	1.6	1.9	1.5	1.8
Dissolved arsenic	.020	.008	.011	.019	.020
Dissolved barium	--	--	--	--	--
Dissolved iron	.090	.12	.10	.20	.11
Dissolved lithium	--	--	--	--	--
Dissolved manganese	--	--	--	--	--
Dissolved strontium	--	--	--	--	--
Dissolved sulfide	--	--	--	--	--

Table 14. Major-ion, nutrient, and selected trace-element concentrations in pore-water samples from core MB-7-30, Main Bay, Devils Lake, July 30, 1991

[All concentrations in milligrams per liter except pH (standard units); cm, centimeters; --, not analyzed]

Property or constituent	0-2 (cm)	2-4 (cm)	4-6 (cm)	6-8 (cm)	8-10 (cm)	10-12 (cm)
pH	8.5	8.5	8.5	8.4	8.6	8.4
Dissolved calcium	48	51	58	66	54	--
Dissolved magnesium	160	160	180	210	180	--
Dissolved sodium	710	730	810	930	760	--
Dissolved potassium	83	95	98	110	100	110
Dissolved bicarbonate	705	769	915	1,110	1,210	1,120
Dissolved carbonate	0	0	0	0	0	0
Dissolved sulfate	1,400	1,500	1,600	1,900	1,600	1,900
Dissolved chloride	290	310	330	360	310	340
Dissolved fluoride	<.1	<.1	<.1	<.1	<.1	<.1
Dissolved silica	30	37	45	51	43	--
Dissolved nitrite, as nitrogen	<.01	<.01	<.01	.01	.022	<.01
Dissolved nitrite plus nitrate, as nitrogen	.086	<.05	<.05	<.05	.11	.064
Dissolved ammonia, as nitrogen	1.2	4.3	7.0	8.0	6.3	7.0
Dissolved ammonia plus organic nitrogen, as nitrogen	--	--	--	--	--	--
Dissolved phosphorus	--	--	--	--	--	--
Dissolved orthophosphate, as phosphorus	.31	1.2	1.4	1.5	1.3	1.2
Dissolved arsenic	.044	.037	.042	.06	.053	.075
Dissolved barium	.053	.057	.065	.075	.065	--
Dissolved iron	<.03	.074	.071	.053	.14	--
Dissolved lithium	.24	.26	.30	.33	.30	--
Dissolved manganese	.26	.38	.54	.68	.52	--
Dissolved strontium	.52	.38	.43	.46	.35	--
Dissolved sulfide	3.5	17	58	86	54	66

Table 15. Major-ion, nutrient, and selected trace-element concentrations in pore-water samples from core MB-8-27, Main Bay, Devils Lake, August 27, 1991

[All concentrations in milligrams per liter except pH (standard units); cm, centimeters; --, not analyzed]

Property or constituent	0-2 (cm)	2-4 (cm)	4-6 (cm)	6-8 (cm)	8-10 (cm)	10-12 (cm)
pH	8.4	8.6	8.3	8.3	8.3	8.4
Dissolved calcium	55	59	--	63	--	69
Dissolved magnesium	180	190	--	210	--	220
Dissolved sodium	800	840	--	900	--	900
Dissolved potassium	--	--	--	--	--	--
Dissolved bicarbonate	542	708	1,060	1,100	1,090	957
Dissolved carbonate	72	96	0	0	77	77
Dissolved sulfate	1,800	1,700	1,800	1,800	2,200	2,100
Dissolved chloride	410	420	440	450	500	440
Dissolved fluoride	.8	.8	.8	.8	.8	.8
Dissolved silica	32	43	--	50	--	51
Dissolved nitrite, as nitrogen	.031	.052	.13	.13	.16	.031
Dissolved nitrite plus nitrate, as nitrogen	<.05	.052	.13	<.05	.10	<.05
Dissolved ammonia, as nitrogen	2.2	5.4	6.2	7.5	9.8	8.6
Dissolved ammonia plus organic nitrogen, as nitrogen	8.5	10	8.2	9.7	13	13
Dissolved phosphorus	.72	1.1	1.4	1.6	1.9	1.9
Dissolved orthophosphate, as phosphorus	.21	.29	1.3	.72	1.0	1.3
Dissolved arsenic	.028	.035	--	.027	--	.090
Dissolved barium	.057	.061	--	.059	--	.060
Dissolved iron	.062	.13	--	.077	--	.10
Dissolved lithium	.32	.034	--	.37	--	.37
Dissolved manganese	.29	.36	--	.53	--	.66
Dissolved strontium	.43	.43	--	.48	--	.47
Dissolved sulfide	26	48	72	78	82	81

Table 16. Major-ion, nutrient, and selected trace-element concentrations in pore-water samples from core MB-10-8, Main Bay, Devils Lake, October 8, 1991

[All concentrations in milligrams per liter except pH (standard units); cm, centimeters; --, not analyzed]

Property or constituent	0-2 (cm)	2-4 (cm)	4-6 (cm)	6-8 (cm)	8-10 (cm)	10-12 (cm)
pH	8.6	8.6	8.4	8.2	8.4	8.3
Dissolved calcium	44	42	49	51	56	58
Dissolved magnesium	160	150	170	170	190	190
Dissolved sodium	720	690	760	750	790	810
Dissolved potassium	100	96	90	99	100	100
Dissolved bicarbonate	383	425	532	708	903	1,080
Dissolved carbonate	34	34	29	29	38	34
Dissolved sulfate	1,500	1,600	1,500	1,500	1,600	1,500
Dissolved chloride	280	320	310	310	320	330
Dissolved fluoride	<.01	<.01	<.01	<.01	1.8	<.01
Dissolved silica	19	20	29	38	46	48
Dissolved nitrite, as nitrogen	<.01	.01	.01	.09	.02	.09
Dissolved nitrite plus nitrate, as nitrogen	<.05	<.05	<.05	.14	<.05	.16
Dissolved ammonia, as nitrogen	.13	.59	1.4	5.6	8.4	9.4
Dissolved ammonia plus organic nitrogen, as nitrogen	2.4	2.6	4.0	8.1	11	12
Dissolved phosphorus	.16	.36	.75	1.3	2.0	2.3
Dissolved orthophosphate, as phosphorus	.16	.34	.77	1.3	2.0	2.2
Dissolved arsenic	.021	.018	.022	.020	.020	.019
Dissolved barium	.042	.044	.048	.052	.057	.056
Dissolved iron	<.03	<.03	<.03	<.03	<.03	.050
Dissolved lithium	.27	.36	.30	.30	.34	.34
Dissolved manganese	.078	.13	.26	.37	.46	.050
Dissolved strontium	.35	.33	.36	.36	.38	.38
Dissolved sulfide	0	.09	7.0	26	54	72

Table 17. Selected physical properties for sediment cores from Main Bay, Devils Lake

[Depth in centimeters; pH in standard units; redox potential in millivolts (calculated using the sulfide/sulfate redox couple); porosity and mean porosity in percent (calculated by loss of weight by drying; mean porosity was calculated as the average of all samples in a core); and pore-water temperature in degrees Celsius (temperature of near-bottom water sample from water column profile data); --, no data]

Date	Core	Depth	pH	Redox potential	Porosity	Mean porosity	Pore-water temperature
May 23, 1991	MB-5-23	0-3	8.2	--	--	84	15
May 23, 1991	MB-5-23	3-6	8.0	--	86	--	--
May 23, 1991	MB-5-23	6-9	8.2	--	82	--	--
May 23, 1991	MB-5-23	9-12	8.2	--	75	--	--
July 30, 1991	MB-7-30	0-2	8.5	-295	91	87	21
July 30, 1991	MB-7-30	2-4	8.5	-301	90	--	--
July 30, 1991	MB-7-30	4-6	8.5	-304	88	--	--
July 30, 1991	MB-7-30	6-8	8.4	-299	87	--	--
July 30, 1991	MB-7-30	8-10	8.6	-310	84	--	--
July 30, 1991	MB-7-30	10-12	8.4	--	80	--	--
August 27, 1991	MB-8-27	0-2	8.4	--	93	88	23
August 27, 1991	MB-8-27	2-4	8.6	--	90	--	--
August 27, 1991	MB-8-27	4-6	8.3	--	90	--	--
August 27, 1991	MB-8-27	6-8	8.3	--	87	--	--
August 27, 1991	MB-8-27	8-10	8.3	--	84	--	--
August 27, 1991	MB-8-27	10-12	8.4	--	81	--	--
October 8, 1991	MB-10-8	0-2	8.6	--	94	89	9
October 8, 1991	MB-10-8	2-4	8.6	-267	92	--	--
October 8, 1991	MB-10-8	4-6	8.4	-267	90	--	--
October 8, 1991	MB-10-8	6-8	8.2	-257	89	--	--
October 8, 1991	MB-10-8	8-10	8.4	-269	86	--	--
October 8, 1991	MB-10-8	10-12	8.3	-268	83	--	--

Sulfate concentrations (fig. 9) and chloride concentrations (fig. 10) tend to increase with depth. Although the increases are not regular, minimum concentrations tend to be near the top of the cores, and maximum concentrations tend to be near the bottom of the cores. Vertical variations in sulfate and chloride concentrations were not as great as variations in bicarbonate concentrations.

Pore-water concentrations of dissolved nutrients were determined for the four cores. In all samples, nitrite and nitrite plus nitrate concentrations were near or less than detection levels. Ammonia was the dominant nitrogen species in the pore water, and concentrations (fig. 11) tended to increase with depth. Ammonia concentrations in pore-water samples from near the sediment surface (0 to 6 cm) were largest in the summer (MB-7-30 and MB-8-27) and smallest in the fall. Near-surface concentrations of orthophosphate (fig. 12) were similar in cores MB-7-30, MB-8-27, and MB-10-8.

Pore-water samples from three of the cores (samples were not analyzed for MB-7-30) were analyzed for dissolved ammonia plus organic nitrogen (fig. 13) and dissolved phosphorus (fig. 14). In general, dissolved ammonia plus organic nitrogen (fig. 13) was greater than dissolved ammonia (fig. 11) in all three cores. The differences were largest in the near-surface samples. The fact that the concentration of ammonia plus organic nitrogen was greater than the concentration of ammonia is an important consideration in determining the importance of bottom-sediment contributions of nitrogen to Devils Lake. Calculated nitrogen fluxes based only on ammonia concentration may underestimate the actual flux of nitrogen from bottom sediments to the lake.

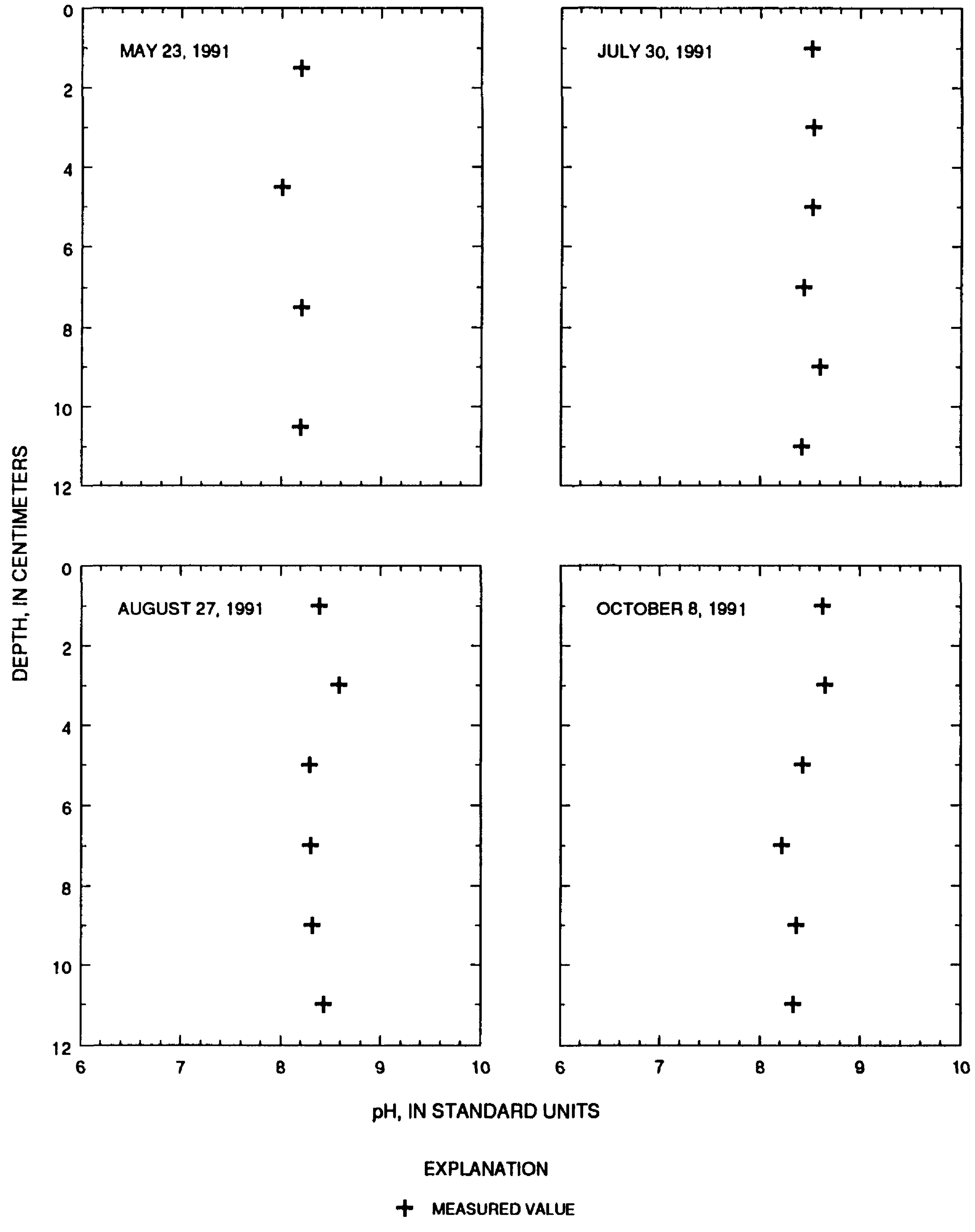

Figure 3. pH of pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

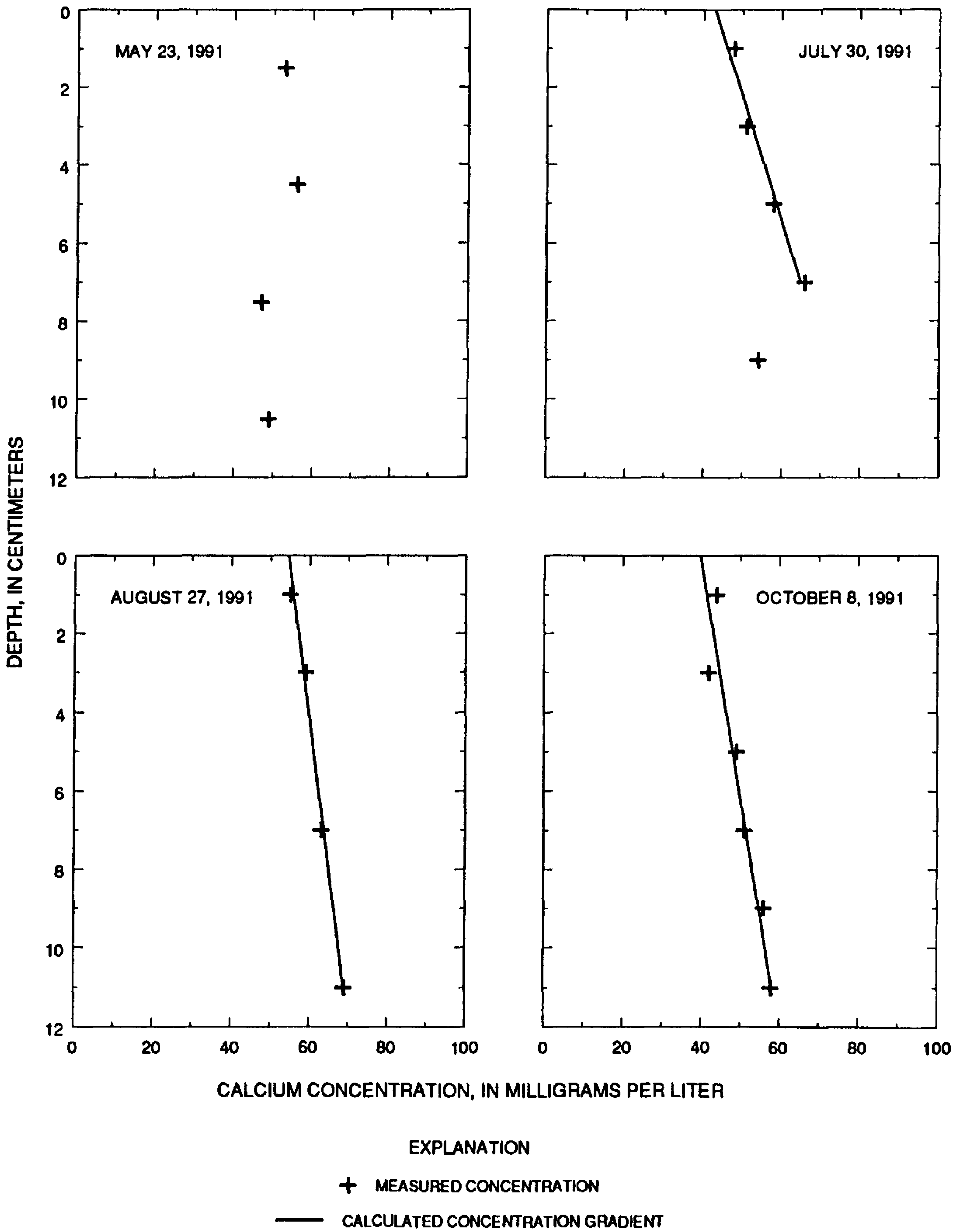

Figure 4. Calcium concentrations of pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

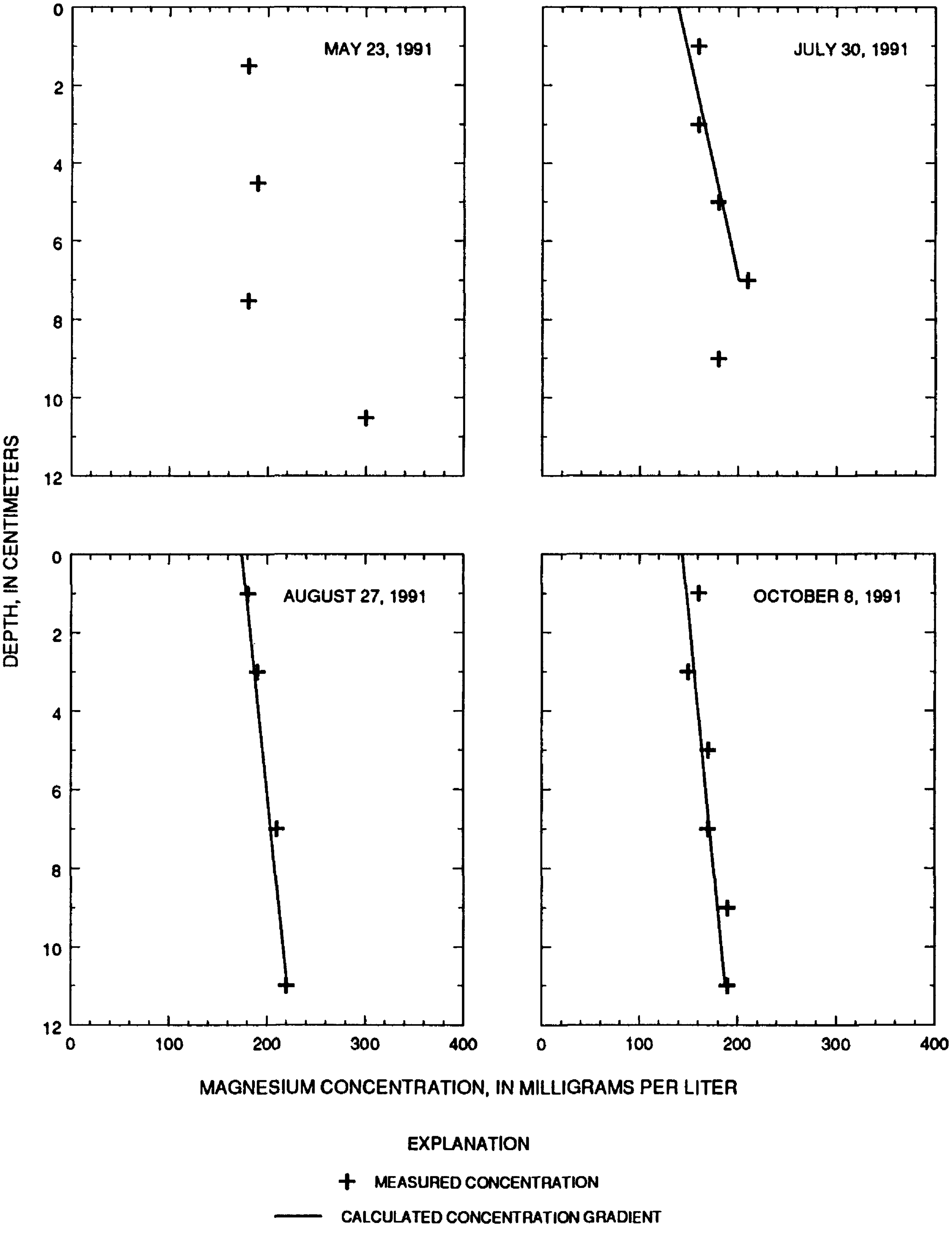

Figure 5. Magnesium concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

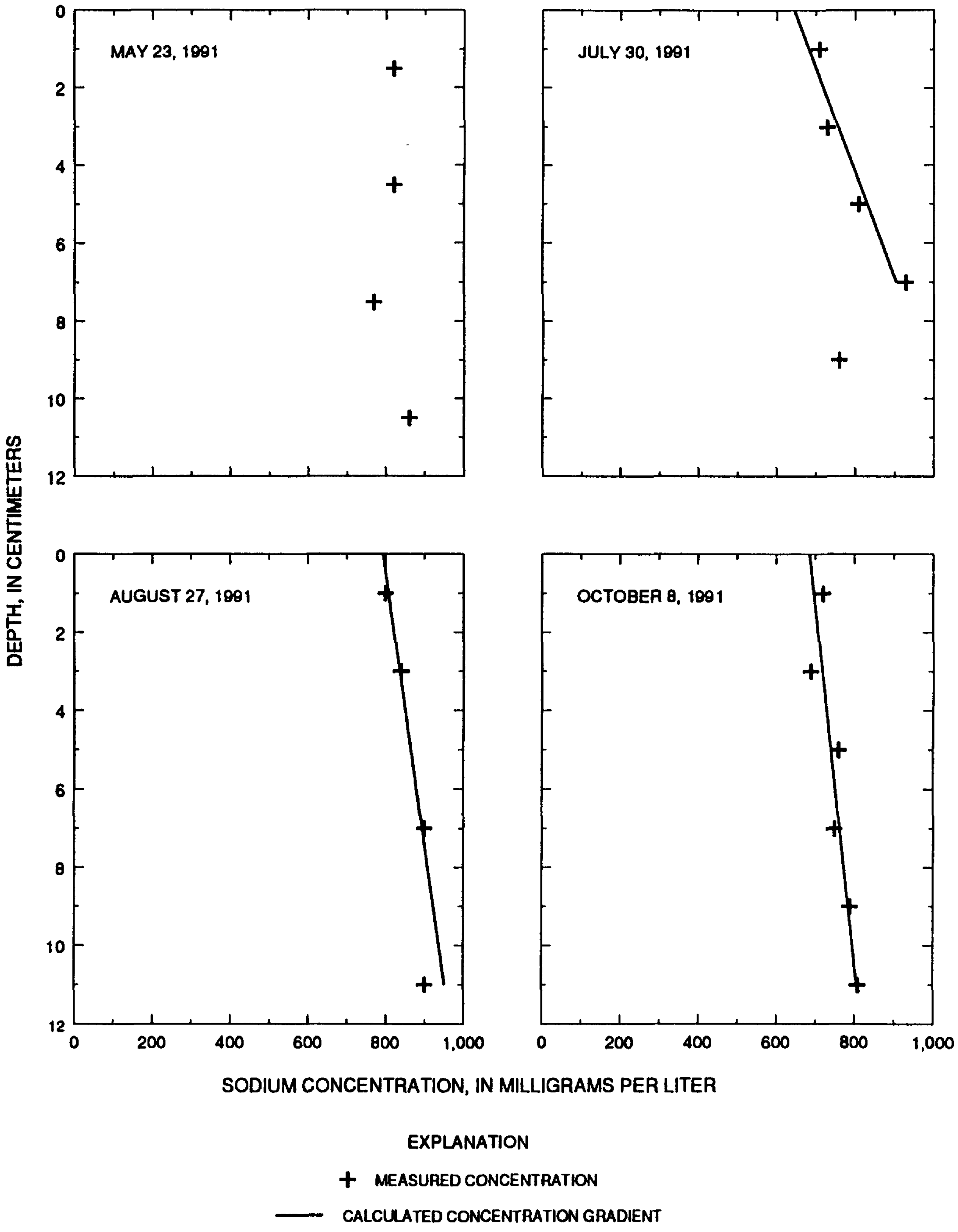

Figure 6. Sodium concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

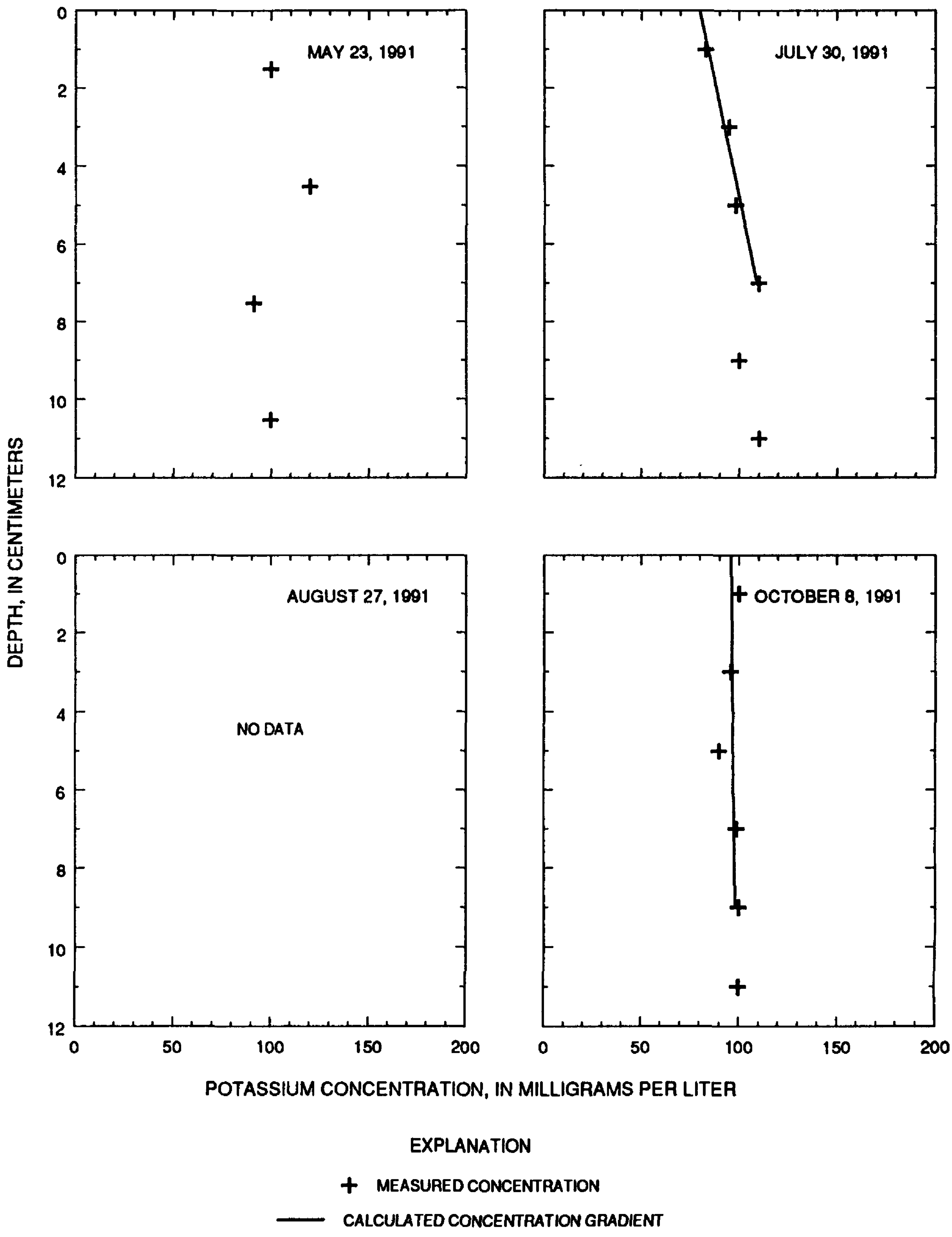

Figure 7. Potassium concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

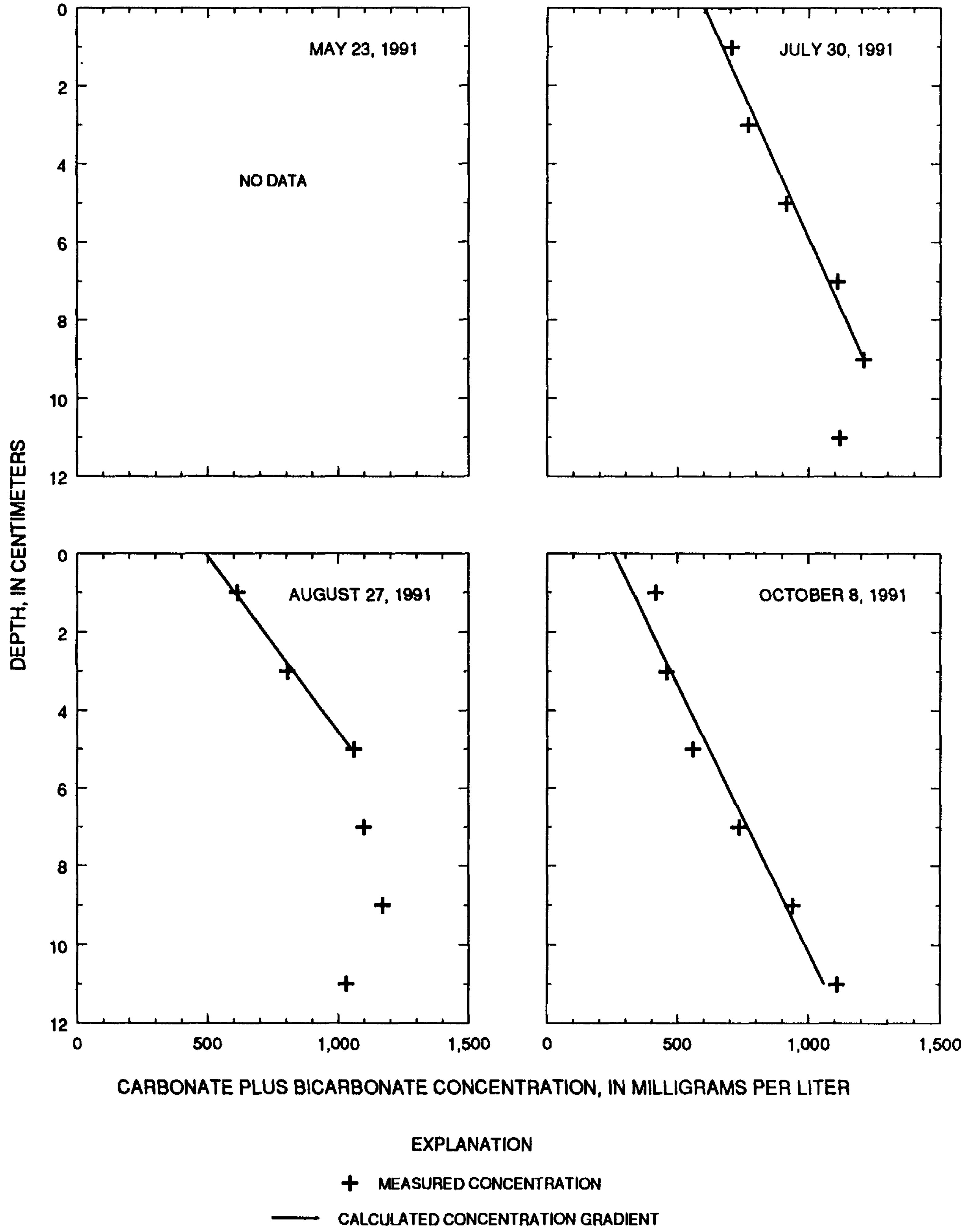

Figure 8. Carbonate plus bicarbonate concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

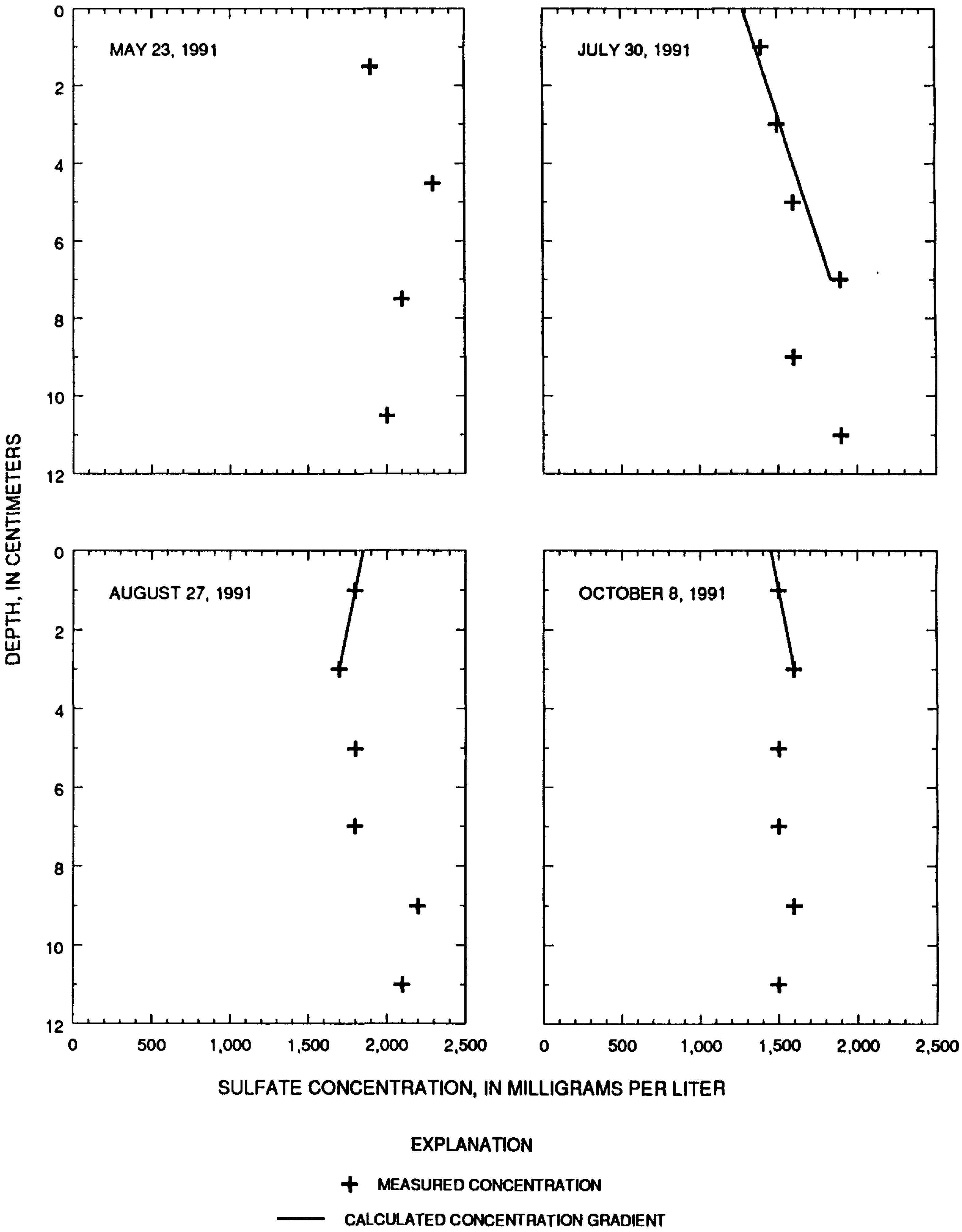

Figure 9. Sulfate concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

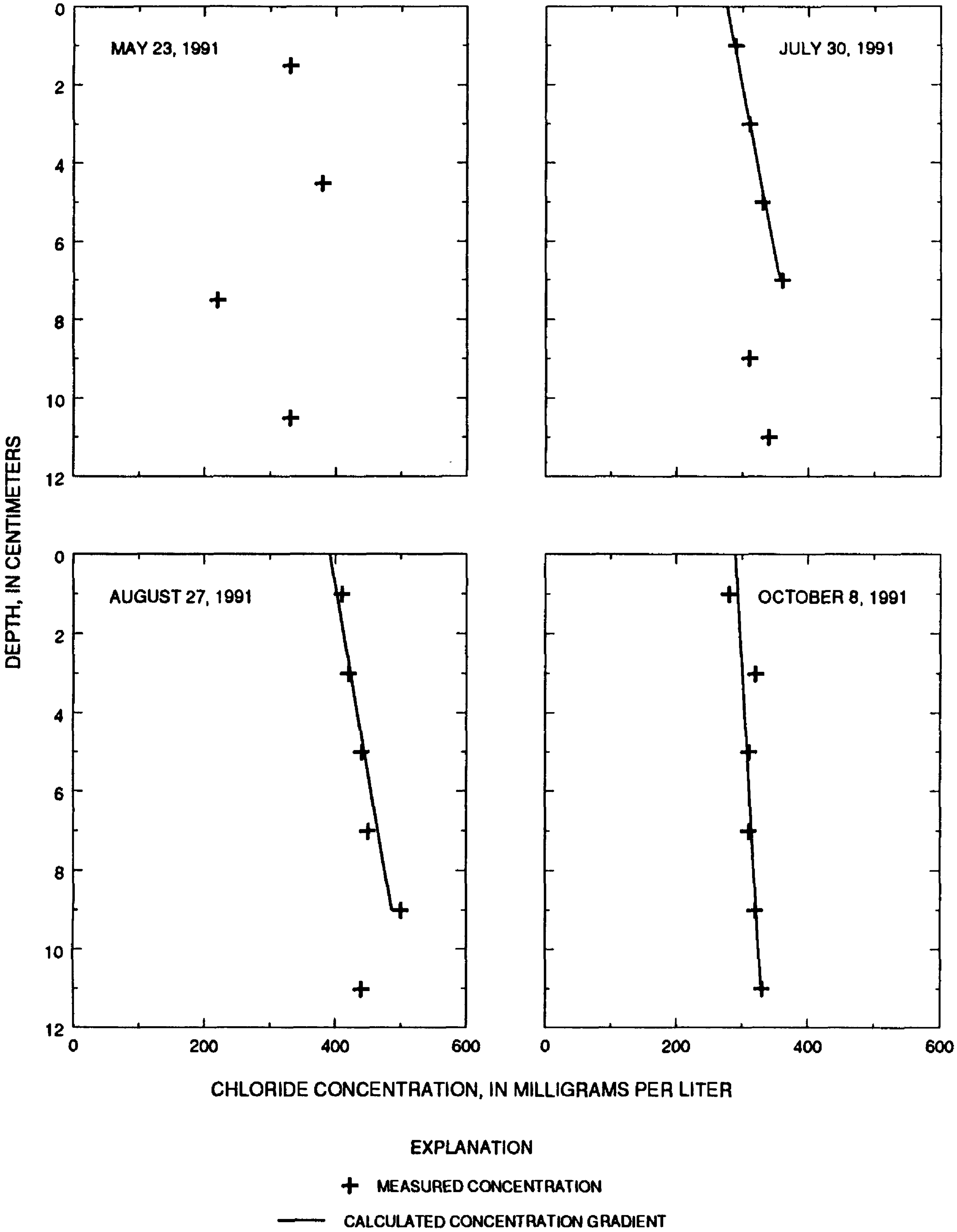

Figure 10. Chloride concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

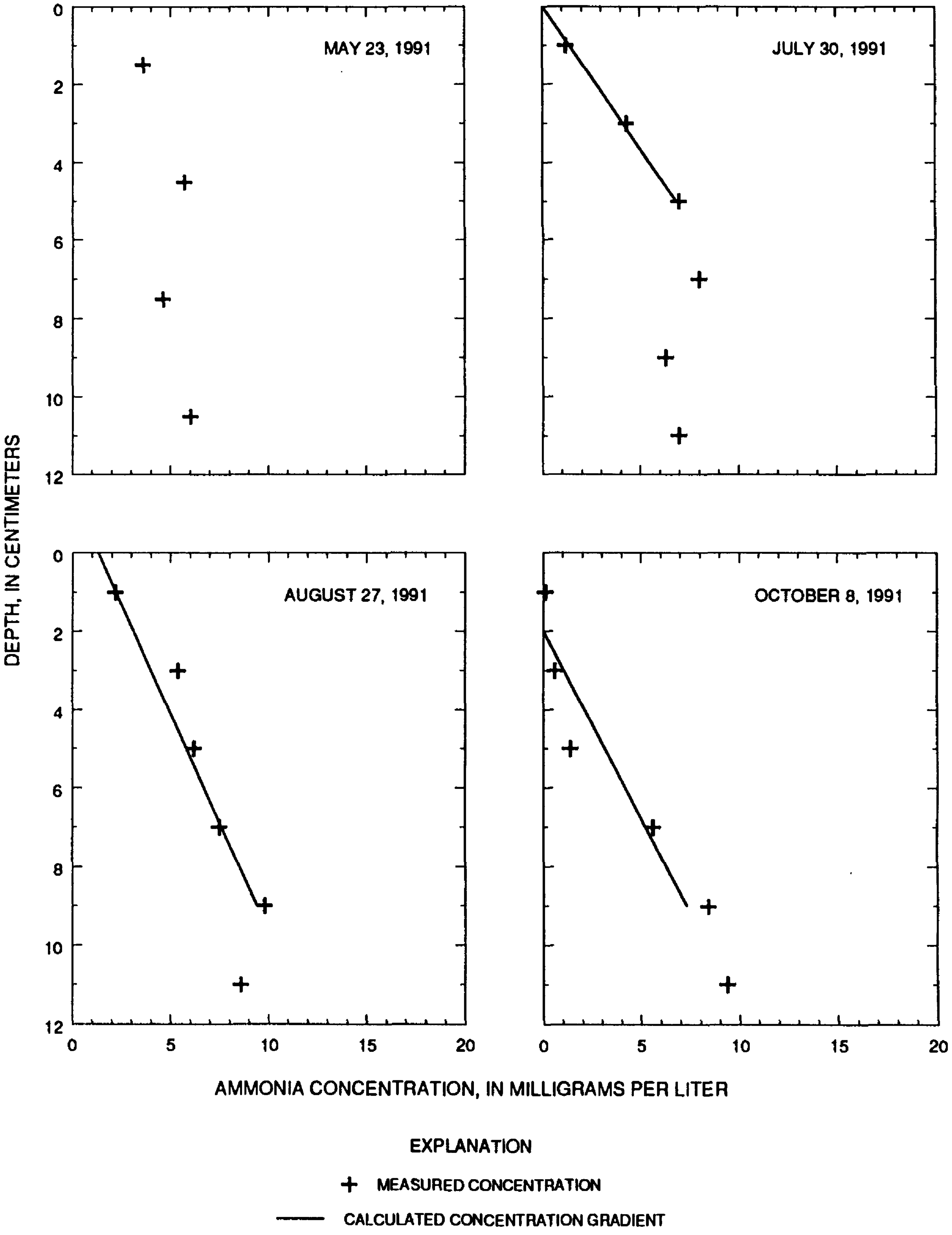

Figure 11. Ammonia concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

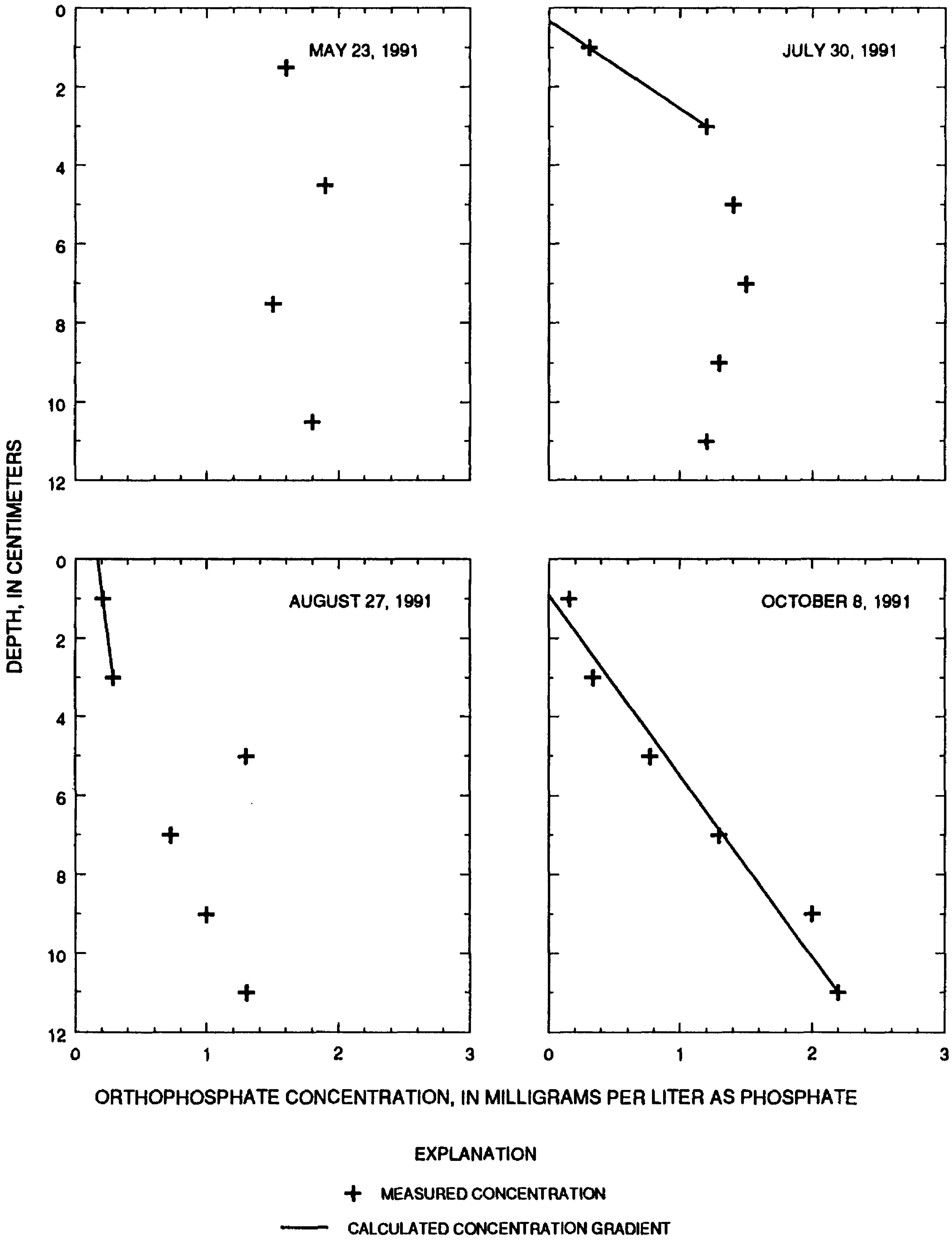

Figure 12. Orthophosphate concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

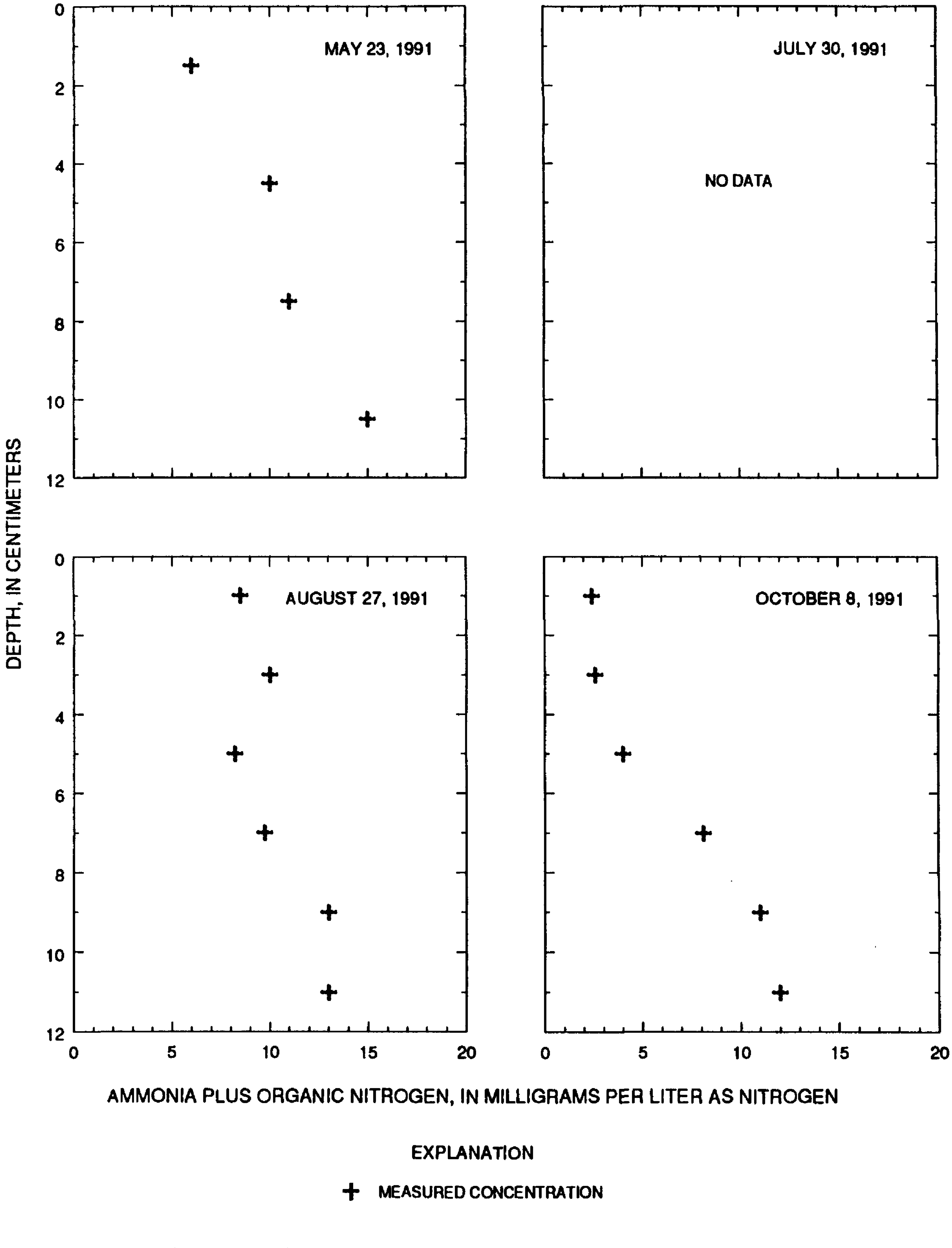

Figure 13. Ammonia plus organic nitrogen concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

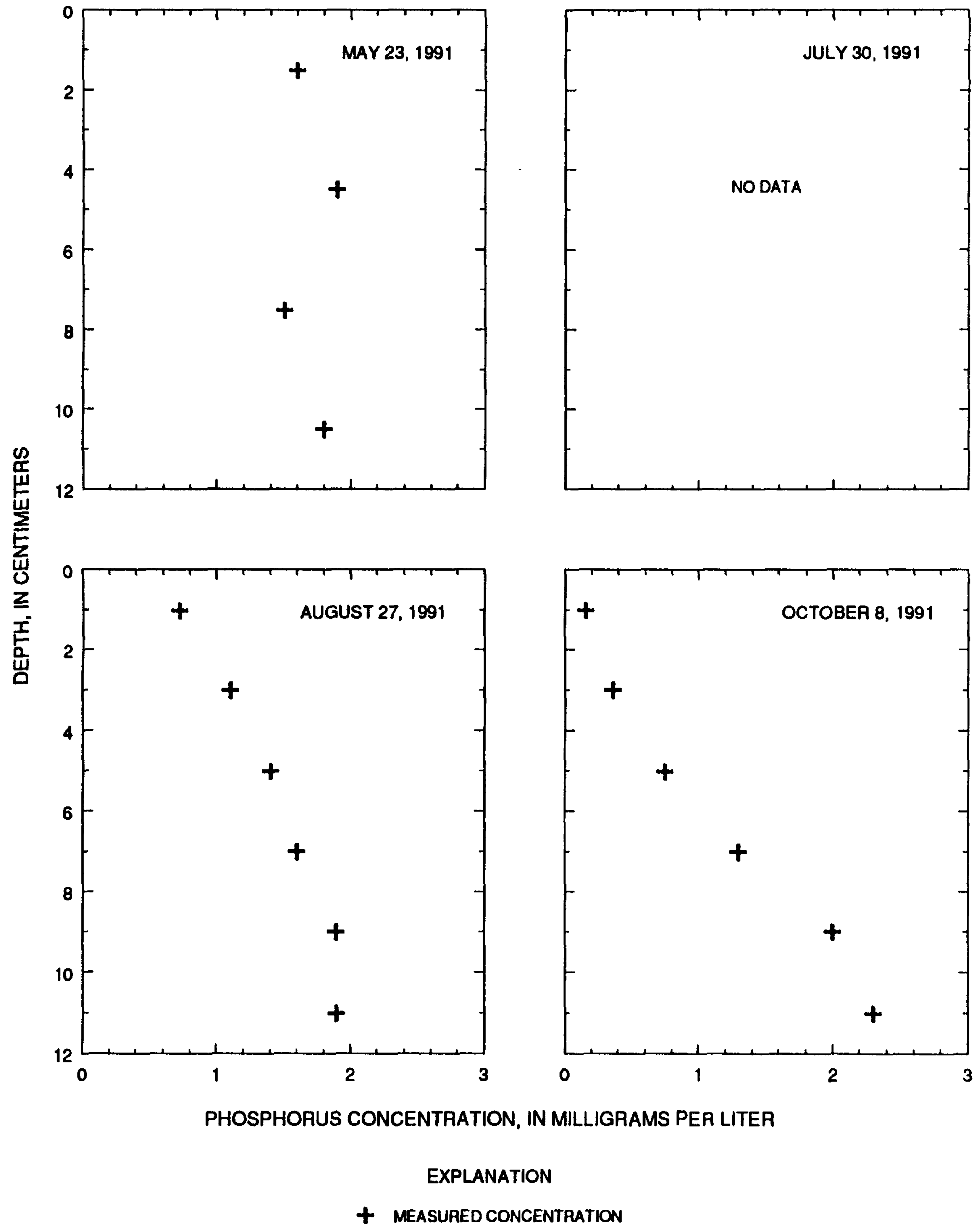

Figure 14. Phosphorus concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

Generally, dissolved phosphorus concentrations (fig. 14) among cores were similar, and dissolved phosphorous concentrations were similar to dissolved orthophosphate concentrations (fig. 12). The only notable exception was in the upper two samples in core MB-8-27, where dissolved phosphorus concentrations were about three to four times larger than dissolved orthophosphate concentrations.

Sulfide concentrations were measured in three of the cores (fig. 15). In general, sulfide concentrations were similar among the cores in the deeper samples and had the most variations in the near-surface samples. The vertical (downcore) difference in sulfide concentrations was largest in core MB-10-8 where sulfide was not detected in the near-surface sample and increased to 72 mg/L in the bottommost sample. The smallest vertical difference in sulfide concentrations was in core MB-8-27, where sulfide concentrations were 26 mg/L at 0 to 2 cm and 81 mg/L at 10 to 12 cm.

The results of the pore-water analyses support the conclusions of Lent (1992) and Komor (1992; 1994). Important processes in the bottom sediments include microbially mediated sulfate reduction, which is responsible for sulfide production and increased concentrations of bicarbonate, ammonia, orthophosphate, organic nitrogen, and phosphorus in sediment pore water. In addition, the dissolution of sulfate and carbonate minerals, along with the burial of saline pore water, results in increased concentrations of calcium, magnesium, bicarbonate, and sulfate in sediment pore water relative to the lake water.

WATER-QUALITY TRENDS

Water-Column Profiles

Thermal data collected from the center of Main Bay during this study and from July 1986 through October 1990 (Sether and Wiche, 1989; Sando and Sether, 1993), are summarized in figure 16. The X-axis is time (July 1986 through October 1991) and the Y-axis is depth in meters in the water column. Single points represent individual temperature measurements, and vertical rows of points are single thermal profiles. The long-term variation in the depth of the thermal profiles (length of Y-axis) is the direct result of variations in water depth (fig. 2). The lines in figure 16 are lines of equal temperature. When the lines of equal temperature are vertical (parallel to the Y-axis), the water column is well mixed. In contrast, when the lines of equal temperature are horizontal (parallel to the X-axis), the water column is thermally stratified. In general, Devils Lake is well mixed (vertical lines) during open-water periods (spring through fall) and becomes stratified during the winter. The lack of detailed data for ice-covered periods makes it difficult to determine the timing and degree of winter thermal stratification.

Specific-conductance data collected from the center of Main Bay during this study, along with additional specific-conductance data collected from September 1986 through October 1990, are summarized in figure 17. Two general trends can be identified in figure 17. The specific conductance of Main Bay was smallest near the beginning of the data-collection period (1986), and generally increased with time to a maximum at the end of the period (1991). The data indicate that dissolved-solids concentrations in the lake have increased with decreasing lake level. In addition, the lines of equal specific conductance tend to be vertical during the summer and indicate that the water column is well mixed during open-water months. During the winter when the lake stratifies, bottom water tends to have elevated specific-conductance values.

Other lakes have similar increases in bottom-water dissolved-solids concentrations during winter months (Sholkovitz, 1985). These increases reflect the flux of dissolved constituents into the water column

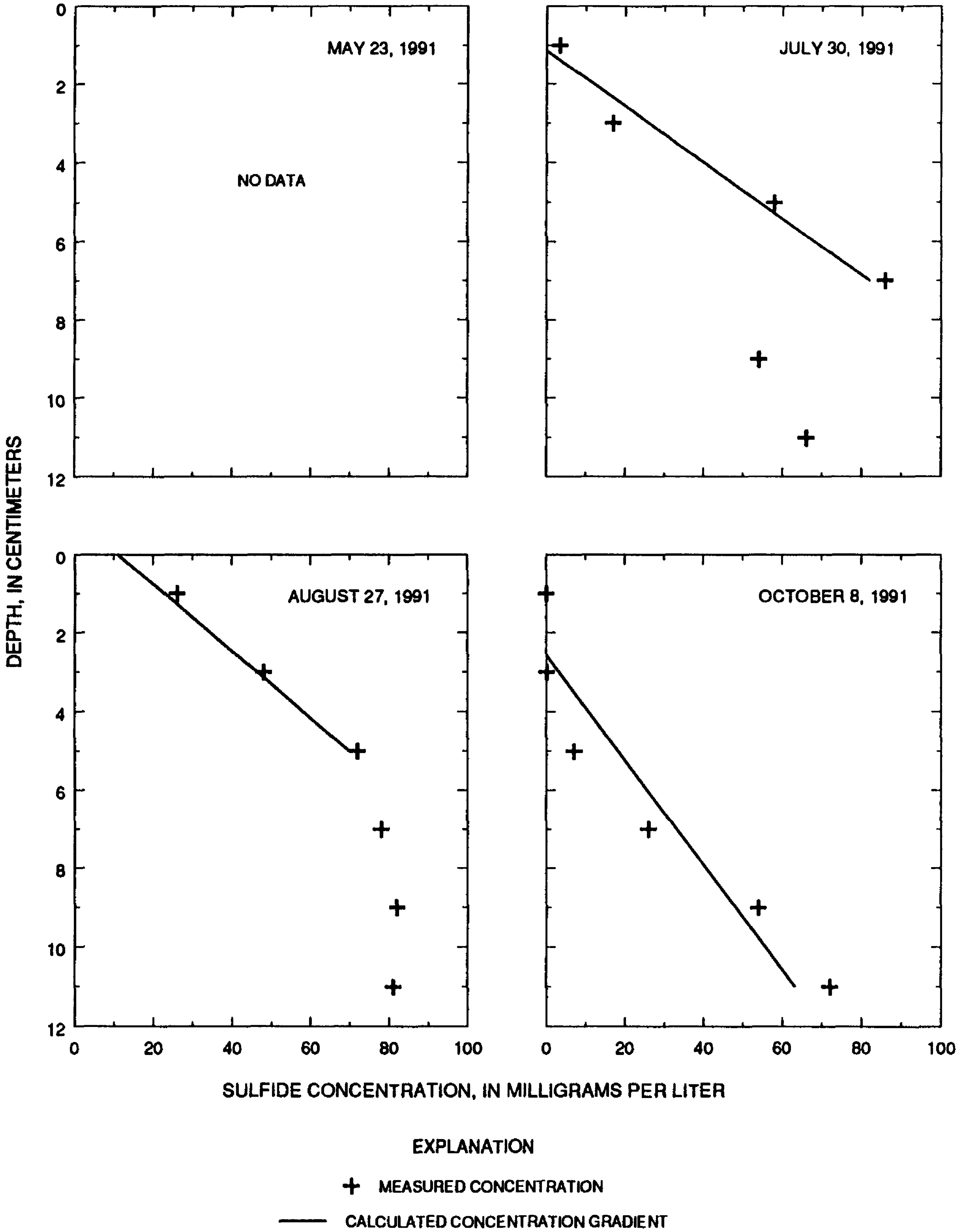

Figure 15. Sulfide concentrations in pore-water samples from sediment cores collected from Main Bay, Devils Lake, 1991.

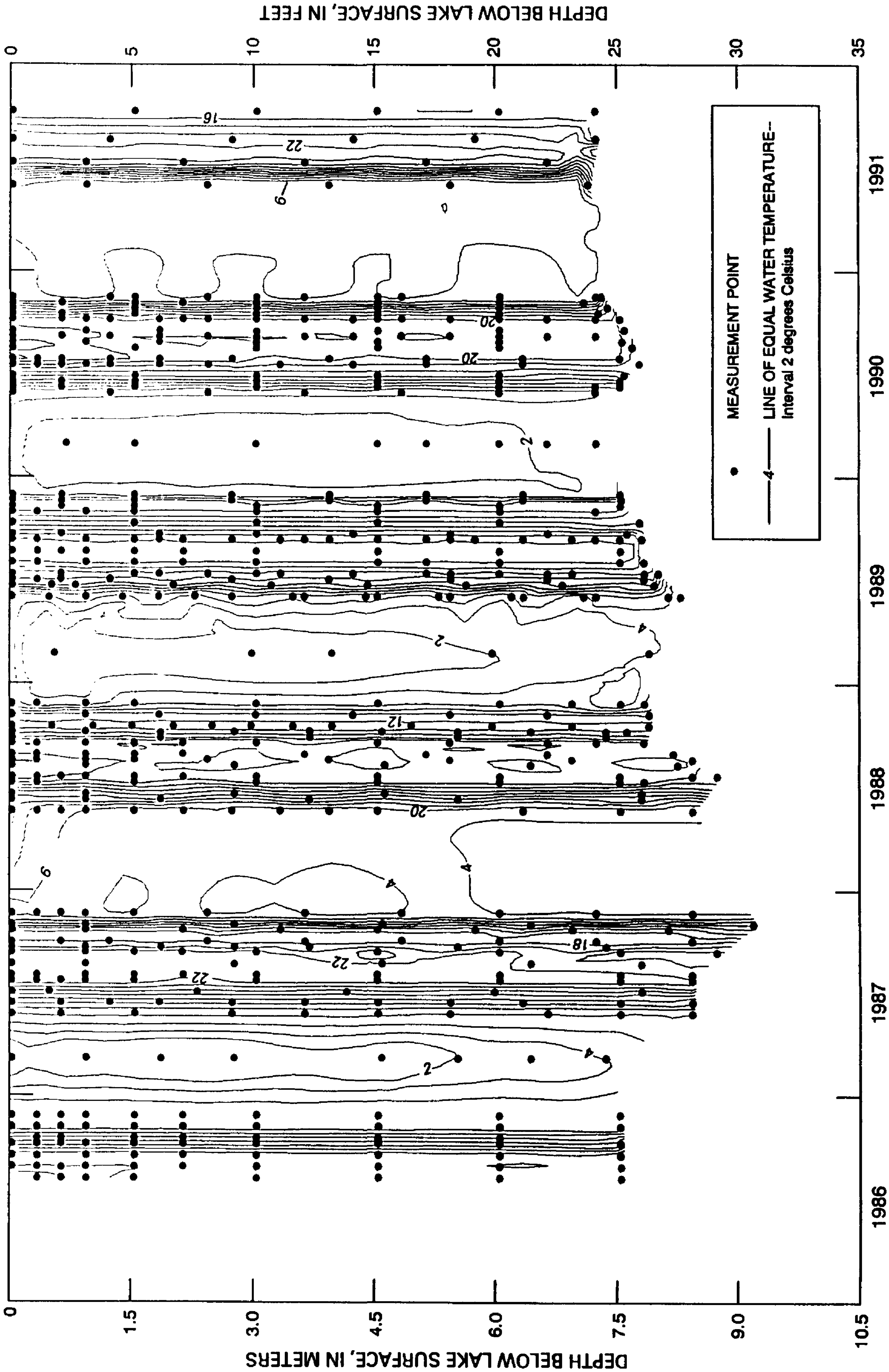

Figure 16. Water temperature in Main Bay, Devils Lake, 1986-91.

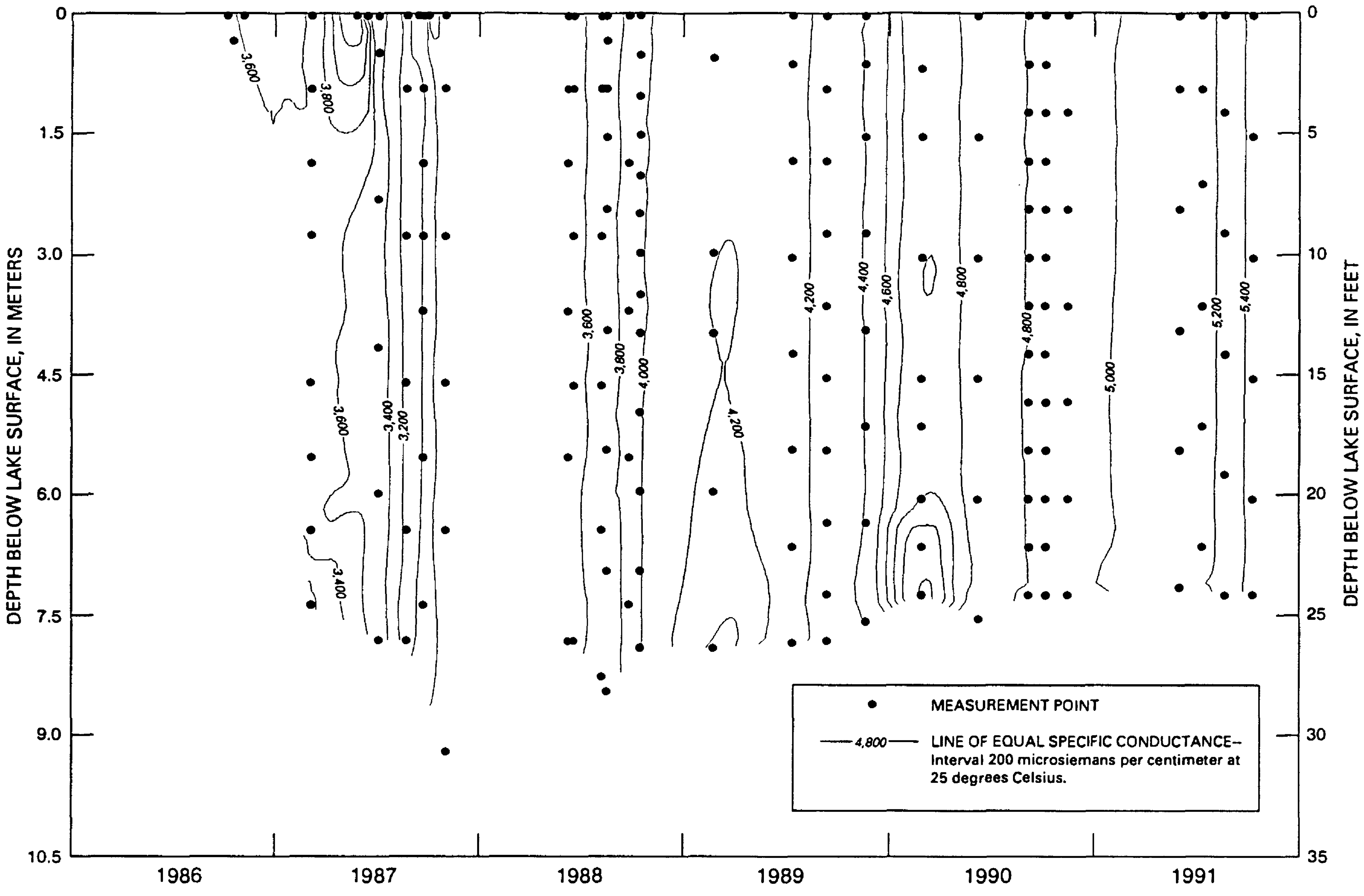

Figure 17. Specific conductance in Main Bay, Devils Lake, 1986-91.

as a result of bottom-sediment processes. However, because sediment cores were not collected for pore-water analyses during winter months, this conclusion is based solely on indirect evidence. On the basis of the specific-conductance data alone, it is impossible to determine whether elevated concentrations of dissolved solids in Devils Lake bottom water are the result of ephemeral processes that occur only during ice-covered periods or are the result of processes that occur continuously but are noticeable only during periods of extended water-column stability.

The pH data collected from the center of Main Bay during this study, along with additional pH data collected from February 1987 through October 1990, are summarized in figure 18. In general, periods of open water are characterized by homogeneous pH values, while ice-covered periods are characterized by vertical pH gradients. For example, during the winter of 1988-89, the pH decreased to less than 8.2 near the sediment/water interface. This decrease in pH probably is related to microbial activity near the sediment/water interface.

Dissolved-oxygen data collected from the center of Main Bay during this study, along with additional dissolved-oxygen data collected from February 1987 through October 1990, are summarized in figure 19. The lines of equal dissolved oxygen in Devils Lake are consistent with the lines of equal temperature and specific conductance. During open-water periods, the water column generally is well mixed with oxygen. The notable exception to this trend was during the summer of 1987 when dissolved oxygen near the bottom of Devils Lake was strongly depleted. Variations in dissolved-oxygen concentration are related to biological processes and, to a lesser degree, variations in the solubility of dissolved oxygen with temperature (Wetzel, 1983). In addition, near-surface water during the summer often is enriched in dissolved oxygen relative to the rest of the water column. This phenomena probably is due to dissolved oxygen produced by photosynthesis in the near-surface water (Wetzel, 1983). During the winter, the bottom water in Main Bay becomes depleted in dissolved oxygen as a result of microbial aerobic respiration that occurs near the sediment/water interface.

Secchi-Disk Depth

Secchi-disk depth measurements made from January 1989 through October 1991 are shown in figure 20. The data from the 3 years indicate similar seasonal variations. In general, Secchi-disk depths are large during the winter and much smaller during the warmer months. Secchi-disk depths were relatively large in June 1989 and 1991. The decreased Secchi-disk depth during early May and from July through September may be due to seasonal blooms of diatoms in the spring and blue-green algae during late summer. These decreases are consistent with other northern prairie lakes (Barica, 1975).

Earlier studies of Devils Lake have included Secchi-disk depth measurements (Anderson, 1969; Shubert, 1976). The recent data combined with data collected during earlier studies should provide insight concerning the trophic states of Devils Lake at different lake-level elevations. Data for this study were collected during a period of decreasing lake level following the recent lake-level maximum in 1987. Anderson (1969) collected 4 years of Secchi-disk depth measurements from 1965-68 (fig. 21). These measurements were made near the end of the most recent period of low lake level (fig. 2). Shubert (1976) collected 2 years of Secchi-disk depth measurements in 1974-75 (fig. 22). Shubert's study was made near the end of a period of rapid lake-level rise in the early 1970's (fig. 2). Therefore, the three data sets provide information about trophic states during three hydrologically distinct periods in the history of Devils Lake.

Similar patterns of seasonal variations in Secchi-disk depth are identifiable in all three data sets. In general, from winter to spring (in most years May or June) Secchi-disk depths decrease to early summer minimums. As previously noted, this decrease probably is related to increasing diatom populations in the lake. The midsummer (usually June or July) increase in Secchi-disk depths may be related to decreasing

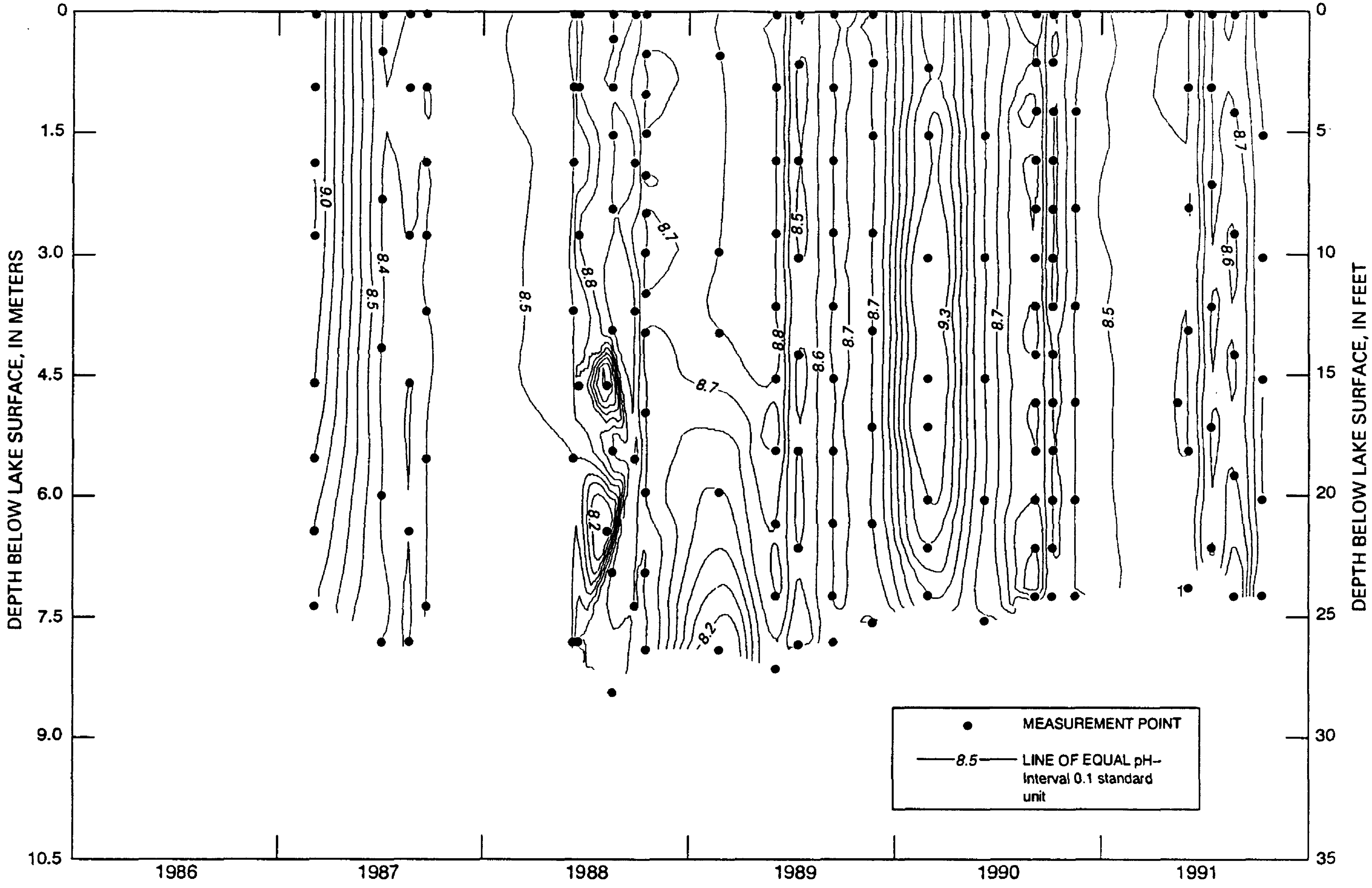

Figure 18. pH in Main Bay, Devils Lake, 1987-91.

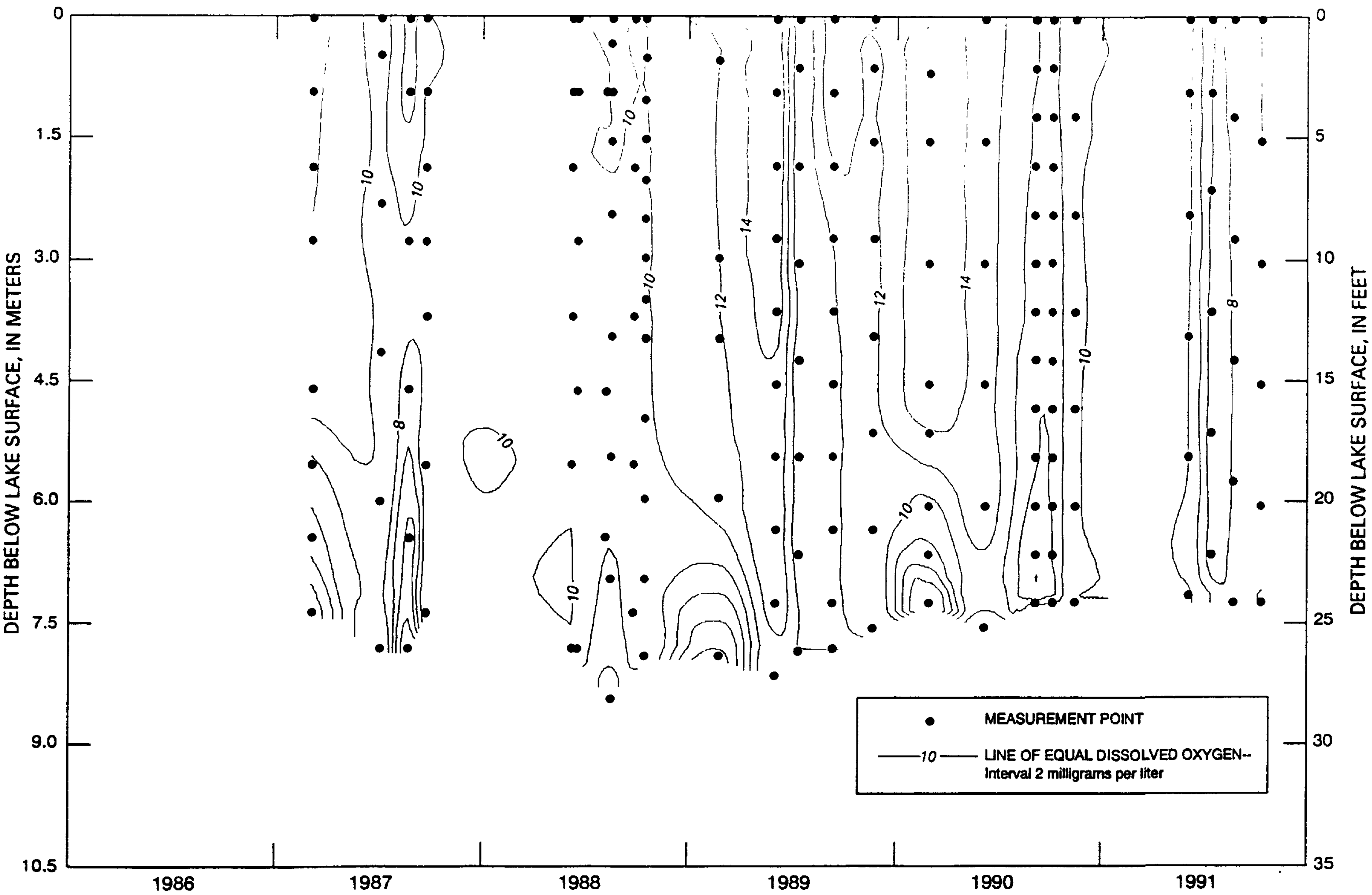

Figure 19. Dissolved oxygen in Main Bay, Devils Lake, 1987-91.

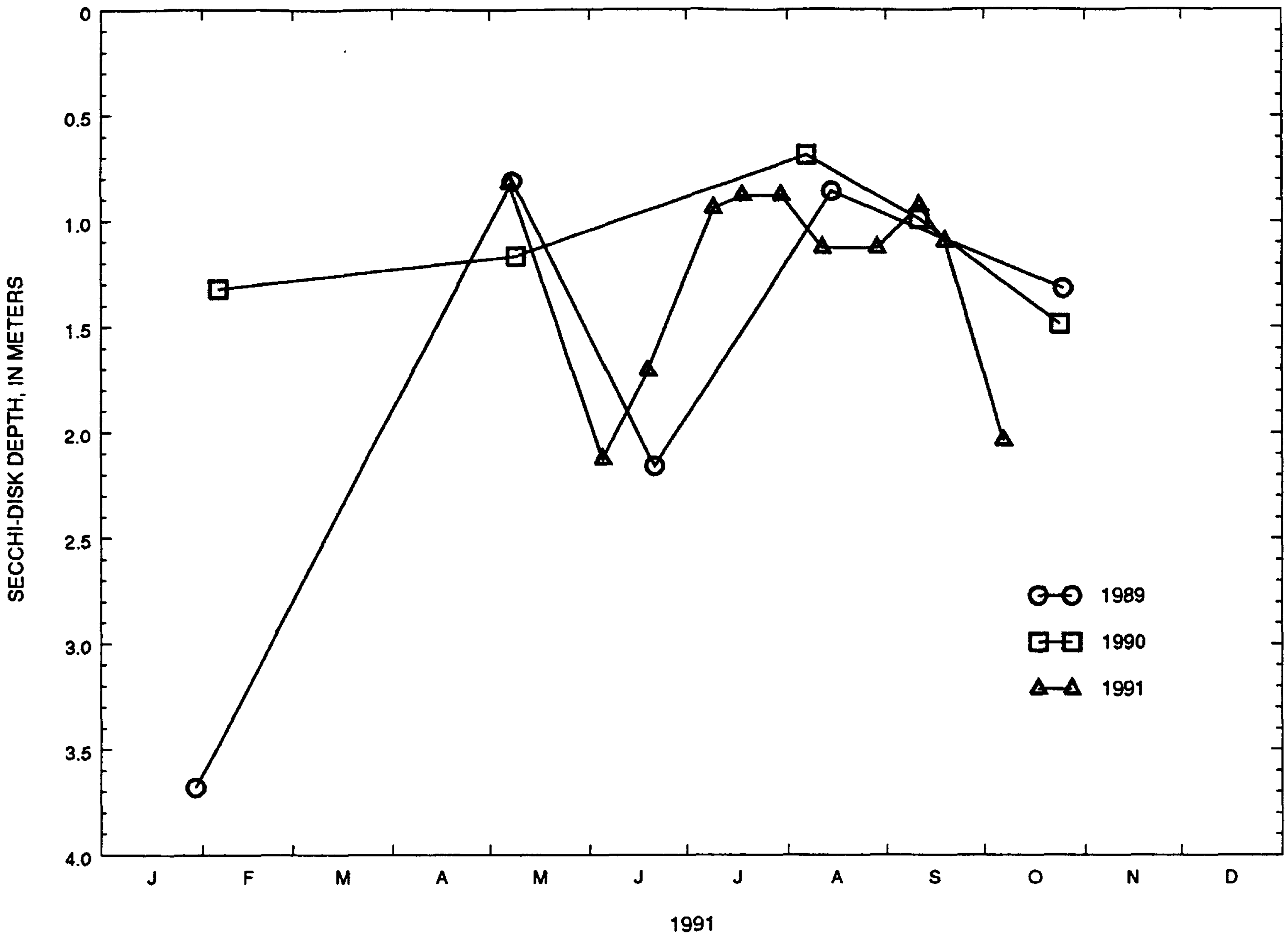

Figure 20. Secchi-disk depths in Main Bay, Devils Lake, 1989-91. (Data for January 1989-October 1990 from Sando and Sether, 1993.)

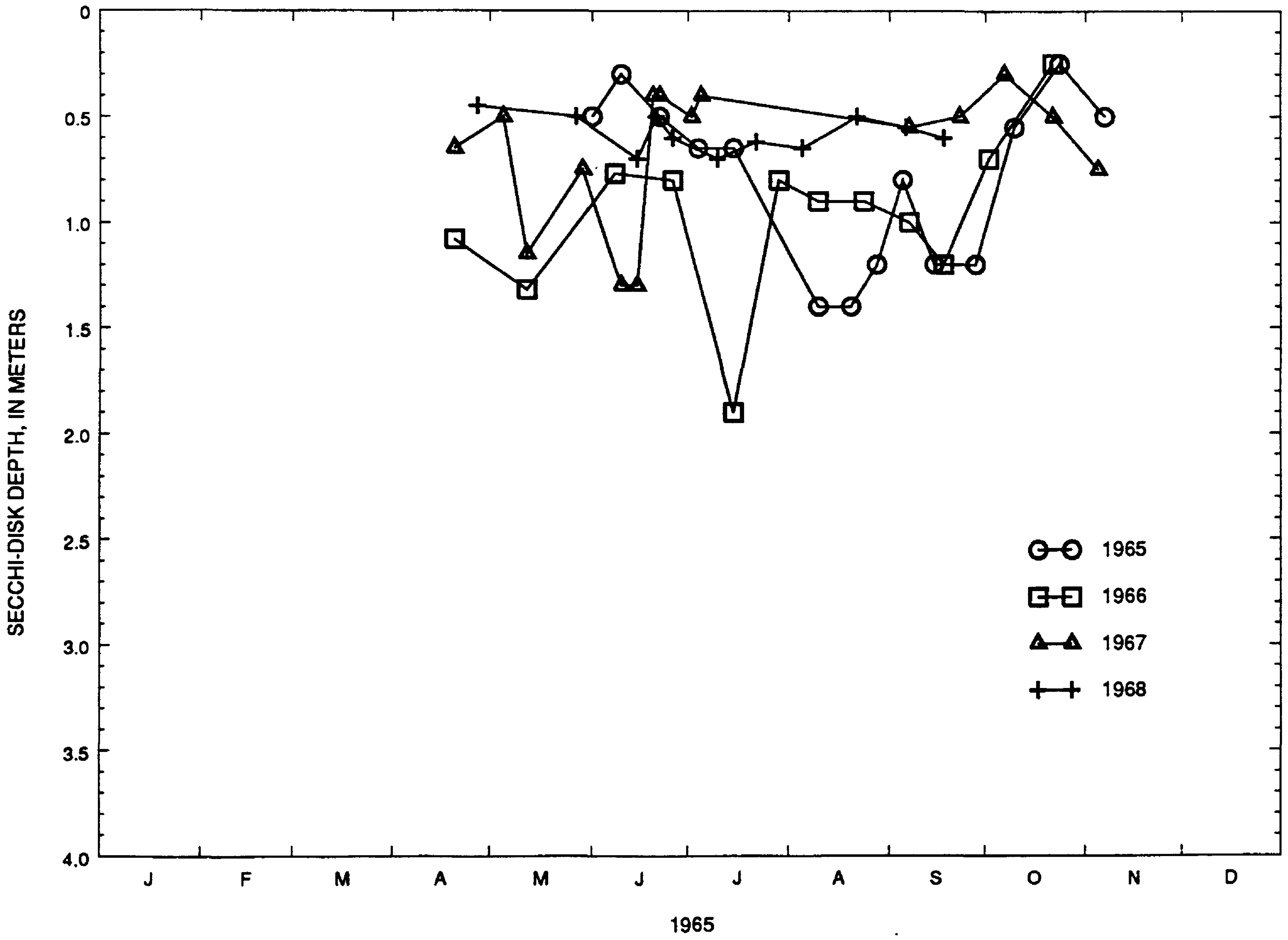

Figure 21. Secchi-disk depths in Main Bay, Devils Lake, 1965-68. (Data from Anderson, 1969.)

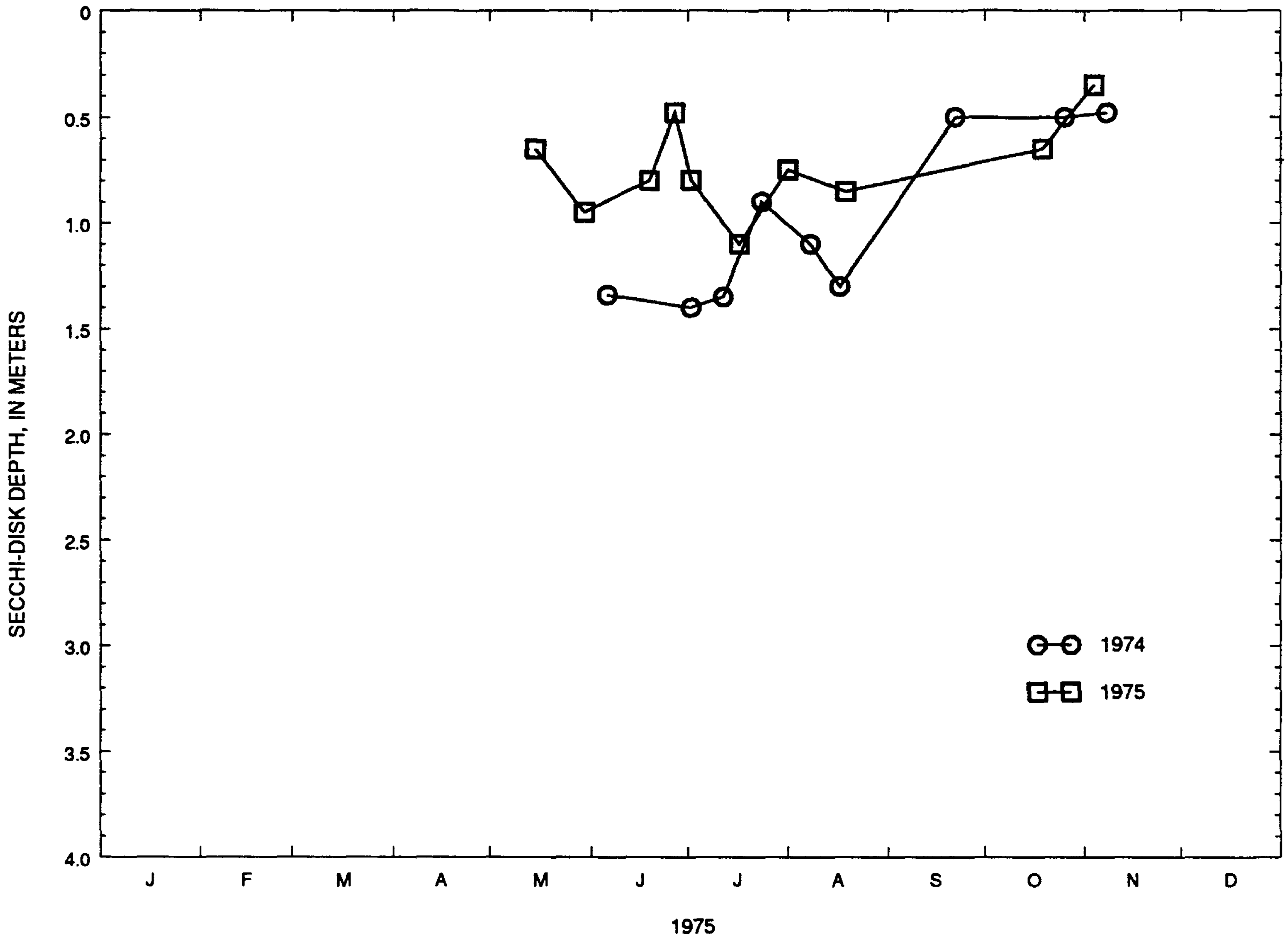

Figure 22. Secchi-disk depths in Main Bay, Devils Lake, 1974-75. (Data from Shubert, 1976.)

diatom populations and a shift to the production of blue-green algae. In late summer or fall (usually occurring between July and October) there is a second period of decreased Secchi-disk depths, possibly related to increased blue-green algae populations.

Secchi-disk depths generally have increased from the 1960's to the present (1989-91). The increased Secchi-disk depths may indicate that trophic conditions in the lake are inversely proportional to lake level. This could be the result of a number of processes, including dilution of nutrient concentrations by fresh water and a resulting decrease in phytoplankton populations. An alterative explanation is that long-term variations in Secchi-disk depths are not related to variations in trophic conditions, but instead are the result of bottom-sediment resuspension during periods of low lake level.

Gross Primary Productivity

The GPP rates determined for Main Bay in 1965-68 by Anderson (1969) varied from near zero for December 1965, 1966, and 1967 to a maximum of 5.14 (gC/m^2)/d on July 29, 1965. The mean GPP rate for May through October for each of the 4 years was 0.89 (gC/m^2)/d in 1965, 1.68 (gC/m^2)/d in 1966, 1.43 (gC/m^2)/d in 1967, and 1.34 (gC/m^2)/d in 1968. These rates are consistent with GPP rates for other eutrophic lakes (Bloesch and others, 1977; Premazzi, 1980; Tilzer, 1983; Stabel, 1985).

General ranges of mean daily GPP rates for lakes of differing trophic categories were reported by Wetzel (1983). Oligotrophic lakes have mean daily GPP rates between 0.05 and 0.300 (gC/m^2)/d. Mesotrophic lakes have mean daily GPP rates between 0.250 and 1.00 (gC/m^2)/d. Hypereutrophic lakes have mean daily GPP rates between 0.50 and 1.00 (gC/m^2)/d. Eutrophic lakes have mean daily GPP rates >1.00 (gC/m^2)/d.

Wetzel's general ranges are for the entire year. In contrast, the mean data reported by Anderson (1969) for Devils Lake are for May through October and do not include the ice-covered months when GPP rates are near zero. As a result, the GPP rates from his study are overestimates of the mean daily rates. Therefore, the GPP rates for Devils Lake indicate that the lake is hypereutrophic to eutrophic, which is in agreement with the conclusions reached by Sando (1992) who found, based on nutrient data, that Devils Lake is hypereutrophic. The similarities between the GPP-rate data in this study and the mid-1960's GPP-rate data from Anderson indicate that while hydrologic and geochemical conditions in Devils Lake have varied substantially, rates of GPP in the lake have remained relatively constant.

CALCULATION OF BENTHIC-FLUX RATES

Sulfate reduction and mineral dissolution in bottom sediments enrich pore water in major ions and nutrients relative to lake water and create well-defined chemical-concentration gradients in near-surface pore water (Eugster and Jones, 1979; Davison, 1985; Kuivila and others, 1989; Dillon and others, 1990). These concentration gradients in turn are responsible for molecular diffusion of major ions and nutrients into the bottom water of the lake. Numerous studies have used measured pore-water gradients in conjunction with empirical and theoretical data to calculate the flux of specific ions across the sediment/water interface. A limited number of studies have used pore-water measurements concurrent with *in situ* flux-chamber measurements to validate these calculations (Callender and Hammond, 1982).

Benthic-flux rate calculations were based on Fick's First Law of diffusion (Berner, 1980):

$$j_i = \varphi_0 D_{i,0}^{sed} \frac{dCi}{dx} \tag{2}$$

where j_i is the benthic flux (milligram per square centimeter per day),

φ_0 is the sediment porosity in the top 2 cm (percent),

$D_{i,0}^{sed}$ is the whole-sediment diffusion coefficient (square centimeter per second), and

$\frac{dCi}{dx}$ is the concentration gradient projected to the sediment-water interface (milligram per liter per centimeter).

$D_{i,0}^{sed}$ includes the effects of tortuosity but does not include the effects of adsorption (Berner, 1980). Two separate methods were used to calculate $D_{i,0}^{sed}$. $D_{i,0}^{sed}$ was calculated using the method outlined by Li and Gregory (1974) and Callender and Hammond (1982) using the expression

$$D_{i,0}^{sed} = \frac{D_i^0}{\varphi_0 F'} \tag{3}$$

where D_i^0 is the diffusion coefficient at infinite dilution (square centimeter per second).

F' is the modified formation factor (unitless):

$$F' = 1.28\varphi^{-2} \tag{4}$$

where φ is the average sediment porosity (percent).

D_i^0 also was calculated using the method developed by Lasaga (1979) where D_i^0 is corrected for electrical and ion-pairing effects (Lasaga, 1979; Berner, 1980). Although this method does account for the effects of electrical and ion pairing, it assumes that the composition of the pore water is near sea-water composition. In addition, chloride and sulfide fluxes cannot be calculated using this method.

Initially, lines were fitted through the entire profiles by linear regressions of the entire data sets. However, many of the profiles, particularly the nutrients, sulfate, and carbonate profiles were not linear through the entire profile. As a result, lines fitted through the entire profile were not always representative of concentration gradients near the sediment/water interface. Therefore, pore-water gradients (*dC/dx*) were calculated by fitting a line through the upper part of the measured pore-water profiles. The intervals used were determined by trial and error to maximize both the number of samples used and the correlation coefficient of the regression. The parts of the pore-water profiles used in the linear regression calculations are shown in figures 4 through 12, and 15.

The results of both sets of calculations are shown in tables 18 and 19. Positive values indicate a flux from the sediments to the bottom water, and negative values indicate a flux from the bottom water to the sediments. In general, the benthic fluxes calculated using the method described by Lasaga (1979) are larger than the fluxes calculated using the diffusion coefficients taken from Li and Gregory (1974). Benthic fluxes calculated using the method described by Lasaga (1979) generally are larger for calcium, magnesium, bicarbonate, and phosphate than the benthic fluxes calculated using the diffusion coefficients taken from Li and Gregory (1974). The potassium flux calculated using the diffusion coefficient from Li and Gregory, however, is larger than the flux calculated using the method from Lasaga (1979). Benthic fluxes calculated using both methods are similar for sodium, sulfate, and ammonia.

The effects of electrical and ion pairing are apparent in the calculated sodium fluxes (tables 18 and 19). The calculated sodium flux for the core collected in Creel Bay in 1990 is positive (from the sediments into the water) using the diffusion coefficient from Li and Gregory (1974), and negative (from the water into the sediments) using the method described by Lasaga (1979). This difference in the direction of the benthic flux probably is due to the negative sulfate gradient in the pore water. The other constituents are affected to a lesser degree.

Table 18. Calculated pore-water benthic-flux rates in Devils Lake using diffusion coefficients from Li and Gregory (1974) for sediment cores collected in 1990-91. Positive values indicate that the flux is from sediments into bottom water, and negative values indicate that the flux is from bottom water into the sediments. Data for 1990 from Komor, (1994)

[Flux rates in milligrams per square meter per day; --, no data]

Constituent	Creel Bay July 25, 1990	Main Bay July 26, 1990	Main Bay July 30, 1991	Main Bay August 27, 1991	Main Bay October 8, 1991
Calcium	16	6.7	12	5.2	5.6
Magnesium	14	14	31	15	12
Sodium	47	170	140	59	38
Potassium	38	38	24	--	4.1
Bicarbonate	3,300	2,500	470	810	440
Sulfate (as SO_4)	-1,000	-1,500	410	-260	240
Chloride	130	35	110	110	32
Ammonia (as N)	26	130	9.0	7.1	7.1
Phosphate (as P)	3.9	2.9	9.8	.16	.24
Sulfide (as S)	110	27	51	43	24
Sulfur (as SO_4)	-730	-1,400	560	-131	310

Table 19. Calculated pore-water benthic-flux rates in Devils Lake using diffusion coefficients from Lasaga (1979) for sediment cores collected in 1990-91. Positive values indicate that the flux is from sediments into bottom water, and negative values indicate that the flux is from bottom water into the sediments. Data for 1990 from Komor, (1994)

[Flux rates in milligrams per square meter per day; --, no data]

Constituent	Creel Bay July 25, 1990	Main Bay July 26, 1990	Main Bay July 30, 1991	Main Bay August 27, 1991	Main Bay October 8, 1991
Calcium	57	28	34	17	22
Magnesium	46	15	89	32	47
Sodium	-36	430	310	130	52
Potassium	47	34	16	--	1.2
Bicarbonate	5,200	4,000	720	1,200	810
Sulfate (as SO_4)	-1,200	-1,800	480	-300	340
Ammonia (as N)	47	230	15	12	15
Phosphate (as P)	33	24	4.8	1.3	2.4

Without supporting benthic-flux data from *in situ* measurements, it is difficult to determine which of the two diffusion-coefficient calculation methods is the most accurate for Devils Lake bottom sediments. However, the following discussions of flux rates, and the subsequent mass-balance calculations, will be based on the fluxes calculated using the diffusion coefficients from Li and Gregory (1974). The reason for this choice is twofold. First, the fluxes based on the diffusion coefficients from Li and Gregory (1974) generally are less than the fluxes calculated using the method described by Lasaga (1979). Therefore, the calculated fluxes using the diffusion coefficients from Li and Gregory (1974) are more conservative estimates of the actual fluxes. Secondly, Li and Gregory (1974) reported diffusion coefficients for chloride and sulfide. The benthic fluxes of chloride and sulfide cannot be calculated using the method described by Lasaga (1979). It should be noted that all subsequent calculations and discussions may underestimate the importance of benthic fluxes.

SEASONAL VARIATIONS IN THE BENTHIC FLUXES OF BIOLOGICALLY ACTIVE CONSTITUENTS

Seasonal variations in the rate of nutrient regeneration by microbial activity in bottom sediments has been identified in other northern lakes (Barica, 1974; 1975) and reservoirs (Billen and others, 1989). The downcore decrease in sulfate concentrations in the two cores collected in July 1990 (Komor, 1992) is convincing evidence that sulfate reduction is occurring in Devils Lake bottom sediments. Comparisons of the pore-water profiles of sulfate, sulfide, bicarbonate, phosphate, and ammonia and the calculated benthic fluxes of these constituents between 1990 and 1991 (table 18) indicate substantial seasonal and yearly differences in sulfate-reduction rates. Sulfate-reduction rates inferred from the two cores collected in 1990 were substantially larger than the apparent rates of sulfate reduction in Main Bay in 1991. Only one of the three cores collected in 1991 indicated a net sulfate flux from the lake into the sediments [-260 $(mgSO_4/m^2)/d$ collected on August 27]. In addition, the calculated negative sulfate fluxes in the two cores collected in 1990 were substantially more negative than the calculated negative sulfate flux for this core (table 18). The calculated benthic fluxes of bicarbonate, ammonia, and phosphate also were noticeably larger in 1990 than in 1991 (table 18).

Data from the three cores collected in 1991 indicate that the fluxes of biologically active constituents in Main Bay generally were consistent throughout the 1991 study period. The large differences between flux rates for 1990 and 1991 may indicate that the environmental factors that affect sulfate-reduction rates differed between the 2 years. It is possible that sulfate-reduction rates in Devils Lake bottom sediments depend on the stabilization of the water column in the lake. Short periods of calm wind conditions could result in water-column stabilization, decreased dissolved-oxygen concentrations at the sediment/water interface, and increased sulfate-reduction rates in near-surface bottom sediments. This possibility is consistent with observations made by Anderson (1969) in July 1965. During a 4-day period at the end of July, wind velocities on Devils Lake were negligible. Near the end of this 4-day calm period, primary productivity, nutrient concentration, and dissolved iron increased, and dissolved-oxygen concentrations decreased. All of the changes could be attributed to increased microbiologic activity in the bottom sediments of Devils Lake. The fact that they occurred after 4 days of unusually calm conditions supports the contention that water-column stabilization can enhance sulfate-reduction rates in the bottom sediments of the lake.

Lent (1992) described the spatial variability of major-ion and nutrient concentrations in bottom sediments in East Bay, Devils Lake (table 20). There are noticeable differences between the calculated fluxes of major ions and nutrients for East Bay (Lent, 1992) and for Main Bay and Creel Bay (Komor, 1992; 1994). Lent (1992) attributed these differences to variations in sulfate-reduction rates.

SOURCE OF MAJOR IONS TO PORE WATER

Previous investigators (Lent, 1992; Komor, 1992; 1994) concluded that dissolution of evaporite minerals is the most likely source of dissolved major ions to Devils Lake bottom sediments. The results of this study agree with their conclusion. Generally, the concentrations of major ions were largest near the bottoms of the cores, consistent with dissolution of saline sediments and diffusion of saline pore water.

Comparisons of the calculated benthic fluxes of major ions between the cores collected in Main Bay in 1990-91 (table 18) indicate that although the calculated benthic fluxes of most major ions (excluding sulfate and bicarbonate) are similar, there are some notable differences. These differences may be the result of (1) the addition of major ions to pore water as a result of decomposition of organic matter; (2) clay-mediated exchange of calcium, magnesium, sodium, and potassium for ammonia, which is produced by microbial activity; and (3) adsorption/desorption reactions related to redox reactions, including reduction of iron and manganese oxyhydroxides (Kinniburgh and Jackson, 1981; Sholkovitz, 1985). All of these processes probably occur in the near-surface bottom sediments of Devils Lake at the depth of sulfate reduction (generally less than 8 cm based on the sulfide and sulfate profiles).

Table 20. Calculated pore-water benthic-flux rates in Devils Lake using diffusion coefficients from Li and Gregory (1974) for sediment cores collected in East Bay, Devils Lake, in 1986 (Lent, 1992). Total sulfur was calculated as the sum of sulfate and sulfide. The average benthic-flux rates for the three cores collected in Main Bay in 1991 are shown for comparison. Positive values indicate that the flux is from sediments into bottom water, and negative values indicate that the flux is from bottom water into the sediments

[Flux rates in milligrams per square meter per day; --, no data]

		East Bay			
Constituent	**Main Bay 1991**	**Core 1**	**Core 2**	**Core 3**	**Core 4**
Calcium	7.6	10	14	250	390
Magnesium	19	27	24	320	160
Sodium	79	1,400	250	2,800	1,300
Potassium	14	660	39	430	220
Bicarbonate	570	220	260	420	240
Total sulfur (as SO_4)	250	300	410	3,900	620
Ammonia (as N)	7.7	4.1	5.1	10	4.2
Phosphate (as P)	3.4	.31	.53	-.34	-.37

RESPONSE TIMES OF MAJOR IONS AND NUTRIENTS IN DEVILS LAKE

One of the primary reasons for undertaking this study was to better understand the role of bottom-sediment processes in the cycling of major ions and nutrients in Devils Lake based on chemical mass-balance calculations. Chemical mass-balance calculations are expressed as

$$\Delta(M) = \Sigma(I) - \Sigma(O) \tag{5}$$

where $\Delta(M)$ is the change of mass of a particular constituent in solution,
$\Sigma(I)$ is the sum of the inputs of the constituent, and
$\Sigma(O)$ is the sum of the outputs of the constituent.

Chemical mass-balance calculations in this form can be used to determine if all the important mass-transfer processes occurring in a system have been identified. These types of mass-balance calculations also can be used to estimate the relative importance of undetermined processes.

A second type of mass-balance calculation involves the determination of the response time of a chemical constituent in a system. The response time is an estimate of the time period it would take to replace the mass of dissolved solids in Devils Lake by tributary inflow. In a closed basin such as Devils Lake, the response time for a constituent can be determined by the relation

$$T = \frac{(CDAl)}{(cEAl_{avg})} \tag{6}$$

where T is the response time, in years;
C is the concentration of dissolved constituent, in grams per cubic meter;
D is the mean depth, in meters;
Al is area of the lake, in square meters;
c is the input concentration, in grams per cubic meter;
E is the net evaporation, in meters; and
Al_{avg} is the average area of the lake over time, in square meters per year.

Chemical mass-balance calculations in this form can be used to calculate the accumulation time for a constituent in a lake. Using theoretical equations to solve for c, Langbein (1961) calculated the response time for dissolved solids in Devils Lake in the late 1950's as 800 years. Using inflow data from Swenson and Colby (1955), Langbein also calculated the response time for dissolved solids and sulfate as 2,200 years and 2,100 years, respectively. During the late 1950's, the water level of Devils Lake was substantially lower than in 1991. The surface area of the lake was smaller and limited to Main Bay and Creel Bay. The two shortcomings of these calculations are that they were made for periods of low lake level and the results may not be applicable to 1991 conditions, and that they do not include the contributions of bottom-sediment/water-column interactions.

In order to calculate the response times for specific dissolved constituents in Devils Lake, two potential external sources of major ions and nutrients--surface runoff (primarily through Big Coulee and Channel A), and direct precipitation onto the lake--need to be considered. In addition to these external sources, internal loading as a result of bottom-sediment processes also should be considered. Previous water-quality work for Devils Lake (Lent, 1992) indicated that bottom-sediment processes are major sources of major ions and nutrients to the respective chemical budgets. Chemical mass-balance calculations for Devils Lake can be simplified based on the following observations: (1) Lent (1992) determined that input of major ions from precipitation is negligible compared to bottom-sediment contributions; (2) Sando (1992) determined that contribution of nutrients by precipitation or surface-water inflow was much less than the internal loading of nutrients; and (3) during this study, surface-water inflow was minimal and, therefore, the potential effects of surface-water input were minimal.

Spatial variations in water quality and benthic-flux rates also need to be considered in determining response times. Devils Lake can be divided into three sections on the basis of water-quality information. The western section of the lake consists of West Bay (Minnewaukan Flats). The middle section of the lake consists of Main Bay, Sixmile Bay, and Creel Bay. The eastern section of the lake consists of Mission Bay and East Bay. Because benthic-flux-rate data are not available for West Bay or Sixmile Bay, they will not be included in the response-time calculations. As used in the following discussion, Main Bay consists of Main Bay and Creel Bay, and East Bay consists of East Bay and Mission Bay. The following equation was developed to calculate the response time for each water-quality constituent in Devils Lake:

$$T = \frac{[V(MB)c(MB) + V(EB)c(EB)]}{[A(MB)J(MB) + A(EB)J(EB)]} \tag{7}$$

where T is the response time, in days;
$V(MB)$ is the volume of Main Bay, in cubic meters;
$c(MB)$ is the concentration of a selected constituent in Main Bay, in grams per cubic meter;
$V(EB)$ is the volume of East Bay, in cubic meters;
$c(EB)$ is the concentration of a selected constituent in East Bay, in grams per cubic meter;
$A(MB)$ is the area of Main Bay, in square meters;
$J(MB)$ is the benthic flux of a selected constituent in Main Bay, in grams per square meter per day;
$A(EB)$ is the area of East Bay, in square meters; and
$J(EB)$ is the benthic flux of a selected constituent in East Bay, in grams per square meter per day.

The area and volume values for Main Bay and East Bay (table 21) were obtained from existing area/elevation and capacity/elevation curves (Wiche, 1986). The dissolved-solids and nutrient concentrations for Main Bay (table 22) are averages of the surface-water quality data from this study (tables 3, 4, 5, and 6). The dissolved-solids concentrations for East Bay (table 22) are the average concentrations from three water samples collected on May 7, July 30, and September 19, 1991. The total ammonia plus organic nitrogen and total phosphorus concentrations were used to approximate the concentrations of nitrogen and phosphorus in the lake. The benthic-flux rates used in the calculations for Main Bay are the average flux rates for the three cores collected in 1991 (table 20). The 1990 data were not included in the calculations because the apparent sulfate-reduction rates were much larger and resulted in large fluxes of cations, bicarbonates, and nutrients from the sediments to the lake and large fluxes of sulfate from the lake to the sediments. Because the conditions necessary for the large apparent sulfate-reduction rates to occur are rare, it was felt that inclusion of these data would result in overestimation of long-term flux rates. The benthic-flux rates used in the calculations for East Bay are the average flux rates for the four cores collected in 1986 (table 20). The masses and the fluxes of the individual constituents were calculated for Main Bay and East Bay (table 23). These masses and fluxes were used to calculate the response times for individual constituents in Devils Lake (defined as Main Bay, Creel Bay, Mission Bay, and East Bay, excluding West Bay and Sixmile Bay), and in Main Bay (defined as Main Bay and Creel Bay).

Table 21. Area, volume, and mean depth of the major bays in Devils Lake

[Also shown are area, volume, and mean depth of the parts of the lake used in the response-time calculations (Main Bay minus Sixmile Bay and East Bay plus Mission Bay)]

Location	Area (square meters)	Volume (cubic meters)	Mean depth (meters)
West Bay	$3.2\text{x}10^7$	$1.2\text{x}10^8$	3.8
Main Bay	$7.3\text{x}10^7$	$2.5\text{x}10^8$	3.4
Sixmile Bay	$8.4\text{x}10^6$	$1.5\text{x}10^7$	1.8
Mission Bay	$7.2\text{x}10^6$	$3.3\text{x}10^7$	4.6
East Bay	$5.8\text{x}10^7$	$2.2\text{x}10^8$	3.8
Main Bay minus Sixmile Bay	$6.5\text{x}10^7$	$2.3\text{x}10^8$	3.6
East Bay plus Mission Bay	$6.5\text{x}10^7$	$2.5\text{x}10^8$	3.9
Devils Lake	$1.8\text{x}10^8$	$6.4\text{x}10^8$	3.6

The calculated response times for major ions in Devils Lake ranged from 6.7 years for bicarbonate to 34 years for sulfur (table 24). In contrast, the response times calculated for dissolved solids (2,200 years) and sulfate (2,100 years) by Langbein (1961) were substantially longer. The fact that the response times based on benthic-flux data and the dissolved-ion mass in the lake are three orders of magnitude less than response times based on the dissolved-ion mass in tributary inflow and in the lake illustrates the importance of bottom-sediment processes to the dissolved-solids budgets in Devils Lake.

An examination of the data in table 23 reveals that while the total major-ion masses in the two bays are reasonably similar, the total flux rates for East Bay generally are greater than the comparable rates in Main Bay. To illustrate the importance of the differences in total flux rates between East Bay and Main Bay, the response times for major ions in Main Bay were calculated (table 24). Main Bay response times for calcium, magnesium, sodium, potassium, and sulfur generally are two to ten times longer than the response times calculated for Main Bay and East Bay together (i.e. Devils Lake). Nonetheless, the response times for Main Bay are still two orders of magnitude smaller than the response times Langbein (1961) calculated for Devils Lake. The differences in the calculated response times between Devils Lake and Main Bay illustrate the larger major-ion fluxes in East Bay relative to Main Bay. Main Bay response times for bicarbonate, total nitrogen, and total phosphorus are less than the response times calculated for Main Bay and East Bay together (table 24). The relatively short response times for nitrogen (4.2 years) and phosphorus (0.95 year) indicate that nutrients are recycled more rapidly between the bottom sediments and the lake than are the major ions.

Table 22. Major-ion and nutrient concentrations used in the response-time calculations and calculated pore-water benthic-flux rates for major ions and nutrients for sediment cores collected in Main Bay and East Bay, Devils Lake

[mg/L, milligrams per liter; (mg/m^2)/d, milligrams per square meter per day]

	Concentration (mg/L)		Flux [(mg/m^2)/d]	
Constituent	**Main Bay**	**East Bay**	**Main Bay**	**East Bay**
Dissolved calcium	53	65	7.7	170
Dissolved magnesium	190	280	19	130
Dissolved sodium	880	1,400	80	1,400
Dissolved potassium	110	170	14	340
Dissolved bicarbonate	570	520	570	280
Dissolved sulfur (as SO_4)	2,000	3,200	250	1,300
Total nitrogen (as N)	2.7	3	7.7	5.8
Total phosphorus (as P)	.16	.16	3.4	.033

Table 23. Major-ion and nutrient masses in Main Bay and East Bay and calculated total annual pore-water benthic-flux rates for major ions and nutrients for sediment cores collected in Main Bay and East Bay, Devils Lake

	Mass (grams)		Total annual flux (grams per year)	
Constituent	**Main Bay**	**East Bay**	**Main Bay**	**East Bay**
Calcium	1.2×10^{10}	1.6×10^{10}	1.8×10^{8}	3.9×10^{9}
Magnesium	4.4×10^{10}	7.0×10^{10}	4.6×10^{8}	3.1×10^{9}
Sodium	2.0×10^{11}	3.5×10^{11}	1.9×10^{9}	3.4×10^{10}
Potassium	2.5×10^{10}	4.2×10^{10}	3.3×10^{8}	8.0×10^{9}
Bicarbonate	1.3×10^{11}	1.3×10^{11}	1.4×10^{10}	6.8×10^{9}
Sulfur as (SO_4)	4.6×10^{11}	8.0×10^{11}	5.9×10^{9}	3.1×10^{10}
Total nitrogen (as N)	6.2×10^{8}	7.5×10^{8}	1.8×10^{8}	1.4×10^{8}
Phosphorus (as P)	3.7×10^{7}	4.0×10^{7}	8.0×10^{7}	7.7×10^{5}

Table 24. Calculated major-ion and nutrient response times for Devils Lake (defined as Main Bay plus East Bay) and Main Bay

Constituent	Response time (years) Devils Lake	 Main Bay
Calcium	6.7	63
Magnesium	32	95
Sodium	15	110
Potassium	8.1	76
Bicarbonate	13	9.6
Sulfur (as SO_4)	34	78
Total nitrogen (as N)	4.2	3.4
Total phosphorus (as P)	.95	.46

NUTRIENT CYCLES IN DEVILS LAKE

One of the original objectives of this project was to collect data four times during 1991 in order to construct detailed chemical budgets for nutrient cycling in Devils Lake. The intention was to compare the relative magnitudes of different fluxes, such as nutrient uptake during primary production, settling rates of organic matter, decomposition rates of organic matter in the water column, and nutrient regeneration in bottom sediments. Due to the difficulty in obtaining all of the different measurements simultaneously, and to the relatively large variability in the results, this framework was not practical. However, information about the nutrient cycles in Devils Lake can be derived through comparisons of the different fluxes of organic carbon and nutrients calculated for this study. It should be noted that data were collected only four to six times during the study period (late spring to early fall) and may not be representative of the wide variety of environmental conditions that occur in the lake.

Three sets of flux data were calculated for this study: GPP, settling rate of organic matter, and benthic-flux rate. These data can be used to calculate total carbon, nitrogen, and phosphorous uptake by photosynthesis; total carbon, nitrogen, and phosphorous settling rates; and bicarbonate, ammonia, and orthophosphate benthic-flux rates. It can be assumed that bicarbonate, ammonia, and orthophosphate benthic-flux rates are similar to those for total carbon, nitrogen, and phosphorous, respectively. These data are summarized in table 25.

Table 25. Calculated carbon, nitrogen, and phosphorus fluxes for Main Bay, Devils Lake, May through October 1991

[All fluxes are reported as grams per square meter per day; NA, not available]

Flux	Carbon	Nitrogen	Phosphorus
Uptake by photosynthesis	0.87	0.15	0.02
Settling	11	.84	.06
Bottom-sediment benthic flux	.46	.011	.001
Burial in sediments	.24	.045	NA

Recent (1992) work by the U.S. Geological Survey in the Devils Lake Basin involved the collection of six sediment cores from lakes in the Devils Lake Basin. One of these cores was collected from the middle of Main Bay. Chemical analyses of the cores included lead-210 and cesium-137 for sedimentation-rate determinations and total organic carbon content. The average sedimentation rate for the core collected in the middle of Main Bay in 1992 was 0.15 (g/cm^2)/yr. The total organic carbon content of the sediment was 9.3 percent at 0 to 2 cm and decreased to 6.2 percent at 4.5 cm. The mean value for the top 48 cm of the core was 5.8 percent. On the basis of the sedimentation rate of 0.15 (g/cm^2)/yr and the average total organic carbon content of 5.8 percent, the burial rate of organic carbon can be calculated as 0.24 (gC/m^2)/d. The burial rate of total nitrogen can be estimated from existing data. Lent (1992) determined that the molar ratio of carbon to nitrogen in Main Bay bottom sediments is 6.2. From these data, the burial rate of nitrogen can be calculated as 0.045 (gN/m^2)/d.

The calculated rate of carbon, nitrogen, and phosphorus uptake by photosynthesis is greater than the corresponding benthic-flux rates and the burial rates of carbon and nitrogen. This indicates that a substantial amount of organic matter degradation occurs in the water column during settling or at the sediment/water interface prior to burial. Deviations of the composition of settling organic matter collected in the sediment traps from the Redfield ratio support this conclusion.

Nutrient uptake by photosynthesis is significantly less than the settling rate of organic carbon measured in the sediment traps. This may be explained in four ways: (1) GPP measured in the middle of Creel Bay may be an underestimate of the true rate of GPP in Main Bay; (2) plants growing along the shore or attached to the lake bottom may contribute to GPP; however, it seems unlikely that their contribution could explain the differences between GPP and settling rate of organic carbon; (3) there could be additional sources of organic carbon to the lake, including detrital organic matter and organic matter produced elsewhere in the lake; and (4) the sediment-trap data are an overestimate of the settling rate of primary organic carbon. This overestimation could be due to resuspension of bottom sediments or, "overtrapping" by the sediment traps. Overtrapping is a process where settling particles are focused into the traps. It is doubtful, however, that overtrapping is a problem, due to the configuration of the traps. The fact that only slight differences were measured between the upper and lower sediment traps indicates that the majority of organic-matter degradation occurs at or below the sediment/water interface.

During the study period, benthic fluxes appeared to be the dominant source of nutrients to Devils Lake. However, surface-water inflow was minimal during the study period. During periods of increased precipitation, runoff could carry enough dissolved solids and nutrients to materially affect the chemical budgets of the lake. The long-term effects of the benthic fluxes on the lake composition could be evaluated by examination of existing historic water-quality information. Long-term variations in concentrations and masses of major ions and nutrients in Devils Lake and quantification of the major-ion and nutrient compositions of precipitation and runoff could be used to construct chemical mass balances of major ions and nutrients in Devils Lake. These data are available for the past 80 years.

SUMMARY

Devils Lake is a saline lake in a large, closed drainage basin in northeastern North Dakota. Previous studies determined that major-ion and nutrient concentrations in Devils Lake are strongly affected by microbially mediated sulfate reduction and dissolution of sulfate and carbonate minerals in the bottom sediments. These studies documented substantial spatial variability in the magnitude of calculated benthic fluxes coincident with the horizontal salinity gradient in Devils Lake. The purpose of the present study is to evaluate seasonal variability in benthic-flux rates, and to understand the effect of these fluxes on the major-ion and nutrient chemistries in Devils Lake from May 1991 through October 1991.

The results of water-column profiling (specific conductance, pH, temperature, and dissolved oxygen) and water-quality sampling (between May and October 1991) were used to evaluate the effects of geochemical and biogeochemical bottom-sediment processes on the water-quality of Devils Lake. During the study period the water column was well mixed, and specific conductance, pH, and temperature did not vary with depth. Dissolved oxygen was enriched near the lake surface due to photosynthesis.

Comparisons of existing water-column profile data (1986-90) to the water-column profile data collected during this study were used to evaluate seasonal effects of geochemical and biogeochemical bottom-sediment processes on the water-quality of Devils Lake. Dissolved-solids concentrations increased with decreasing lake level. Open-water periods are characterized by homogenous pH values while ice-covered periods are characterized by vertical pH gradients with pH values decreasing near the sediment/water interface. During open-water periods, the water column generally is well mixed with oxygen. In contrast, during ice-covered periods and during brief calm periods during the summer, the water column was stratified, and the effects of the bottom-sediment diagenetic processes were observed. Specific-conductance values increased near the lake bottom as a result of increased major-ion concentrations from bottom sediments. At the same time, pH and dissolved oxygen decreased near the bottom as a result of microbially mediated reactions.

Secchi-disk depth varied from 0.82 meter on May 7, 1991, to 2.13 meters on June 5, 1991. The mean Secchi-disk depth during the study period was 1.24 meters. Seasonal variations in Secchi-disk depths were attributed to variations in primary productivity and phytoplankton communities. Seasonal variations in Secchi-disk depth in 1990 were similar to Secchi-disk depth data from earlier studies. However, Secchi-disk depths generally have increased from the 1960's to the present (1989-91). The trend in Secchi-disk depth may indicate that trophic conditions in the lake are inversely related to lake level, or that bottom-sediment resuspension is important during periods of low lake levels.

During the study period, major-ion and nutrient concentrations did not vary with depth. Because vertical water-quality profiles obtained during this study represent open-water periods, the profiles reflect well-mixed conditions. However, the first and last profiles for the study period did document near-bottom maxima of major cations.

Nutrient cycles in Devils Lake were evaluated using gross primary productivity rate data, sediment-trap data, and major-ion and nutrient benthic-flux rate data. During the study period, gross primary productivity rate was smallest in May (0.076 gram of carbon per square meter per day) and largest in September (1.8 grams of carbon per square meter per day). Average gross primary productivity for the study period was 0.87 gram of carbon per square meter per day. Average gross primary productivity rate for this study is consistent with historic data from Devils Lake and with data from other eutrophic lakes. The similarities between the gross primary productivity rate data in this study and gross primary productivity rate data from the mid-1960's indicate that while hydrologic and geochemical conditions in Devils Lake have varied, gross primary productivity rates in the lake have remained relatively constant.

Sediment traps were deployed to determine the carbon, nitrogen, and phosphorus composition of settling organic matter. The average flux of organic carbon for the study period was 12 grams per square meter per day. The average fluxes of organic nitrogen (0.84 gram per square meter per day) and phosphorus (0.06 gram per square meter per day) were used to evaluate the composition of sediment-trap organic matter. The calculated carbon to nitrogen to phosphorus ratio (317:25:1) is similar to the Redfield ratio (106:16:1); therefore, most organic matter probably is derived from lacustrine phytoplankton.

Sediment cores were used to assess the effect of geochemical and biogeochemical processes in the bottom sediment on the water quality of the lake. Pore-water samples were alkaline and reducing. Important geochemical and biogeochemical processes included microbially mediated sulfate reduction, dissolution of sulfate and carbonate minerals, and burial of saline pore water. These processes have created well-defined major-ion and nutrient pore-water gradients that were used to calculate benthic-flux rates of major ions and nutrients.

Calculated benthic-flux rates indicated that bottom sediments are important sources of major ion and nutrients to Devils Lake. Only one of the cores collected in this study indicated a net sulfate flux from the lake into the sediments. Seasonal variations in major-ion and nutrient benthic fluxes generally were small. However, there were important differences between the calculated benthic fluxes for this study and the calculated benthic fluxes for 1990. Calculated benthic fluxes of bicarbonate, ammonia, and phosphorus for this study were smaller than calculated benthic fluxes for 1990. The large differences between fluxes for 1990 and 1991 were attributed to calm, stratified water-column conditions in 1990 and well-mixed water-column conditions in 1991.

The role of benthic fluxes in the chemical mass balances in Devils Lake was evaluated by calculating response times for major ions and nutrients in Devils Lake. The calculated response times for major ions in Devils Lake ranged from 6.7 years for bicarbonate to 34 years for sulfur (as SO_4). These response times are significantly shorter than previous estimates that did not include benthic fluxes. The relatively short response times for nitrogen (4.2 years) and phosphorus (0.95 year) indicate that nutrients are recycled rapidly between bottom sediments and the lake. During the study period, benthic fluxes were the dominant source of major ions and nutrients to Devils Lake, and greatly reduced the response times of all major ions and nutrients for Devils Lake. As a result, bottom-sediment processes appear to buffer major-ion and nutrient concentrations in the lake. Any future attempt to evaluate water quality in Devils Lake should include the effects of bottom-sediment processes.

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