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Long-Term Studies of Lakes and Watersheds in the Sierra Nevada, Patterns and Processes of Surface-Water Acidification

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD
Research Division

**LONG-TERM STUDIES OF LAKES AND WATERSHEDS IN THE
SIERRA NEVADA, PATTERNS AND PROCESSES OF
SURFACE-WATER ACIDIFICATION**

**Final Report
Contract No. A932-060**

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ABSTRACT

The atmospheric deposition, hydrology, hydrochemistry and zooplankton of seven high altitude Sierran catchments have been studied for two years (1989-1991) to assess potential effects of acidic deposition. Atmospheric deposition of water and solutes was determined by event collections of rain and by snow sampling at the time of maximum accumulation. Year-round bimonthly samples for solutes and zooplankton were obtained from each lake. Lake outflows were sampled bimonthly except during snowmelt when collections were made every one to two weeks. Continuous records of outflow discharge were obtained. All major solutes in atmospheric deposition (H, NH₄, Ca, Mg, Na, K, NO₃, SO₄, Cl, formate and acetate) and lake and stream water (H, NH₄, Ca, Mg, Na, K, NO₃, SO₄, Cl, acid neutralizing capacity [ANC] and silica) were measured. A rigorous quality assurance-quality control protocol was followed.

Sierra snow is slightly acidic (seasonal average among sites, pH 5.2 to 5.4), and rain is usually more acidic (seasonal average among sites, pH 4.6 to 5.5). Volume-weighted mean annual pH ranged from 5.1 to 5.4 among the seven catchments. The acidity is caused by weak organic acids and strong acids of nitrate and sulfate.

All seven catchments retain annually the atmospheric input of H and export ANC and similar amounts of basic cations. Hence, the weathering and exchange processes in the catchments are sufficient to buffer current acidic atmospheric deposition on an annual basis. During snowmelt pH and ANC minima occur each year. Zooplankton species known to be intolerant of acidification occur in all seven lakes, and their presence is evidence that Sierran lakes are not currently showing chronic biological effects of acidic deposition.

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DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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SUMMARY AND CONCLUSIONS

Our research on seven high-elevation catchments of the Sierra Nevada has focused on 1) identifying patterns in surface-water chemistry and acidic deposition in seven high-altitude watersheds in the Sierra Nevada; 2) quantifying the year-round susceptibility of Sierran lakes to acid deposition and 3) detecting changes in zooplankton populations induced by hydrochemical changes. To attain these objectives we employed hydrological measurements and chemical and biological sampling at regular intervals throughout a two year period with more intensive study during snowmelt. The seven catchments each with a lake spanned the length of the high-elevation Sierra Nevada. The catchments range in area from 18.5 ha to 424 ha, and the lake elevations vary from 2475 m to 3426 m.

The major processes in lakes and their catchments that contribute to the neutralization of acidic atmospheric deposition include chemical weathering, ion exchange and redox reactions. Year-round sampling in Sierran lakes and their outflowing streams has characterized the regional seasonal patterns in hydrochemical conditions and permitted identification of the relative importance of neutralization processes. When combined with measurements of atmospheric deposition of solutes and water and discharge of the outflowing stream, the relative magnitude of acidic inputs and acidic neutralizing capacity of the catchment and lake was determined. Hence, we can evaluate the susceptibility of a regionally representative set of alpine Sierran catchments to acidic deposition.

Solute concentrations in the lakes were greatest during winter months, declined to minima during snowmelt and increased gradually through the summer and autumn. This pattern is most conspicuous for ANC, basic cations and conductance. Other solutes diverged from this pattern in some lakes. In Emerald and Pearl lakes, pH showed little annual variation in water year 1990. pH declined gradually throughout the entire study period in Crystal Lake, and during water year 1990 in Ruby and Spuller lakes.

The strength and longevity of a lake's thermal stratification influences the extent of oxygen depletion and subsequent increase in ANC in the hypolimnion. Lost and Topaz lakes had only slight stratification of temperature and dissolved oxygen and almost no vertical differences in ANC. In Crystal and Emerald lakes, hypolimnetic oxygen depletion during winter and summer was mild and resulted in only slight accumulations of ANC. The hypolimnion of Pear Lake was low in dissolved oxygen during the entire study period; hypolimnetic accumulations of ANC were

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Zooplankton species known to be intolerant of acidification occur in all seven lakes, and their presence is evidence that Sierran lakes are not currently showing chronic biological effects of acidic deposition.

moderate in the winter of 1990 but low in the winter of 1991. Ruby Lake had depressed dissolved oxygen concentrations during winter and had increased hypolimnetic ANC.

In the outflowing streams, ANC was generally highest prior to the onset of snowmelt and declined as discharge increased. pH also declined during the period often in connection with increases in nitrate and sulfate. Almost all the export of solutes from the catchments occurs during the period from March to August.

The chemical composition of snow was similar among the catchments; pH ranged from 5.2 to 5.4, and the dominant solutes were H, NH_4 and NO_3 . The concentration of solutes in rain was more variable and about ten times greater than in the snow; pH ranged from 4.6 to 5.5. On an annual basis, the pH of Sierran atmospheric deposition ranged from 5.1 to 5.4. The acidity is caused by weak organic acids and strong acids of nitrate and sulfate.

Net annual yields of H, ANC and base cations per ha of catchment provide an integrative metric of the current capacity of the catchments to neutralize acidic inputs. All the catchments retain H and export ANC and a similar amount of basic cations. Hence, the weathering and exchange processes in the catchments are sufficient to buffer current atmospheric deposition of H on an annual basis.

Zooplankton communities are expected to respond to lake acidification via alterations in community composition and the relative abundance of species. Numbers of crustacean and rotifer species can be expected to decline during lake acidification, but predictions for single species vary. Zooplankton species coinciding with the period of maximum discharge and resultant minima in ANC during snow melt are the most likely to experience periods of lowered pH. The overall utility of monitoring zooplankton in order to detect early signs of acidification will depend in part on the predictability of observing species during this part of the hydrological cycle and on their tolerance to low pH. Among crustacean zooplankton, *Macrocyclus albidus* was the most often observed zooplankton species during snow melt periods. *Bosmina longirostris* and *Diaptomus signicauda* were the second and third most frequently encountered crustacean zooplankters during snow melt periods.

Based on the available descriptive and experimental information, certain changes in community structure are reasonable to predict if our survey lakes become subjected to chronic acid stress. *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicauda* are likely to be removed if pH levels reach as low as 5.0. In the lakes in which these species overlap seasonally

Time series analysis

Hydrochemical measurements of streams, lakes and atmospheric inputs spanning 10 years for Sierran catchments are appropriate for statistical analyses of temporal trends. We recommend examination of interannual variations and trends.

Zooplankton as bio-indicators of lake acidification

To evaluate episodic acidification during snowmelt, more information about the pH tolerance range of *Macrocyclops albidus* is required. To detect initial stages of chronic acidifications continued sampling from June to November will indicate abundance of species most sensitive to initial pH reductions in Sierran lakes.

RECOMMENDATIONS

Hydrochemical and hydrological measurements of Sierran catchments

We recommend continuation of the hydrochemical and hydrological measurements in the seven Sierran catchments currently being studied (i.e. Emerald, Topaz, Pear, Ruby, Crystal, Spuller and Lost) through water year 1993. To aid interpretation of long-term data we recommend use of automatic samplers to obtain samples of streams for selected sites on a daily basis during snowmelt and on a weekly basis. To aid geochemical analyses we recommend further measurements of Al species and dissolved inorganic and organic carbon.

To improve estimation of atmospheric deposition, dry deposition should be calculated with available meteorological and aerosol and gas measurements.

To improve interpretation of weathering reactions as a major source of ANC, stoichiometry of important rocks from specific catchments should be determined.

Watershed characteristics

To evaluate the role of catchment processes in determining acidification of streams and lakes further characterization of the geology, soils and vegetation of each catchment is recommended. Digital elevation maps are required to improve calculation of snow deposition and runoff routing. Meteorological measurements should be combined with topographic data to calculate evaporative losses.

Hydrochemical modeling

Models for hydrochemical processes developed for alpine regions are now mature and appropriate for application to the Sierra Nevada. We recommend validating the models with data from the Sierra and then using the models to predict changes in hydrochemical conditions as a function of atmospheric deposition of solutes.

The major objectives of our current research are as follows:

1. Identify trends and patterns in surface-water chemistry and acidic deposition in seven high-altitude watersheds in the Sierra Nevada.
2. Quantify the year-round susceptibility of Sierran lakes to acid deposition. A major component of this objective is the construction of watershed mass-balances.
3. Detect changes in biological populations induced by water quality changes.
4. Provide results to be used in establishing deposition standards for the Sierra Nevada.

Site Descriptions

Figure 1 shows the location of the seven study sites in California. A summary of the watershed and lake characteristics is contained in Table 1.

Emerald Lake (36°35'49"N, 118°40'30"W) is located in Sequoia National Park. The watershed is granitic and composed mainly of granodiorite, with some mafic inclusions, aplite dikes and pegamite veins (Sisson and Moore 1987, Clow 1987). Poorly developed soils cover 20% of the watershed, and these are acidic and weakly buffered (Huntington and Akeson 1987, Lund *et al.* 1987). There are three major inflowing streams to the lake. Vegetation is sparse (Rundel *et al.* 1988), including scattered coniferous trees and short woody shrubs and grasses found in areas with soils. A naturally reproducing population of brook trout occur in the lake and its outflow.

Pear Lake (36°36'2"N, 118°40'00"W) is located in Sequoia National Park about 0.5 km from Emerald Lake. The majority of the watershed is composed of coarse-grained granite containing sparse mafic inclusions of widely variable size and texture; the remainder of the basin is underlaid by medium-grained, porphyritic granodiorite (Sisson and Moore 1987). Owing to the steepness of the terrain, a large portion of the watershed lies at higher elevations. The lake is fed by one major stream during most of the year and probably receives a significant portion of its water during snowmelt from sheet flow off the large areas of granitic bedrock surrounding the lake. A naturally reproducing population of brook trout is present.

Topaz Lake (36°37'30"N, 118°38'11"W) is in Sequoia National Park in a region known as the Tablelands, about 6 km north-northwest of Emerald Lake. Vertical relief in the basin is small, and it has a southern exposure. Portions of the upper basin have extensive meadows and ponds during snowmelt. There is a small stand of Foxtail pines in the upper eastern portion of the

Chapter I

INTRODUCTION

Project Background and Objectives

Acid precipitation is falling on California's coast, inland valleys and montane regions (California Air Resources Board 1988). Evaluating the potential harm posed by acid deposition in California required an assessment of the status of its aquatic resources and their possible responses to acidification. The California Air Resources Board (ARB) approached the problem in several ways. The ARB determined the geographic extent of weakly buffered aquatic habitats by conducting state-wide surveys of lakes and streams. An Integrated Watershed Study (IWS) of the Emerald Lake watershed in the Sierra Nevada was carried out between 1984 and 1988. Baseline data were collected and experiments conducted to determine the possible consequences of acidification of California's montane lakes (*see* Melack *et al.* 1987, Melack *et al.* 1989, Dozier *et al.* 1989). Near the conclusion of the Emerald Lake IWS, a year-round study of four additional high-altitude watersheds in the Sierra Nevada was begun and continued for two years (Sickman and Melack 1989). This study was designed to assess the generality of the intensive Emerald Lake study and to characterize the year-round susceptibility of a larger population of lakes to acid deposition.

Montane watersheds of the Sierra Nevada are among the habitats in California most susceptible to anthropogenic acidification. Because of the large annual and interannual variability in surface-water chemistry and acidic deposition in these catchments, long-term data are necessary to detect trends in water quality. Montane lakes in the Sierra Nevada vary considerably in their capacity to generate acid-neutralizing capacity (ANC). Therefore, assessment of the influence of acidic deposition on aquatic chemistry and biota in these waters must include data from a representative sample of Sierran lakes.

Spuller Lake (37°56'55"N, 119°17'2"W) is located in the Hall Research Natural Area near Tioga Pass. This area is administered by the U.S Forest Service. The watershed has a predominantly southeast aspect and large vertical relief. The lake is supplied by one major inflow. The lower portions of the watershed are composed of ancient tuffaceous lake beds. These beds are fine-grained and thin and composed chiefly of volcanogenic sediment. Common minerals include plagioclase, quartz, biotite, hornblende and opaque minerals; calcareous layers contain calcite, diopside, hornblende, epidote and trace amounts of sheelite. The upper portion of the watershed is composed of talus slopes. These rocks are dark-colored medium-grained hornblende-biotite granodiorite (Bateman *et al.* 1983). The watershed is completely devoid of trees and vegetation is confined to a small meadow at the inflow to the lake. A small population of reproducing brown trout is present.

Lost Lake (38°51'37"N, 120°5'48"W) is located in the northern Sierra Nevada near Lake Tahoe in the Desolation Wilderness of Eldorado National Forest. The lake is lowest in altitude and the smallest in volume and surface area of the seven study lakes. The lake's basin is also the smallest and has the least vertical relief of the study lakes. Hemlock, Lodgepole pine and Western White pine line the shore of the lake and are present in all but the uppermost portions of the watershed. Two main inflows occur during the spring. The watershed has a north-facing aspect. A healthy population of brook trout is present.

watershed (~25 trees). The geology of the basin is dominated by fine-grained, granodiorite containing abundant mafic inclusions. The phenocrysts include potassium feldspar, hornblende, biotite and plagioclase (Sisson and Moore 1987). Because of the gentle relief around the lake, it tends to expand during snowmelt and floods a meadow, forming a shallow bay. As the summer progresses the lake level declines and the water retreats from this bay. No fish occur in the lake.

Ruby Lake (37°24'50"N, 118°46'15"W) is situated on the eastern slope of the Sierra Nevada in the John Muir Wilderness of the Inyo National Forest. It is the largest and deepest of the study lakes and lies at the highest altitude, has the largest watershed, greatest lake volume and most watershed relief. The basin has a northwestern exposure and is composed predominantly of quartz monzonite. This rock is typically coarse-grained and strongly porphyritic and contains minor amounts of hornblende and sphene (Lockwood and Lido 1975). The higher cirques of the basin contain talus fields and small glaciers. These glaciers are actively eroding the watershed, and there is glacial flour in the major inflow to the lake. Besides this major inflow, two other significant runoff channels have been identified. The cirque inflow drains a portion of the watershed southwest of the lake composed of talus and boulders. The Mono Pass inflow originates from the northern portion of the watershed which is primarily weakly developed soils and gravel. This portion of the watershed is the only one with trees which are limited to a stand of Whitebark and Lodgepole pine. The majority of the watershed is within the alpine zone. The outflow from Ruby Lake flows year-round. A stunted population of brook trout is present.

Crystal Lake (37°35'36"N, 119°01'5"W) is located about 10 km southwest of the town of Mammoth Lakes. The watershed area is lightly forested for about half its area with a mixture of Whitebark and Lodgepole pines. The basin has a north-facing aspect. The eastern and southern portions of the basin are dominated by a granitic dome and talus. These rocks range in composition from granodiorite to alaskite with an average composition of mafic quartz monzonite. The rocks are generally coarse-grained and commonly porphyritic with phenocrysts of potassium feldspar. The remaining portion of the basin is dominated by ash and soils of volcanic origin. These rocks are a series of interbedded andesitic flows, cinders and rubble. The flow rock is commonly vesicular and essentially nonporphyritic (Huber and Rinehart 1965). Three major runoff channels enter the lake. Inflow #1 and the main inflow drain the eastern and southern portions of the basin. Inflow #2, draining the western region of the watershed, is minor in comparison. These inflow streams and the outflow are ephemeral and flow only during snowmelt or shortly after autumn precipitation; during the winter outflow is usually absent. A naturally reproducing population of golden trout is present.

column, conductivity detection and a micro-membrane suppressor. Calcium, magnesium, sodium and potassium were measured by flame atomic-absorption spectroscopy using a Varian model AA6 spectrophotometer. Silicate was determined on a filtered subsample using the silico-molybdate method (Strickland and Parsons 1972).

Precipitation Sampling and Analyses

Samples of the snowpack were obtained by digging pits to the ground and collecting duplicate, contiguous, vertical sections every 40 cm using a clear PVC tube (5 cm diameter, 50 cm long, with a sharp, beveled cutting edge). The sampling coincided with the period of maximum snow accumulation. In each basin two pits located in portions of the watersheds with different exposure and altitude were sampled.

Each 40 cm section was placed into a separate polyethylene bag. Bags and sampling apparatus were soaked in deionized water for several days before use and kept scrupulously clean. All snow samples were kept frozen at -20 °C until they were placed into polyethylene buckets and thawed at 5 °C. After melting, pH, ANC and specific conductance were determined using unfiltered samples employing the same equipment and techniques as used for the lake and stream samples. All samples for major solutes and nutrients were filtered through Nuclepore polycarbonate filters (1.0 micron pore size). A separate filtered subsample was made for organic anions and preserved with chloroform. Anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_2^- and CH_3CO_2^-) were determined on the ion chromatograph. Cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by the flame atomic absorption technique. Ammonium ion was determined within 24 hours of melting using filtered samples by the indophenol blue method (Strickland and Parsons 1972).

In order to estimate snow water equivalence for each catchment, snow density and snow-covered area were determined. Snow density was determined in vertical 10 cm intervals in each sampling pit using a wedge shaped, stainless steel cutter and a portable electronic balance (Dozier *et al.* 1987). All cutters were calibrated and found to have less than 1% error in volume. Snow depth was determined along transects from the lakes' edges to the boundaries of the watersheds; approximately 300 depth measurements were made in each basin. Snow-covered area was estimated from aerial photographs.

During the ice-free seasons, precipitation quantity was measured at or near each lake using a tipping-bucket rain-gauge (Qualimetrics model 6011-B) connected to a solid-state datalogger. Alter-type shields were used on the rain gauges at Emerald and Spuller Lakes and near Lost Lake. Wet only precipitation was collected on an event basis at or near all watersheds using Aerochemetrics collectors. Ionic loading was calculated from rainfall amounts measured in or near

Chapter II

HYDROCHEMICAL AND HYDROLOGICAL METHODS and QUALITY ASSURANCE and CONTROL

Lake and Stream Sampling and Chemical Analyses

Emerald, Pear, Topaz, Ruby, Crystal, Spuller and Lost Lakes were sampled approximately bimonthly during the period from October 1989 through November 1991. Samples for chemical analyses were collected from five depths in Pear Lake, four depths in Emerald, Crystal, Ruby and Spuller Lakes and from three depths in Topaz and Lost Lakes. A single sampling station, overlying the deepest portion of each lake was used. Outflow samples were collected bimonthly when possible. During the snowmelt periods of 1990 and 1991 (April through June) outflow samples were collected every one to two weeks at each watershed. Major inflows to the lake were also sampled at this time.

Lake samples were obtained from a small inflatable boat (ice-free seasons) using an all-plastic peristaltic pump connected to Tygon tubing. The tubing was weighted with a rubber stopper and lowered to the proper depth. At least two tubing volumes were flushed before sample collection. During periods of ice cover, an ice auger was used to reach the lake water. Water from each sampling depth was placed into large polyethylene bottles and then split into filtered and unfiltered subsamples for transport. Vertical profiles of dissolved oxygen and temperature (meter intervals) were measured using a portable meter (Yellow Springs Instruments [YSI] Model 58) equipped with polarographic oxygen electrode and thermistor.

All apparatus and bottles used in sampling were rinsed with deionized water and then soaked in deionized water for several days. Major solute and nutrient samples were filtered with Nuclepore polycarbonate filters (1.0 micron pore size). All samples were kept cool and in the dark during transport. For long-term storage, major solute and nutrient samples were held at 5 °C.

A Gran titration (Talling 1973) and pH measurement were done on unfiltered subsamples within 72 hours of collection using a Orion model 920 meter and Ross (Orion) combination electrode. Specific conductance of unfiltered water was measured with a YSI Model 34 conductivity bridge and electrode (cell constant = 0.1) and readings corrected to 25°C. Ammonium was determined on filtered samples generally within 72 hours by the indophenol blue method (Strickland and Parsons 1972). Chloride, nitrate and sulfate were measured by ion chromatography on a DIONEX model 2010i ion chromatograph, employing an AS4A separation

Where:

H is the depth of flow through the weir in cm

Q is discharge in cubic meters per second

The weirs were constructed of plywood and attached to the streambed and bank using angle-iron, concrete and steel bolts. The wetted perimeter of the weirs was a plate of quarter inch steel honed to a sharp edge. This edge consisted of a narrow surface at right angle to the upstream face of the plate and a 45-degree chamfer at the downstream edge. There was adequate fall of water to ensure that the weirs would not be submerged at high flows.

In order to develop relationships between the pressure transducers and outflow discharge a lengthy calibration of the transducers was made using salt dilution estimates of discharge. The salt dilution technique is described in detail by Dozier *et al.* (1987). Discharge measurements were conducted during bimonthly sampling trips and intensively during the snowmelt periods. New rating curves were developed every few years because of changes in channel morphology and because of electronic drift in the pressure transducers. Two different rating curves for Topaz and Ruby Lakes are shown in Figure 2 and illustrate the changes of these rating curves from year to year. Table 2 summarizes all the rating curves used to convert transducer voltages to discharge.

When no weir was present, outflow discharge was calculated by converting transducer voltage (time-step, one hour) directly into discharge using the appropriate rating equation. At Emerald and Spuller lakes transducer hourly voltages were first converted into units of depth of flow through the weir (see Figure 3). The equations that relate transducer voltage to discharge are as follows:

Emerald Lake transducer 1 (5 psi): Voltage = $0.0143(H) + 1.584$

Emerald Lake transducer 2 (1 psi): Voltage = $0.0650(H) + 3.069$

Spuller Lake transducer 1 (1 psi): Voltage = $0.0683(H) + 2.747$

Spuller Lake transducer 2 (1 psi): Voltage = $0.0654(H) + 2.792$

Where:

H is depth of flow through weir in cm

psi is pressure per square inch

Gauging Method Comparison

The accuracy of the salt dilution technique could be determined by comparing discharge determined by salt dilution to the measurements of flow made by the weirs. Individual flow

each watershed and from samples analyzed chemically as described for snow. Rain chemistry from the collector at Emerald Lake site was used at Emerald, Pear (1 km; 104 m altitude difference) and Topaz (6 km; 419 m altitude difference) lakes. Chemistry from a collector at Eastern Brook Lake was used at Ruby Lake (4 km; 280 m altitude difference). At Crystal Lake chemistry from Mammoth Mountain (5 km, 25 m altitude difference) was used. Data from a collector at the Carnegie Institute Field Station was used at Spuller Lake (3 km, 134 m altitude difference). Rain chemistry at Lost Lake was collected at Angora Lakes (3 km; 189 m altitude difference).

Outflow Discharge

At each lake there is an automatic hydrological station. The station consists of an Easylogger field computer (Omnidata International) powered by a durable, weather-proof battery pack. The field computers were mounted in trees, or at Spuller Lake on a metal tower, adjacent to the outflow streams. Stream stage was continuously monitored using micro-pressure transducers (Montedero Whitney), installed in the stream bed and attached to the loggers. Starting in 1991 there were two transducers at each lake. In 1990, thermistors were installed in the outlets of all lakes to provide a continuous record of outflow temperature. Also in 1990, v-notch weirs were constructed at the outflows of Emerald and Spuller lakes. The weir at Emerald Lake had an angle of 120 degrees; the weir at Spuller had an angle of 90 degrees. These types of weirs have the ability to measure low discharges accurately, to cover a wide range of flows, have a stable and constant coefficient of flow which is wholly dependant on their geometry. The recommended discharge equations from Herschy (1978) for the weirs are:

$$\text{Emerald:} \quad Q = 4.33 H^{2.5}$$

$$\text{Spuller:} \quad Q = 2.50 H^{2.5}$$

Where: H is the depth of flow through the weir in feet
 Q is discharge in cubic feet per second

Converting into metric terms for H and Q yields:

$$\text{Emerald:} \quad Q = (2.39 \times 10^{-5}) H^{2.5}$$

$$\text{Spuller:} \quad Q = (1.38 \times 10^{-5}) H^{2.5}$$

Lake Morphometry

Bathymetric maps of lakes were prepared from echo soundings. A graduated line was strung across each lake's surface between prominent landmarks. Transects were run from landmark to landmark across the lake surfaces by following this graduated line and taking echo soundings at 5 m intervals. Between 5 and 8 transects and a total of 200 to 400 individual measurements were made at each lake. The maps were drawn by hand and then digitized using a digitizing tablet and appropriate software. The volumes of the lakes were estimated from their hypsographic curves.

Meteorological Measurements

To improve the accuracy of the water and mass balance calculations for the catchments, water lost through sublimation and evapotranspiration must be accounted for. To estimate these losses climate data are needed. Meteorological data are available from existing stations near some of the watersheds (Mammoth Mountain near Crystal Lake, Eastern Brook Lake near Ruby Lake). Two meteorological stations were constructed; one at Emerald Lake (to provide climate data for the Sequoia N.P. lakes) and another at Spuller Lake. Climate parameters measured include air temperature, relative humidity, wind speed and direction and incident radiation. Two radiation sensors were used; a pyrgeometer to measure longwave radiation (4-50 μm) and a pyranometer to measure solar radiation (285-2800 nm). These sensors are connected to Easylogger units and record data on an hourly basis. A summary of the instrumentation is contained in Table 3.

Quality Assurance and Control

A long-term effort investigating regional differences in precipitation or surface water chemistry requires a strong quality assurance (QA) plan for sampling and analysis. The QA plan comprises rigorous field and laboratory quality control (QC) procedures which are prerequisite to the production of credible data. UCSB has implemented a QA program to ensure the integrity of precipitation and surface water samples collected in the field and to produce reliable analytical data for samples analyzed in the laboratory.

In an assessment of methods for monitoring snowfall, Berg et al (1989) employing UCSB's quality assurance protocols for precipitation and surface water samples documented guidelines for sampling interval, collection, storage, transport and processing of snow. These protocols have been used by Sickman & Melack (1989) in monitoring the chemistry of Sierra Nevada lakes and were followed here.

measurements made by both methods and the stage-discharge relationships generated by the two methods were compared.

Figures 4 and 5 show the relationship between stage (as indicated by transducer voltage) and discharge measured by salt dilution and by weir for Emerald and Spuller lakes. The stage-discharge relation for weir measurements is precisely defined. The stage-discharge relationship for salt dilutions is not as precisely defined. Comparing individual measurements of flow shows that salt dilutions can both over- and under-estimate discharge. However, on average, salt dilutions over-estimate discharge by 2% at Emerald Lake and by 10% at Spuller Lake (Figure 6). The discrepancy between the methods appears to grow as discharge increases. The apparent over-estimate by salt dilution at Spuller lake may be caused, in part, by slight leakage around the weir.

Watershed Mass Balance

The mass balance of solutes for a watershed consisted of two components: loading of solutes by atmospheric deposition and outflow solute losses. Loading was divided into two types: snow and non-winter precipitation which were calculated separately. Solute loading by snow was calculated from the volume-weighted mean concentration of each solute multiplied by the total volume of snow at maximum accumulation. The solute flux for non-winter precipitation was calculated by multiplying the volume-weighted mean concentration for this precipitation by its total volume. Total solute loading is then sum of snow and non-winter precipitation loading.

Mass flux in the outflow of each lake was calculated from daily outflow discharge and outflow chemistry. Chemistry was assigned to discharge mainly on the basis of the timing of major hydrological events in the watersheds. For instance, if the outflow from a lake was sampled in December and then sampled again in the middle of the snowmelt period, the early winter chemistry would be applied to the outflow up until the onset of snowmelt, and the snowmelt chemistry would be extrapolated back to the beginning of melt.

Using the mass balance components, the yield of solutes from the watershed was calculated using the following equation:

$$\text{Watershed Yield} = [(\text{Output} - \text{Input}) \div \text{Watershed Area}]$$

where Output equals the mass flux in the outflow of each lake and Input equals the sum of snow and non-winter precipitation solute deposition. Yield is expressed as equivalents per hectare per year. A positive yield indicates that the loss of the ion from the watershed was greater than the supply; a negative yield indicates that the loss of the ion was less than the supply.

In addition to the above procedures, the internal consistency of our chemical data is validated by adherence to the following criteria (Drouse et al 1985). Tests for consistency of data include departure from electroneutrality and comparison of calculated and measured specific conductance. Charge balance is evaluated as an ion balance ratio and as the absolute value of the sum of positive ions minus the sum of negative ions. Theoretical specific conductance is calculated from measured ion concentrations and compared with measured specific conductance as the conductance deficit (measured conductance minus calculated conductance). If measured ionic concentrations are accurate and all the major constituents measured, the sum of cations should equal the sum of anions. If measured conductance is the same as theoretical conductance, then our analytical protocol determines all the important ionic species and our measurements are not biased.

Specific conductance—The YSI 3402 cell ($K = 0.1 \text{ cm}^{-1}$) was calibrated with 10^{-4}N KCl throughout the measurement period of 1990-1991. The specific conductance of the KCl standard was always within 12% of the theoretical value of $14.9 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C . Overall precisions for 1990 and 1991 were 4.9 and 3.8 percent relative standard deviation, respectively.

pH—The Orion EA 920 meter equipped with a Ross 8104 electrode was first calibrated with NBS traceable pH 7.00 and pH 4.00 buffers. A further calibration with various concentrations of HCl prepared from certified 10^{-2}N HCl (Fisher-SA62-1) solution was then performed. Overall precision computed from pH 4.0 and pH 4.7 HCl standards were 0 and 1.1 percent relative standard deviation, respectively. Precisions of 0.5 and 0.6 percent relative standard deviation for pH measurements on a single day were computed using replicate measurements of snowmelt samples and of a USGS simulated snowmelt sample, respectively.

Accuracy of determination of anions—Accuracy was assessed by comparing measured values with certified values of NBS 2694-II simulated rainwater and also by recovery after known addition to duplicates of natural samples. The values measured for the NBS control which was included in each analytical run for lake and stream water indicated no bias in Cl or NO_3 and a slight positive bias (6%) in SO_4 for 1990-91 (Table 5). Overall accuracy for 1990 was 93 ± 20 , 98 ± 8 , and 112 ± 7 percent recovery for Cl, NO_3 and SO_4 , respectively. In 1991, overall percent recoveries of 92 ± 12 , 100 ± 11 and 102 ± 15 were realized for Cl, NO_3 and SO_4 , respectively. The snow data (Table 6) include replicates from the "Wet Deposition in Alpine Areas of the Sierra Nevada Project" (ARB contract A932-081). Comparison of measured values with the certified values of the NBS control indicated no bias in the determination of any anion. Overall accuracy for 1990 was 91 ± 15 , 106 ± 18 , and 95 ± 23 , percent recovery for Cl, NO_3 and SO_4 , respectively. In 1991,

Our QC procedures include the following components: Identical instruments are used and adherence to standardized data collection procedures and field analysis protocols are emphasized with the field staff at all sites (Table 4); the sampling procedures are described in the methods section of this report. Procedural variability in the field is assessed by duplicate cores and replicate samples at 5% frequency for snow and lake water, respectively, and by means of field blanks obtained on each and every sampling trip. In the laboratory, blanks include deionized water processed through plastic bottles, filters and buckets which assess contamination from buckets employed to melt snow, from the membranes used to filter melted snow, and from bottles used to contain lake water.

Our analytical procedures incorporate a variety of internal and external checks to generate precision and accuracy statistics. The following is a summary of the internal checks used for each analysis.

pH: After a two point calibration with NBS-traceable buffers, the accuracy of the electrode is checked using dilute solutions of HCl (10^{-4} and 10^{-5} N).

ANC: After electrode calibration and accuracy checks as with pH, a titration is performed with NaOH (ANC, $30 \mu\text{eq L}^{-1}$).

Specific Conductance: A 10^{-4} M KCl conductivity standard, which has a theoretical specific conductance of $14.7 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C is measured frequently. In 1990 two audits (high and low, 118 and $6.5 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C , respectively) were prepared from Orion low ionic strength buffers and measured throughout a six month period.

Cations and Anions: Duplicate samples are run at a 5% frequency in each assay session for estimation of within-run precision. Known additions are made to samples and standards in duplicate at a 5% frequency in each assay session for estimation of within-run accuracy.

We employ two different independent (external) checks on the accuracy of our chemical analyses. Routine analysis of standard reference materials from the National Bureau of Standards is performed. This material is synthetic rain-water with certified concentrations for major cations and anions. The second independent check on our chemical data involves participation in the U.S. Geological Survey's Analytical Evaluation Program. Twice yearly the USGS distributes a water sample to participants at laboratories and universities nationwide for major cations and anions analysis. Participants return their results to the USGS. The USGS assigns a score to each laboratory based on how close their results come to the mean value obtained from all participants.

Based on limited replicates precision was 2 and 4 percent relative standard deviation for cations and anions, respectively. A more concerted effort to generate quality assurance data with higher replication is in progress.

Field blanks—Prior to snow sampling the polycarbonate snow corers were rinsed three times with deionized water ($\leq 1 \mu\text{S}\cdot\text{cm}^{-1}$, 25°C) and a final, fourth rinse was collected for chemical analysis. Contamination with major ions was undetectable ($< 0.1 \mu\text{eq}\cdot\text{L}^{-1}$). Prior to installation, Aero Chemetrics collectors were rinsed three times with deionized water ($\leq 1 \mu\text{S}\cdot\text{cm}^{-1}$, 25°C). A final, fourth rinse with ca. 150 ml was collected for a chemical analysis. Contamination with major ions was negligible ($0.1\text{-}0.3 \mu\text{eq}\cdot\text{L}^{-1}$).

Laboratory blanks—Plasticware blanks included samples from ziplock bags, 125 ml and 30 ml high density polyethylene bottles, and filters at ca. 10% frequency. Plasticware was soaked in deionized water ≥ 3 days and then rinsed 5 times with deionized water. Filter blanks were obtained from the buckets used to melt snow by filtering (1.0 micron polycarbonate membrane) a ca. 100 ml portion of the 250 ml of deionized water kept in contact at 4°C with the bucket for 24 hours. No significant contamination was detected in any of these blanks.

Overall accuracy and overall precision of analysis of each cation and of each anion for 1990 and for 1991 are tabulated in Table 9.

The internal consistency of the chemical data is validated by the application of two criteria to the data set. Lack of departure from zero for electroneutrality indexed as the absolute value of the sum of positive ions minus the sum of negative ions affirms that measured ionic concentrations are accurate and that all major constituents are measured. Figures 7 through 11 depict the frequency distribution of cations minus anions for lake and stream, snow and rain samples. For lake and stream samples a mean of $-2.2 \mu\text{eq}\cdot\text{L}^{-1}$ as bias toward negative charge is observed (Figure 7). This represents 1.7% of total ions or percent ion difference present in a sample. The average total charges for a lake and stream sample was $126 \mu\text{eq}\cdot\text{L}^{-1}$. For snow samples a mean of $+4.4 \mu\text{eq}\cdot\text{L}^{-1}$ as bias toward positive charge is observed (Fig. 8 and 9); this represents a 23% ion difference. The average total charges for a snow sample was $19 \mu\text{eq}\cdot\text{L}^{-1}$. For rain a mean of $+0.2$ and $+0.8 \mu\text{eq}\cdot\text{L}^{-1}$ is observed for 1990 and for 1991, respectively (Fig. 10 and 11). This represents average percent ion differences of 2.3% and 4.0% for 1990 and 1991, respectively. The average total charges for rain samples was $164 \mu\text{eq}\cdot\text{L}^{-1}$ (1990) and $205 \mu\text{eq}\cdot\text{L}^{-1}$ (1991).

percent recoveries of 96 ± 16 , 101 ± 11 and 103 ± 7 were realized for Cl, NO₃ and SO₄, respectively.

Precision of determination of anions—Within run precision was computed as the percent relative standard deviation of the means of three kinds of samples. Randomly selected samples were analyzed in duplicate as natural and as augmented (known addition) samples. A synthetic laboratory control (LC) consisting of known addition to a calibration standard was analyzed in duplicate in each run: For lake and stream water, overall precision on Cl, NO₃ and SO₄ for 1990 (n = 25) and for 1991 (n = 33) was 4.8, 3.2, 2.5 and 3.4, 2.7, 2.9 percent relative standard deviation, respectively. For snow, overall precision on Cl, NO₃ and SO₄ for 1990 (n = 45) and for 1991 (n = 28) was 11.2, 2.4, 3.2 and 4.9, 1.3, 1.8 percent relative standard deviation, respectively.

Accuracy of determination of cations—Accuracy was assessed by comparing measured values with certified values of NBS 2694-II simulated rainwater and also by recovery after known addition to duplicates of natural samples: For lake and stream water, the values measured for the NBS control indicated a slight positive bias for Ca (20%) in 1990; no bias was detected for Mg, Na or K in 1990 or 1991 (Table 7). Overall accuracy for 1990 (n = 12) was 100 ± 11 , 104 ± 3 , 104 ± 4 , and 102 ± 6 percent recovery for Ca, Mg, Na and K, respectively. In 1991 (n = 11), overall percent recoveries of 94 ± 11 , 99 ± 5 , 105 ± 14 and 101 ± 7 were realized for Ca, Mg, Na and K, respectively. For snow, comparison of measured values with the certified values of the NBS control indicated no bias in the determination of any cation (Table 8). Overall accuracy for 1990 (n = 8) was 102 ± 11 , 101 ± 8 , 114 ± 9 , and 102 ± 9 percent recovery for Ca, Mg, Na and K, respectively. In 1991 (n = 9), overall percent recoveries of 101 ± 8 , 110 ± 4 , 114 ± 11 , and 108 ± 0 were realized for Ca, Mg, Na and K, respectively.

Precision of determination of cations—Within run precision was computed as the percent relative standard deviation of randomly selected natural and augmented samples analyzed in duplicate: For lake and stream water, overall precision on Ca, Mg, Na, and K for 1990 (n = 24) and for 1991 (n = 22) was 1.4, 0.7, 1.5, 1.9, and 0.7, 1.2, 0.6, 1.4 percent relative standard deviation, respectively. For snow, overall precision on Ca, Mg, Na and K for 1990 (n = 16) and for 1991 (n = 18) was 3.4, 2.9, 2.9, 1.2 and 2.5, 2.2, 2.0, 1.2 percent relative standard deviation, respectively.

Quality assurance on ion analysis of rain samples—Replication of analysis of cations and anions on rain samples was difficult because of highly variable concentrations of each ion in a sample.

Chapter III

SEASONAL PATTERNS in HYDROCHEMICAL CONDITIONS and ANNUAL SOLUTE YIELDS of CATCHMENTS

The major processes in lakes and their catchments that contribute to the neutralization of acidic atmospheric deposition include chemical weathering, ion exchange and redox reactions (Schnoor and Stumm 1985). Year-round sampling for two years in seven alpine Sierran lakes and their outflowing streams has characterized the regional seasonal patterns in hydrochemical conditions and permitted identification of the relative importance of neutralization processes. When combined with measurements of atmospheric deposition of solutes and water and the discharge of the outflowing streams, the relative magnitude of acidic inputs and acidic neutralizing capacity of the catchment and lake was determined. Hence, we can evaluate the susceptibility of a regionally representative set of alpine Sierran catchments to acidic deposition.

In this chapter, we present time series plots of the solute concentrations in each lake and outflow to document seasonal patterns. Special attention is given to the period of snowmelt runoff. In addition, we present annual, volume-weighted mean concentrations of solutes in rain, snow and outflows, and use these data to do analyses of ion enrichment by catchment processes. Combined with hydrologic measurements, these hydrochemical data are used to calculate annual yields from the catchments and annual atmospheric deposition. Results for water years 1990 and 1991 (e.g. WY 90, 1 October 1989 to 30 September 1990) are presented for all seven lakes. For comparison, annual yields are presented for water year 1987 for Crystal, Ruby, Emerald, Pear and Topaz lakes based on revised hydrological calculations with data from Sickman and Melack (1989). Because measurements of the seven catchments are continuing for water years 1992 and 1993, further analysis in progress under our current ARB contract will combine all the years and provide the information necessary for thorough time series statistics and syntheses.

Lake Chemistry

For each lake, time-series plots of volume-weighted mean (VWM) concentrations of pH and ANC, nitrate and sulfate, sum of calcium, magnesium, sodium, potassium (SBC) and silica, and chloride and specific conductance for the period October 1989 to November 1991 are presented to show the seasonal patterns of these constituents (Figures 12 through 15). These figures also show the duration of ice-cover on the lakes. Owing to the wide variation in lake chemistry, the vertical axes have different scales.

The second criterion applied to the data set is the computation of the conductance deficit (calculated conductance minus measured conductance). If the conductance deficit is zero, then all important ionic species have been determined and measured without bias. The mean conductance deficit for lake and stream samples was $1.9 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C (Fig. 7). This indicates that an excess of ions was measured and coupled with the ion difference bias toward negative charge suggests that an anion was overestimated. A reanalysis of acid neutralizing capacity (ANC) on 15 filtered lake samples whose ion difference was large yielded ANC values lower than values obtained from unfiltered samples. This suggests that particulate ANC is contributing negative charge to the dissolved anion pool when the summation is computed.

The mean conductance deficit for snow was 0.02 and $0.34 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C for 1990 and 1991, respectively (Figures 8 and 9). The negative conductance deficit coupled with the positive ion difference suggests an underestimation of anions. Unmeasured bicarbonate is a possible contributor to the charge imbalance. Because our detection limit for the Gran titration is $2 \mu\text{eq}\cdot\text{L}^{-1}$, we have not detected HCO_3^- when snow has been analyzed for acid neutralizing capacity. An overestimation of H^+ effects the same bias. Results from 1992 on 350 measurements of pH on melted snow under Argon and after four hours exposure to ambient CO_2 levels in the laboratory demonstrate up to $3 \mu\text{eq}\cdot\text{L}^{-1}$ (mean = $1.5 \mu\text{eq H}^+\cdot\text{L}^{-1}$) more H^+ in the latter samples. The mean conductance deficit for rain samples was -0.95 and $+1.42 \mu\text{S}\cdot\text{cm}^{-1}$ at 25°C in 1990 and in 1991, respectively (Fig. 10 and 11). The conductance deficit and positive ion difference obtained for 1990 may suggest an underestimation of anions. We have demonstrated loss of organic anions in chloroform preserved rain samples maintained at 4°C . In 1991 chloroform preserved rain samples were kept frozen until analysis. In 1991, both the conductance deficit and the percent ion difference were positive, and very small.

the lake is masked during snowmelt but its impact on the lake's chemistry becomes more pronounced during late autumn and winter.

In Topaz Lake, pH decreased from October through June and increased from July to October (Figure 12). The lowest pH observed was 5.6 and was measured during April 1991. ANC in Topaz Lake had peaks during early spring followed by moderate declines during snowmelt. Maximum ANC values recorded were between 50 and 65 $\mu\text{eq L}^{-1}$ under ice-cover. Minimum values occurred after snowmelt and were between 24 and 35 $\mu\text{eq L}^{-1}$. Periods of increasing ANC and decreasing pH were observed during autumn and winter of both water years. In water year 1991 the inverse relationship lasted for over six months. However, in contrast to Spuller Lake, the ANC buildup was relatively small and was not associated with low dissolved oxygen (Figure 22).

In Crystal Lake, pH declined during the study period from a high of 6.7 in October 1989 to 6.1 in November 1990 (Figure 12). The lowest pH measured was 5.9 which occurred prior to snowmelt in April 1991 (Figure 26). ANC in Crystal Lake had little change during water years 1990 and 1991 and ranged from 56 to 82 $\mu\text{eq L}^{-1}$. ANC increased in the lake beginning in the summer, peaked prior to snowmelt in the early spring and declined slightly during snowmelt. ANC increases during periods of stratification were slight and the water column was well oxygenated throughout (Figure 16). Vertical distribution of ANC in the water column was uniform.

In Emerald Lake, from October 1989 until January 1991 pH was remarkably constant ranging from 6.2 to 6.3 (Figure 12). From January 1991 pH declined and reached a minimum of 5.7 in April at the onset of snowmelt (Figure 26). From April 1991 until the end of the study period pH increased gradually and reached 6.1 in November 1991. In contrast to pH, an annual pattern of ANC in Emerald Lake was evident. In both water year 1990 and 1991, ANC increased in the summer, autumn and winter with maximum ANC reached in the early spring. During snowmelt, ANC fell sharply and reached minima in the summer. The range of ANC observed in Emerald Lake during the 26 months of the study was 20 to 44 $\mu\text{eq L}^{-1}$. Both ANC and oxygen concentrations were consistent throughout the water column in Emerald Lake during most of the study period (Figure 17).

In Lost Lake, pH ranged from a high of 6.3 to a low of 5.4 recorded in late April 1991 (Figure 12). In water year 1990, pH reached a minimum of 5.9 in June while in water year 1991 the lowest pH was measured in April 1991. pH maximum occurred in the winter during water

The volume-weighted mean concentrations at Pear Lake are based on samples taken at 5 depths; at Emerald, Crystal, Ruby and Spuller lakes 4 depths were used and at Topaz and Lost lakes samples from 3 or 4 depths were used. To calculate VWM concentrations, the value from each depth was applied to a stratum of the lake on the basis of temperature and oxygen stratification. The volume of each stratum was calculated from a hypsographic curve (determined from bathymetric maps). In general, surface samples had greater influence on VWM chemistry than samples collected near a lake's bottom because strata near the surface of the lake have greater volume per meter of depth.

Seasonal Patterns of pH and ANC. In Ruby Lake, pH declined gradually from October 1989 (6.6) until a minimum of 6.2 was reached in June 1990 (Figure 12). After June, pH increased slightly and remained constant until February 1991 (ca. 6.2). Between February and April pH declined to 5.8; pH increased to 6.1 in July 1991 and was steady for the remainder of the study period. During winter 1989-90 and 1990-91, ANC increased and reached maxima during early spring. During the snowmelt seasons, ANC declined and reached minima during midsummer (Figure 12), the time of greatest outflow discharge (Figures 23 and 26). Over the study period, ANC ranged from 55 to 80 $\mu\text{eq L}^{-1}$. ANC increased while pH declined. ANC increased in the hypolimnion under low oxygen conditions (Figure 20).

In Spuller Lake, seasonal patterns of pH were similar to those in Ruby Lake (Figure 12). The pH declined from October 1989 (6.7) until June 1990 (6.1) followed by a slight increase which continued through the summer and autumn. pH peaked again in January 1991 (6.2) then declined during snowmelt and reached a minimum of about 5.8 in late July. For the remainder of the study period VWM pH was between 6.0 and 6.2. For both water year 1990 and 1991, ANC was lowest in midsummer (37 $\mu\text{eq L}^{-1}$ and 36 $\mu\text{eq L}^{-1}$ respectively). ANC maxima were observed in the early spring prior to snowmelt during both years with values of 123 and 117 $\mu\text{eq L}^{-1}$ respectively. These ANC maxima were followed by sharp declines induced by snowmelt flushing of the lakes (Figures 23 and 26).

As in Ruby Lake, ANC had an inverse relationship with pH during periods of lake stratification. During the period October 1989 until March 1990 pH declined as ANC increased. In contrast to Ruby Lake, oxygen concentrations in Spuller Lake were relatively high (between 4 and 7 mg L^{-1} (Figure 21)), and the buildup of ANC and reduction of pH were observed throughout the lake. Glacial moraines and talus fields comprise a large percentage of the Spuller watershed and may store an appreciable amount of snowmelt runoff. This groundwater input to

Several perennial springs have been observed in the Ruby catchment. These springs have much higher ANC and solute concentrations than other inflows to the lake (Sickman and Melack 1989). During winter periods, slightly elevated levels of ANC have been observed just below the ice. We believe that springwater flows into the lake and, being near 0 °C, mix only with the upper few meters of the lake. Because the volume of these inputs is a small fraction of the lake's volume, groundwater has only a slight effect on VWM ANC in Ruby Lake.

Groundwater inputs to Spuller Lake have a major effect on lake chemistry. Spuller Lake is shallow with a small volume and groundwater inputs mix throughout the water column. After snowmelt diminishes, groundwater inputs gradually increase the ANC and solute concentrations of the lake.

Seasonal Patterns of Nitrate and Sulfate - In Ruby Lake, sulfate had little seasonal variation (Figure 13) and ranged from 7.4 to 10.3 $\mu\text{eq L}^{-1}$. Sulfate concentrations were well regulated in Ruby Lake although there was a slight decrease during the snowmelt period of water year 1990. Slight decreases in nitrate were also observed during the water year 1990 snowmelt in Ruby Lake. Nitrate levels in the lake were low and ranged from 0.05 to 2.9 $\mu\text{eq L}^{-1}$. During water year 1991, nitrate concentrations increased from November 1990 until a maximum was reached in July 1991. During the remainder of the study nitrate declined.

In Spuller Lake, annual variability of sulfate was large and had a regular pattern of peaks during early spring and minima during early to mid-summer (Figure 13). Snowmelt discharge caused steep declines in sulfate, reducing values by more than 20 $\mu\text{eq L}^{-1}$ in three months. The highest sulfate value measured was 29.5 $\mu\text{eq L}^{-1}$ during April 1991. In contrast to sulfate, nitrate levels in Spuller Lake were low and ranged only from 0.05 to 4.2 $\mu\text{eq L}^{-1}$ (Figure 13). Nitrate concentrations increased during snowmelt (maxima were reached in July 1990 and August 1991) and declined from midsummer through autumn. Nitrate concentrations were at or near the detection limit by the end of autumn. During portions of snowmelt 1990 and 1991, nitrate concentrations increased as sulfate concentrations declined. This relationship is due to input of meltwater having lower sulfate and higher nitrate concentrations than lake-water.

In Topaz Lake sulfate increased during the late summer and reached peak values in late winter (Figure 13). During snowmelt, sulfate declined and reached lowest levels during the summer. Sulfate ranged from 3.6 to 9.9 $\mu\text{eq L}^{-1}$. Nitrate concentrations varied in Topaz Lake from 66.7 $\mu\text{eq L}^{-1}$ during October 1989 to levels below detection during the summers 1990 and

year 1990 and during late autumn in water year 1991. ANC had a consistent pattern in Lost Lake with peaks during winter and minima in early summer. During both water years, snowmelt induced a steep decline in ANC. ANC ranged from 16 to 60 $\mu\text{eq L}^{-1}$ with similar annual minima in both water years. ANC had no vertical heterogeneity in Lost Lake (Figure 18).

In Pear Lake, the seasonal pattern of pH was similar to that in Emerald Lake although pH was slightly lower in Pear Lake (Figure 12). As in Emerald Lake pH varied less than 0.1 units from October 1989 until January 1991. After January 1991, pH declined and reached a minimum of 5.6 in mid-April 1991. Thereafter pH increased until midsummer and then declined through the remainder of the study. Greatest ANC was observed just prior to snowmelt and minima were reached in early summer. ANC ranged from 21 to 39 $\mu\text{eq L}^{-1}$ during water years 1990 and 1991. During times of thermal stratification, low oxygen concentrations were measured in the hypolimnion of the lake, and ANC levels near bottom were from 10 to 80 $\mu\text{eq L}^{-1}$ higher than in surface waters (Figure 19).

Factors regulating ANC in Sierran lakes - Snowmelt runoff, groundwater inputs and in-lake processes are the major factors likely to control seasonal patterns of ANC in montane lakes of the Sierra Nevada. In the study lakes, snowmelt runoff was an important factor influencing ANC. Rapid ANC depletion during snowmelt was followed by gradual recovery through the rest of the year. In-lake processes and groundwater inputs can influence lake ANC during non-snowmelt periods.

Most of the lakes had some hypolimnetic ANC buildup but only in the deep lakes, Pear and Ruby, was the increase substantial (Figures 19 and 20). These deep lakes had longer and stronger periods of stratification. In addition, deep lakes may be more biologically productive per unit area resulting in greater rates of decomposition in the hypolimnion. Decomposition of organic matter consumes oxygen. Long periods of anoxia allow a relatively large amount of ANC to accumulate in deep lakes.

Of the seven study lakes, five have outflowing streams which cease flowing by August of each year. Only the outlets to Ruby and Spuller lakes flowed in the autumn and early winter and only Ruby's outlet flows year-round which suggests that these lakes receive prolonged inputs from groundwater. The impact of groundwater on lake chemistry is variable and is related to lake volume.

However, unlike Spuller and Topaz lakes, sulfate in Lost Lake continued to decline during the summer and minimum values were reached in the autumn. The range of sulfate concentrations in Lost Lake was 3.2 to 8.2 $\mu\text{eq L}^{-1}$. Nitrate concentrations are at or near the detection limit most of the time. The highest level recorded was 1.4 $\mu\text{eq L}^{-1}$ during November 1991. Nitrate in the lake did not increase during snowmelt.

In Pear Lake, sulfate varied moderately during water years 1990 and 1991 (Figure 13). Some depression in sulfate concentrations occurred during snowmelt, and peak values were generally measured during winter and early spring. During water year 1990, nitrate levels peaked during snowmelt, which corresponded with the sulfate minimum. In water year 1991, peaks in nitrate coincided with sulfate peaks. The range of nitrate in Pear Lake was from below detection to 3.3 $\mu\text{eq L}^{-1}$.

To summarize, sulfate concentrations varied least in the larger and deep lakes (Ruby, Crystal, Emerald and Pear) and most in the lakes with lowest volumes (Spuller, Topaz and Lost). Larger lakes tend to moderate the effects of inputs of sulfate from inflows and groundwater and from in-lake processes near lake sediments. Depending on depth and volume, inputs from groundwater and inflows can mix through the entire water column (Spuller Lake) or be confined to certain lake-strata due to thermal stratification (eg. Emerald and Ruby lakes). Sulfate declined during snowmelt in all lakes due to dilution by melting snow with lower sulfate concentration.

Nitrate concentrations in the seven study lakes were low. Nitrate uptake within the catchments and by aquatic plants may explain the low levels observed. During snowmelt, nitrate increased at most lakes due to inputs of streamwater enriched with nitrate. In addition to atmospheric deposition, in-lake processes such as nitrification of ammonium or re-inundation of lake sediments can supply large amounts of nitrate to lakes under certain conditions (eg. Topaz Lake).

Seasonal patterns of base cations and silica - In Ruby Lake, the concentration of the sum of base cations (calcium, magnesium, sodium, potassium) varied little during the 26 months of the study; the range observed was 64 to 78 $\mu\text{eq L}^{-1}$ (Figure 14). SBC decreased during snowmelt and increased through the remainder of the year. Peak SBC concentrations occurred in the spring, prior to snowmelt. There was a close relationship between SBC and silica in Ruby Lake (Figure 14) with peaks in spring followed by declines through snowmelt. Silica concentrations ranged from 28 to 39 μM .

1991. Nitrate concentrations were low most of the year and, excluding data from October 1989, the highest level measured was $2.9 \mu\text{eq L}^{-1}$.

There are several probable explanations for the high nitrate concentrations in Topaz Lake: atmospheric inputs, in-lake processes that produce nitrate, evapoconcentration of the lake or a combination of the three. Of these explanations, atmospheric inputs and evapoconcentration are, by themselves, unlikely to be the cause since there were no large rainstorms observed during the autumn of 1989 and rain which did fall in this period had low nitrate concentration. If the nitrate in the lake was derived entirely from atmospheric deposition we would also expect sulfate concentrations to be high, since sulfate is a major component of summer rain. If evapoconcentration were the primary factor, all major ions should have increased, but this was not observed. The more likely explanation for the excess nitrate in Topaz Lake is nitrification of ammonium produced in the lake itself.

In Crystal Lake, the range of values of sulfate was the smallest of the seven study lakes: from 5.7 to $7.3 \mu\text{eq L}^{-1}$ (Figure 13). No clear annual pattern was discernable but sulfate did decrease slightly during snowmelt. Similarly, nitrate in Crystal Lake was constant with concentrations below detection for most of the study period, and being above this level only during autumn and early winter 1989 and 1991 (Figure 13). The highest nitrate concentration measured in Crystal Lake was $1.1 \mu\text{eq L}^{-1}$.

In Emerald Lake, sulfate was usually moderated during the study period, varying from 5.6 to $7.8 \mu\text{eq L}^{-1}$. An exception was the high level of sulfate found at a depth of 1 meter in March 1990. The sulfate concentration at this depth was $27.6 \mu\text{eq L}^{-1}$; the rest of the water column had concentrations between 7.6 and $8.0 \mu\text{eq L}^{-1}$. It is uncertain what caused this high sulfate concentration although it is likely that inflowing water with high sulfate is responsible. This water, being near 0°C , would be confined to the upper meters of the lake because of temperature stratification (Figure 17). Nitrate in Emerald Lake had a consistent pattern during water years 1990 and 1991 (Figure 13). Levels increased gradually from early winter through the following snowmelt period and then declined during the summer and autumn. These decreases were probably due to biological uptake. As with nitrate in Spuller Lake, the maximum nitrate levels in Emerald Lake tended to coincide with minimum sulfate levels. Nitrate in Emerald Lake ranged from below detection to $3.9 \mu\text{eq L}^{-1}$.

In Lost Lake, as in the other small lakes (Spuller and Topaz), seasonal patterns of sulfate were well defined with peaks in early spring and steep declines during snowmelt (Figure 13).

autumn and winter of 1990 and during the autumn of 1991. The overall range of silica concentrations in Lost Lake was 13 to 46 μM .

In Pear Lake, the times-series of base cations and silica resembles that for Ruby Lake (Figure 14). Both constituents varied relatively little during the study period. Peak concentrations for both variables occurred in early spring and declines were observed during snowmelt. Silica generally varied directly with base cations; inverse correlations were noted during late summer and winter 1990 and during autumn 1991. The range of concentrations measured was 28 to 44 $\mu\text{eq L}^{-1}$ for base cations and 14 to 24 μM for silica.

In summary, seasonal patterns of base cations and silica were dominated by snowmelt runoff. Peak concentrations for both usually occurred in the early spring, prior to snowmelt runoff. However, there were some exceptions to these generalizations. At Crystal Lake, silica levels increased in the lake during the snowmelt periods of 1990 and 1991. In addition, base cations and silica concentrations were inversely related at all lakes (especially at Crystal Lake) for some time during the study period. Inverse relationships generally occurred during the autumn and early winter periods. In most lakes, base cation concentrations dropped more during snowmelt than did silica concentrations.

Seasonal patterns of chloride and specific conductance - In Ruby Lake, chloride during the snowmelt period of water year 1990 reached a minimum during July and increased during the remainder of the water year (Figure 15). During water year 1991, chloride concentrations declined the entire year; no steeper decline was observed during snowmelt. Specific conductance (SC) in Ruby Lake increased throughout most of water year 1990 and during the first part of water year 1991. SC peaked in late January 1991 then declined during snowmelt, reaching a minimum in July. For the remainder of the study period SC increased.

In Spuller Lake, there was a clear seasonal pattern in chloride concentrations: peaks prior to snowmelt, minima near the end of snowmelt runoff (Figure 15). In contrast to other solutes such as sulfate, base cations and ANC, the range of chloride concentrations observed was small: from 1.5 to 3.2 $\mu\text{eq L}^{-1}$. The relatively small range of chloride concentrations in Spuller Lake is indicative of the conservative nature of chloride in catchment processes. Specific conductance in Spuller Lake had a pattern similar to chloride except that its minimum during water year 1991 occurred about one month earlier. The overall range of SC in Spuller Lake was large: from 4.9 to 15.4 $\mu\text{S cm}^{-1}$.

In Spuller Lake, base cations had a large annual change in concentration (Figure 14). As was the case with other solutes, the large increase observed during non-snowmelt periods can probably be attributed to groundwater inputs. During snowmelt, SBC declined sharply, reaching minimum values in early to mid summer. In Spuller Lake, SBC ranged from 44 to 138 $\mu\text{eq L}^{-1}$. Silica concentrations in Spuller Lake did not have a regular seasonal pattern although some decrease occurred during snowmelt (Figure 14). The magnitude of the silica decline during snowmelt was much smaller than the decline for base cations. Interestingly, there were periods where silica declined or stayed constant as base cations increased. This inverse relationship was observed mainly during autumn and winter periods.

In Topaz Lake, base cations generally decreased during snowmelt and increased through the remainder of the year (Figure 14). In October 1989, however, base cations levels were high. The overall range of base cations observed in Topaz Lake (excluding October 1989) was 33 to 74 $\mu\text{eq L}^{-1}$. Variations in silica concentration were smaller than those for base cations (Figure 14). No clear seasonal pattern was evident except for a slight depression during snowmelt.

In Crystal Lake, base cations followed a seasonal pattern: declines during snowmelt, and increases at other times of the year (Figure 14). The range of SBC observed in the lake was 69 to 92 $\mu\text{eq L}^{-1}$. In contrast to base cations, silica in Crystal Lake increased during the snowmelt periods of water year 1990 and 1991 (Figure 14). In addition there were periods when silica declined as base cations increased. Overall there was a strong inverse relationship between these constituents in Crystal Lake. Silica concentrations ranged from 48 to 70 μM .

In Emerald Lake, base cation concentrations followed the general, snowmelt influenced trend with decreases during snowmelt and increases during the rest of the year (Figure 14). The range of base cation concentrations was 30 to 59 $\mu\text{eq L}^{-1}$. Silica levels in Emerald Lake varied only from 26 to 40 μM . Peak concentrations were measured in early spring and declines occurred during snowmelt. During the period of August 1990 through March 1991 and the period after July 1991, there was an inverse relationship between silica and base cations in Emerald Lake.

In Lost Lake, as in the other smaller lakes, base cations had a regular annual pattern (Figure 14). Peak concentration occurred in the late winter in water year 1990 and in early spring during water year 1991. Snowmelt runoff induced steep drops in SBC levels. The overall range of base cations was relatively large (25 to 70 $\mu\text{eq L}^{-1}$). During most of the study period, silica concentrations varied directly with base cation levels. An inverse relationship occurred during the

altitude and relief. Certain lake-specific parameters appear to have a large effect on lake chemistry. A lake's response to water inputs during both snowmelt and non-snowmelt periods is related to its volume and depth.

Large, deep lakes moderated chemical changes induced by snowmelt and groundwater inputs while small, shallow lakes had large annual changes in solute chemistry. These smaller lakes tended to become more dilute during snowmelt and were more enriched by groundwater inputs. Of the seven study lakes, Spuller Lake had the greatest annual variation in water chemistry because of the lake's small size and the large amount of groundwater the lake receives during non-snowmelt periods.

The dominant event in the annual cycle of Sierran lakes is the period of snowmelt runoff. In most lakes, the majority of the solutes decreased during snowmelt due to dilution. The notable exception was nitrate which commonly increased during snowmelt runoff. During snowmelt, the lakes' chemistry tended to become more like that of the snowpack: lower pH, ANC, base cations and relatively enriched in nitrate.

Using post-snowmelt pH, ANC and base cations as indices of a lake's sensitivity to acidification, Pear and Lost lakes appear to be the most vulnerable and Ruby and Crystal lakes the least vulnerable. Lost Lake consistently had the lowest VWM mean pH and ANC (pH, 5.46; ANC, $16 \mu\text{eq L}^{-1}$). In addition, during snowmelt runoff, ANC concentrations in the major inflows to Pear and Lost lakes are very low. For example, during the period of 15 May to 3 June 1991, the ANC in the main inflow to Pear Lake ranged from 6 to $8 \mu\text{eq L}^{-1}$. At Ruby and Crystal lakes, ANC in the inflows stayed above $20 \mu\text{eq L}^{-1}$ during snowmelt runoff.

Outflow Discharge, Chemistry and Solute Flux

Outflow discharge during snowmelt 1990 - In Ruby Lake, snowmelt began in early May and increased rapidly in early June (Figure 23). Peak daily discharge occurred during the period from mid June to mid July. Snowmelt gradually diminished through August. Snowmelt runoff in the Ruby catchment occurs late into the water year with long periods of high runoff because of the large size and high altitude of the watershed (Table 1).

At Spuller Lake, outflow discharge increased from base flow levels in early May (Figure 23). Peak daily flows occurred during June and early July and then declined rapidly.

In Topaz Lake, both chloride and specific conductance had peaks during late winter to early spring and then declined during snowmelt periods. Declines during melt were followed by increases during the summer and autumn. Both parameters were high during October 1989.

In Crystal Lake, chloride declined during the autumn of 1989 then remained constant until the summer of 1990 (Figure 15). During autumn 1990, chloride concentrations declined slightly. Chloride concentrations during water year 1991 followed a more familiar pattern: peak during early spring, decline during snowmelt and a post-melt recovery. In Crystal Lake, SC declined for much of water year 1990, reaching minimum in June 1990. For the balance of the water year SC increased. During water year 1991, SC increased steadily from October 1990 until a maximum value in April 1991 and then it declined sharply during snowmelt. After snowmelt 1991, SC increased gradually for the remainder of the study.

In Emerald Lake, chloride and specific conductance followed the usual pattern of peaks in early spring and declines during snowmelt periods. During non-snowmelt periods both parameters generally increased. Overall, SC ranged over $8 \mu\text{S cm}^{-1}$ in Emerald Lake and there was a strong relationship between chloride and SC in the lake.

In Lost Lake, the seasonal patterns of chloride and specific conductance were regular: declining during snowmelt and increasing during non-snowmelt periods. The range of values were large, with chloride ranging from 1.7 to $10.0 \mu\text{eq L}^{-1}$ and SC ranging from 2.9 to $8.8 \mu\text{S cm}^{-1}$.

In Pear Lake, chloride concentrations increased during non-snowmelt periods reaching maximum values in late winter or early spring. During snowmelt periods of both water years, chloride declined rapidly and reached minima during the summer and autumn. Specific conductance in Pear Lake had a similar pattern except that SC minima occurred at the end of snowmelt in the summer.

To summarize, both chloride and specific conductance followed the same patterns as the other solutes with peak values prior to snowmelt and large declines during runoff. The range of values for both parameters tended to be greater in the smaller lakes (Spuller, Topaz and Lost) except that chloride concentrations in Spuller Lake ranged only $1.7 \mu\text{eq L}^{-1}$.

Summary - The lakes of this study are a representative cross-section of lakes found in the Sierra Nevada. They varied in surface area, depth and volume and their catchments ranged in area,

In Spuller outflow, pH declined slightly at the onset of snowmelt and reached a minimum of 6.0 on May 28 (Figure 23). The pH in the outflow increased as discharge increased during the beginning of June, then held steady until a moderate decline in mid June. This drop in pH was short-lived and pH levels increased slightly and held steady for the remainder of the snowmelt period. Two conspicuous declines in outflow ANC occurred: one at the onset of snowmelt and one during the large increase of discharge in early June. The minimum value of ANC recorded was 35 $\mu\text{eq L}^{-1}$. After June, ANC gradually increased in the outflow.

In Topaz outflow, the sampling intensity was low during April (Figure 23). During May, pH in the outflow declined during high runoff early May and then was variable for the remainder of snowmelt. ANC in the outflow declined slowly during the first phase of snowmelt and more rapidly during peak flows in early May. After peak discharge in May, ANC gradually increased and then stabilized through the remainder of snowmelt.

In the Crystal Lake outflow, pH was variable during snowmelt although there was a gradual decline during the first half of snowmelt (Figure 23). ANC declined only slightly during snowmelt; the overall range of values was from 65 to 81 $\mu\text{eq L}^{-1}$.

In the outflow to Emerald Lake, few samples were collected during March and April (Figure 23). Starting in early May, pH declined slightly then gradually rose as runoff increased during May and June. ANC in the outflow generally declined throughout the snowmelt period. Periods of ANC recovery occurred during periods of rapidly increasing runoff in early May and early June. The lowest pH and ANC measured in the outflow to Emerald Lake during snowmelt 1990 were 6.0 and 23 $\mu\text{eq L}^{-1}$ respectively.

In the Lost Lake outflow, pH declined at the onset of snowmelt during March (Figure 23). Following a minimum of pH 5.8 during April, pH increased gradually through the end of May, then declined again as discharge increased in early June. As melt runoff declined in June, pH rose sharply. In the outflow to Lost Lake, ANC gradually declined during March and April and reached a minimum of 20 $\mu\text{eq L}^{-1}$ in mid May. ANC in the outflow recovered for a short period in the last half of May then declined again as discharge peaked in early June.

Sampling of the outflow of Pear Lake was infrequent during April 1990. Starting in late April, pH declined and reached a minimum value of 5.8 just before mid May. Following this minimum, pH gradually increased and then stabilized during the remainder of snowmelt despite a large increase in the runoff in June. ANC in the lake's outflow declined during two periods during

At Topaz Lake, snowmelt in 1990 had large fluctuations in daily discharge (Figure 23). The melt period had three phases: an early phase in April with moderate flow rates, a middle phase in early May with high flows of short duration, and a phase from late May through June of relatively low flows. In contrast to Ruby and Spuller Lakes, snowmelt at Topaz Lake was rapid and resulted in flow rates as high as 40,000 m³ per day. The outlet to Topaz Lake was dry by July 1990.

At Crystal Lake, snowmelt began in late April, continued at a moderate rate during May and increased rapidly in early June (Figure 23). The hydrographs during May and June at Crystal and Spuller lakes are quite similar. After mid June, outflow discharge declined rapidly at Crystal Lake and no flow continued after late July. Despite having a relatively large watershed (Table 1), peak daily discharge and the period of snowmelt runoff are small. Water balances constructed for the catchment indicate that a significant proportion of water exits the catchment as groundwater and is not measured by the gauging station.

At Emerald Lake, the snowmelt hydrograph had large daily changes (Figure 23). Snowmelt began in March (the small peak observed in February was caused by displacement of lake water by snow loading on the frozen lake) and increased to high to moderate rates in April. By early May snowmelt was proceeding rapidly with peak daily discharge occurring in mid June. The snowmelt runoff was almost over by the end of June.

At Lost Lake, snowmelt began in late March, gradually increased through April and May, and peaked in the first half of June (Figure 23). After mid June runoff declined and the outlet was dry by the end of July. Because of the small size of the catchment, peak outflow discharge at Lost Lake was never more than 5500 m³ per day.

At Pear Lake, the lake water displaced by the February snowstorm is obvious in the hydrograph (Figure 23). Snowmelt began in March, increased gradually through April and May, and reached peak flows during early June. By August the outflow to Pear Lake was dry.

Patterns of pH and ANC during snowmelt 1990 - In Ruby outflow, pH declined slightly at the onset of snowmelt (6.2) and then remained stable during the remainder of the snowmelt period (Figure 23). ANC declined sharply during the first weeks of snowmelt and reached a minimum of 52 µeq L⁻¹. From late May until late June, ANC gradually increased, then decreased sharply reaching a minimum of 48 µeq L⁻¹ in early July.

In the Lost Lake outflow, sulfate increased slightly at the onset of snowmelt and had a second peak as discharge increased rapidly during early June (Figure 24). Following these peaks sulfate declined as discharge continued to increase. Nitrate levels were below the detection limit for the majority of the snowmelt period. The highest value was recorded in mid April ($2.1 \mu\text{eq L}^{-1}$).

In the outflow to Pear Lake, it appeared that sulfate remained constant from March until the end of April despite infrequent sampling (Figure 24). From late April until mid May, sulfate declined as runoff increased and then concentrations were variable through the remainder of the melt period. The time series of nitrate in the outflow of Pear Lake was very similar to that at Emerald outflow. Nitrate increased from less than 1 to over $10 \mu\text{eq L}^{-1}$ from late April until late May and then declined quickly as runoff increased in early May. From mid May until mid June nitrate declined only slightly.

Patterns of base cations and silica during snowmelt 1990 - In the outflow to Ruby Lake, SBC declined smoothly during the early part of snowmelt, recovered slightly near the mid-point of melt and then remained constant during the remainder of melt (Figure 25). Silica concentrations began declining at the onset of melt and continued to gradually decline well into July. Between mid July and late August, snowmelt runoff diminished and silica concentrations rose slightly.

In the Spuller Lake outflow, SBC declined at the onset of snowmelt and then increased for a short period of time near the end of May when discharge declined (Figure 25). As runoff grew during June and July, SBC declined steadily reaching a minimum during late June and then increased through the remainder of the period as discharge declined. The overall range of SBC observed in the outflow of Spuller Lake was relatively large (46 to $87 \mu\text{eq L}^{-1}$). Changes in silica concentration in the Spuller outflow generally followed those of SBC except during the period of highest runoff during mid June to mid July. During this period silica levels rose as SBC concentration declined. Silica concentrations in the outflow ranged from 11 to $57 \mu\text{M}$ during the melt period.

In the Topaz Lake outflow, the change in SBC and silica concentrations were smooth and closely followed changes in ANC (Figure 23 and 25). Both constituents declined rapidly during the period of high runoff in May and then increased slightly as discharge declined during the remainder of the melt period.

snowmelt 1990: during the first half of melt and during the period of greatest runoff near the beginning of June. The lowest ANC valued measured was $15 \mu\text{eq L}^{-1}$.

Patterns of sulfate and nitrate during snowmelt 1990 - In Ruby outflow, sulfate concentrations had little variation other than a slight depression at the beginning of melt and a slight increase as runoff peaked in late June (Figure 24). Sulfate concentrations ranged from 7.9 to $10.1 \mu\text{eq L}^{-1}$. Nitrate concentrations in the outflow of Ruby Lake were more variable. Nitrate increased as snowmelt runoff increased during May and reached a peak of $6.8 \mu\text{eq L}^{-1}$. Following this peak, nitrate declined as runoff increased rapidly and reached a minimum of $0.7 \mu\text{eq L}^{-1}$ at mid June.

In the Spuller Lake outflow, sulfate declined during the earliest part of snowmelt, then increased slightly as runoff declined in late May (Figure 24). As discharge rapidly increased in June, sulfate concentrations declined falling from 16.5 to $5.9 \mu\text{eq L}^{-1}$ in about one month. Sulfate gradually increased as snowmelt runoff diminished in July and August. Nitrate concentrations in the outflow gradually increased during the early part of melt, peaking ($11.0 \mu\text{eq L}^{-1}$) as runoff grew in early June. Following this peak, nitrate declined until it was below detection in early July and, as runoff declined, increased gradually in July and August.

At Topaz Lake, sampling of the outflow was infrequent during April. During the remainder of snowmelt, sulfate declined with the greatest decrease occurring during peak discharge in early May (Figure 24). Nitrate concentration in the outflow was higher in late April compared to March. From late April through the end of snowmelt, nitrate declined to levels below detection. Coarse sampling in April makes it difficult to characterize the behavior of sulfate and nitrate during the early portion of snowmelt.

In the outflow of Crystal Lake, sulfate and nitrate were remarkably constant (Figure 24). Sulfate concentrations varied less than $1 \mu\text{eq L}^{-1}$ during snowmelt despite a seven-fold increase in outflow discharge. Nitrate was below the detection limit for the majority of the period, becoming measurable only for a brief period during peak runoff in June.

In Emerald outflow, sulfate concentrations varied little but were not as constant as at Crystal Lake (Figure 24). Overall, sulfate declined during snowmelt in a stair-step fashion which did not appear to be related to discharge volume. Nitrate levels in the outflow to Emerald Lake varied from below detection to $7.1 \mu\text{eq L}^{-1}$ during the runoff period, increasing greatly during the rising limb of the snowmelt hydrograph. As runoff reached high levels in early May, nitrate began to decline and reached minimum concentrations of about $4 \mu\text{eq L}^{-1}$ from mid May until mid June.

After being dry for several months, the outlet to Crystal Lake began to flow during the latter part of May (Figure 26). Runoff increased rapidly, reaching peak daily flows by mid June. Following this peak, runoff declined during late June and then peaked again in early July. The outlet to the lake was dry in early August. The snowmelt period was shorter and peak daily flows greater in 1991 compared to 1990.

At Emerald Lake, snowmelt began in late April during 1991. During the first weeks of May, runoff was variable but as May progressed flows increased sharply (Figure 26). Peak daily discharges occurred during June and were followed by a brief decline in runoff at the end of June. During the first week of July, outflow discharge increased and peaked again; snowmelt was mostly over by the end of July. The snowmelt period of 1991 began later and ran longer than in 1990.

At Lost Lake, runoff from snowmelt began in early May and grew slowly during May and early June with peak discharges measured mid June until early July (Figure 26). Following peak runoff in June there was a brief decline in discharge and then an increase in melt during the first part of July. In contrast to 1990, snowmelt in 1991 occurred in a shorter span of time and peak daily discharges were higher.

At Pear Lake, outflow discharge began to rise in late April and rose and fell during much of May (Figure 26). By the end of May, runoff began to rise rapidly and peak daily discharge occurred in mid June. The late June decline in runoff that was observed at Crystal, Emerald and Lost lakes also occurred at Pear Lake. Despite being separated by hundreds of miles, the snowmelt hydrographs for these four lakes and Topaz Lake had many similarities which suggests large scale meteorological events affect the timing and rate of snowmelt runoff.

Patterns of pH and ANC during snowmelt 1991 - In the outflow to Ruby Lake, pH increased during rising discharge in late May and then declined as runoff reached high levels in early to mid June (minimum = 5.8; Figure 26). From mid June until mid July, pH increased to 6.4 then declined again on the falling limb of the hydrograph and then increased slightly in early autumn. The acid neutralizing capacity in the outflow to Ruby Lake decreased from the onset of snowmelt until a minimum of $36 \mu\text{eq L}^{-1}$ was reached in the latter half of June. Following this minimum, ANC increased and then remained stable through the remainder of the melt period. The ANC change in the outflow observed during the snowmelt period was $46 \mu\text{eq L}^{-1}$.

In the outflow to Crystal Lake, base cation concentrations were well moderated, varying from 69 to 83 $\mu\text{eq L}^{-1}$ during the snowmelt period (Figure 25). The greatest change occurred during the rapid increase of runoff during early June. In contrast to SBC, silica concentrations in the outflow to Crystal were variable during most of the snowmelt period, becoming stable on the falling limb of the hydrograph after mid June. The overall range of silica values measured was from 38 to 76 μM .

In the Emerald Lake outflow, base cation concentrations declined throughout most of the snowmelt period with the steeper declines occurring during periods of rapidly increasing runoff (Figure 25). Silica concentrations in the outflow to Emerald Lake declined at the onset of snowmelt reaching minimum values in mid May, and then increased until runoff peaked in early June. As snowmelt runoff decreased in June, so did silica concentrations.

In the Lost Lake outflow, base cations and silica had consistent declines in concentration from February until mid May (Figure 25). Following mid May, these solutes briefly increased in concentration but then declined again as runoff steeply increased in early June.

In the Pear Lake outflow, beginning in late April, both base cation and silica concentrations declined as runoff increased, recovering for a short time as melt declined in mid May. During the remainder of the melt period, both constituents declined while runoff was high. The range of concentrations measured was from 17 to 30 μM for silica and from 26 to 36 $\mu\text{eq L}^{-1}$ for base cations.

Outflow discharge during snowmelt 1991 - At Ruby Lake, snowmelt began in 1991 during late May and increased rapidly until mid June (Figure 26). From mid June through July, daily discharge remained above 15,000 m^3 per day; runoff began to decline thereafter. In comparison to water year 1990, the snowmelt period of 1991 occurred about one month later.

At Spuller Lake, snowmelt began in early May and runoff increased rapidly in early June (Figure 26). Peak daily discharges of nearly 20,000 m^3 per day were measured during early July; runoff declined rapidly thereafter.

At Topaz Lake, snowmelt runoff during 1991 was less variable than in 1990 (Figure 26). Melt began a little later in 1991 and runoff grew slowly from mid April to mid May. Peak discharge occurred in mid June and was followed by a large decline in runoff during the remainder of June; the outflow to Topaz Lake was dry by the end of July.

In the outflow to Pear Lake, pH gradually increased throughout the snowmelt period of 1991 (Figure 26). The timing of sampling and peaks in runoff did not coincide (as was the case at Topaz Lake), therefore it is difficult to interpret the effect of runoff on outflow pH at Pear Lake. ANC in the outflow to the lake declined sharply in the first half of melt, reaching a minimum of $9.6 \mu\text{eq L}^{-1}$ which was the lowest ANC measured of any outflow or lake during the study period. Following this minimum, pH rose as runoff peaked and was then stable as snowmelt declined.

Patterns of sulfate and nitrate during snowmelt 1991 - In the outflow to Ruby Lake, sulfate concentrations varied little except for an increase as runoff rapidly grew during early June (Figure 27). Following this peak, sulfate concentrations declined very slightly then increased very slightly as runoff diminished. Nitrate concentrations in the outflow to the lake were much more variable. A large increase in nitrate occurred as runoff increased in early June and these high levels (ca. $10 \mu\text{eq L}^{-1}$) persisted for most of June. Following this period, nitrate levels fell sharply as snowmelt runoff peaked in early July and then increased slightly as outflow discharge declined during the summer and early autumn.

In the Spuller Lake outflow, sulfate and nitrate concentration closely followed one another (Figure 27). During the latter part of May, sulfate declined from 24 to $6 \mu\text{eq L}^{-1}$ and nitrate declined from 14 to $1 \mu\text{eq L}^{-1}$. Later both anions increased as runoff grew in early June. Following these peaks, sulfate and nitrate concentrations declined gradually but sulfate increased again as runoff rapidly grew in early July. Overall, sulfate and nitrate concentrations increased during periods of rapid increase in outflow discharge.

In Topaz outflow, sulfate concentrations during the snowmelt period of 1991 were well moderated, showing only a small depression during peak runoff in June (Figure 26). Nitrate concentrations in the outflow were very high during the first trickle of runoff in April ($40 \mu\text{eq L}^{-1}$) then declined as snowmelt grew. Nitrate levels were below the detection limit during the height of snowmelt, then increased slightly as runoff diminished in July.

In the outflow to Crystal Lake, sulfate concentrations varied, during the snowmelt period of 1991, in a remarkably linear fashion (Figure 27). From the onset of snowmelt until shortly after peak runoff in June, sulfate in the outflow decreased at a constant rate ($-0.13 \mu\text{eq L}^{-1}$ per day, $r^2 = 0.9999$). From mid June through the remainder of snowmelt, the variability of sulfate concentration in the outflow was within the analytical precision of our sulfate assay. Nitrate concentration in the outflow to the lake was highest in the earliest runoff ($2.1 \mu\text{eq L}^{-1}$), then

In the Spuller Lake outflow, pH declined during the first part of snowmelt, reaching 5.8 during early June (Figure 26). For most of June pH was constant but then rose to 6.2 near the end of the month. Following this peak, pH declined as runoff levels peaked in the first part of July and then as runoff declined, pH levels rose and then stabilized. At the onset of melt, ANC in the outflow to Spuller Lake declined steeply, dropping from 100 to 23 $\mu\text{eq L}^{-1}$ in less than one month. Following this decline, ANC recovered slightly during the last half of June, declined again as runoff peaked and then gradually increased on the falling limb of the hydrograph.

In the outflow to Topaz Lake, pH gradually increased during the snowmelt period of 1991 (Figure 26). However, the interval between samples was relatively large and no samples were taken during peak runoff in late May and mid June, making interpretation of these data problematic. ANC in the outflow had a smooth decline during snowmelt, falling to 9.6 $\mu\text{eq L}^{-1}$ in mid June. During the remainder of the melt period, ANC increased slightly as runoff declined.

Compared to other constituents, pH in the outflow to Crystal Lake was quite variable during the snowmelt period of 1991 (Figure 26). During the first trickle of runoff (less than 10 m^3 per day) pH declined, then as runoff increased rapidly, pH rose from 5.6 to 6.3 and then declined again as discharge peaked in mid June. During the short lull in snowmelt near the beginning of July, pH increased, then fell again as runoff increased and finally increased again as melt ended. Runoff intensity had a significant and clear effect on outflow pH at Crystal Lake. In contrast, ANC in the outflow was very stable, only dropping from 80 to 59 $\mu\text{eq L}^{-1}$ during the snowmelt period.

In the Emerald Lake outflow, pH declined slightly during the initial phase of melt reaching a minimum of 5.6 by mid May. Thereafter pH increased as discharge grew then fell again as runoff peaked in mid June. pH in the outflow to the lake gradually increased during the decline of melt in June and July. ANC declined slightly from early April to early May and then declined more steeply as runoff increased near the beginning of June, reaching a minimum of 12.2 $\mu\text{eq L}^{-1}$, and thereafter generally increased as snowmelt decreased.

In the Lost Lake outflow, pH declined as runoff increased in early June, reaching a minimum of 5.4 which was the lowest pH of any outflow or lake sample collected during the study period (Figure 26). Thereafter pH increased until late June as runoff decreased then declined as snowmelt lessened in July. ANC in the outflow to Lost Lake was variable during the melt period with the only clear trend being a large decline early in the period. The range of ANC measured was 12 to 25 $\mu\text{eq L}^{-1}$ during the snowmelt period.

In the outflow to Crystal Lake, base cation concentrations were well moderated except for an initial decline at the earliest phase of snowmelt (Figure 28). Ignoring the first sample of the time-series, SBC concentrations varied less than $10 \mu\text{eq L}^{-1}$ through the end of July. Silica concentrations in the outflow to the lake were similarly stable in the latter part of snowmelt but, underwent a relatively large decline during the first weeks of melt as runoff increased rapidly.

In the Emerald Lake outflow, there was good agreement in the patterns of base cations and silica concentrations (Figure 28). Both constituents declined on the rising limb of the snowmelt hydrograph, reaching minimum concentrations in mid June and then increasing slowly as snowmelt runoff diminished.

In the outflow to Lost Lake, base cations and silica concentrations decreased beginning in late April with minimum values occurring in mid June (Figure 28). After this point, concentrations of both constituents slowly increased through the remainder of snowmelt except for a short dip in concentrations during increased runoff in late June.

In the Pear Lake outflow, base cations and silica concentrations declined on the rising limb of the snowmelt hydrograph, reaching minimum concentrations in early June (Figure 28). From early to mid June, levels of these solutes increased slightly then declined again as runoff increased in early July.

Outflow flux of solutes - At all seven lakes, most solute flux occurred during the months of May and June during water years 1990 and 1991 (Figure 29-35). Peak, monthly solute flux was generally higher in water year 1991 because of greater snowmelt runoff. At Ruby, Topaz and Emerald lakes there was not much difference in peak fluxes between water years 1990 and 1991. The flux of ANC from all catchments is much greater than the flux of hydrogen ion, indicating that the watersheds are producing sufficient ANC to buffer current inputs of acids. The ratio of nitrate flux to sulfate flux is much smaller than the ratio of nitrate to sulfate in precipitation at Crystal and Lost lakes which suggests that these catchments are sinks for nitrate. In other lakes, nitrate flux is higher and often exceeds sulfate flux in the earlier phases of snowmelt. The fluxes of base cations and silica were generally similar but, at Ruby and Spuller lakes, base cation flux was substantially greater than silica flux.

Summary - Outflow chemistry during snowmelt can be divided into three phases: the period from the onset of snowmelt until peak discharge, the period of peak discharge and the period from peak

declined as melt increased initially. As outflow discharge increased further (in early June) nitrate concentrations rose and peaked at the same time daily outflow discharge peaked in mid June. During the remainder of the snowmelt period nitrate levels gradually declined to below the detection limit.

In the Emerald Lake outflow, the sulfate concentration increased slightly during the onset of snowmelt and then declined modestly as runoff increased. Following peak runoff, sulfate concentrations in the outflow were constant. In contrast, nitrate concentrations increased in the outflow to Emerald by $5 \mu\text{eq L}^{-1}$ during the rising limb of the hydrograph. After early June, nitrate levels gradually decline through the remainder of the snowmelt period.

At Lost Lake, no outflow samples were collected during the earliest part of snowmelt in May. Beginning in late May, sulfate and nitrate concentrations declined as runoff grew, reaching minimum values in mid June (Figure 27). For the remainder of the melt period, sulfate concentration were stable and nitrate levels remained near the detection limit.

In the Pear Lake outflow, sulfate concentrations gradually declined during the snowmelt period with the greatest change occurring during the early part of melt (Figure 27). Nitrate concentrations increased from 7 to $14 \mu\text{eq L}^{-1}$ from early April to mid May and then declined rapidly as runoff increased.

Patterns of base cations and silica during snowmelt 1991 - In the outflow to Ruby Lake, base cations and silica concentrations had very similar patterns during the snowmelt period of 1991 (Figure 28). Both constituents decrease sharply as runoff rapidly increased in early June, then recovered slightly towards the middle of June and remained stable for the remainder of the melt period.

In the Spuller Lake outflow, base cations and silica concentrations decreased during the first half of snowmelt with minimum values occurring in mid June (Figure 28). After this point, concentrations of both constituents slowly increased through the remainder of snowmelt except for a brief dip in concentrations during peak runoff in early July.

In the Topaz Lake outflow, base cations and silica concentrations decreased during the snowmelt period of 1991 with the largest declines occurring as snowmelt increased during late May (Figure 28). Minimum values were reached by mid June and then base cation and silica concentrations increased as runoff decreased.

biological demand for nitrate in Crystal and Lost lakes is greater than at the other catchments or these watersheds may lack a source of nitrate other than precipitation.

Base cation concentrations usually declined during the first phase of melt, reaching minimum values at or near peak runoff. During the last phase of snowmelt, base cations increased as snowmelt diminished. Silica concentrations generally followed SBC concentrations, however, silica occasionally increased as snowmelt intensified (eg. Crystal and Emerald lakes 1990, Crystal Lake 1991). Overall silica concentrations were more variable than SBC concentrations.

Monthly fluxes of solutes via the outflows illustrates the strong snowmelt influence on solute export. Almost all export occurs from April through July with essentially no export during the autumn and winter except for Spuller and Ruby lakes. Further discussion of outflow flux will follow in the next portion of this report.

Atmospheric Deposition

The inputs of water via snow and rain to the seven catchments varied considerably among catchments and between years (Tables 10-11). The winter of 1990 deposited more snow than 1991 except in the Ruby Lake catchment. In 1990 the Lost Lake catchment accumulated the most SWE and the Topaz Lake catchment the least; the Crystal, Emerald and Ruby Lake catchments also accumulated low SWE. In 1991, Emerald and Lost lake catchments had the highest SWE and Ruby had the least. Water year 1987 had low SWE for all five catchments sampled (Table 12).

Rain contributed between 8 and 15 percent of total atmospheric deposition of water in water year 1990, and between 7 and 10 percent in water year 1991. As a result of spring rain in water year 1987, rain contributed more of the water in that year (12 to 32 percent of total).

Volume-weighted mean snowpack solute concentrations from snowpits sampled during March and April 1990 and 1991 are presented in Tables 13 to 19. Snow chemistry was similar among watersheds. pH ranged from 5.2 to 5.4. The order of ions based on concentration was also similar among the basins. The dominant cations were H^+ and NH_4^+ which is similar to snowpit chemistry from 1987 through 1989 (Sickman and Melack 1989, Williams and Melack 1991). For anions the usual order was: $NO_3^- > SO_4^{2-} > Cl^- > CH_3CO_2^-$ or HCO_2^- .

The solute concentrations in the Sierran snowpacks are very low. Hydrogen had the highest concentrations in all years in all catchments (5.6 to $2.7 \mu eq L^{-1}$) except for the ammonium

discharge until the end of snowmelt. During the first phase of snowmelt, pH and ANC declined in most outflows during both years with minima being recorded at or near peak runoff (second phase). During the third phase of snowmelt pH and ANC levels generally increased in most lakes. As with lake chemistry, lake volume had a large effect on the magnitude of the pH and ANC changes seen in the outflow during the melt period; small lakes had the greatest range in pH and ANC. The main exception to this pattern was the outflow to Crystal Lake. Although there was a small decrease at the onset of snowmelt, ANC in this outflow generally remained stable during all three phases of snowmelt.

Using outflow pH and ANC minimum values as indices of a catchment's sensitivity to acidification, Lost Lake and Pear Lake catchments are the most sensitive and Crystal Lake and Ruby Lake catchments the least sensitive. In comparing the difference in minimum pH and ANC during snowmelt between water years 1990 and 1991, values were lower in all outflows during 1991, probably because of greater snowfall (and snow water equivalence) in the winter of water year 1991. A larger snowpack during water year 1991 resulted in a longer runoff period with higher peak daily discharge.

Changes in outflow sulfate and nitrate concentrations during snowmelt were more complex than changes in pH and ANC. Sulfate generally declined during the first phase of melt but, remained fairly stable during the second and third phases of snowmelt. Some transient increases in sulfate occurred during all three phases of snowmelt; these increases were associated with temporary decreases in runoff. Incidents when sulfate increased as discharge increased during the first phase of melt (ie. ionic pulse) were not common and only occurred consistently in the outflows to Ruby and Spuller lakes. The stable nature of sulfate during snowmelt suggests there are catchment or lake processes which regulate the concentration of sulfate in surface waters of the Sierra Nevada.

Nitrate concentrations in the outflows to the lakes generally increased substantially during the first phase of snowmelt, with high levels occasionally persisting for one to two weeks. Maximum, outflow nitrate concentrations were often much greater than the concentration of nitrate in the snowpack and occurred well into snowmelt (eg. Ruby Lake 1991, Emerald and Pear lakes 1990) suggesting that there is some source of nitrate independent of precipitation. Usually nitrate concentrations had begun to decline by the second phase of melt, and reached low levels during the final phase of snowmelt. Exceptions to this pattern were the outflows to Crystal and Lost lakes where nitrate concentrations remained low throughout the entire snowmelt period. Perhaps

Simplifying the estimation of evaporation to the evaporation from snow does not make the remaining calculation simple. A review of the literature yields mostly disagreement as to appropriate methods, application of the methodology, and results. The easiest approach is the use of bulk transfer equations of the type:

$$L_v E = D_e \bar{U} z (e_a - e_s) \quad (1)$$

Where: L_v = latent heat of evaporation or sublimation, 2500 KJ kg⁻¹ or 2820 kJ Kg⁻¹ respectively,
 e_a, e_s = vapor pressure of the air and snow surface (mb)

$\bar{U} z$ = mean wind speed at some reference height z , (m s⁻¹)

D_e = bulk transfer coefficient for latent heat transfer (Jm⁻³ mb⁻¹)

Unfortunately, typical values for D_e range from 2 to 25 (Male and Gray 1981). Other easily applied methods, reviewed by Male and Granger [1979], such as the Bowen Ratio and Penman equations also give no reliable or consistent results.

The most promising methodology, turbulent mass transfer (Brutsaert 1982), requires measurements, at short time intervals (15 min. to one hour) of e , air temperature (T) and \bar{U} at two points above the snow surface: preferably one at 0.25 meters above and the other 2 to 3 meters higher. The difficulty of maintaining instruments at these heights under adverse conditions and a constantly changing snow pack depth is obvious. Most studies utilizing this method have elected to measure these parameters at just one point (Marks and Dozier 1992), assuming the second point to be some small roughness height Z_0 above the snow surface, where $T = 0^\circ\text{C}$, $\bar{U} = 0$ and the vapor pressure is at saturation. The surface roughness height for the snow surface alone can vary from 0.0001 to 0.005 meters. This value will change throughout the season, and if nearby vegetation and terrain features are considered it can be much higher.

Application of the mass transfer equations can determine evaporation at a point. This value will then have to be distributed over the entire basin. Decreasing snow covered area with time must also be considered.

The assumption of conditions just above the snow surface layer requires careful consideration. Since we are concerned only with the evaporation that occurs after the snow pack is at its maximum (after the measurement of distributed snow water equivalence) and when air

concentration ($5.5 \mu\text{eq L}^{-1}$) in 1991 at Crystal Lake and occasionally when ammonium equalled the hydrogen concentration. Most other solutes were less than $3 \mu\text{eq L}^{-1}$. These results are much the same as those reported by Williams and Melack (1991) for 1985 through 1988 at Emerald Lake.

Volume-weighted mean solute concentrations in rain are much higher than those in the snow. The dominant cations are NH_4^+ , Ca^{2+} and H^+ . Among the anions, NO_3^- has the highest concentrations followed by sulfate or organic acids. pH ranged from 4.6 to 5.5. Volume-weighted mean pH for the combination of rain and snow ranged from 5.1 to 5.4.

The ratio of NO_3 to SO_4 on an equivalent basis was greater than one in snow, rain and snow plus rain for all catchments in all years except at Emerald Lake in 1990 (ratio = 1.0) and Pear Lake in 1990 (ratio = 0.8). While extending Williams and Melack's (1991) finding for Emerald Lake, this result contrasts with eastern North America where a high NO_3 to SO_4 ratio occurs in snow but a low NO_3 to SO_4 ratio occurs in rain (Chan et al 1987). Apparently, emissions of NO_x in California exceed those of SO_x year round.

The atmospheric deposition data are used in this report to calculate solute mass balances and to conduct ion enrichment analyses (see below). Analyses of regional differences and interannual trends or variations require combination of the data reported here with those from on-going ARB contracts and prior ARB contracts, and will be accomplished as part of upcoming reports.

Evaporation

For an alpine lake basin total evaporation is the sum of four components: evaporation from snow, the lake itself, and the land surface, and transpiration from vegetation in the basin. Kattelmann and Elder (1991) calculated the water balance for Emerald Lake for the 1986 and 1987 water years and concluded that evaporation from the lake combined with evapotranspiration from the land accounted for approximately 4% of the total precipitation to the basin. One of their water years was atypical, with very low snowfall and short snowmelt period; these factors magnify the magnitude of these terms. For the other, more typical year, with about 2.5 meters of total precipitation, evapotranspiration from surfaces other than snow was approximately 3%. Given their estimate of the total error of their methodology at $\pm 15\%$, the effect of these terms on the water balance is negligible. In alpine basins with sparse vegetation, coarse granitic soils, low temperatures, and a relatively short snow and ice free season this conclusion is not unexpected.

$$SWE_s + P = D + E_s$$

Where: SWE_s is the snow water equivalent as of the spring snow survey,
 P is precipitation after this time,
 D is discharge
and E_s is evaporation from snow

The CARB's concurrent mini-watershed study, which is sited directly adjacent to the Emerald Lake basin, also offers a significant opportunity for closure on this problem. With accurate measurement of outflow and weather parameters, these study areas will, in effect, serve as large lysimeters and can provide an excellent check on any method used to calculate evaporation.

temperatures are usually above freezing, the assumption that the temperature just above the snow will be at 0°C does not seem unreasonable. However, others (Male and Granger 1979) have pointed out that there is daytime radiative heating of the air directly adjacent to the snow which may result in much higher temperatures. If the temperature is assumed to be zero, the warmer and lighter air above causes a stable inversion that will minimize evaporation. Warmer temperatures at the surface have the opposite effect and maximize turbulence and evaporation. This difference probably accounts for much of the discrepancy over the importance and magnitude of evaporation from snow reported in the literature. Stewart (1982) reports estimates that vary from 1 to 2% of the snowpack to 50 to 80%.

Despite these obstacles mass transfer offers the best alternative for the calculation of evaporation or sublimation off of snow for this study. The weather instrumentation at Spuller and Emerald Lakes will allow this calculation at these two points. Unfortunately, instrument malfunction during the first winter after installation (water year 1991) left gaps in the measurement record, and most occurred during the critical period of spring snow melt. With data collected since then, and with the continuous weather record maintained at the Log Meadow Ranger Station, we plan to reconstruct the missing data. In a similar fashion, data collected at the Lee Vining Ranger Station may help us repair the Spuller record.

The best approximation of evaporative loss is the percentage values established by Kattelmann and Elder 1991:

1. Loss by evaporation from snow, after the April snow survey, as a percentage of the average snow water equivalence (SWE) of the spring pack, 10% of SWE.
2. Loss by evaporation from the lake and evapotranspiration from snow free land surfaces, after the April snow survey, 4% of SWE.
3. Loss by evaporation from snow over the water year as a percentage of total precipitation, 18%.
4. Total loss by evapotranspiration over the water year as a percentage of total precipitation, 22%.

Continuation of our ARB contract, with more accurate stream gaging at Emerald and Spuller Lakes, along with improved weather data, will allow better approximations. Better data will enable the utilization of the turbulent mass flux method, while more accurate measurement of outflow will provide a check on the results. With loss through ground water flow and other forms of evaporation assumed negligible, the mass balance for the basin reduces to:

The yield of sulfate varied considerably among catchments from retention of 81 eq ha⁻¹ yr⁻¹ (Topaz Lake 1987) to export of 103 eq ha⁻¹ yr⁻¹ (Spuller Lake, 1990). Moreover, Emerald, Pear, Ruby and Topaz lakes' catchments had net retention sulfate in 1987 but net export in 1990 and 1991.

Chloride does not behave conservatively or consistently among years or catchments. All five catchments retained chloride in 1987. All but Crystal Lake's catchment exported chloride in 1990 and 1991.

Interpretation of differences in retention or export observed among the catchments requires information about the vegetation, soils and minerals within the catchments and would benefit from application of modeling of the biogeochemical and hydrological processes. These activities are in progress under ongoing ARB contracts and non-ARB grants.

Very few studies with solute yields from alpine catchments with which to compare our results are available. One of the few was conducted in the Front Range of the Rockies of Colorado at the Loch Vale catchment (Baron 1992). Average yields of HCO₃ (219 eq ha⁻¹ yr⁻¹) and base cations (260 eq ha⁻¹ yr⁻¹) for 1984 through 1988 fall midrange among the Sierran data (Mast 1992). Likewise, NH₄ and H were highly retained. Sulfate had slight net export, and nitrate and chloride had slight net retention.

Ion Enrichment Analysis

Ion enrichment analysis is an application of a simple evapotranspiration and solute mass balance calculation to identify contributions of acidic or basic solutes to observed ANC of waters within a catchment (Baker 1991, Munson and Gherini 1991). This analysis was applied to the seven Sierran catchments for water year 1991 (Table 23), and was applied to Emerald Lake for 1986 and Gem Lake for 1984 by Melack and Stoddard (1991).

The first step in ion enrichment analysis is to calculate the chemical composition of the lake that would result if the lake water was only atmospheric precipitation concentrated by evaporation. Evaporation can be determined from detailed hydrologic and meteorological measurements such as those done at Emerald Lake (Marks and Dozier 1992, Kattelmann and Elder 1991) or be based on the ratio of the concentration of Cl in lake water to atmospheric deposition. The latter approach was used here; calculations derived from hydrologic and meteorological measurements are in progress under an on-going ARB contract.

Annual Solute Yields

Annual yields of solutes per hectare of catchment provide an integrative metric of the current capacity of the catchments to neutralize acidic inputs and retain or export solutes. Annual yields are calculated as the difference between efflux via the outflowing streams and atmospheric deposition (or loading) divided by catchment area. Only snow and rain are included in the atmospheric deposition; hence, summer dry deposition is not included. A negative yield indicates retention or reaction of the solute within the catchment. A positive yield indicates fluvial export exceeds atmospheric inputs, and implies a source for the solute within the catchment.

Annual yields of solutes (H, ANC, NH_4 , Cl, NO_3 , SO_4 and base cations) were calculated for each of the seven catchments for water year 1990 and 1991 (Tables 20 and 21), and for five of the catchments for water year 1987 (Table 22). The combination of these data produces 19 water years of solute yields.

All the catchments in all years retain an amount of H almost equivalent to that deposited from the atmosphere. The amount retained ranged from 16 to 53 $\text{eq ha}^{-1} \text{yr}^{-1}$; Lost Lake's catchment neutralized the smallest proportion of that deposited (i.e. 30% in 1991, but 67% in 1990). However, internal sources of acidity confound interpretation of net retention as a direct measure neutralization of acidic atmospheric deposition.

ANC and similar amounts of base cations are exported from all catchments in all years. Spuller Lake's catchment consistently exports the most ANC (355 to 552 $\text{eq ha}^{-1} \text{yr}^{-1}$). The least ANC exported per year ranged from 115 to 141 $\text{eq ha}^{-1} \text{yr}^{-1}$ and occurred in Emerald, Pear or Crystal lakes' catchments. The net export of ANC which is predominately HCO_3 and base cations indicates that weathering and exchange processes are of sufficient magnitude to buffer current acidic atmospheric deposition.

Essentially all the ammonium deposited from the atmosphere or produced within the catchments is retained. However, nitrate retention varies among the catchments and among years within the same catchment. All catchments retained nitrate except the Spuller Lake catchment in 1990 and 1991 and the Pear Lake catchment in 1991. Net export of nitrate is surprising and implies an internal source and nitrogen saturation of the soils and biota. In the catchments that had net nitrate retention, the proportion of atmospherically deposited nitrate that was retained ranged from 100% (Crystal Lake) to 3% (Emerald Lake).

Negative values of the anion, NO_3 , for all the catchments indicate nitrate consumption, which may be attributed to biological assimilation or denitrification, and is a source of ANC. Conservely, negative values of the cation, NH_4 , represent an ANC sink probably caused by biological uptake of NH_4 . In each catchment the absolute value of the NH_4 decrease exceeds the absolute value of the NO_3 decrease, hence the net contribution of removal of these nitrogen species is a slight loss of ANC.

In summary, the magnitude and similarity of the lake water ANC and basic cation ion enrichment indicates that the dominant biogeochemical mechanisms of ANC generation are associated with release of basic cations in all seven catchments. A minor source of ANC is associated with nitrate consumption. Losses of ammonium and gains in sulfate represent minor ANC sinks. Similar conculsions were reached by Melack and Stoddard (1991) for water year 1986 for Emerald Lake's catchment, and by Turk and Spahr (1991) for the Rockies and Nelson (1991) for the Cascades.

The second step of ion enrichment analysis is to calculate the extent of biogeochemical reaction within the catchment by comparing expected and measured chemical composition of the lake. Enrichment or depletion of relevant solutes was computed as a concentration ($\mu\text{eq L}^{-1}$). Based on electroneutrality, reactions which result in gains in cations or loss of anions increase ANC and, conversely, reactions which remove cations or increase anions decrease ANC.

Three assumptions are made in the ion enrichment analysis done here: (1) Cl is a conservative tracer, (2) all inputs to the catchment occur via atmospheric deposition and (3) the catchment is at steady state. As mentioned above, Cl appears not to be strictly conservative in all the catchments. However, the determination of chemical loading by snowfall was made in April, hence, evapoconcentration by sublimation of the snow had already occurred. Moreover, Melack and Stoddard (1991) based their application of ion enrichment analysis on hydrologic measurements in Emerald Lake's catchment and reported conclusions similar to those here.

Acidic atmospheric deposition is indicated as an input of negative ANC, and ranged from -5.1 to -10.5 $\mu\text{eq L}^{-1}$ among the seven Sierran catchments after evapoconcentration (Table 23). The extent to which basic cations are higher in the lake than in the atmospheric deposition is a measure of a positive contribution to ANC. The concentration of the sum of basic cations after evapoconcentration are positive ranging from 23.0 to 61.7 $\mu\text{eq L}^{-1}$ and are close in concentration to the measured lake water ANC. This result can be interpreted to indicate that weathering reactions and cation exchange are the primary biogeochemical reactions determining ANC and cation concentrations.

Because neutralization of atmospheric inputs of H is insufficient to account for all the basic cation increase, weathering driven by other sources of acidity such as soil respiration probably causes most of the basic cation increase.

Sulfate adsorption or reduction within the catchment results in lake water concentrations lower than those in atmospheric deposition (i.e. negative values in Table 23), and indicates a positive contribution to ANC. A source of sulfate in the catchment (e.g. pyritic material or gypsum) causes a negative contribution to ANC (i.e. positive values in Table 23). Sulfate values of 2.0 (Ruby) and 5.7 (Spuller) (Table 23) are evidence for sources of sulfate within the catchments, and hence are sinks for ANC. The sulfate values for the other lakes are near 0 and may indicate slight sources or sinks of ANC or may be within the error of the technique.

the sensitivity of many Sierra Nevada plankton species to increased acidity (Melack et al. 1987, 1989, Barmuta et al. 1991). In these studies *Diaptomus signicauda*, *Daphnia rosea*, *Holopedium gibberum*, and *Conichilus unicornis* decreased at pH < 5.5 and were intolerant to pH < 5.0. *Bosmina longirostris*, *Keratella taurocephala*, and *Polyarthra vulgaris* experienced increases in abundance at pH levels between 5.5 and ca. 5.0, thus exhibiting greater acid tolerance and the potential to respond numerically to competitive release at intermediate stages of acidification.

The applicability of these results to Sierran lakes in general will depend not only on how widespread known sensitive species are in the Sierra Nevada, but also on the extent to which these species co-occur in similarly structured communities. Zooplankton assemblages in Sierran lakes currently fall into a variety of community types, whose distributions are dependent on a wide range of physical and biological co-variables (Stoddard 1987). Presence of fish, nutrient levels, elevation, lake and basin area, morphoedaphic index and bedrock type are all significant predictors of community distributions and must be considered when evaluating the significance of the distribution of any particular zooplankton species that shows promise as a bio-indicator of lake acidification.

We here report the results of multi-year sampling of zooplankton from seven high altitude Sierra Nevada lakes. The community types present are discussed in terms of other relevant physical or biological factors measured for the lakes. Inter- and intra-annual variation in abundance among species is used to evaluate the utility of year-round sampling as a monitoring activity for zooplankton. Finally, the seasonal patterns of known sensitive species are evaluated in light of the likely timing of episodic acidification.

Methods

Four of the lakes, Crystal, Ruby, Topaz, and Pear, were sampled six to ten times from June 1987 through 1989 and every two months in 1990 and 1991. Although the zooplankton of the fifth lake, Emerald Lake, have been studied since 1984 (Melack et al. 1987, 1989, Barmuta et al. 1991) we here describe only those results from sampling that took place twice in 1989 and every two months in 1990 and 1991. The remaining two lakes, Lost and Spuller, were sampled every two months in 1990 and 1991.

Duplicate vertical tows were taken on each date in each lake from near the bottom to the surface of the lake using a 64 μ m mesh net with a 0.12 m diameter. Zooplankton samples were preserved in the field with 10% formalin. The depth of each tow was recorded and numbers per

Chapter IV

ZOOPLANKTON AS BIO-INDICATORS OF LAKE ACIDIFICATION

Introduction

Zooplankton communities are expected to respond to lake acidification via alterations in community composition and the relative abundance of species. Review of over 100 acidification studies in the eastern U.S., Canada and Scandinavia shows that short-term pH shock affects daphnids most strongly, followed by other cladocerans, copepods and lastly, by chaoborids (Brett 1989). Differences in water permeability appear to explain gross differences in responses to acidification at this taxonomic level (Nilssen et al. 1984). Overall, numbers of crustacean and rotifer species can be expected to decline during lake acidification, but predictions for single species vary somewhat among studies.

Variable tolerance among species to hydrogen ion stress is probably the predominant influence structuring zooplankton communities in acidified lakes which have been reduced to extremely few species. At intermediate stages, other factors related to the acidification process may interact to cause changes in abundance or composition of zooplankton, including metal ion toxicities, shifts in phytoplankton toward inedible species, and shifts in vertebrate or invertebrate planktivore populations. For example, reductions in zooplankton biomass are observed in many acid-stressed ecosystems, but appear to be indirect results of changes in lake productivity rather than strictly pH (Brett 1989). Additionally, the exclusion of some crustaceans from acidified lakes (e.g. *Holopedium*, *Bosmina*, and *Ceriodaphnia*) may be due to the presence of the planktivore *Chaoborus*, which is acid tolerant and may occur when fish are eliminated as part of the acidification process (Nyberg 1984, Stenson and Oscarson 1984).

High elevation lakes in Sierra Nevada of California are not currently experiencing chronic acidification. However, most of the annual precipitation in the region is stored in the winter snowpack, which currently has pH values between 5.2 and 5.4. Depression of pH and acid neutralizing capacity (ANC) occur in lakes during the annual flushing due to springtime snowmelt (Melack et al. 1988). In addition, infrequent convective storms may deliver precipitation with pH as low as 3.7 during the summer (Melack et al. 1982), and have shown to temporarily depress pH in lake inflows (Melack et al. 1989).

Although most acidification studies and surveys of zooplankton have been conducted in eastern North America and Europe, acidification experiments conducted in Emerald Lake evaluated

many small-bodied crustacea common to lakes with trout. *Chydorus sphaericus*, which was negatively associated with lake size in Stoddard's (1987) study, was accordingly absent in the plankton of Ruby Lake, the largest of the lakes in our survey. The occurrence of *Cyclops vernalis* only in Ruby Lake may be explained by its association with lakes with large basins.

Interannual variation in relative abundance—The zooplankton were numerically dominated by rotifers on most sampling dates in most lakes (Tables 24-30). Two exceptions were Lost Lake and Topaz Lake, in which cladocera and copepoda were often more abundant than rotifers. Time series abundance data indicate considerable inter- and intra-annual variation in relative abundance among the zooplankton species present in the seven lakes. Mean abundance for the principal crustacean and rotifer species in each lake were plotted as time series together with periods of snow melt (Fig. 37-43). Snow melt periods were defined for this purpose as beginning in the first week of each year in which discharge began to rise and ending about one week after the maximum discharge values were observed, or after the lowest ANC value was observed, whichever occurred later. Every lake contained crustacean and rotifer species which, although numerically important in one or more years, were not detected in high numbers in every year sampled. The relatively infrequent sampling schedule may not have coincided with the population highs for some species in many years.

Seasonal succession—For the five lakes for which data were available for more than two years, chronologies were constructed identifying portions of the year in which annual peaks in abundance for major species could be expected (Fig. 44-45). These chronologies indicate lake to lake variation in seasonal succession patterns even for numerically dominant species. A few species exhibited more or less consistent seasonal patterns among lakes. *Daphnia rosea* consistently peaked in late summer or early autumn. *Diaptomus signicauda* generally reached its highest numbers in summer or autumn, and overlapped frequently with *D. rosea*. *Holopedium gibberum* showed population peaks anywhere from spring through late autumn, depending on the lake. In three of the lakes, *Bosmina longirostris* was consistently most abundant in winter prior to snow melt, but in the other two lakes, *Bosmina* reached its highest numbers in summer or early autumn, coincident with *Daphnia rosea* (Ruby and Crystal). *Keratella taurocephala* usually became most abundant sometime after snow melt but before October, except in Pear Lake where population highs were also observed under ice cover. *Conichilus* and *Trichocerca* generally peaked in August or September. *Keratella quadrata*, *Keratella cochlearis* and *Polyarthra vulgaris* were especially variable, becoming abundant at almost any time of year.

sample were converted to numbers per cubic meter prior to averaging duplicate tows. The filtration efficiency of the net was assumed to be 100%.

In the laboratory, zooplankton samples were diluted and subsampled with a Stempel or Finn pipette, and zooplankters were identified and counted at 25X under a dissecting microscope. Microcrustaceans and rotifers were subsampled separately because of the generally higher abundance of the latter. Subsample dilutions were adjusted so that at least 100 individuals were counted for each subsample. At least three subsamples were counted per sample, and each subsample usually comprised 5 to 10% and 0.5 to 1% of the microcrustacean and rotifer samples, respectively. In several cases the entire sample was counted.

Results

Community composition—There was considerable overlap among the species present in the seven lakes, which as a group contained five copepod species (excluding benthic harpacticoid spp.), six cladoceran species (excluding occasional appearance of the benthic genera *Alona* and *Macrothrix* in tow samples), and at least 20 rotifer species (Fig. 36). Some species were widespread among the lakes. The calanoid copepod *Diaptomus signicauda* was present in five of the lakes, and the cyclopoid copepods *Macrocyclus albidus* and *Tropocyclops prasinus* were present in six and five of the lakes, respectively. Cladocera present in all lakes were *Daphnia rosea* and *Bosmina longirostris*. *Holopedium gibberum* was present in four lakes. Among rotifers, *Polyarthra vulgaris*, *Keratella quadrata*, and either *Keratella taurocephala* or *Keratella cochlearis*, were abundant in all seven lakes. In all of the lakes except Ruby and Spuller these rotifers were accompanied by *Conichilus unicornis* and *Trichocerca capucina*. In most lakes, one or more other rotifer species were occasionally abundant.

The crustacean zooplankton in the seven lakes contained species that are typical for the region according to Stoddard's (1987) survey of 75 high altitude Sierran lakes. However, the specific complement of species in none of the lakes agreed completely with the community types outlined in Stoddard's study. In lakes with trout, the discrepancies were primarily due to the absence of *Polyphemus*, rarity of *Diaphanosoma*, presence of *Chydorus sphaericus*, and the substitution of *Cyclops vernalis* by *Macrocyclus albidus* in most of the lakes of our survey. *Holopedium gibberum* was highly associated with presence of trout in Stoddard's survey, but was absent from two of the lakes with fish in this study (Ruby Lake and Spuller Lake). The one fishless lake of our survey, Topaz Lake, contained two large-bodied zooplankton characteristic of fishless lakes in the Sierra, (*Diaptomus eiseni* and *Daphnia middendorffiana*), but also also had

The analysis revealed that for the purpose of monitoring species composition in any one lake (based on presence/absence data), there is little necessity of sampling during the winter months. There were only a few cases in which a species was present in at least 50% of the winter samples, but encountered with less frequency during the Spring or Summer seasons. These cases were restricted to *Chydorus sphaericus* in Crystal Lake, *Macrocyclus albidus* in Emerald Lake, and *Bosmina longirostris* and *Notholca* in Topaz Lake. Thus in only these cases are any species at risk of being underrepresented in a sampling program if effort during the winter months (November through March) is entirely omitted. Additionally, only in the latter case (Topaz Lake) were the species involved either numerically important or never more abundant in other seasons. There was no species in any lake that was observed only during a winter month.

Sampling for zooplankton could not be restricted to either the Spring or the Summer period without risking underrepresentation of several species. Many species were better sampled overall during the spring period than during the summer period. These species were predominantly rotifers and included *Asplanchna* and *Synchaeta* in Crystal Lake, *Keratella quadrata* in Emerald Lake, *Asplanchna* in Pear Lake, *Synchaeta* in Spuller Lake, *Macrocyclus albidus* and *Keratella quadrata* in Topaz lake. Lost Lake was the only lake in which a cladoceran species was best sampled during spring period (*Daphnia rosea* and *Holopedium gibberum*), and overall contained 8 species more frequently encountered during spring than during other periods. Every lake contained species which were more reliably sampled in the summer period than during any other period.

Species present during periods of maximum discharge within snow melt periods—Zooplankton species coinciding with the period of maximum lake discharge and resultant minima in ANC during snow melt are the most likely to experience brief periods of lowered pH if an acidification process begins in Sierran lakes. The overall utility of monitoring zooplankton in order to detect early signs of acidification will depend in part on the predictability of observing species during this part of the hydrological cycle and on their tolerance to low pH. For the purpose of determining which species are most susceptible to pH lows during snow melt, all cases in which a species was sampled (at densities of at least 100 organisms per m³) from the initiation of snow melt through peak spring time discharge were pooled among lakes and tabulated. For Crystal Lake, Pear Lake, Ruby Lake and Topaz Lake, 4 snow melt periods were covered in the analysis. For Emerald Lake, 3 snow melt periods were included, and for Lost Lake and Spuller Lake, the analysis included 2 snow melt periods. Among crustacean zooplankton, *Macrocyclus albidus* was the most often observed zooplankton species during snow melt periods (Table 39). *Bosmina longirostris* and *Diaptomus signicauda* were the second and third most frequently encountered crustacean zooplankters during

Species Richness—Due to seasonal succession patterns, and interannual variation in species composition, overall species richness (defined as total number of species collected on a sampling date) varied from month to month and between years in all lakes (Fig. 46-47). Species richness tended to be lower during winter months (Oct. - Mar.) than during spring and summer months (Apr. - Sept.), but this difference was statistically significant for Crystal Lake and Pear Lake only (Table 31). No long term trends were evident in lakes for which multi-year data are available. Species richness is negatively correlated with elevation in Sierra lakes (Stoddard 1987, Melack et al. 1989). Mean species richness (obtained by pooling richness values from all sampling dates for a given lake) showed no clear trend with respect to elevation for the lakes in our survey, nor were the maximum species richness values observed in each lake over time clearly associated with lake elevation (Fig. 48). However, all of our lakes were in the upper montane or alpine zone and separated by a maximum of 1000 m of elevation.

Seasonal occurrence of species in sampling—For each lake, frequency of occurrence of species in samples was determined for three periods defined as follows: Winter (November-March), Spring (April-June), Summer (July-October). Percent occurrence of a species for a particular season was obtained by pooling all sampling events in the time series of one lake which occurred in that season and calculating the percent of those sampling events in which the species appeared. Relative abundance of the species was not taken into consideration; a species needed only to be present to be scored. Species which were observed in less than 10% of all samples from a particular lake were omitted from the analysis.

In each lake, some species were detected in 50% or more of the samples in every season and, thus, likely to be detected in a multi-year sampling program even if conducted irregularly. In every lake, except Crystal Lake, at least one copepod species was likely to be sampled in any season. *Holopedium gibberum* (in one lake) and *Bosmina longirostris* (in three lakes) were the only cladocera observed year round according to this criteria. In Crystal Lake “year-round” species included *Holopedium gibberum*, *Keratella cochlearis*, *Keratella quadrata*, *Polyarthra vulgaris*, and *Kellicottia* sp. (Table 32). In Emerald Lake these species included *Diaptomus signicauda*, *Bosmina longirostris*, *Keratella taurocephala*, and *Polyarthra vulgaris* (Table 33). In Lost Lake, *Diaptomus signicauda*, *Bosmina longirostris*, and *Keratella cochlearis* were likely to be sampled year round (Table 34). In Pear Lake, Ruby Lake, Spuller Lake, the year-round species were *Macrocylops albidus*, *Keratella* spp. and *Polyarthra vulgaris* (Tables 35-37). *Bosmina longirostris* was also present in >50% of the samples of Pear Lake year-round. In Topaz Lake, *Diaptomus signicauda*, *Diaptomus eiseni*, and both *Keratella* species were likely to be sampled in any season (Table 38).

another widespread Sierran species, was shown to decline at pH < 5.5 in Emerald Lake (Melack et al. 1987), and is reduced in acidified Swedish lakes (Almer et al. 1974, 1978).

Many important Sierra microcrustacean and rotifer species have been shown either through surveys or direct experimentation to have a relative advantage during at least the early phases of lake acidification. *Diaphanosoma*, *Bosmina longirostris*, *Holopedium gibberum*, and *Keratella taurocephala* are common dominants in acidic lakes (Brett 1989). Although the evidence is less clear, *Keratella cochlearis*, *Kellicottia longispina*, and *Polyarthra vulgaris* appear to tolerate mildly acidic pHs (5.4 to 4.4). In at least one study, *Syncheata* was codominant with *Keratella taurocephala* in an acidified lake (mean pH 4.0, Yan & Geiling 1983). In Emerald lake, *Bosmina longirostris*, *Holopedium gibberum*, *Keratella taurocephala*, and *Polyarthra vulgaris* were favored in experimental treatments at pHs too low (below 5.5) for the more sensitive *Daphnia rosea* and *Diaptomus signicauda*. Similarly, *Bosmina longirostris*, *Diaphanosoma*, and *Chydorus sphaericus* increased in relative abundance as *Daphnia* collapsed when pH was reduced from 6.4 to 5.3 in a British Colombia lake (Marmorek 1984). *B. longirostris* and *C. sphaericus* likewise increased in low pH treatments in West Virginia by Havens and DeCosta (1985, 1987). These shifts in relative abundance are commonly believed to reflect population increases of competitively inferior species when more acid-sensitive dominants are removed from the community. Community shifts brought about by interaction between pH tolerance and interspecific competition may not persist throughout the acidification process, as temporarily favored species may reach their physiological tolerance limits with further declines in pH.

Based on the available descriptive and experimental information, certain changes in community structure are reasonable to predict if our survey lakes become subjected to chronic acid stress. *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicauda* are likely to be removed if pH levels reach as low as 5.0. In the lakes in which these species overlap seasonally with *Bosmina longirostris*, *Holopedium*, *Diaphanosoma*, *Keratella taurocephala*, or *Polyarthra vulgaris*, increases in the latter, more acid-tolerant, species are fairly certain. Where they occur, *Conichilus unicornis* and the genera *Asplanchna*, *Filinia*, *Ascomorpha*, and *Ploesoma* may be expected to decline, and *Kellicottia* and *Keratella cochlearis* may be expected to increase, but predictions for these taxa remain speculative. However, regardless of the species involved, some increase in rotifer biomass can be expected at least temporarily after a collapse of the crustacean component of zooplankton in an acidified lake (Yan & Geiling 1984, Yan et al. 1982, Brett 1989). In Lost, Pear, Ruby and Topaz lakes, a cyclopoid species (*Macrocyclus albidus* or *Cyclops vernalis*) is currently a frequent dominant. Information is lacking about the acid sensitivity of *Macrocyclus albidus*, and considerable variation in the tolerance level of *Cyclops vernalis* is

snow melt periods. *Polyarthra vulgaris* was the most frequently encountered rotifer during snow melt, followed by *Keratella quadrata* and *Keratella taurocephala* (Table 40).

Discussion

Detection of chronic acidification in Sierra Nevada lakes - The seven Sierran lakes we surveyed contain many species known from other studies to be acid intolerant. In general, *Daphnia* spp. and cyclopoid copepods, especially of the genus *Cyclops*, are much reduced or absent in acidic lakes (Brett 1989). Although *Daphnia rosea* is currently present in all of the seven lakes, experimental evidence indicates that it will be one of the first taxa to be eliminated if Sierran lakes become acidified. In enclosure experiments conducted in Emerald lake, *Daphnia rosea* declined when pH dropped below 5.5 (Melack et al. 1987, 1989, Barmuta et al. 1991). In a similar study, *Daphnia rosea* experienced pronounced mortality in lake enclosures when pH was reduced from 6.4 to 5.3 (Marmorek 1984). In the Emerald Lake experiments, the response of *Diaptomus signicauda* to decreasing pH paralleled that of *Daphnia rosea*. *D. signicauda* is the only widespread small calanoid copepod in the Sierra Nevada range, and it has been suggested that in these lakes it plays the role of *Diaptomus minutus*, another ubiquitous, small bodied calanoid common in other geographical regions (Stoddard 1987). However, *Diaptomus minutus* is characteristic of acidic lakes in north eastern North America, and thus apparently maintains a widespread distribution even during a regional process of lake acidification. The apparent acid intolerance of *Diaptomus signicauda*, and its widespread distribution in the Sierra range, imply that acidification in this region would eliminate the calanoid copepod component in the plankton of many high altitude lakes. The potential responses to low pH by the large-bodied zooplankters of fishless Sierra lakes, *Daphnia middendorffiana*, *Diaptomus eiseni* and *Diaptomus shoshone*, have not been experimentally determined in a Sierra lake to date, although evidence from other studies implies strongly that *D. middendorffiana*, will be negatively impacted by low pH, as are essentially all of its congeners (Havas & Hutchinson 1982, Brett 1989).

Rarely are rotifer species consistently eliminated from acidified lakes. However, a reduction in the number of rotifer species with lowered pH is often cited, and the genera *Asplanchna*, *Filinia*, *Ascomorpha*, and *Ploesoma* are found primarily in circumneutral lakes (Almer et al. 1974, 1978, Brezonik et al. 1984, Brett 1989, Carter et al. 1986, Chengalath et al. 1984, Siegfried et al. 1984). *Keratella cochlearis* declined during experimental acidification of Little Rock Lake (Frost & Montz 1988), and in at least one study was less common in acidic than non-acidic lakes (Carter et al. 1986), indicating some vulnerability as a widespread Sierran species. *Conichilus unicornis*,

Early detection of episodic acidification in Sierra Nevada lakes—There are only two ways in which episodic acidification in Sierra Nevada lakes may take place, pH depression caused by the springtime melting of an acidic snowpack, or by occasionally severe convective summertime rains. The earliest detection of episodic acidification of lakes in the Sierra Nevada will depend on the acid tolerance of zooplankton species which occur in the lakes specifically during these times, which are not necessarily the most sensitive species. The only crustacean zooplankton species which occurred frequently in samples obtained during snow melt periods were *Diaptomus signicauda*, *Macrocyclus albidus*, *Tropocyclops prasinus*, and *Bosmina longirostris*. *Daphnia rosea* was sampled during snow melt only three times during the entire monitoring program to date, making it a particularly unsuitable species for detecting early response to acidic snowmelt. The frequency of *Bosmina longirostris* in snow melt samples is of little use for early detection because of its known acid tolerance. Learning more about the tolerance range of *Macrocyclus albidus* would be useful due to its widespread occurrence and its frequent appearance in samples during snow melt. *Keratella taurocephala*, *Keratella quadrata* and *Polyarthra vulgaris* were the most often encountered rotifers during snow melt periods. However, *Keratella taurocephala*, like *Bosmina longirostris*, is not likely to yield information about early acidification due to its known acid tolerance. Further defining the acid tolerance ranges of *K. quadrata* and *Polyarthra vulgaris* may be important if they are focussed upon as potential indicators of processes during snow melt periods. Although the timing of snow melt varies to some degree from year to year and among lakes, the entire phenomenon could be safely bracketed in a group of lakes by regular sampling between the months of March and June. It seems inadvisable to plan a monitoring program to detect the effect of acidic summer time precipitation on zooplankton due to the unpredictability of storms and the small and ephemeral nature of the pH depressions they cause.

apparent from the literature (Yan & Strus 1980, Carter et al. 1986). Thus, we are unable to predict whether these species will be removed along with known sensitive species, or whether they stand to increase at some point in an acidification process due to competitive release from more sensitive calanoid and cladoceran competitors.

If we restrict predictions to those species for which the most information is available, the following consequences of chronic acidification are probable in the seven Sierra Lakes surveyed. Both Spuller and Ruby Lake lack *D. signicauda*, *Holopedium* and *Keratella taurocephala*, thus an increase in *B. longirostris* following removal of *D. rosea* is the only change that may be expected in these lakes based on available information. In Topaz Lake, *Holopedium* is absent and three species are likely to be removed upon acidification, *D. rosea*, *D. middendorffiana* and *D. signicauda*. Thus in this lake, increases in relative abundance seem probable for *Bosmina longirostris*, *Chydorus sphaericus*, and *Keratella taurocephala*. In Pear Lake, as was observed in Emerald Lake, removal of *D. signicauda* and *D. rosea* may be accompanied by increases in *Holopedium*, *Bosmina*, *Chydorus sphaericus*, and *Keratella taurocephala*. If acidified, the zooplankton responses in Lost Lake and Crystal Lake are likely to resemble those of Pear and Emerald Lakes, with the exception of increases in *Keratella taurocephala* which is absent in these lakes.

In order to achieve the earliest detection of chronic acidification based on zooplankton assemblage it is logical to focus attention on the most sensitive species and concentrate sampling to times of year in which they are characteristically abundant. In the case of *Daphnia rosea*, *Daphnia middendorffiana* and *Diaptomus signicuada*, sampling from June through November would be sufficient in all of the survey lakes to detect major changes in abundance. Upward shifts in abundance of more tolerant species due to competitive release will depend on complex interactions among a number of species, and will probably lag behind decline in sensitive species due to physiologically based mortality. Furthermore, increases in more tolerant species may be hard to detect in a time series, since many of the species involved are already numerically dominant in the survey lakes through much of the year. If detailed monitoring of indirect responses are deemed necessary, a prolonged sampling period may be justified. However, based on the analysis of the efficacy of year-round sampling, it seems prudent to restrict sampling to the months encompassing snow melt through the summer and ice-free autumn months (roughly April-October). More frequent sampling (at least once/month) is advisable in order to ensure the detection of annual population peaks for important species, and to avoid incorrectly designating species as absent at certain times of the year.

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Fig. 2

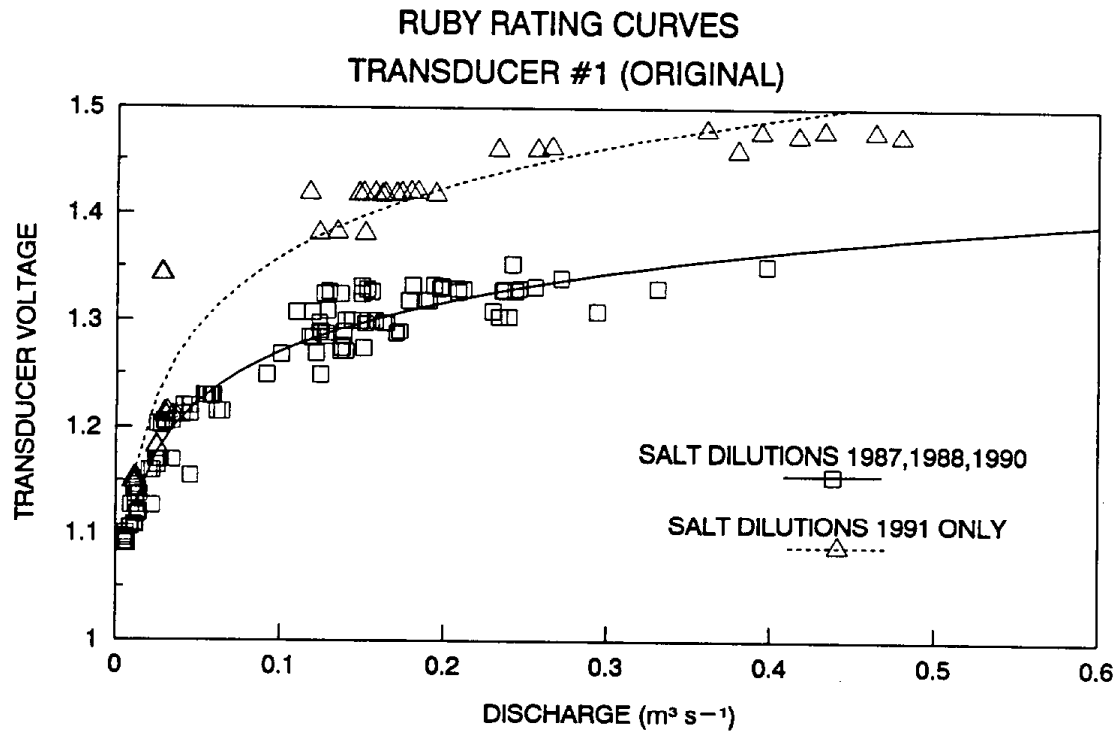
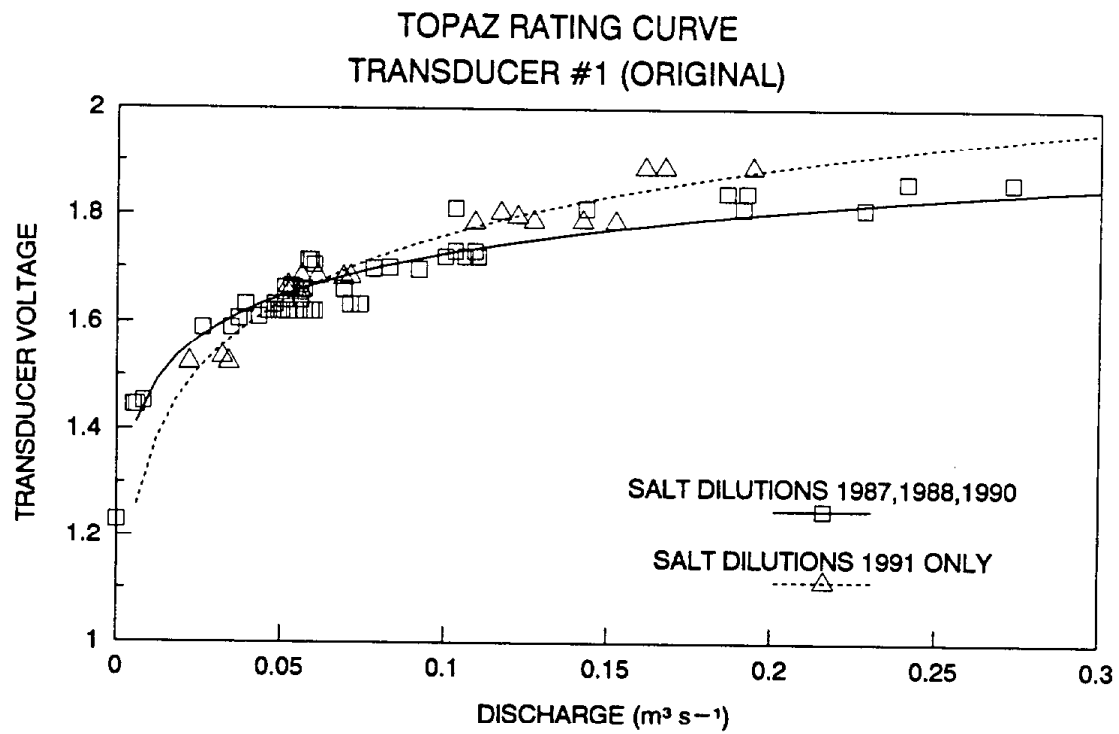
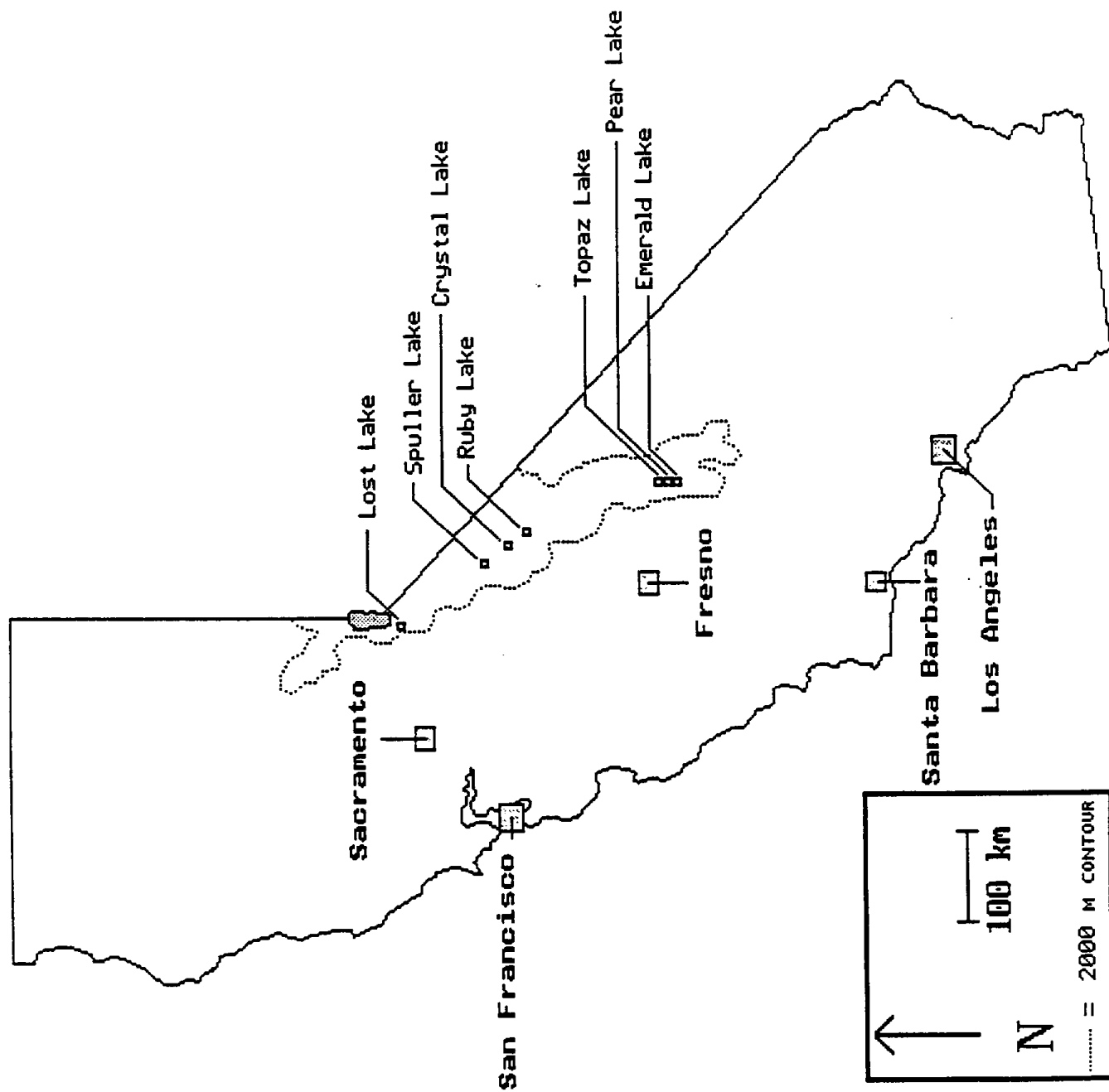
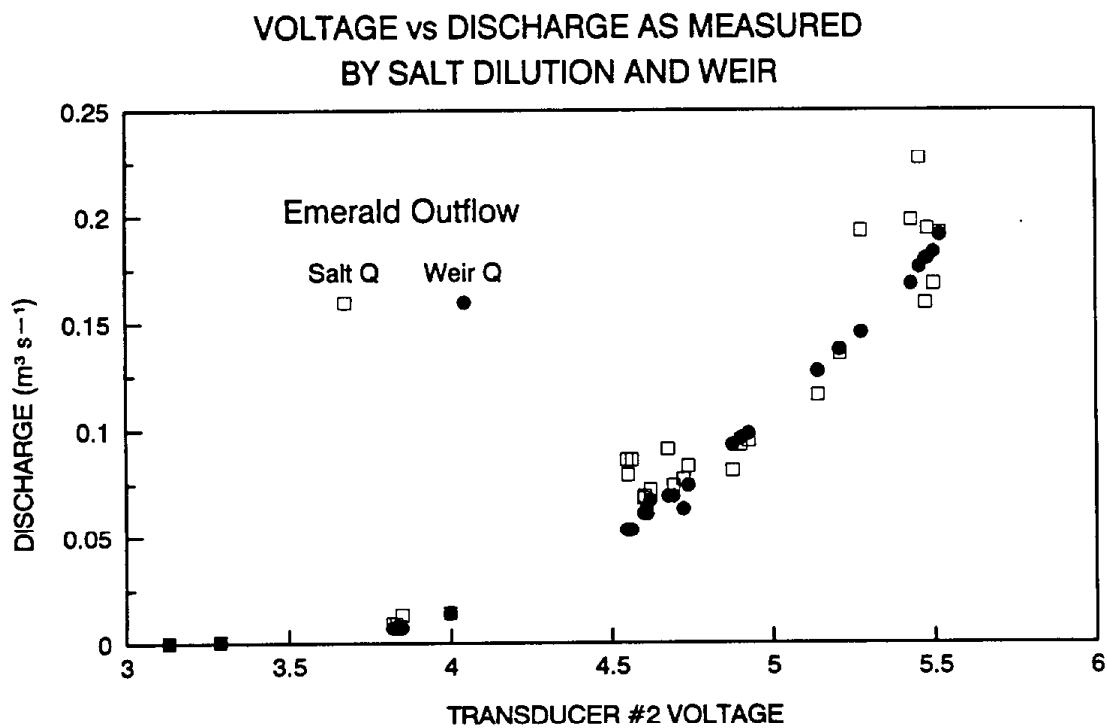
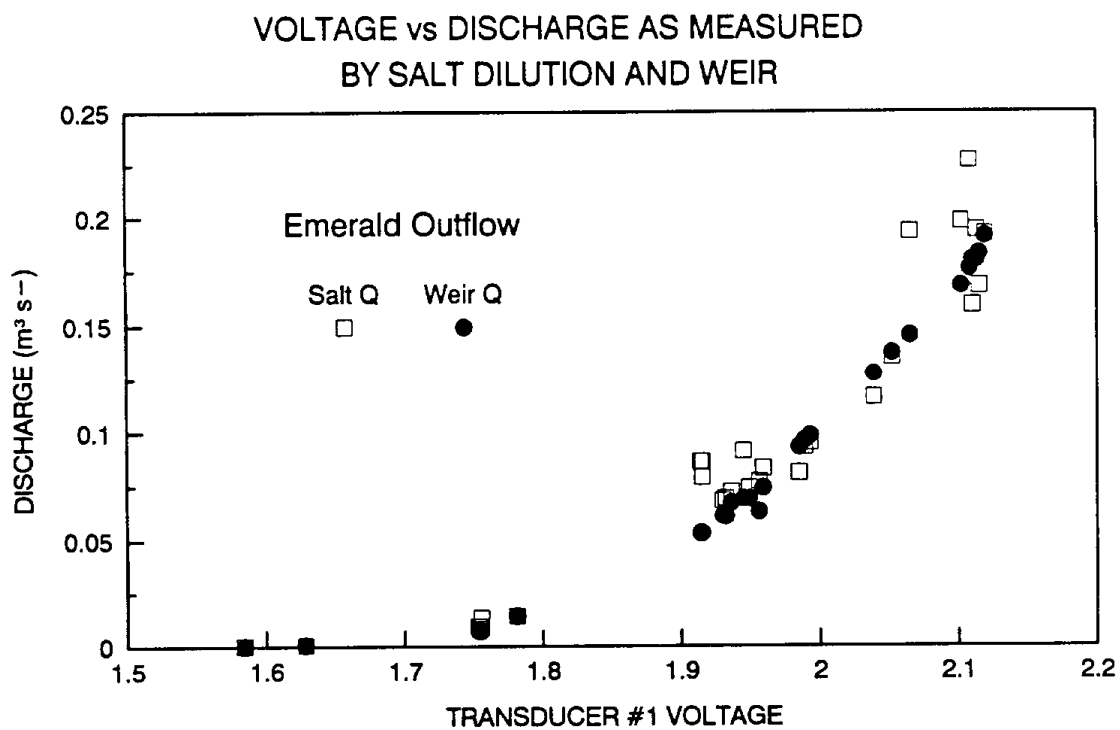


Figure 1





RELATIONSHIP BETWEEN WEIR GAUGE AND TRANSDUCER VOLTAGE

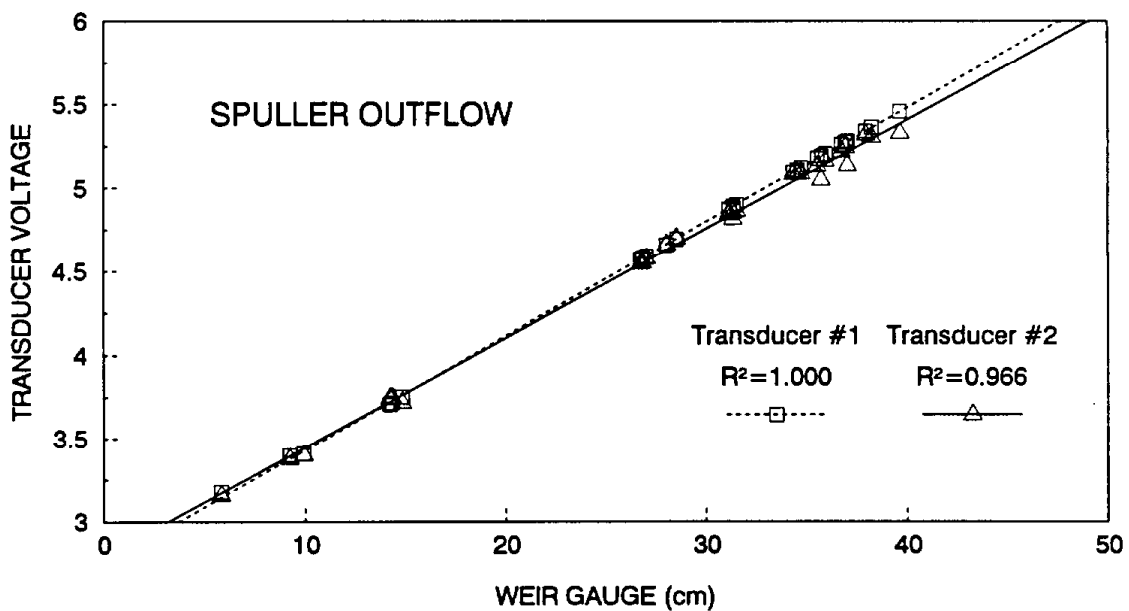
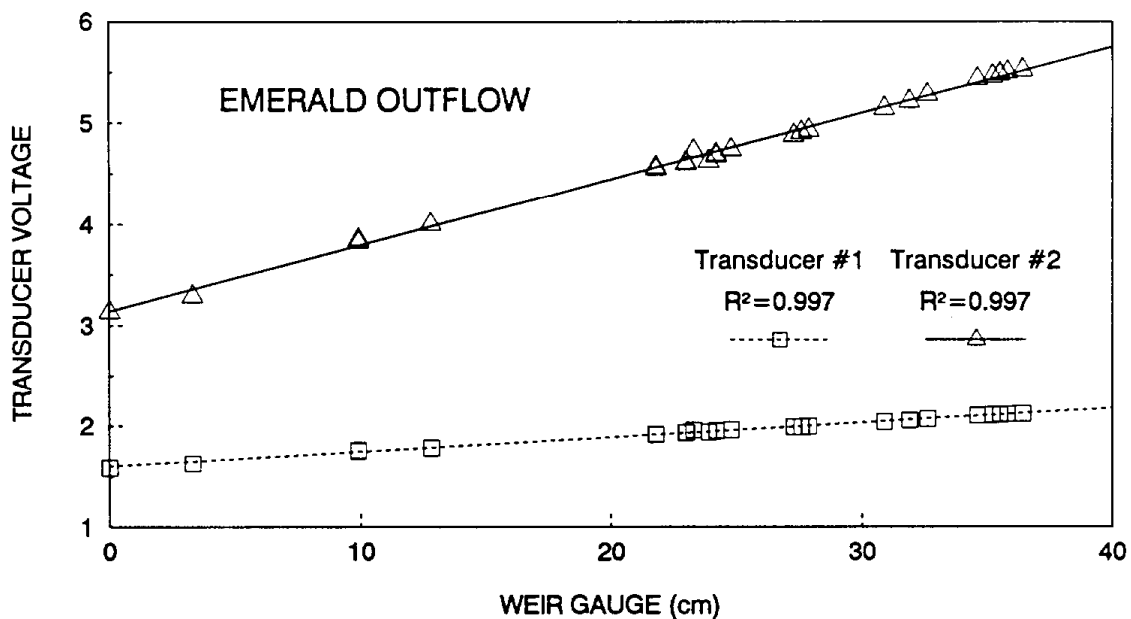


Fig. 6

DISCHARGE BY WEIR vs DISCHARGE BY SALT DILUTION

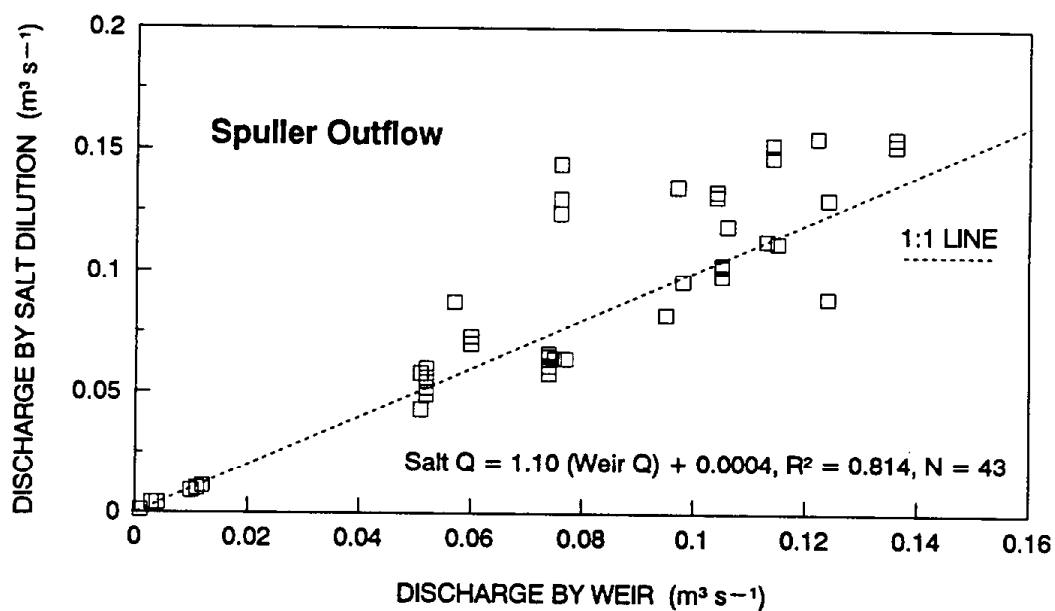
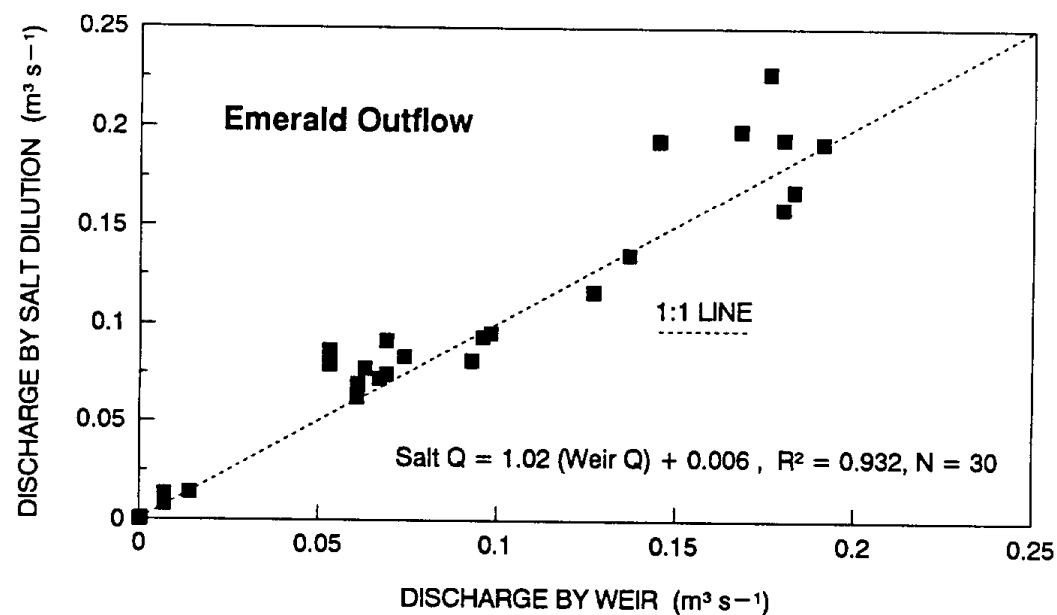
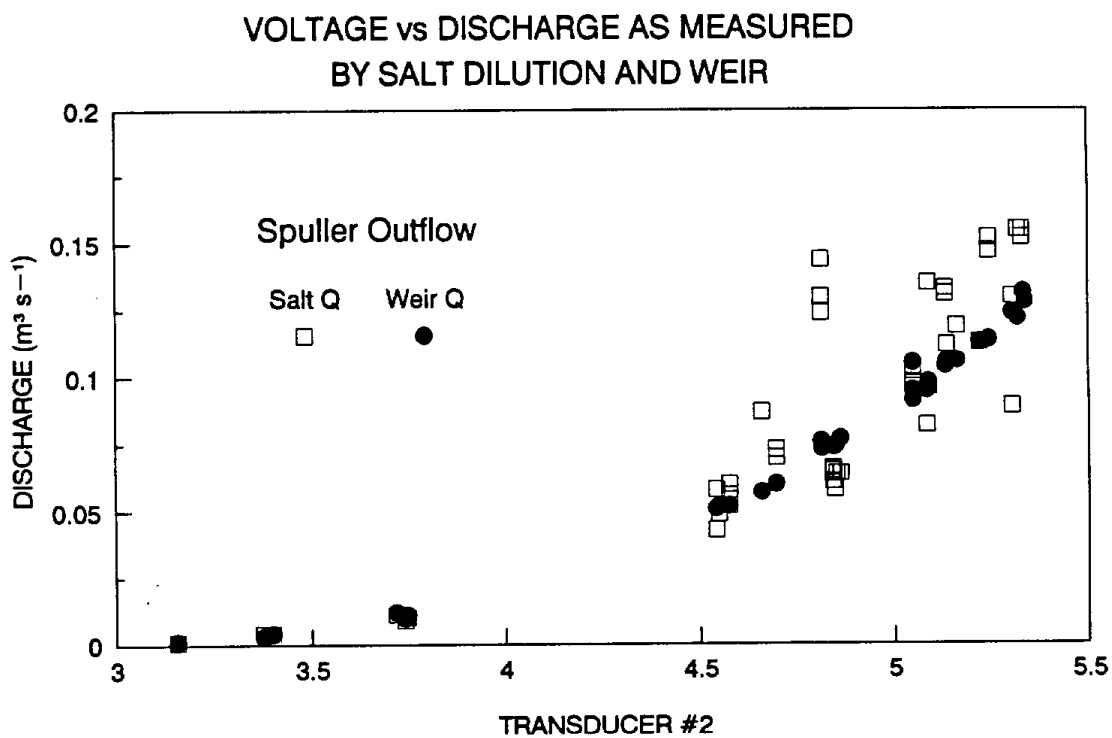
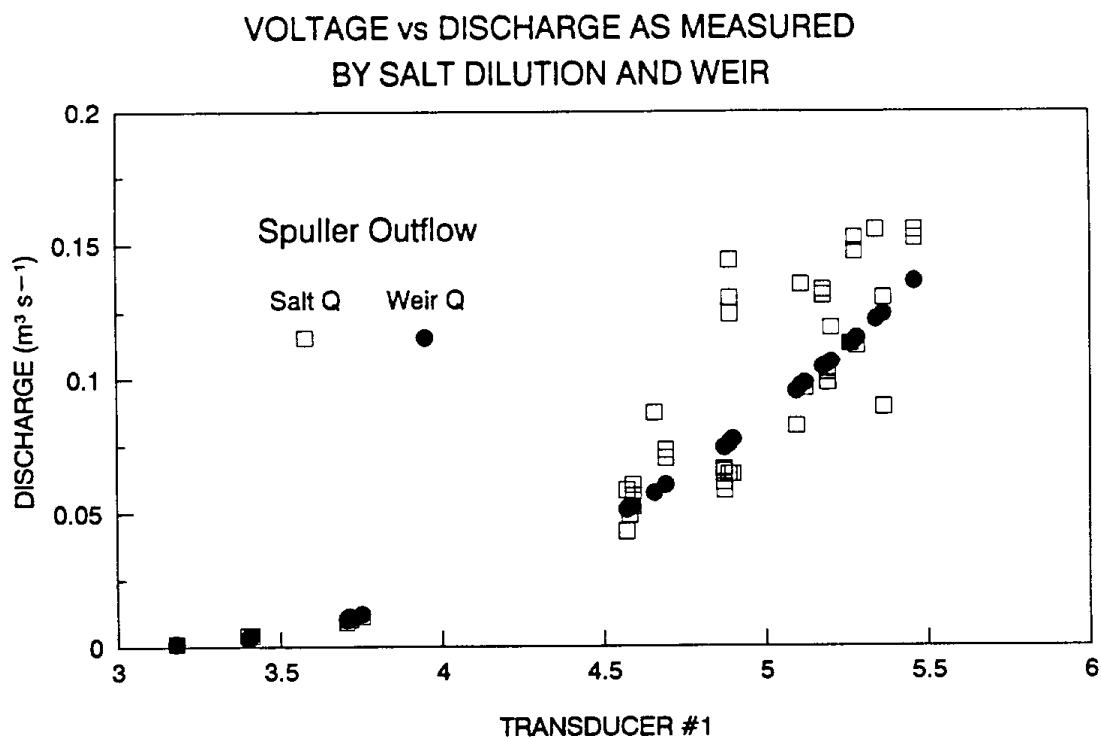


Fig. 5



SNOW SAMPLES SPRING 1990

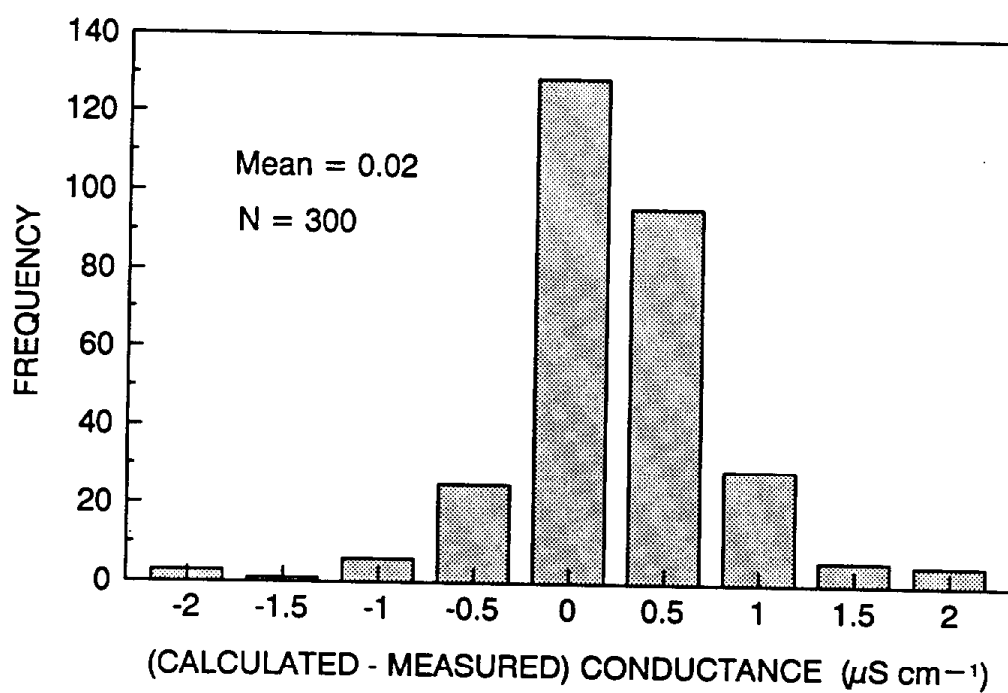
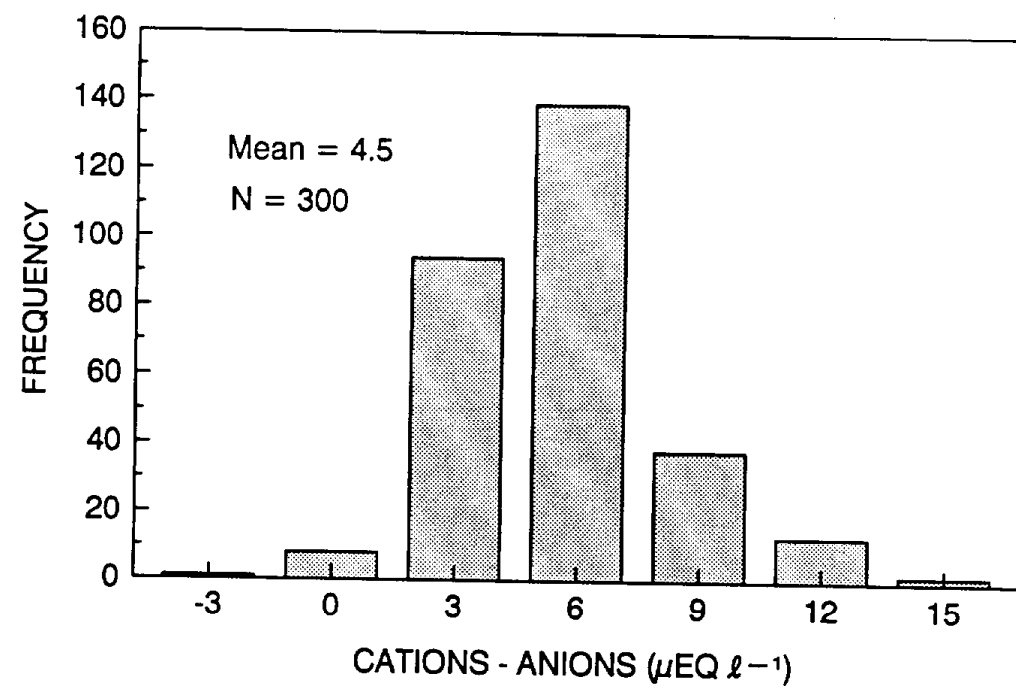
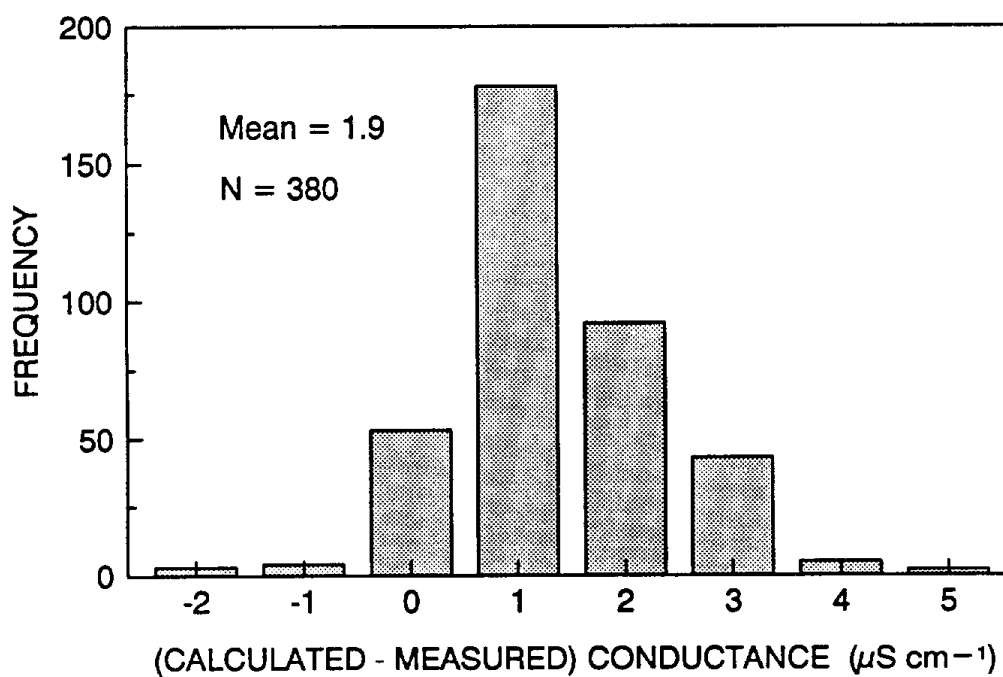
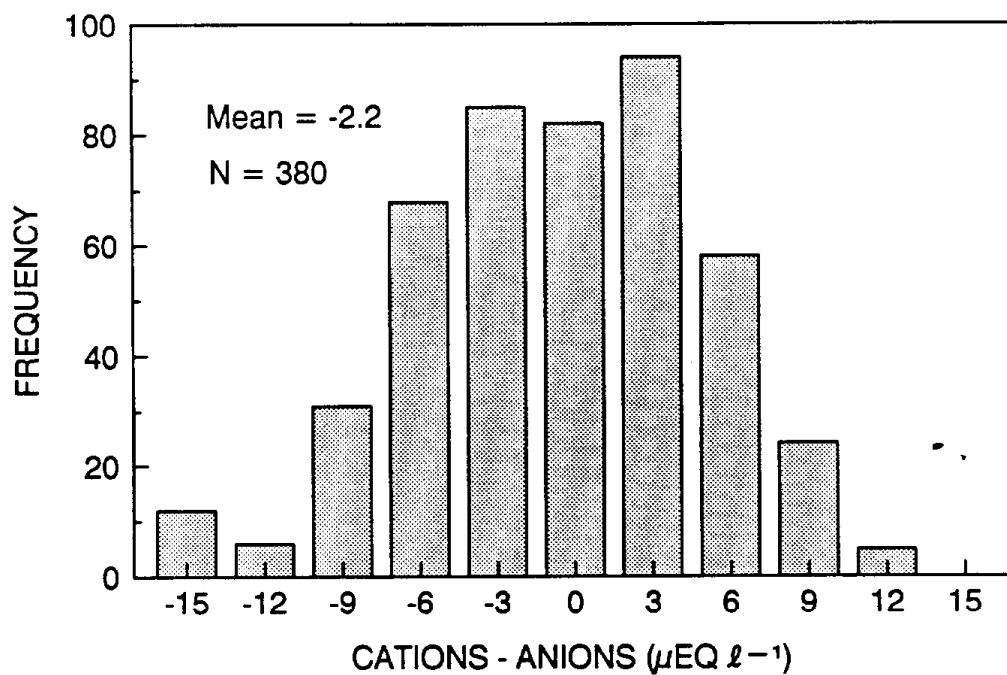


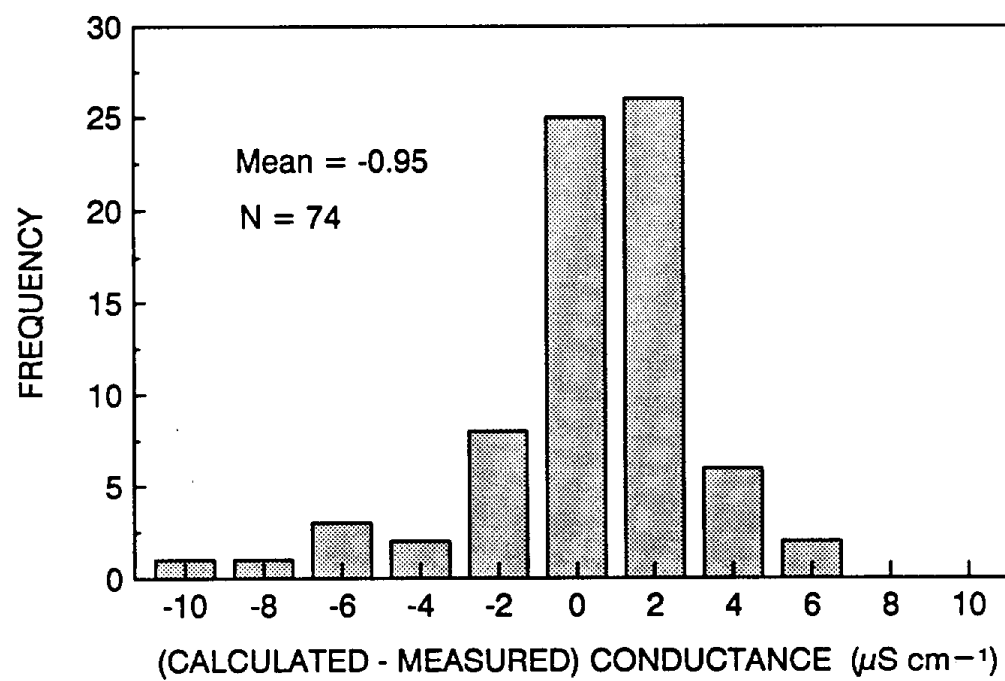
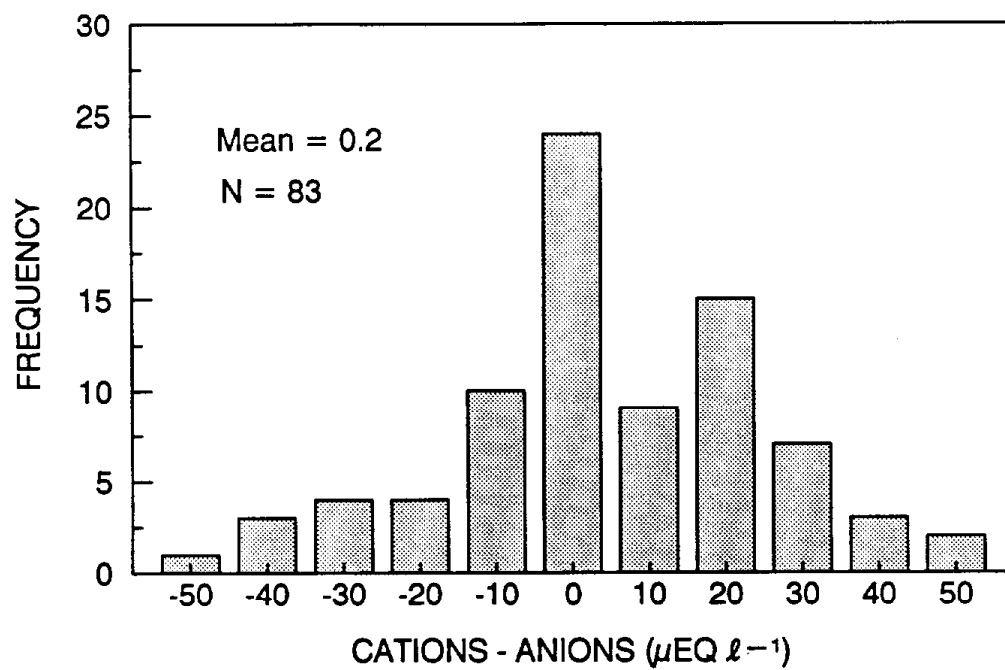
Fig. 7

LAKE AND OUTFLOW SAMPLES OCTOBER 1989 TO NOVEMBER 1991

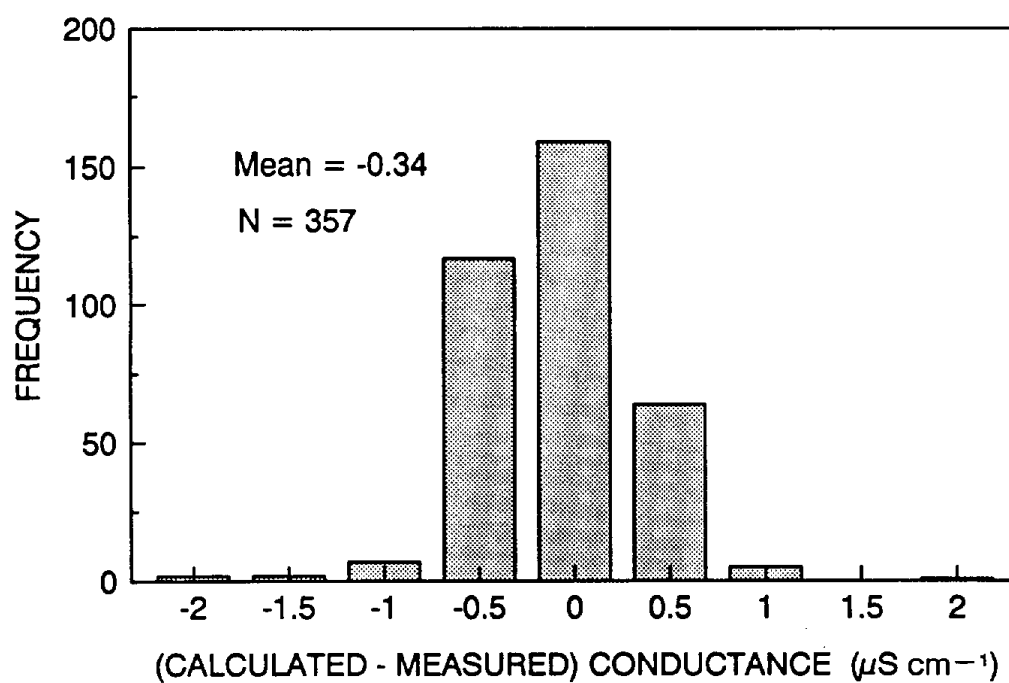
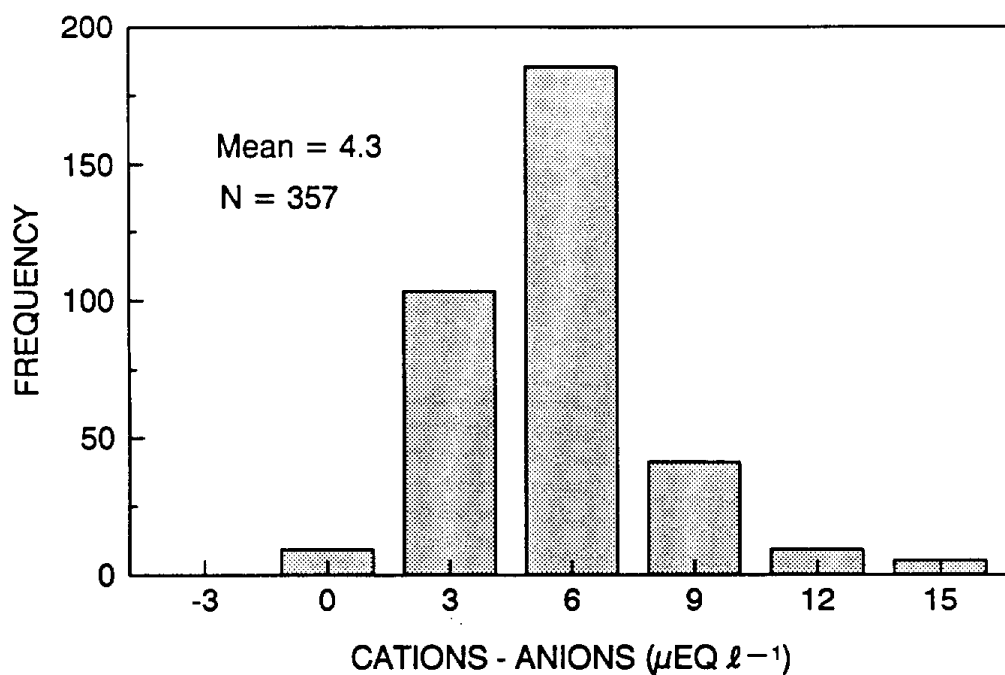


RAIN SAMPLES

1990



SNOW SAMPLES SPRING 1991



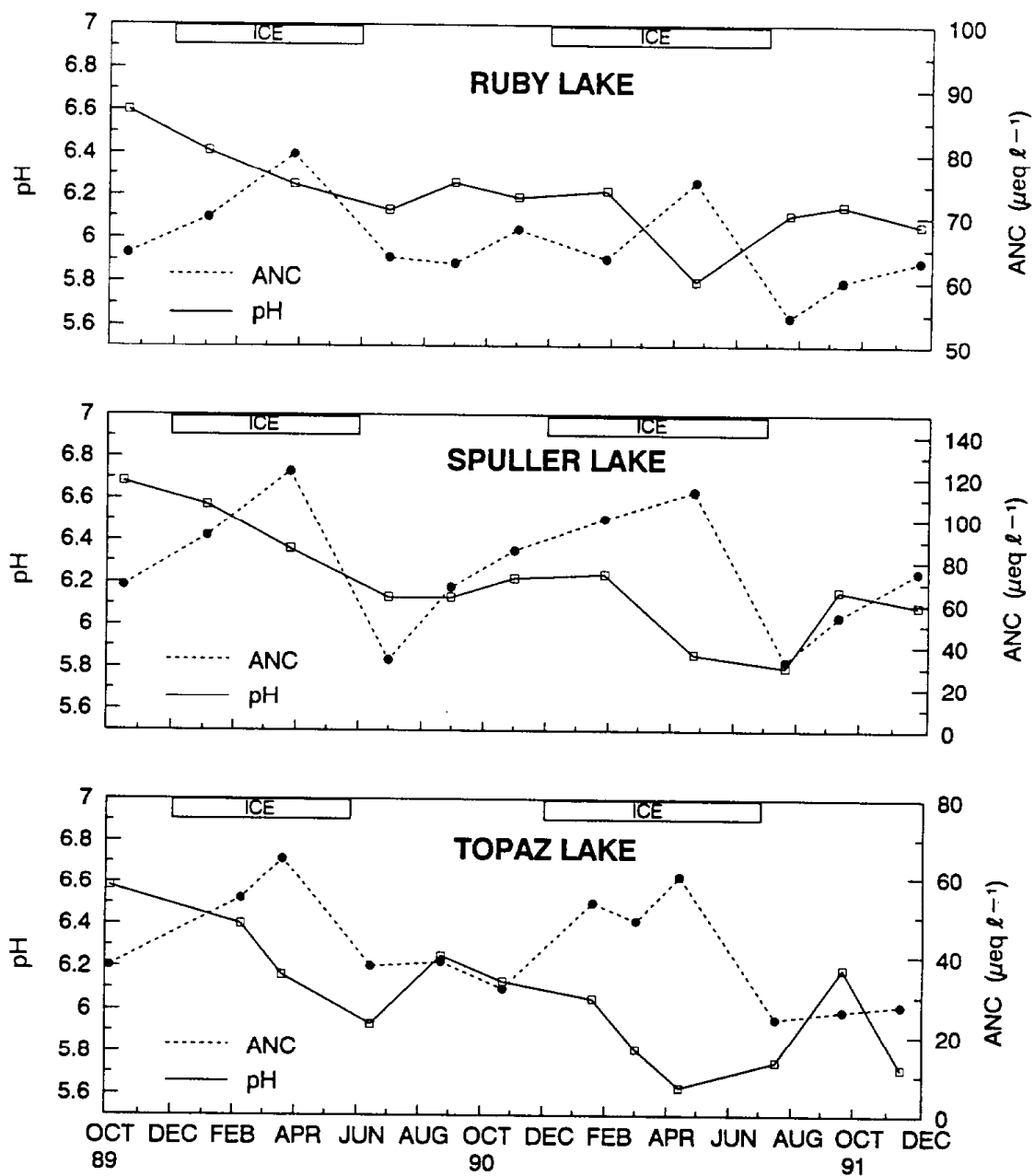
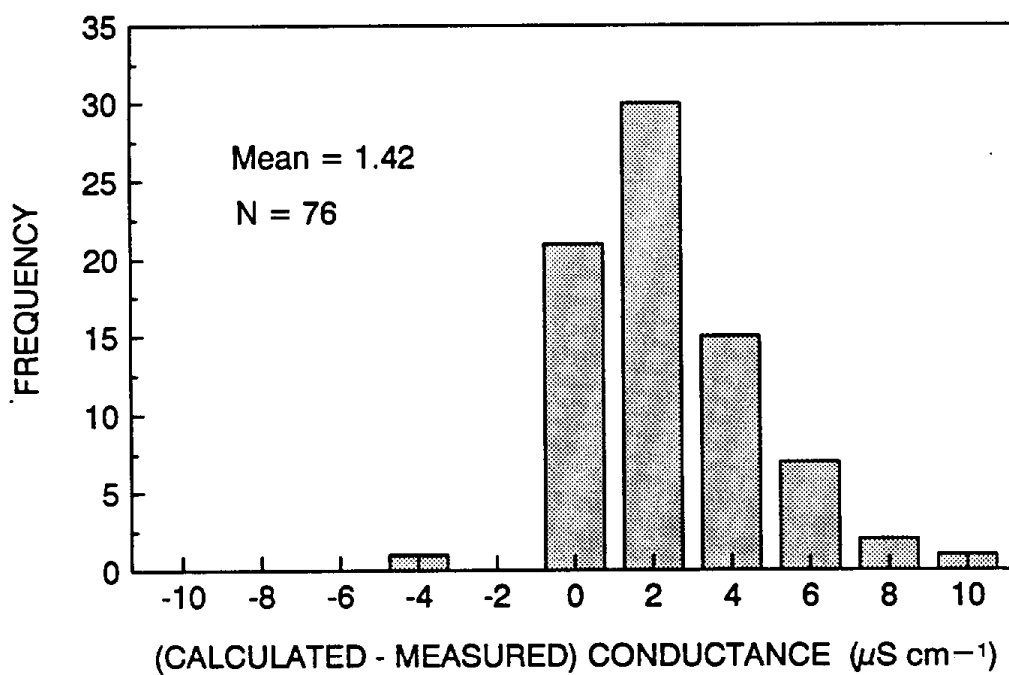
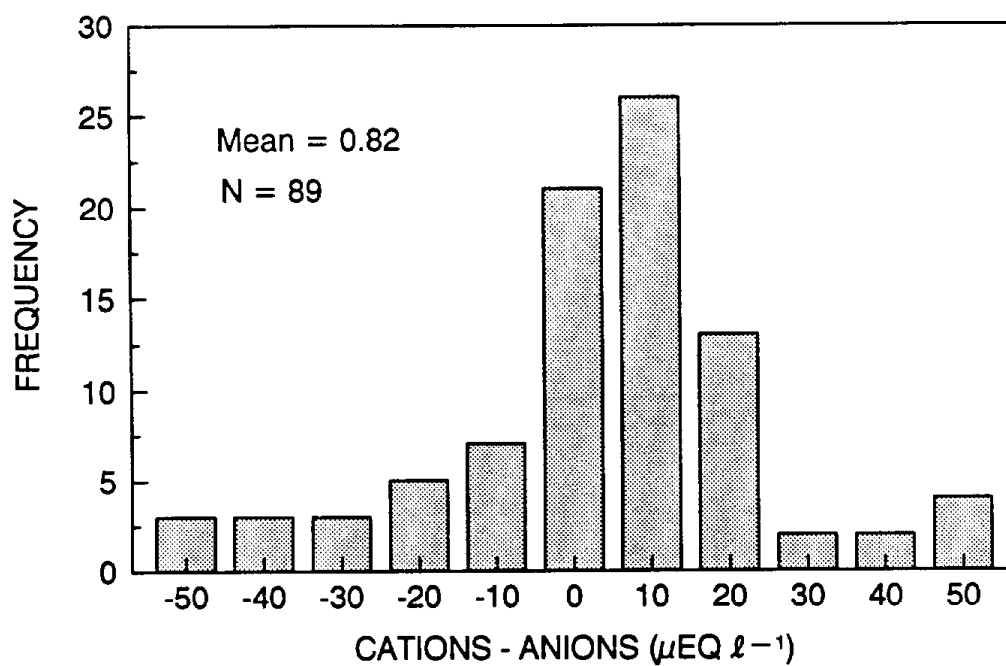


Fig. 12 Volume-weighted mean lake chemistry for the period of October 1989 to November 1991.

RAIN SAMPLES

1991



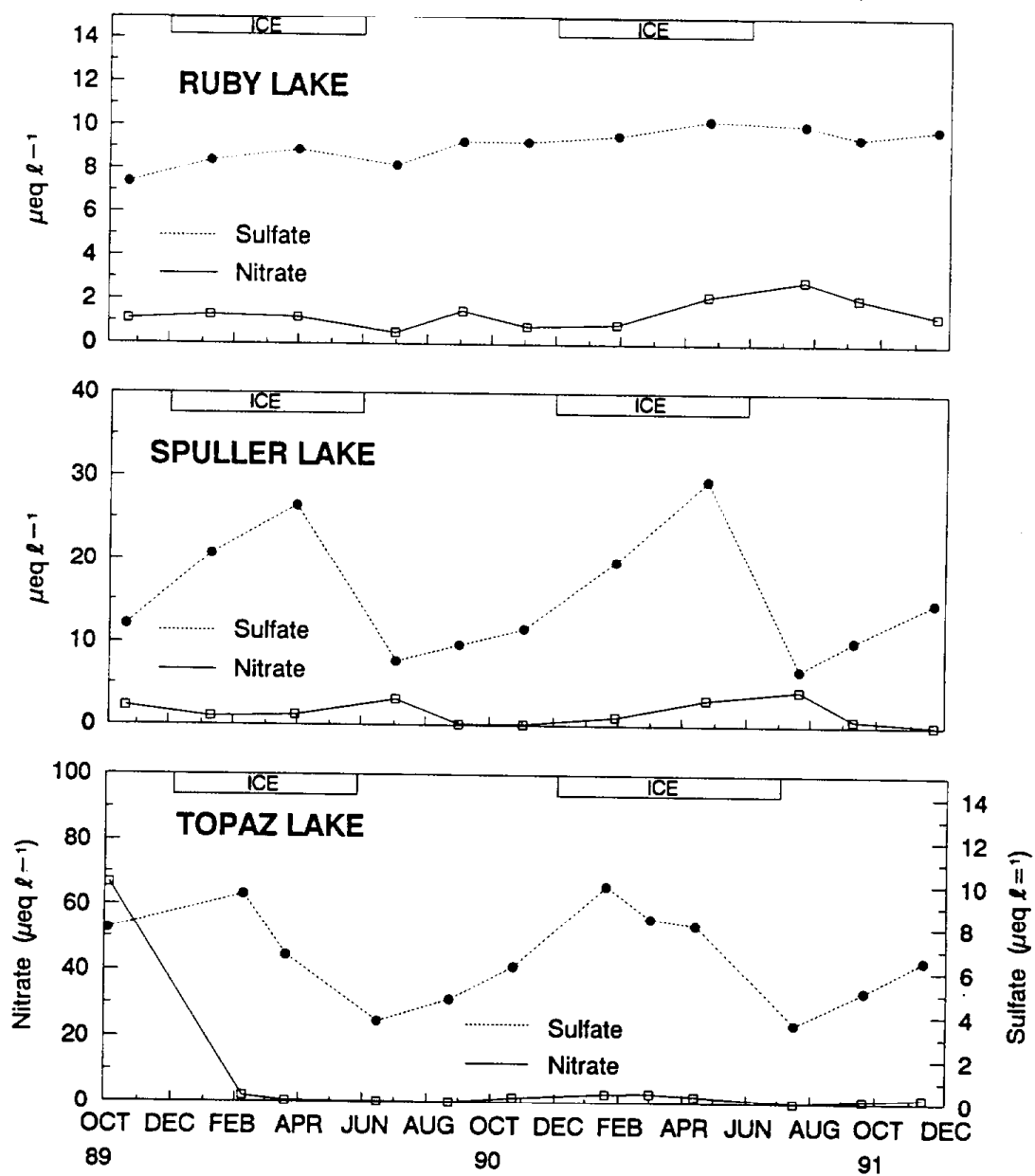
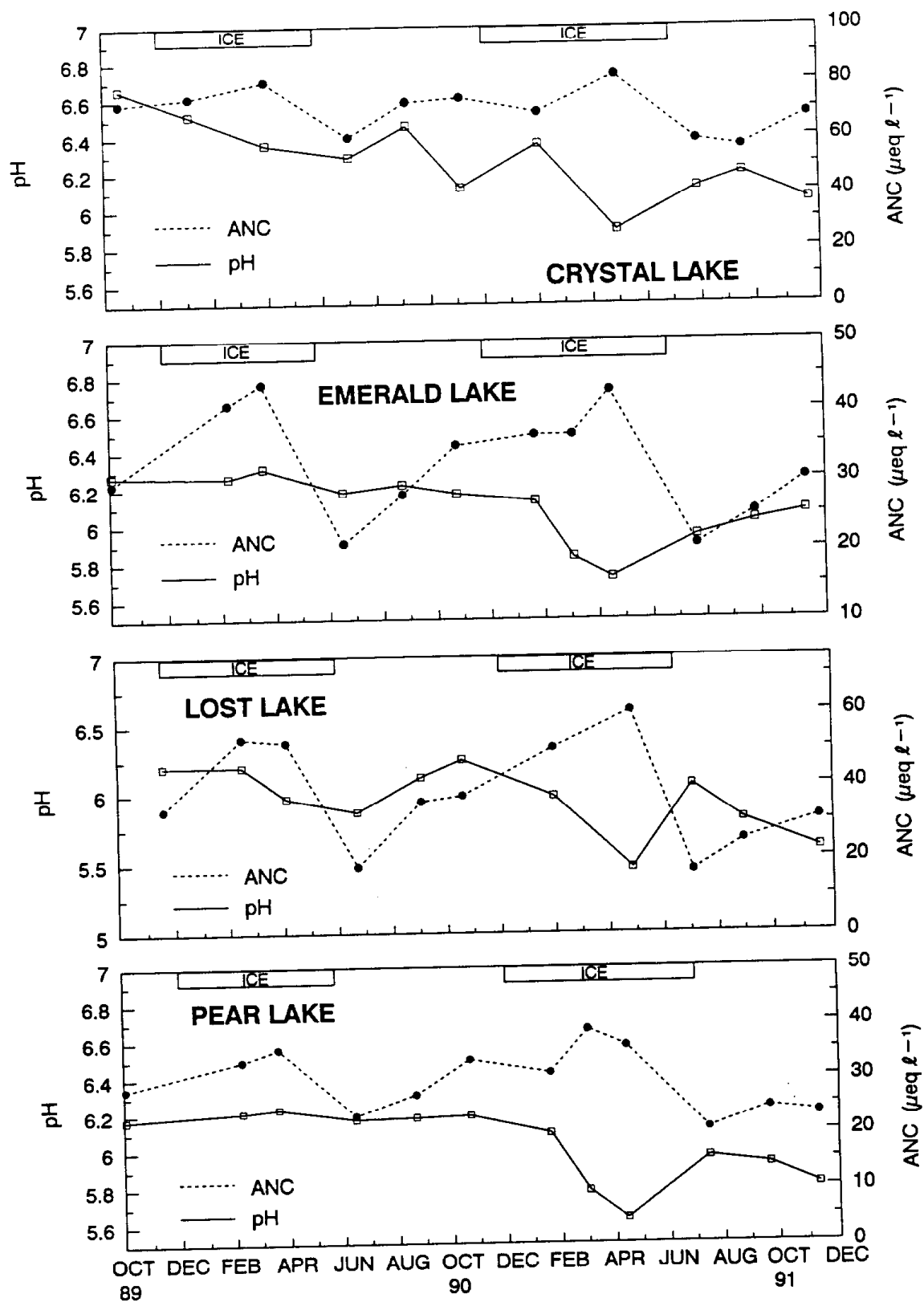


Fig. 13 Volume-weighted mean lake chemistry for the period of October 1989 to November 1991.

Fig. 12



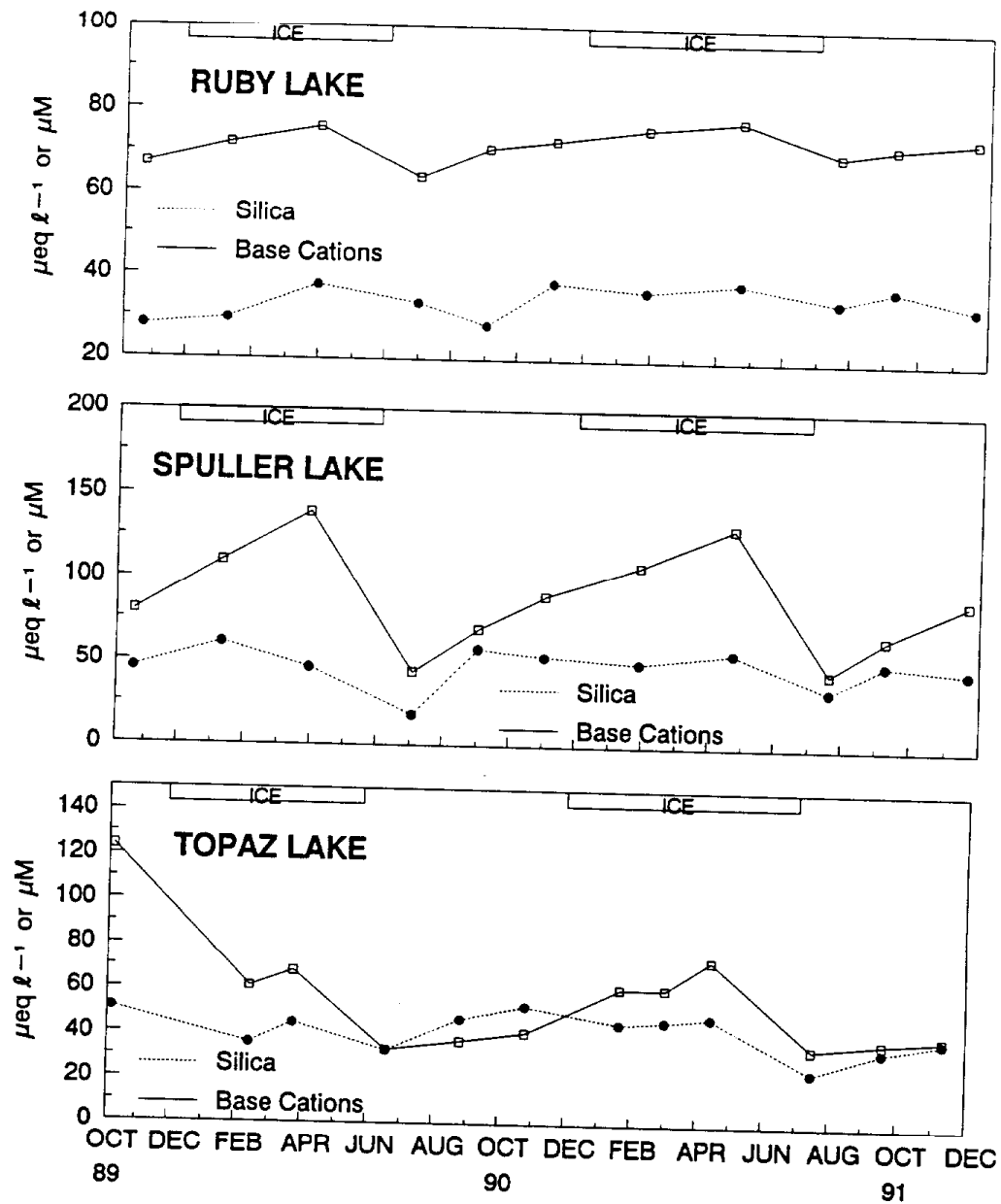
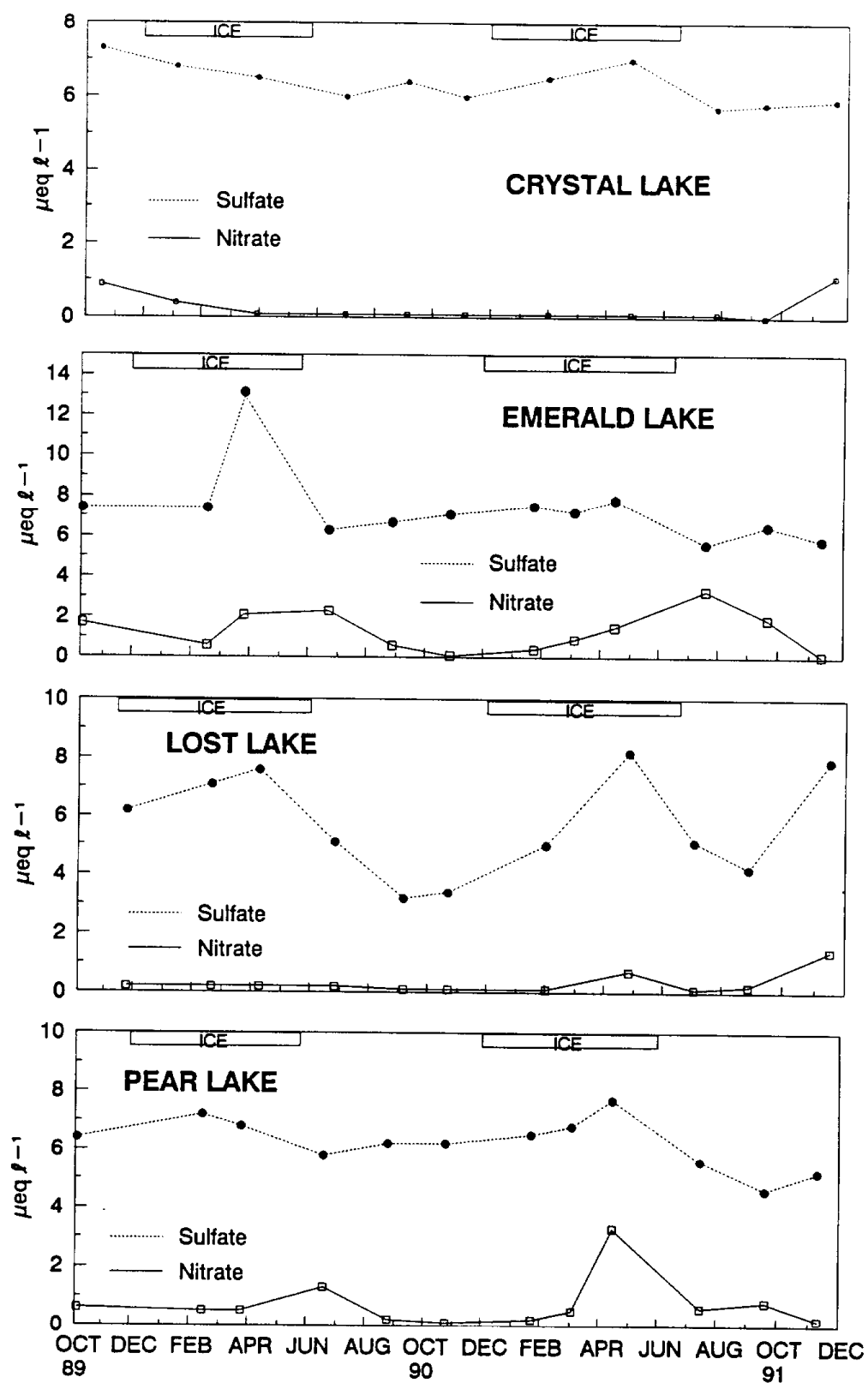


Fig. 14 Volume-weighted mean lake chemistry for the period of October 1989 to November 1991.

Fig. 13



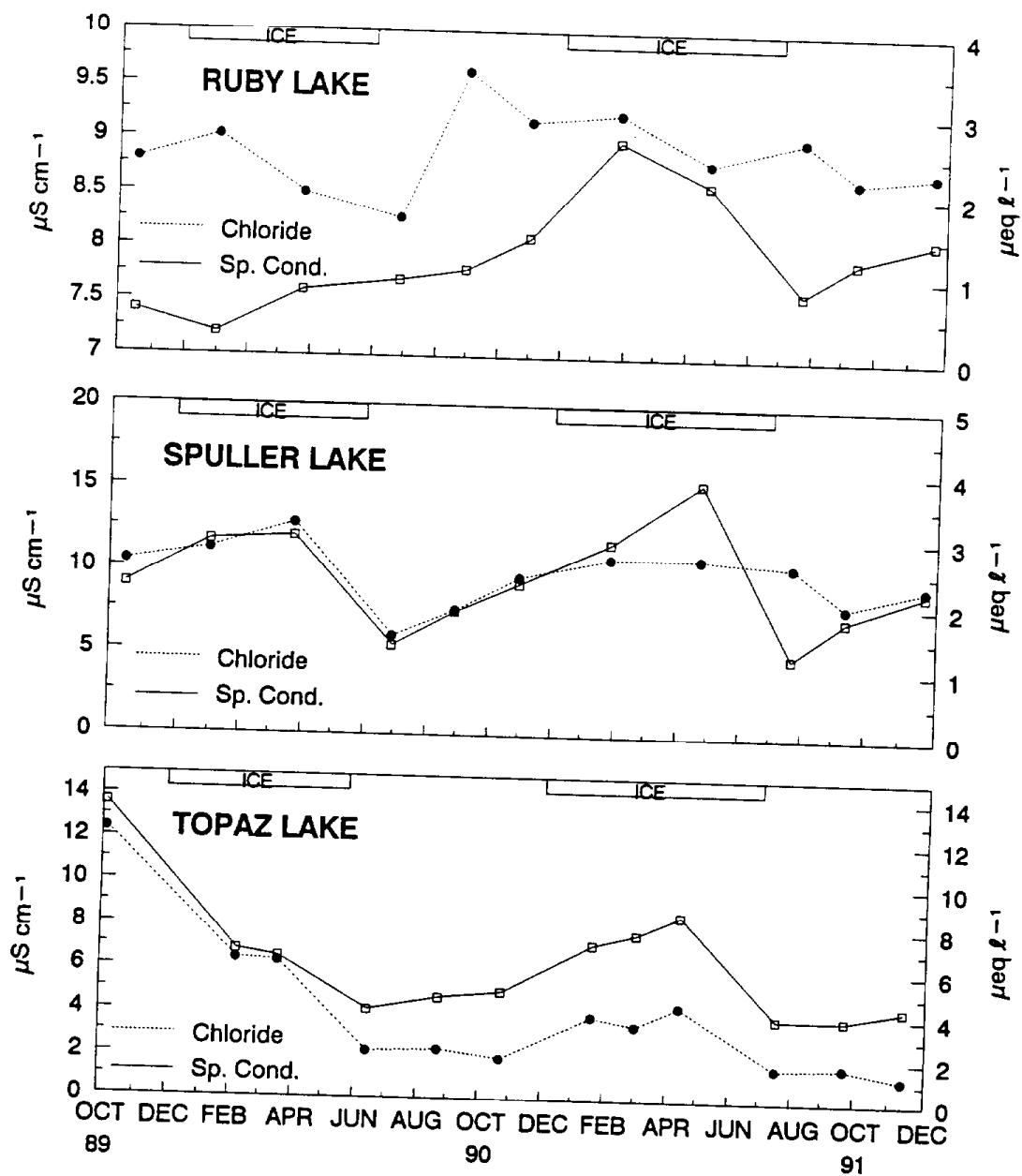


Fig. 15 Volume-weighted mean lake chemistry for the period of October 1989 to November 1991.

Fig. 14

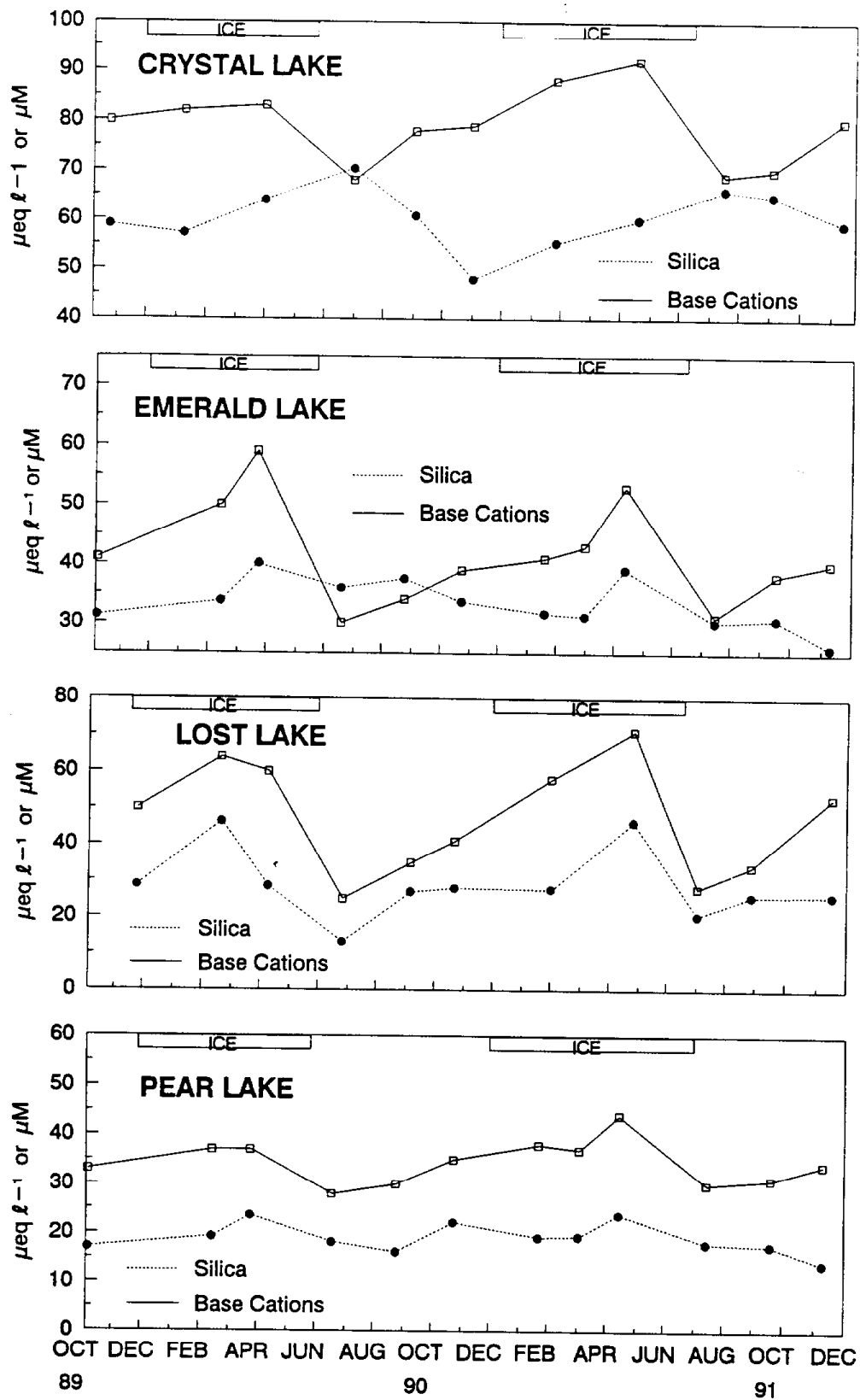


Fig. 16a

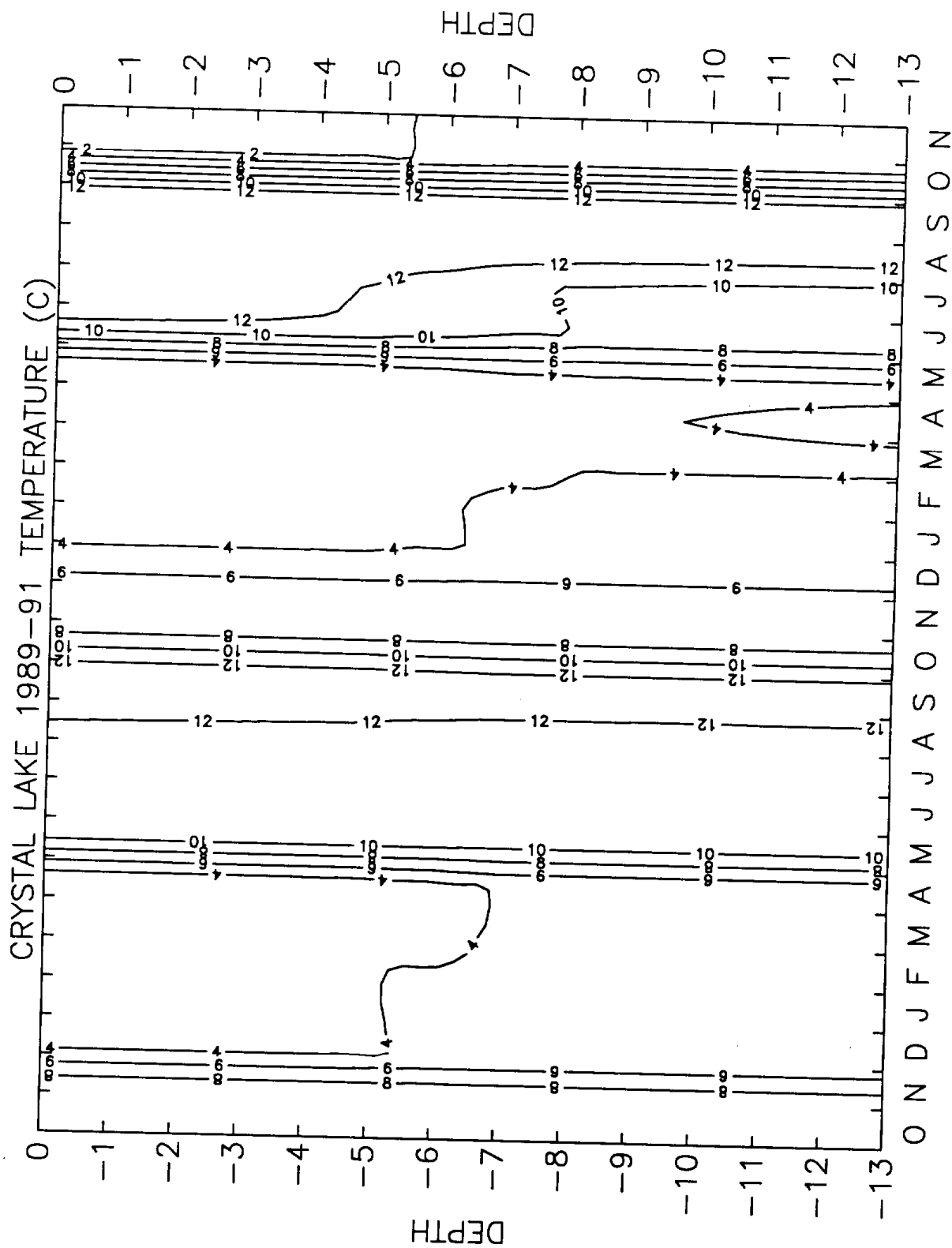


Fig. 15

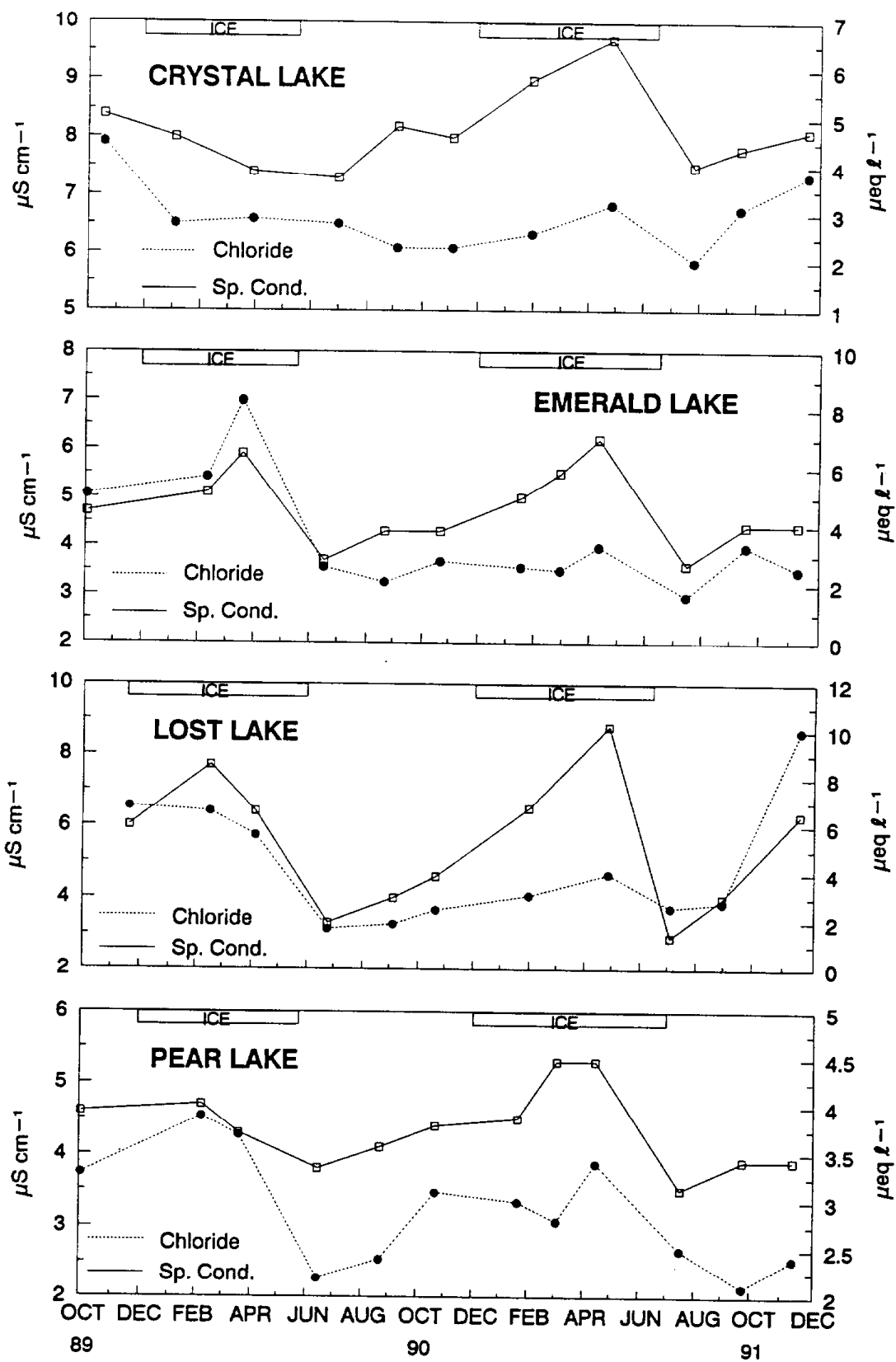


Fig. 16c

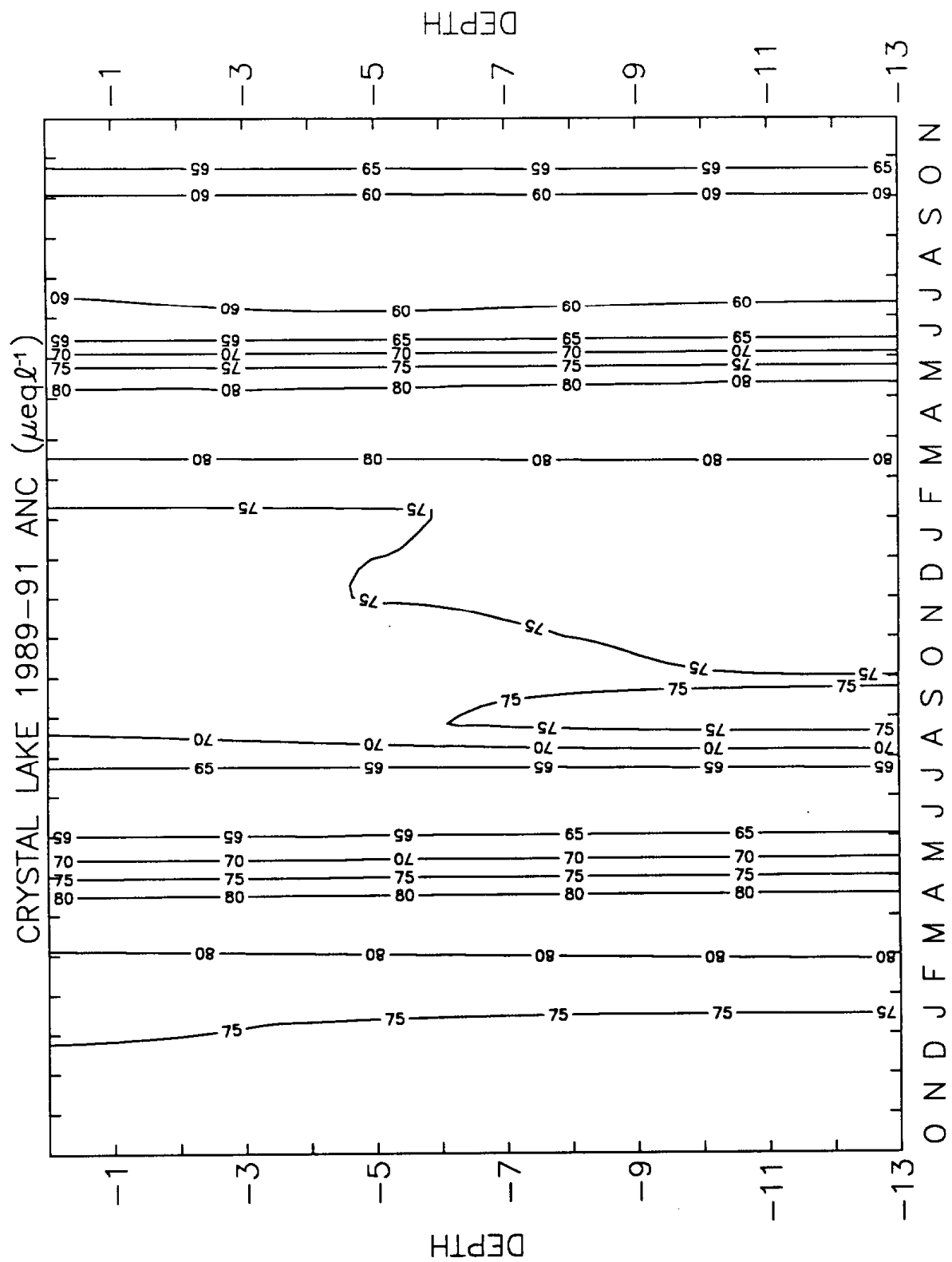


Fig. 16b

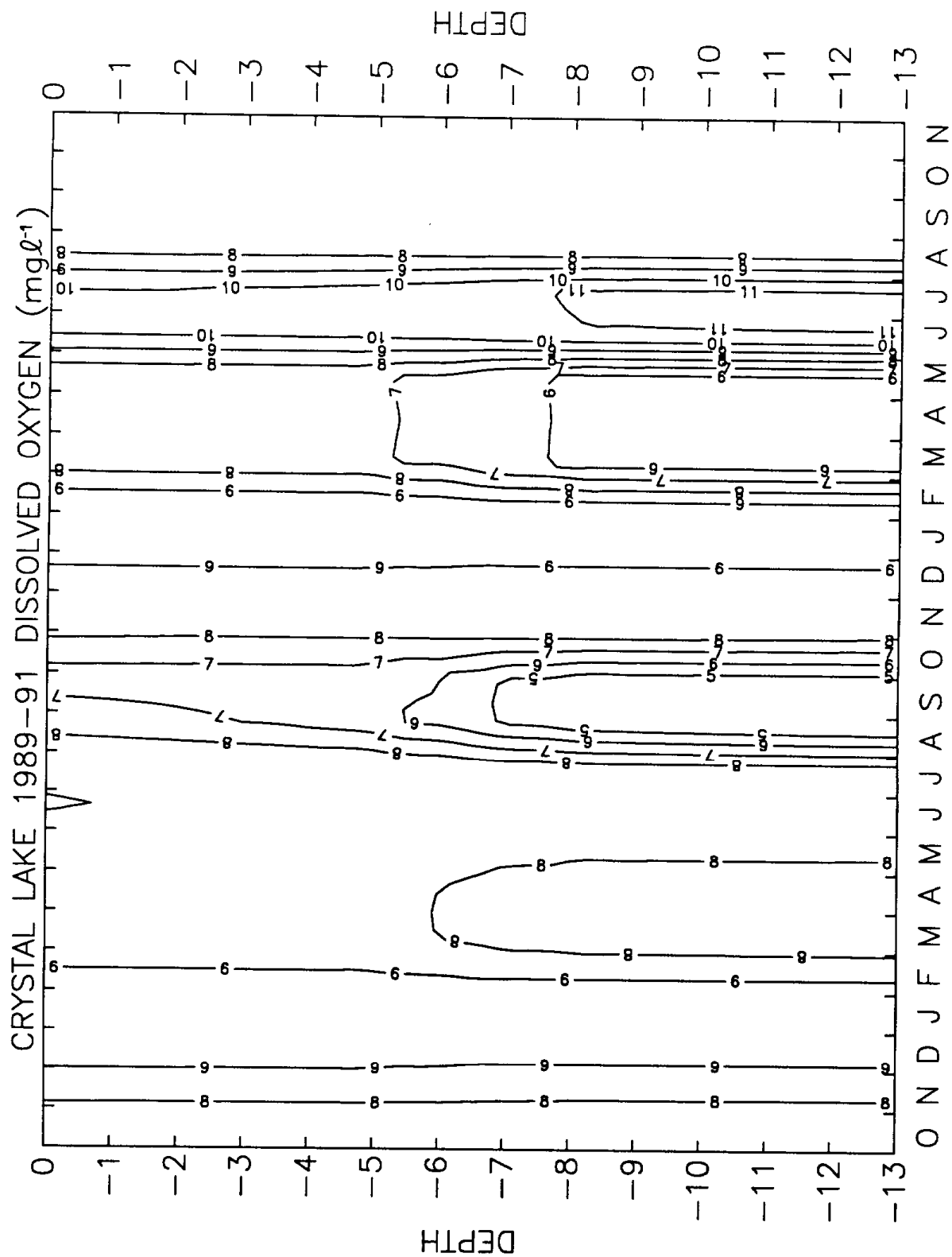


Fig. 17b

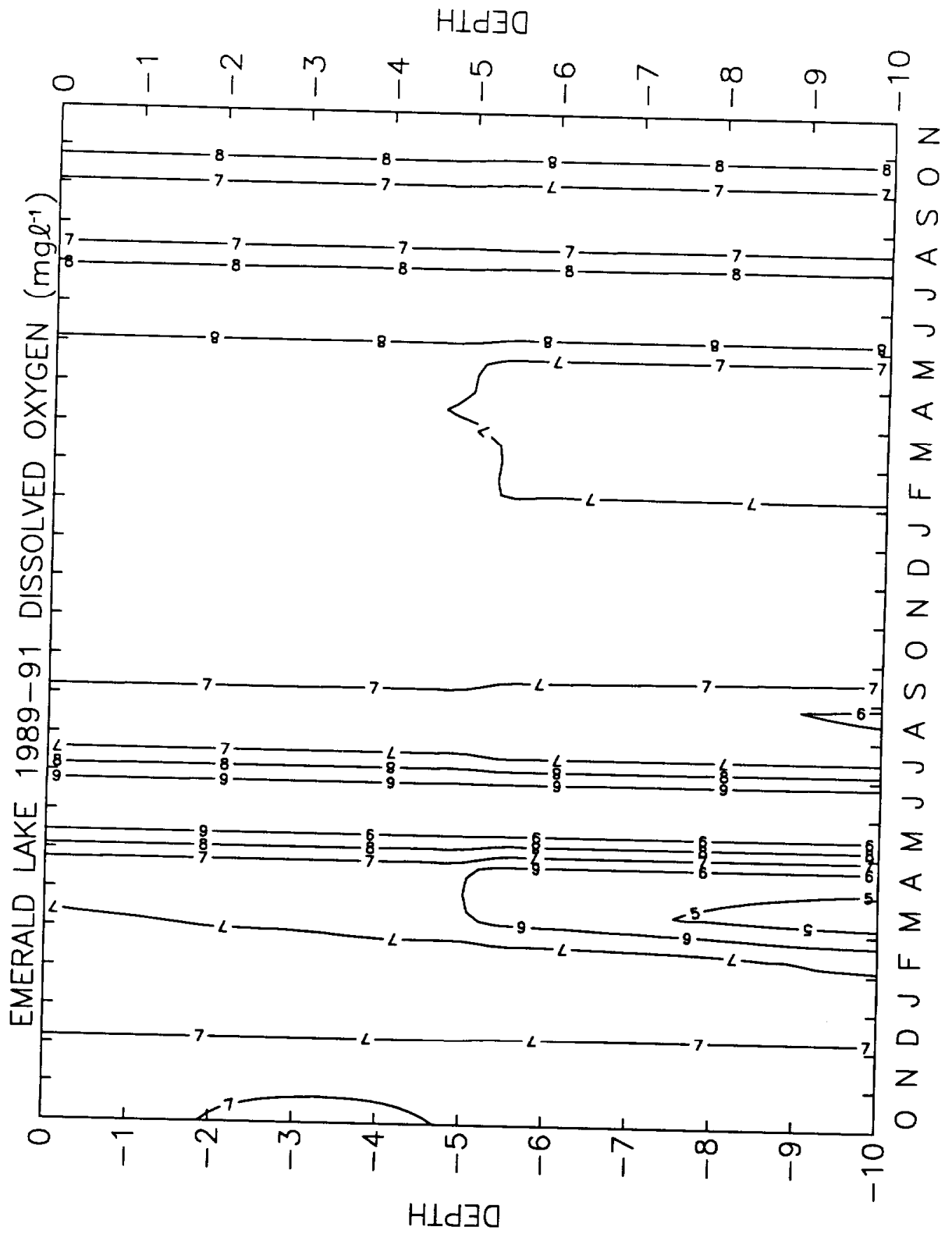


Fig. 17a

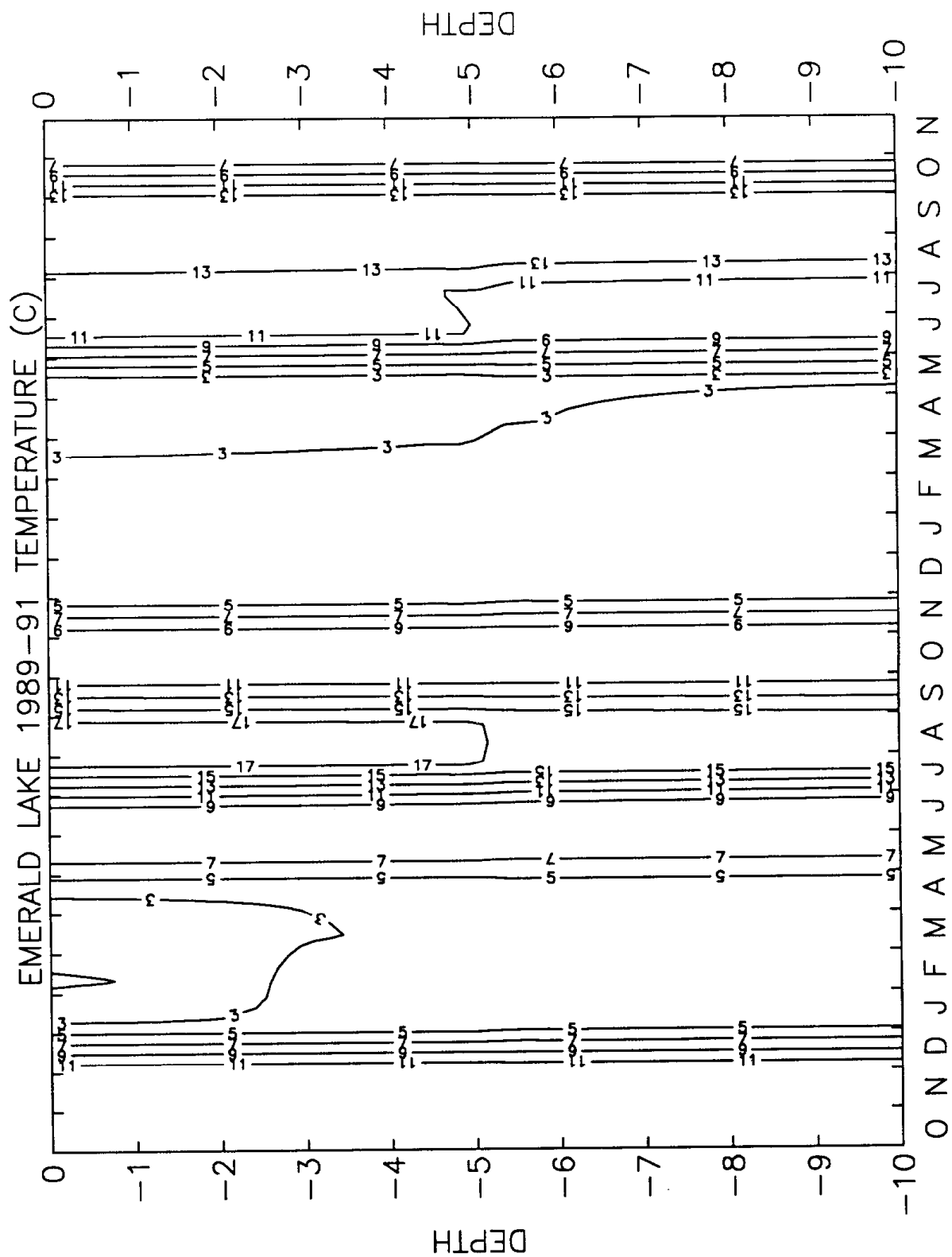


Fig. 18a

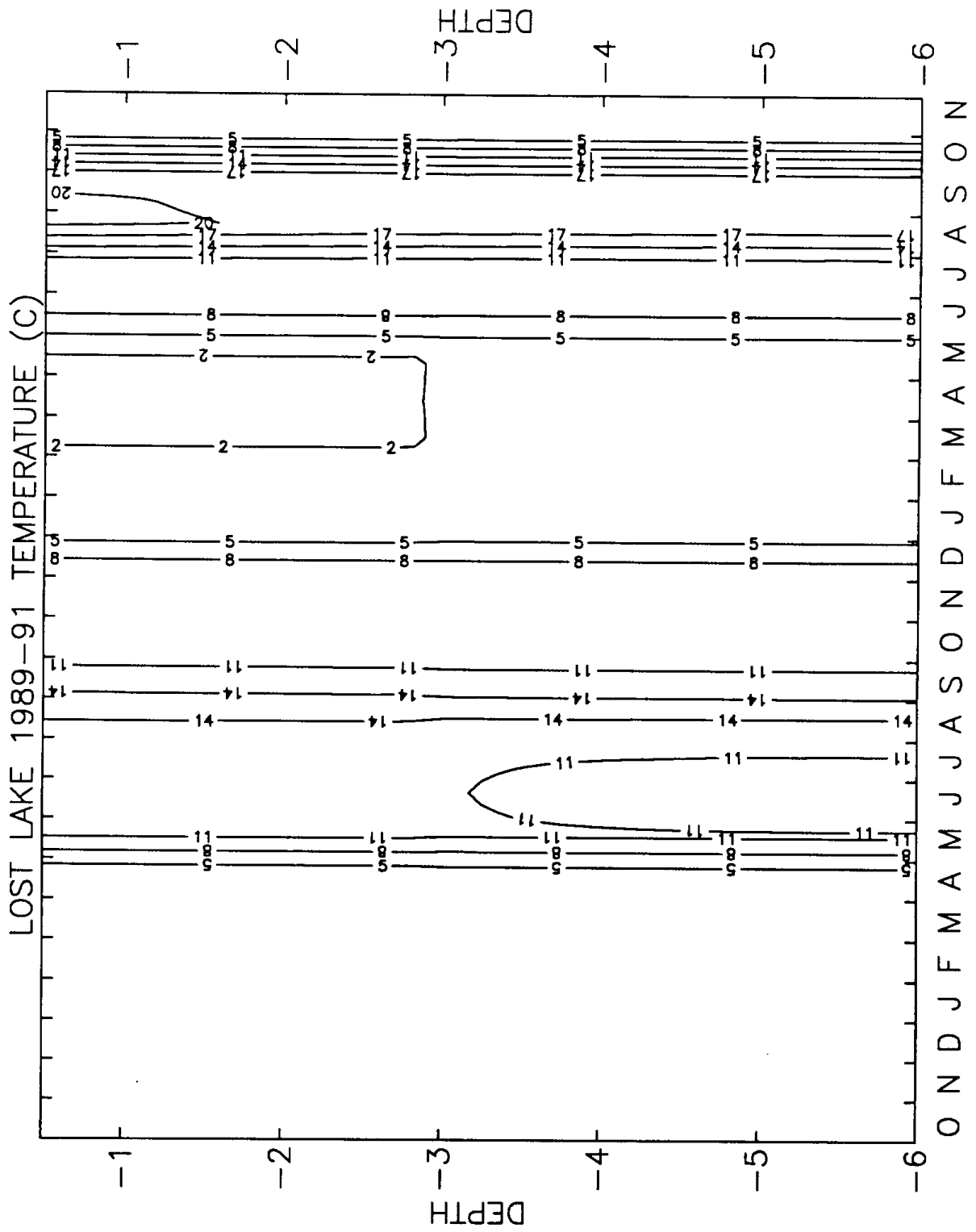


Fig. 17c

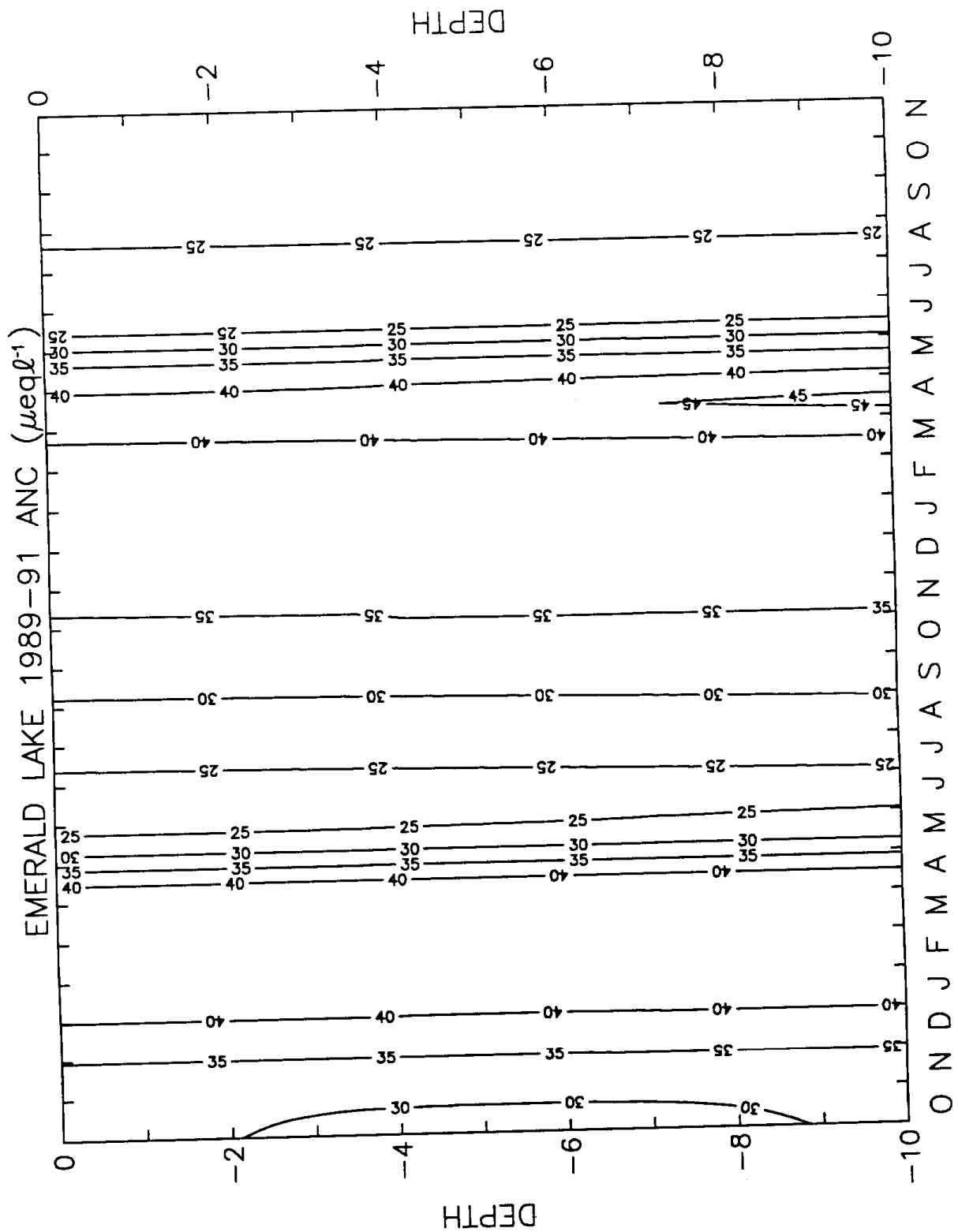


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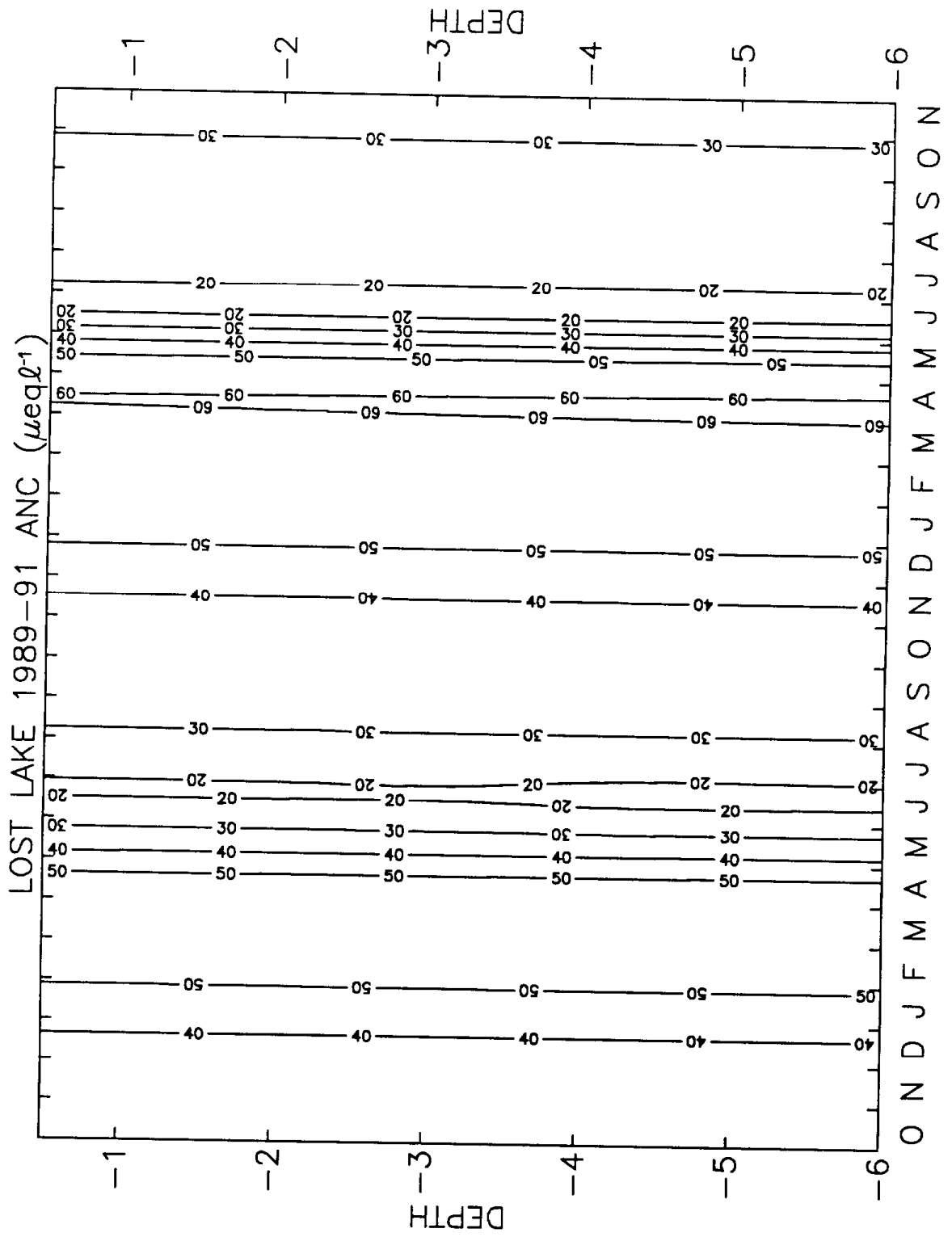
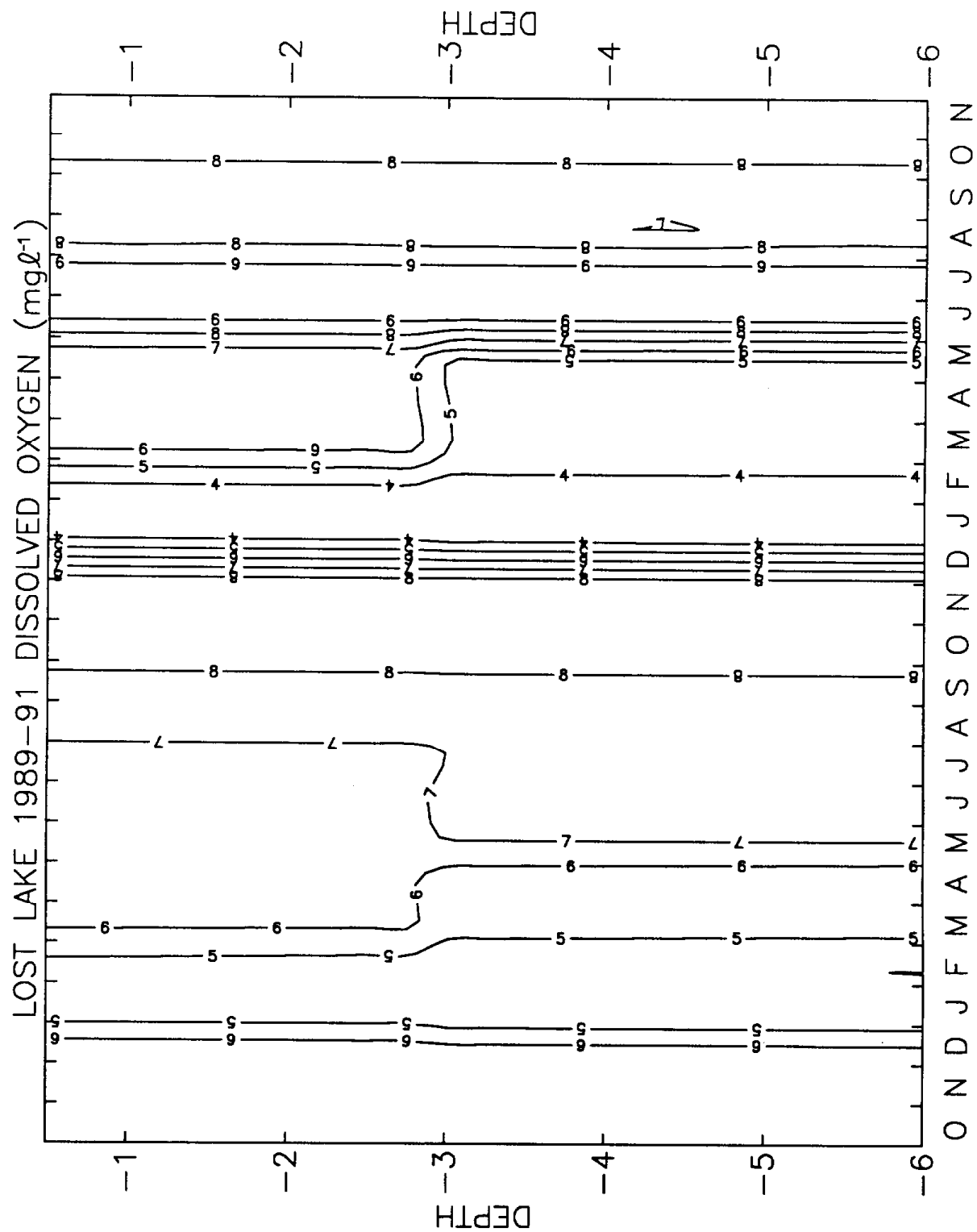


Fig. 18b



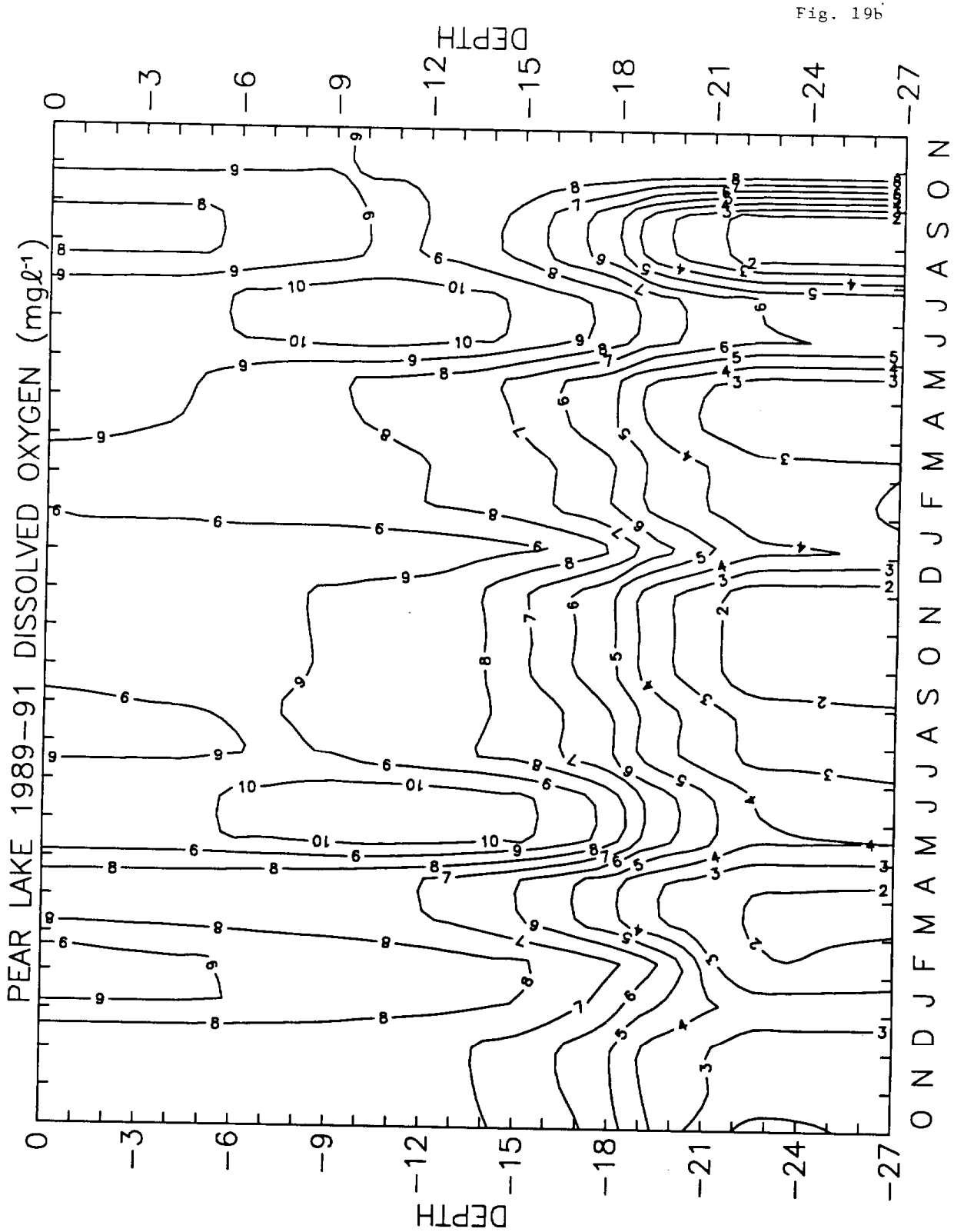


Fig. 19b

Fig. 19a

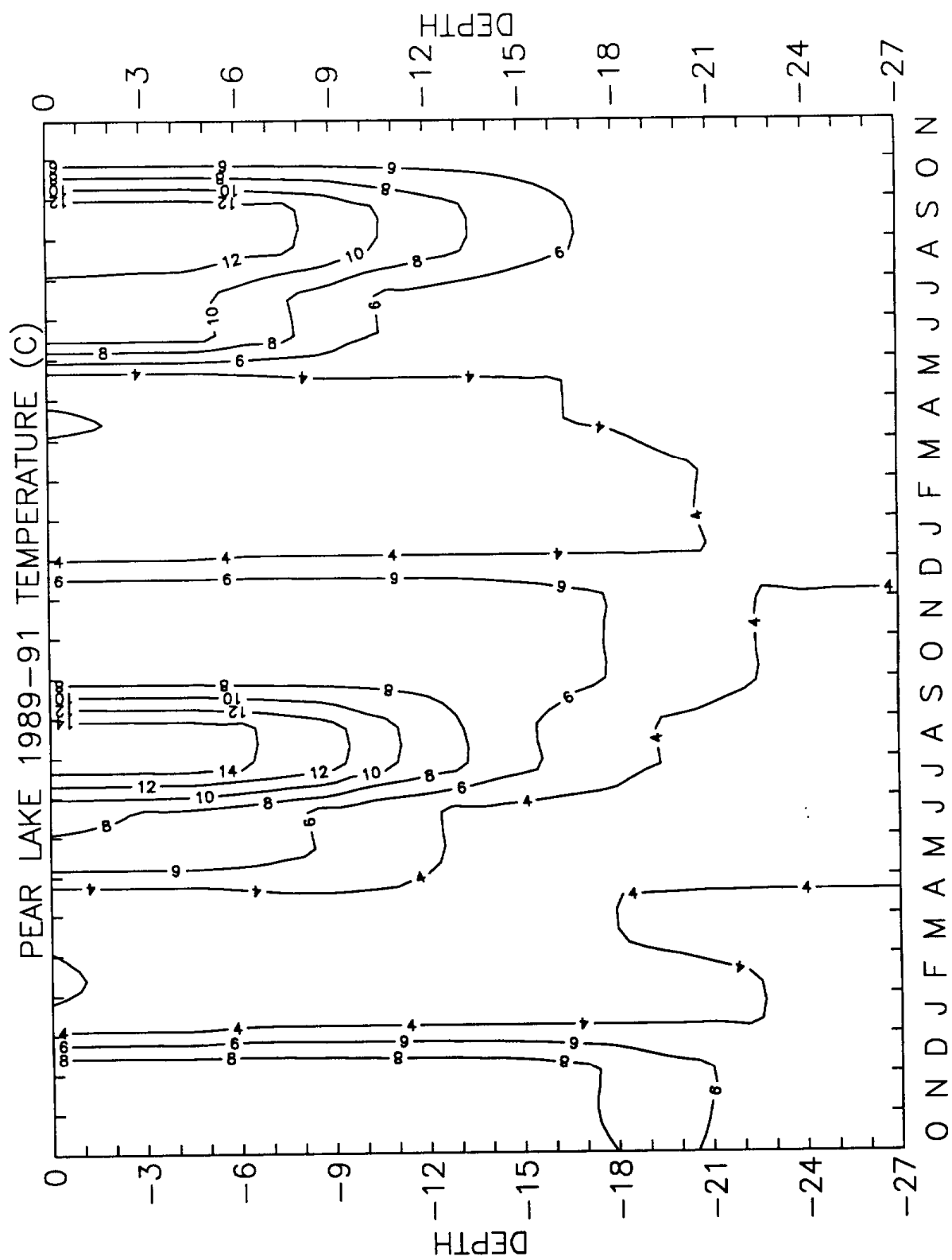


Fig. 20a

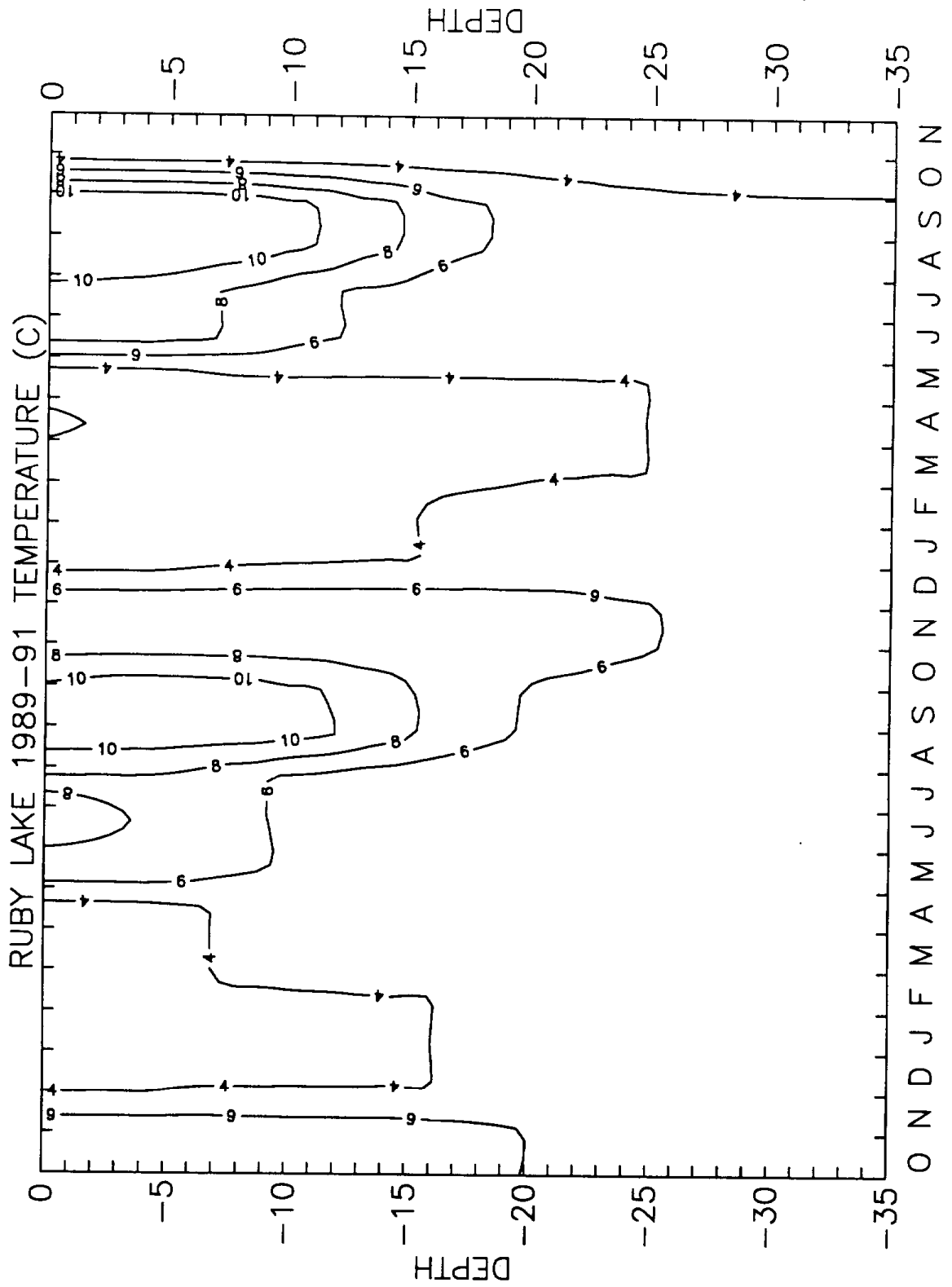


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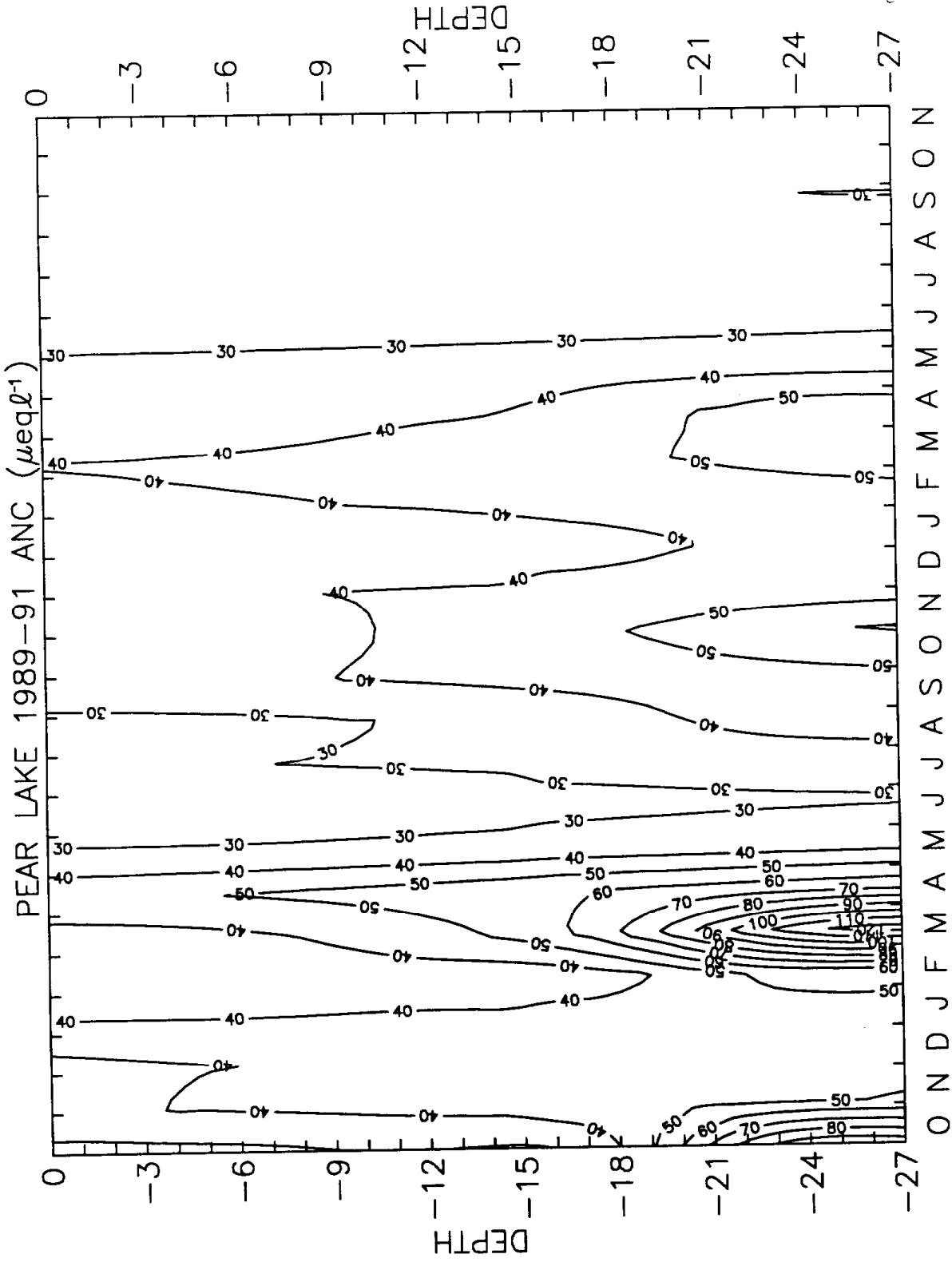
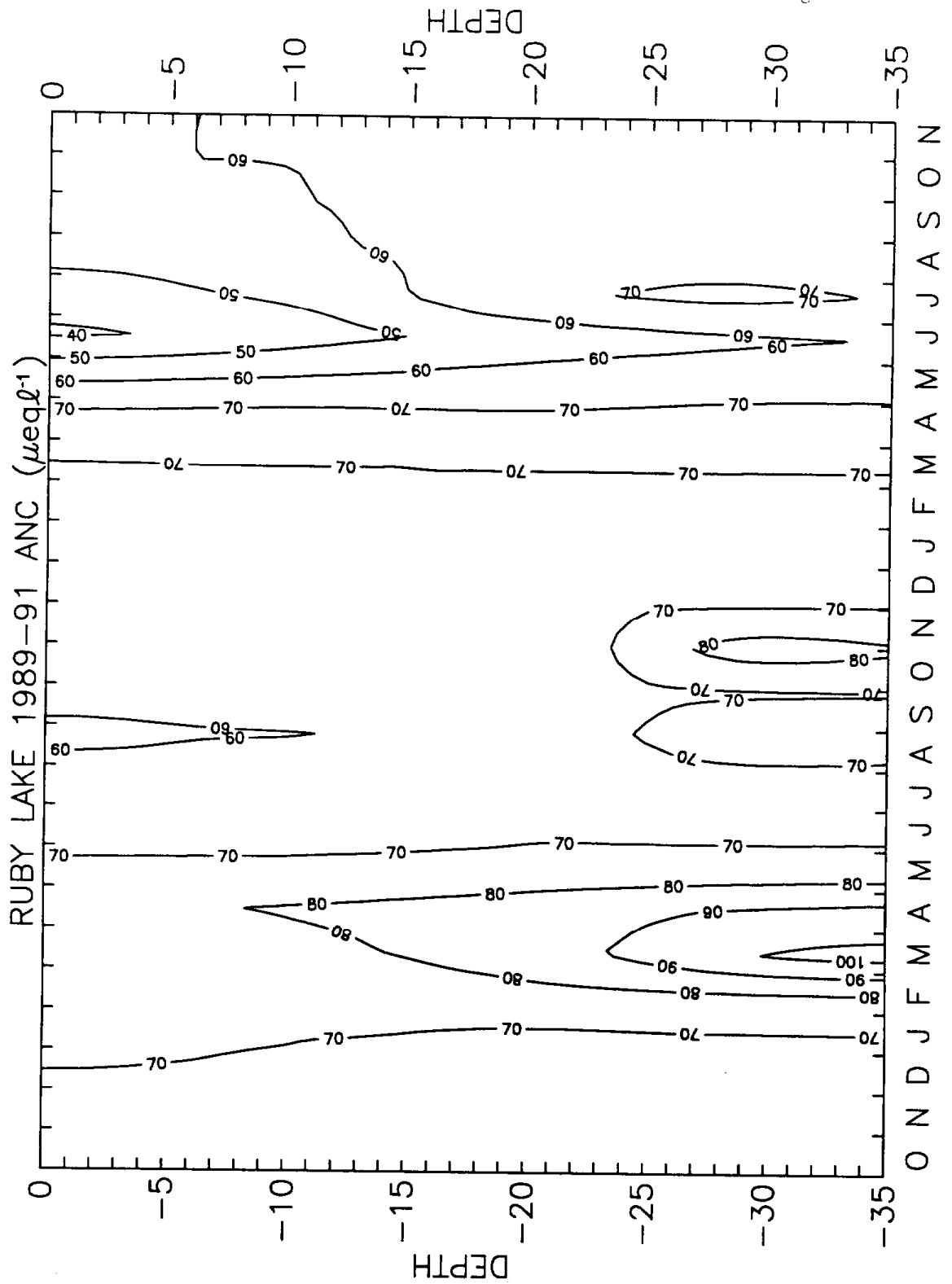


Fig. 20c



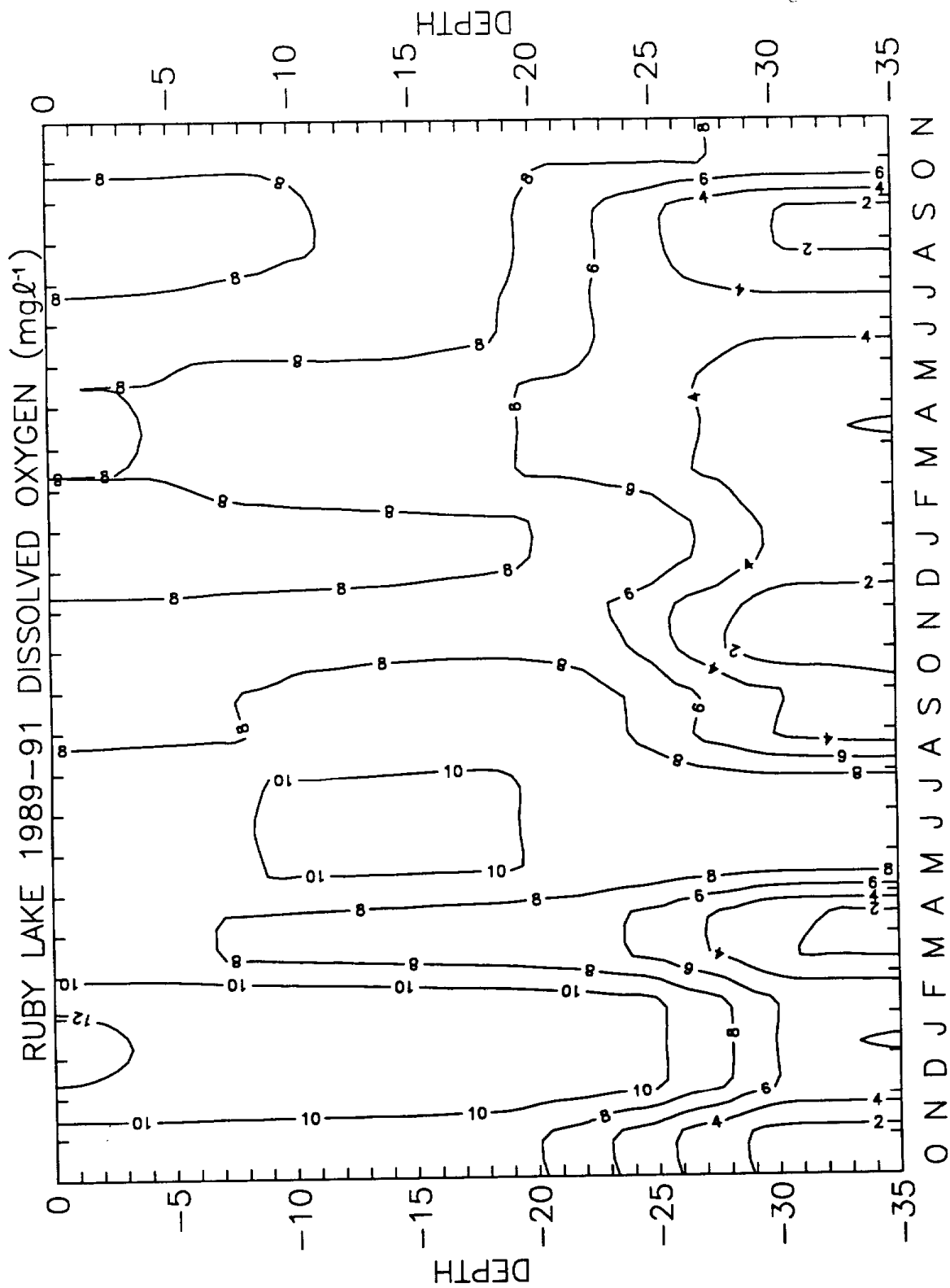


Fig. 20b

Fig. 21b

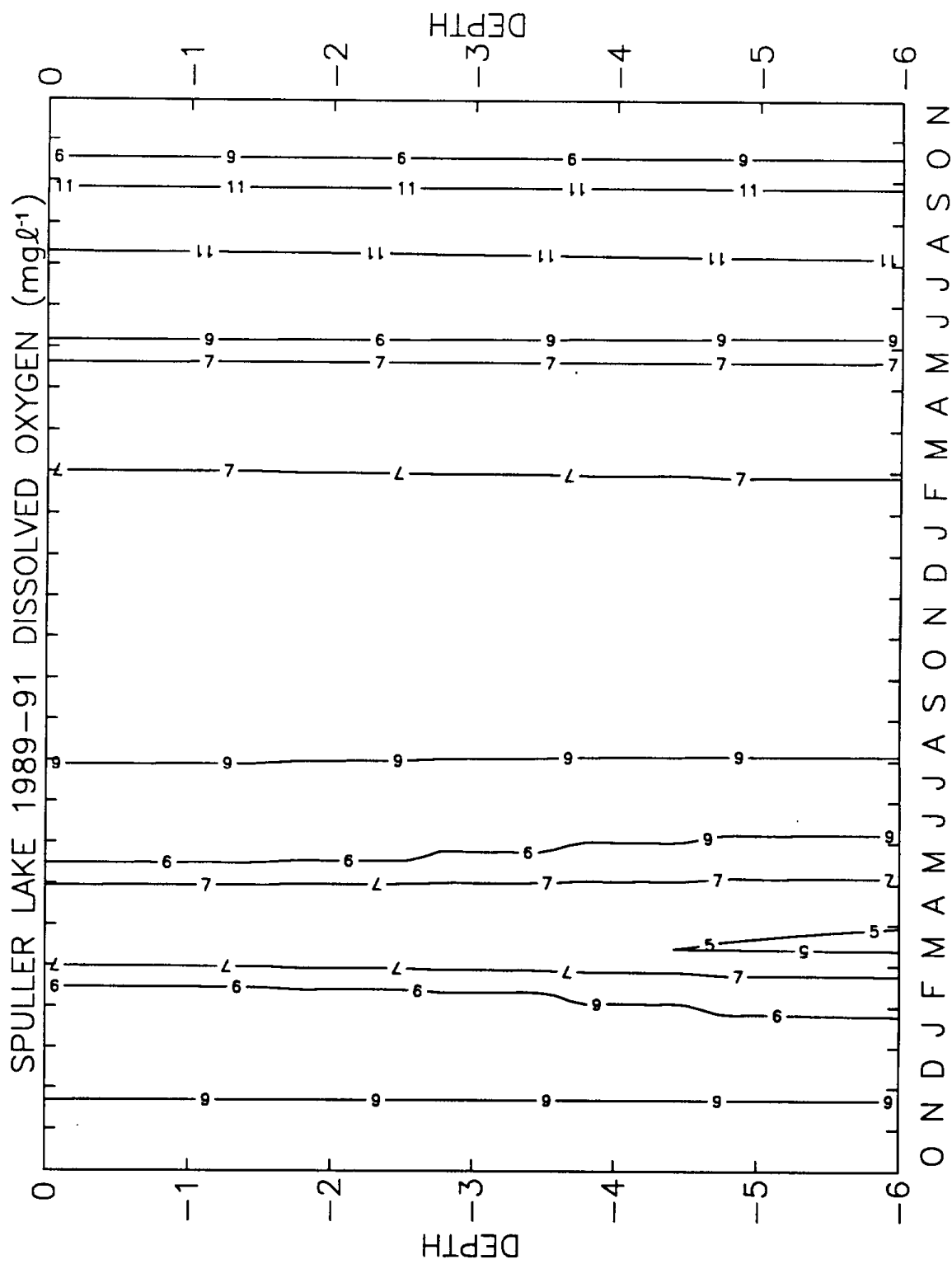


Fig. 21a

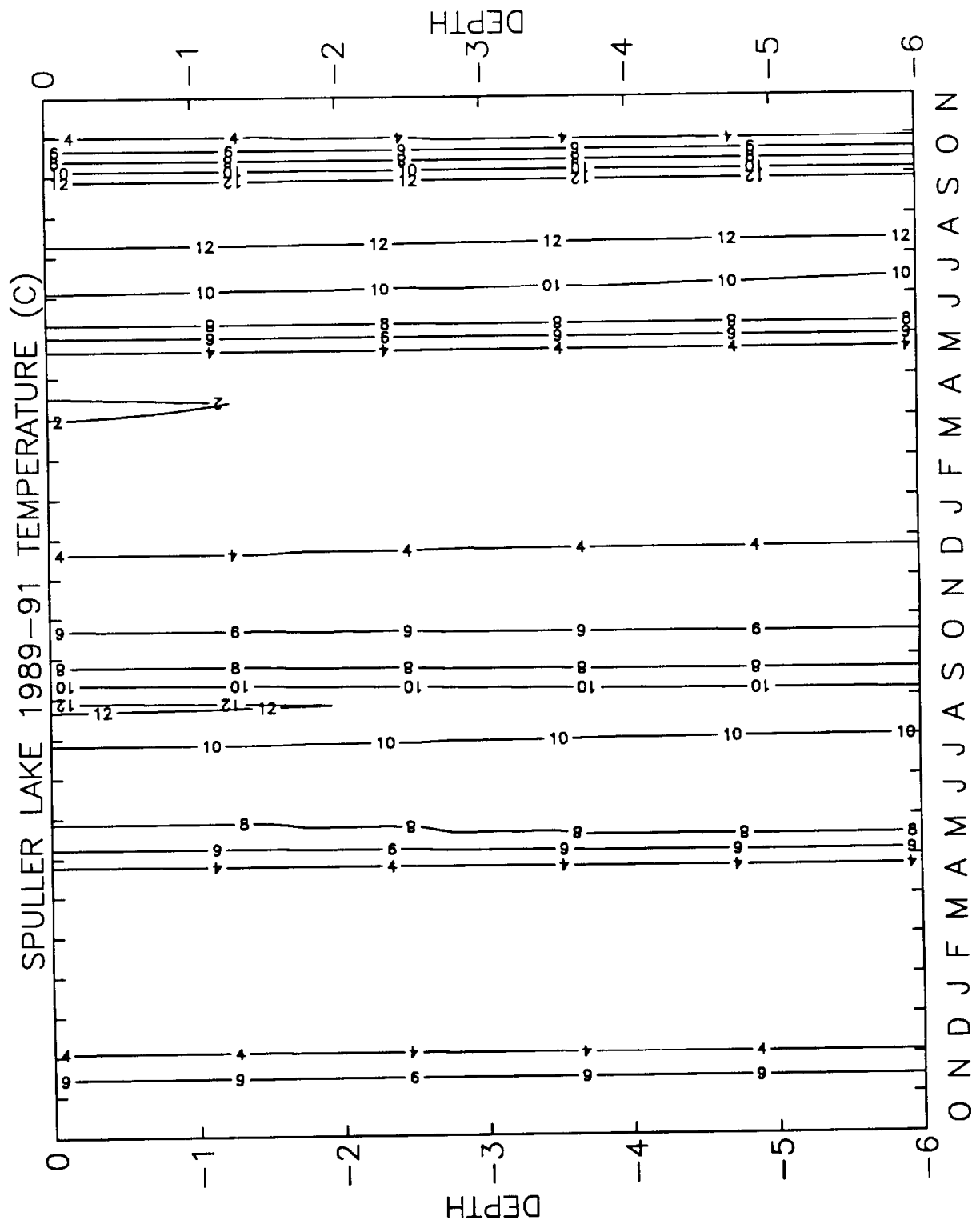


Fig. 22a

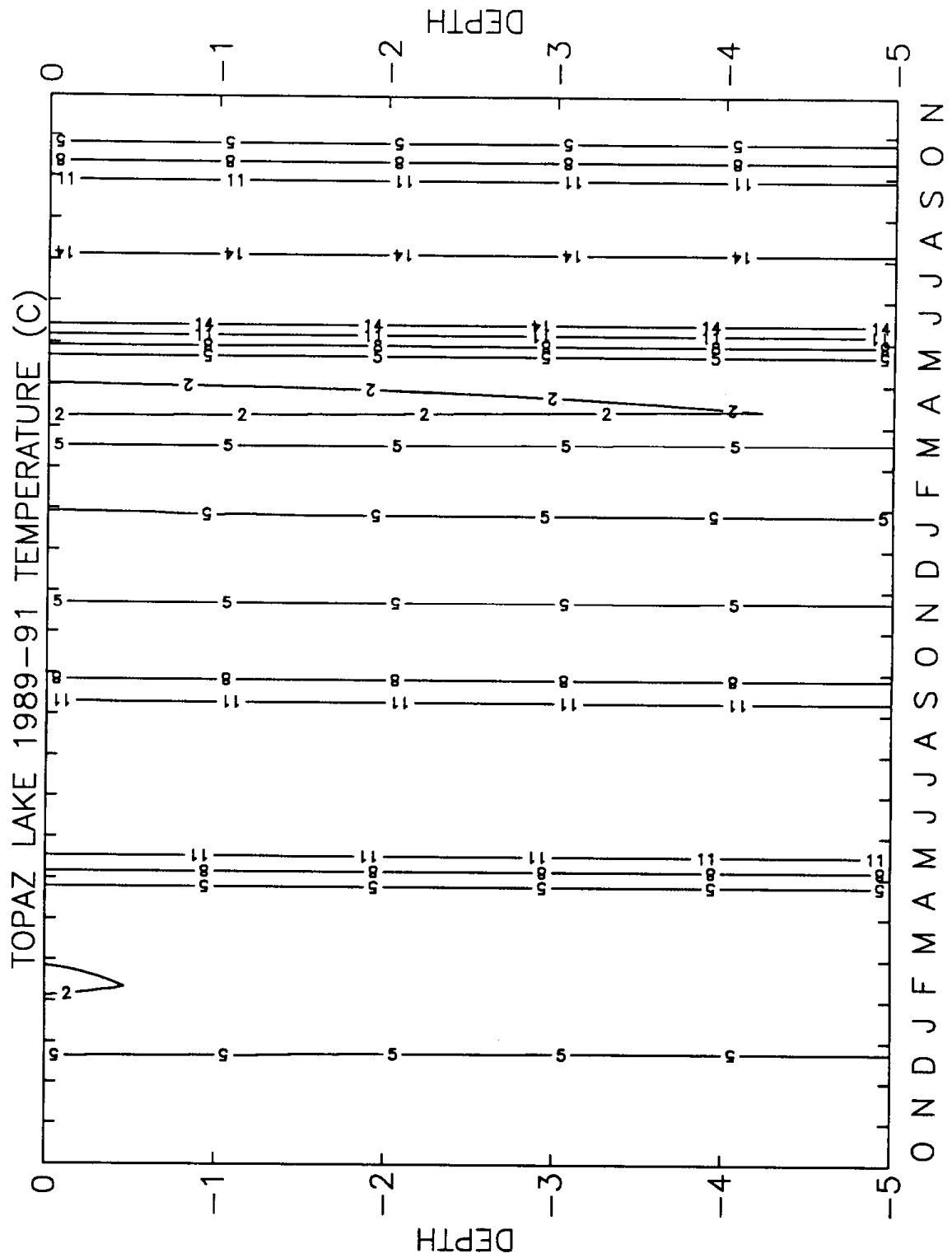


Fig. 21c

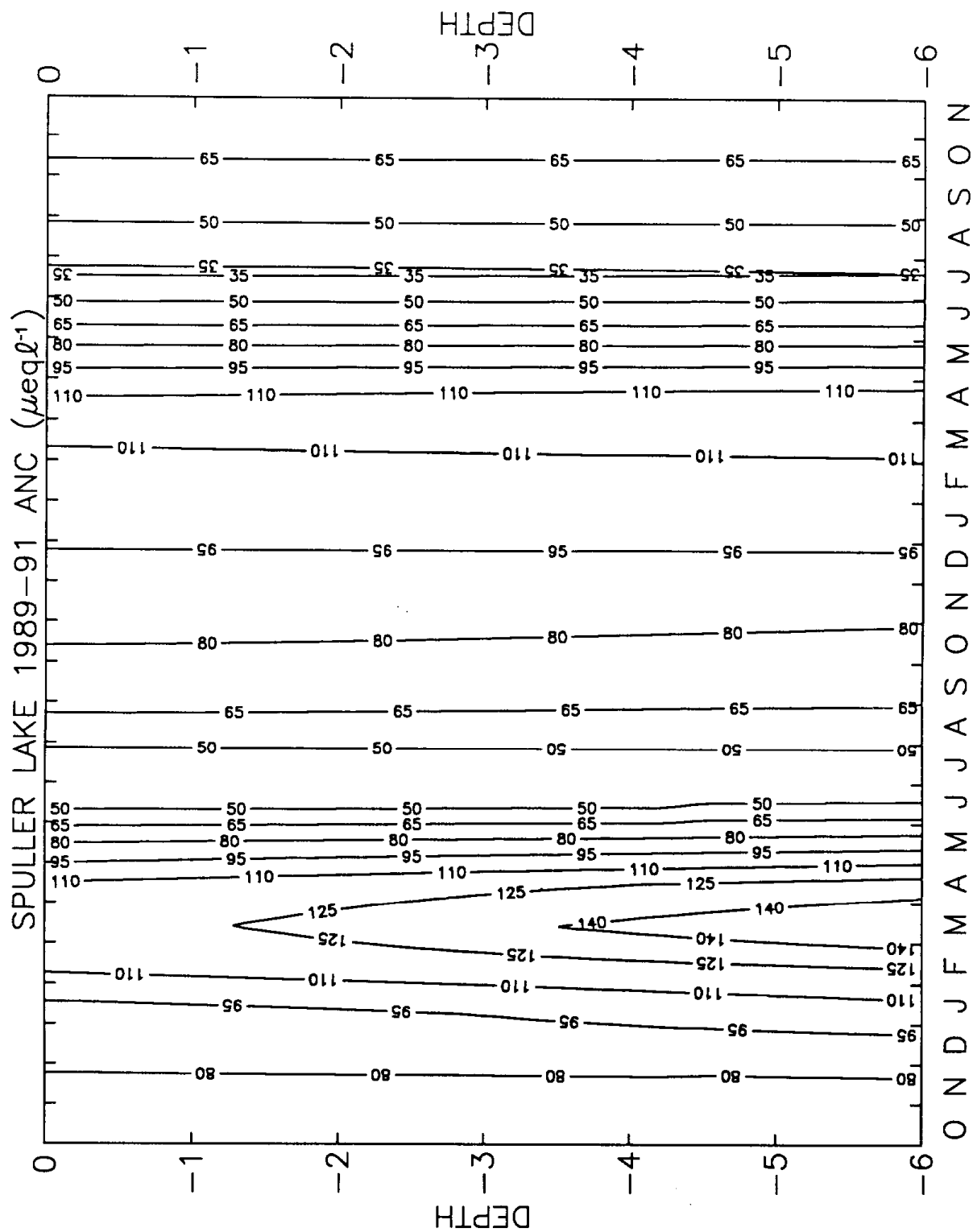


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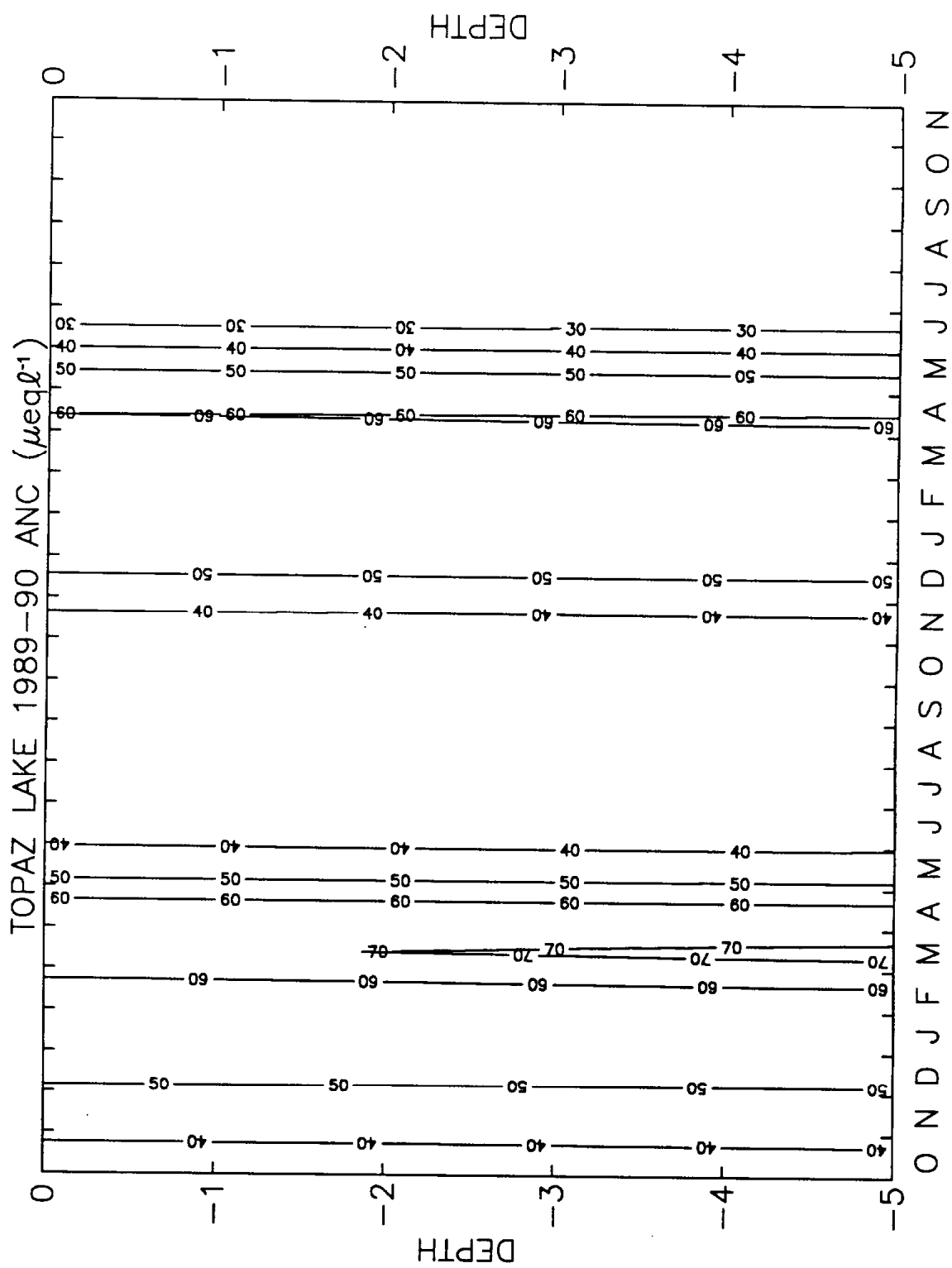


Fig. 22b

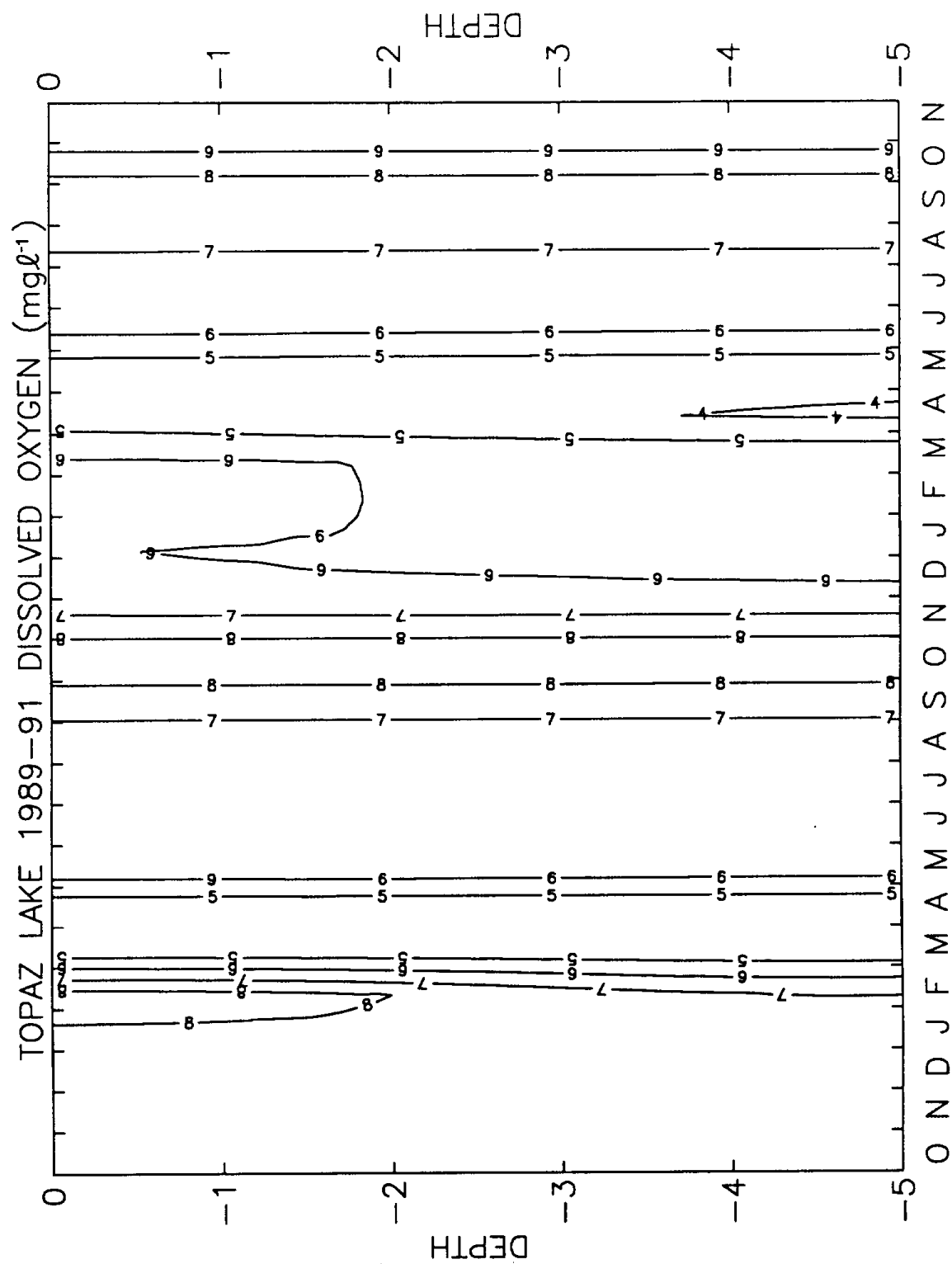
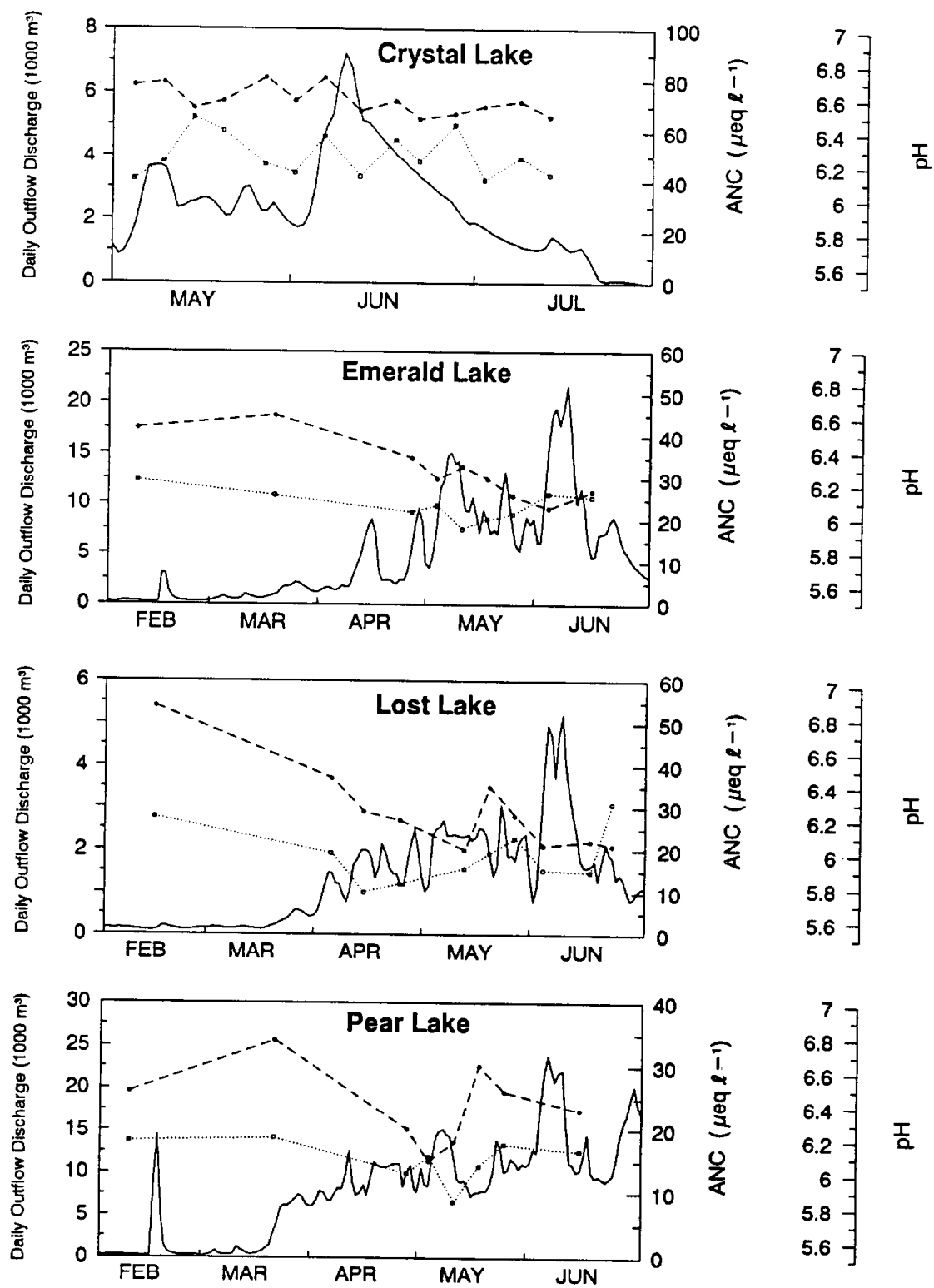
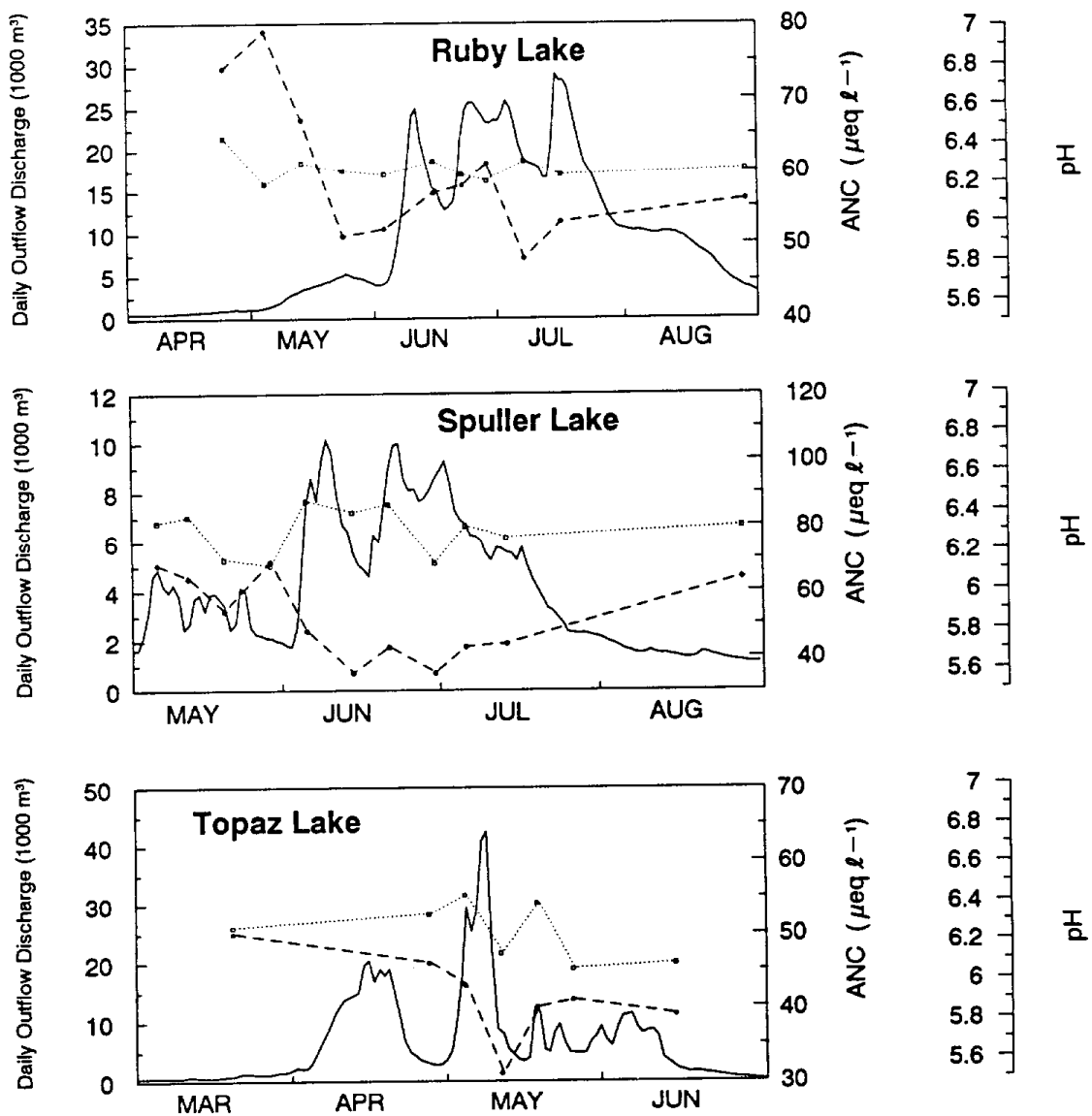


Fig. 23





Outflow Chemistry Snowmelt 1990

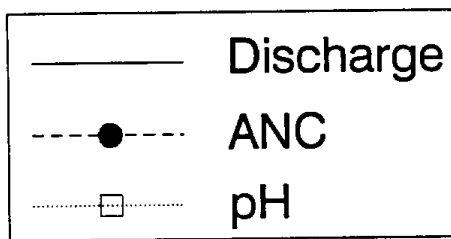
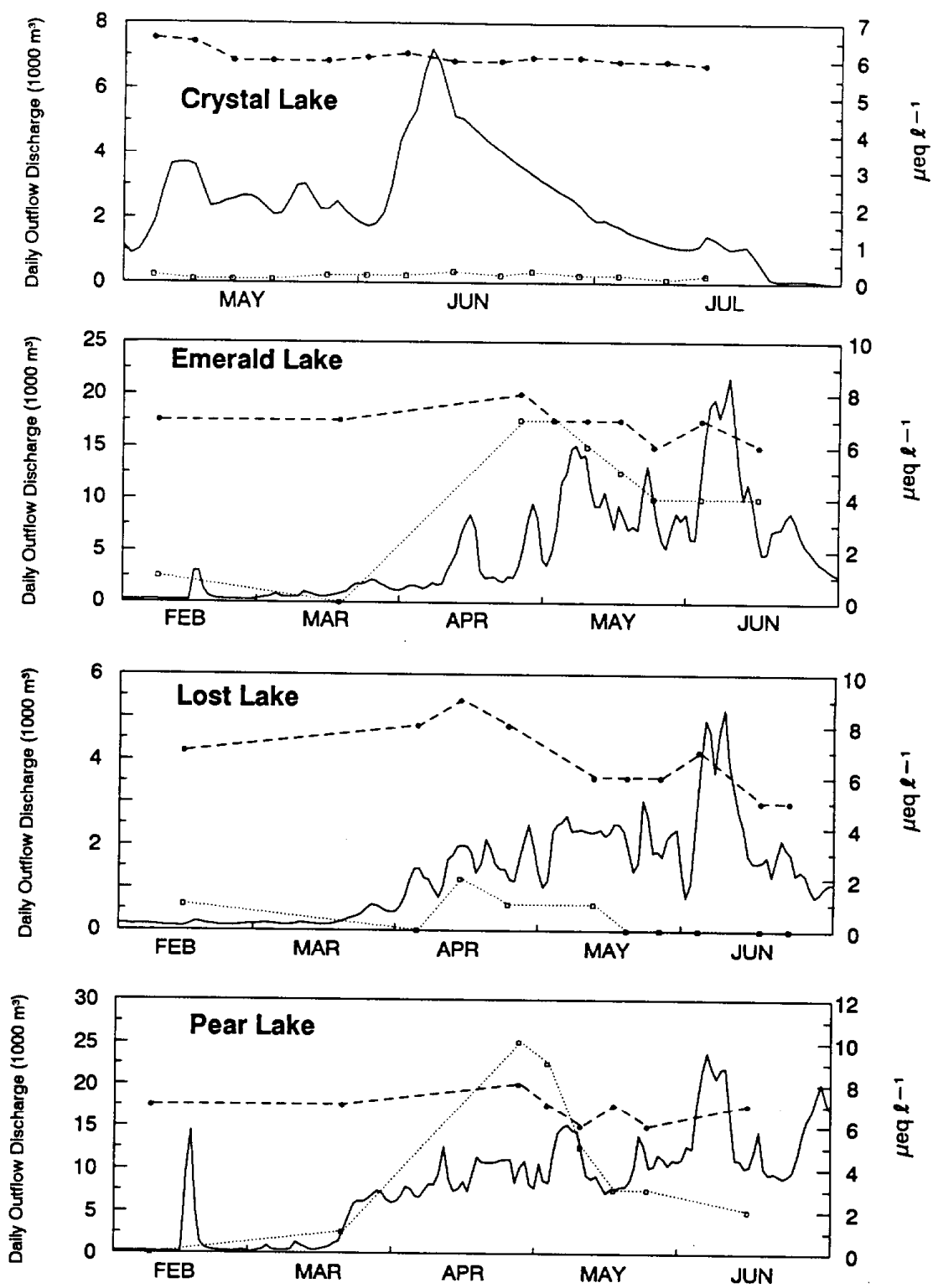
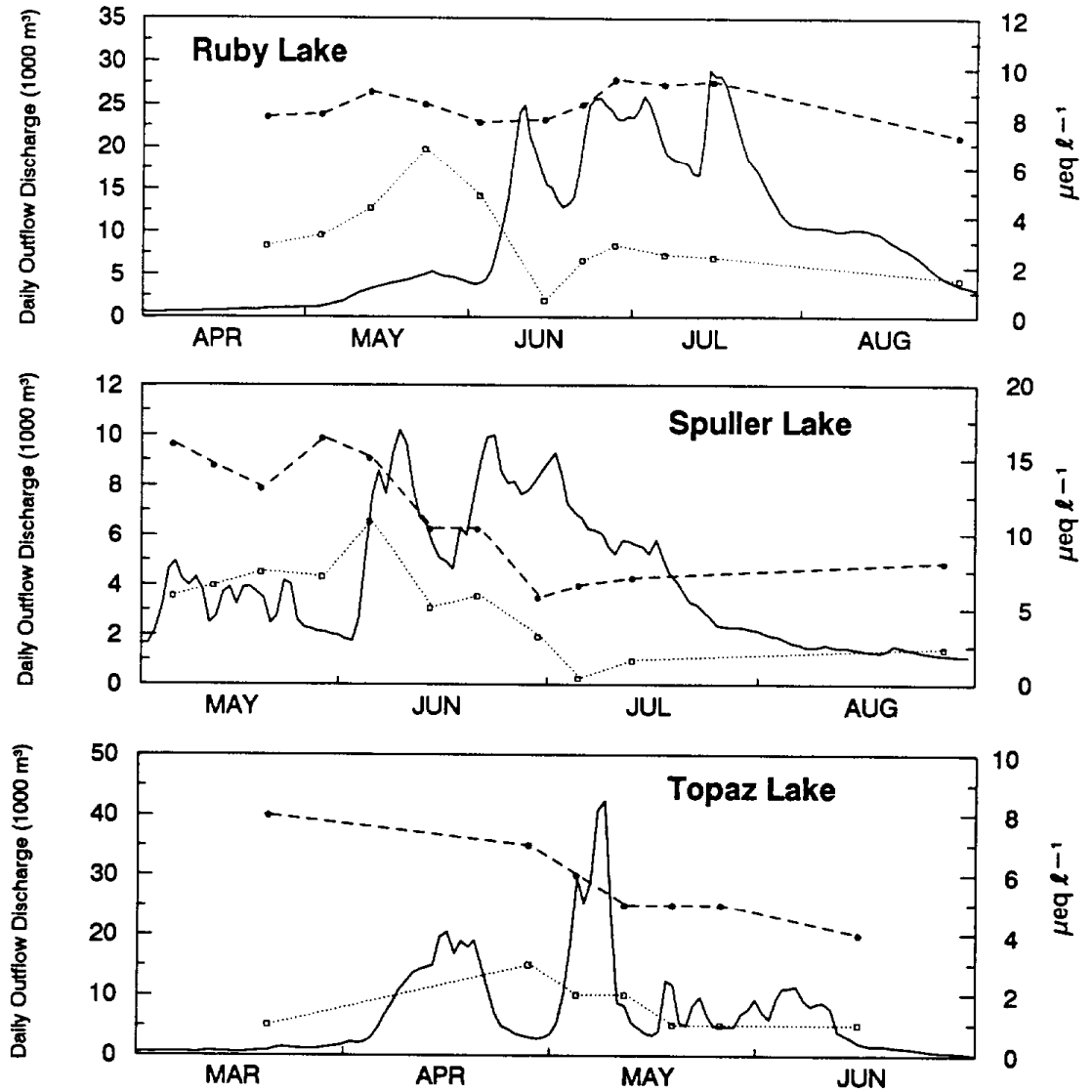


Fig. 23

Fig. 24





Outflow Chemistry Snowmelt 1990

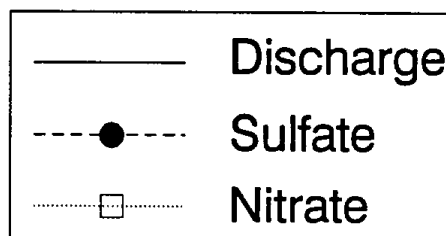
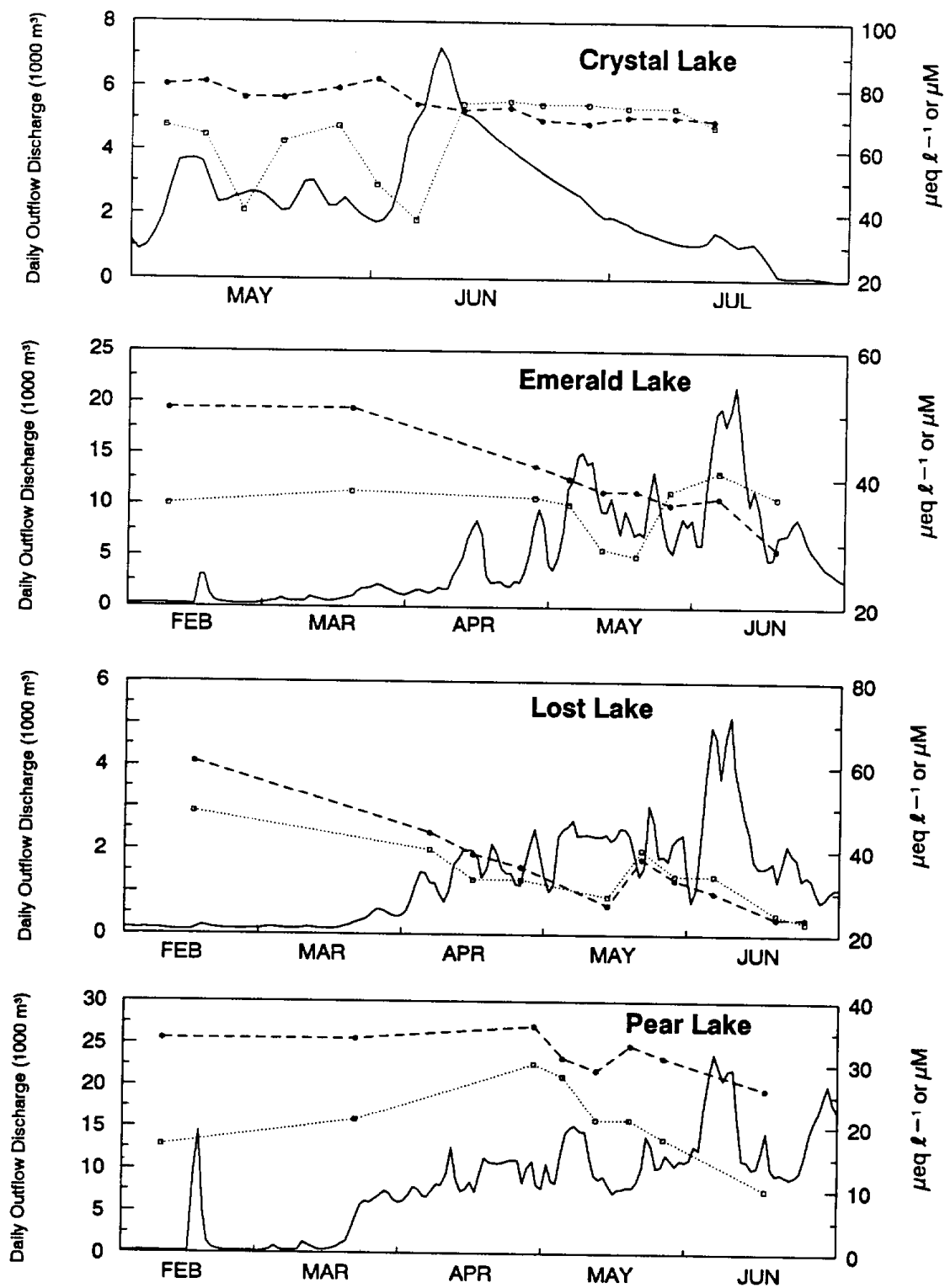
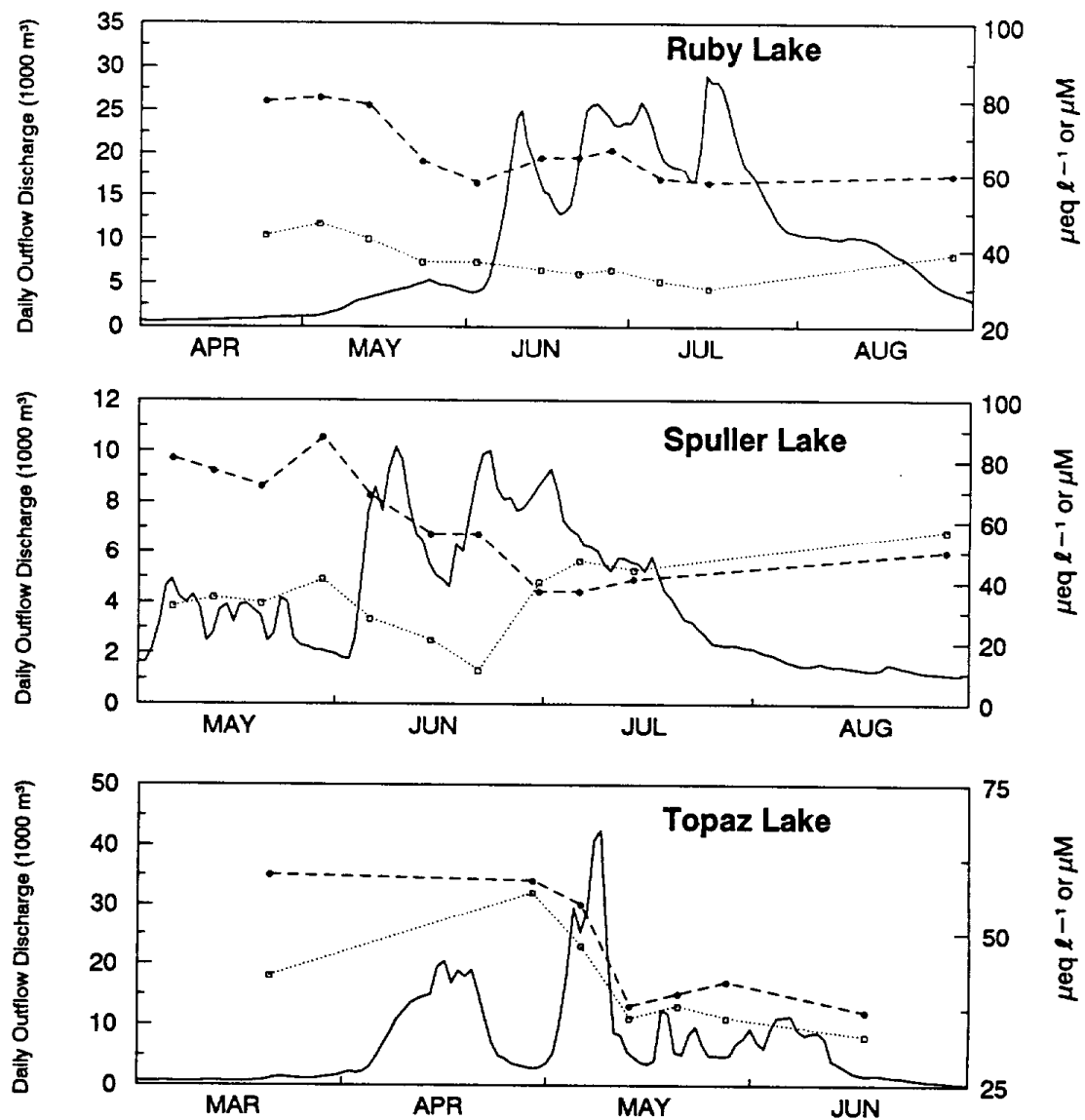


Fig. 24

Fig. 25





Outflow Chemistry Snowmelt 1990

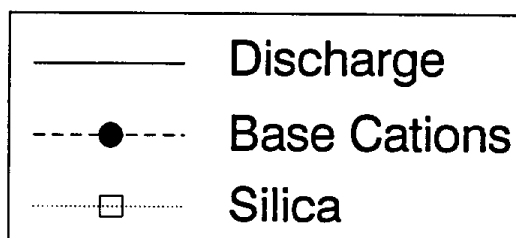
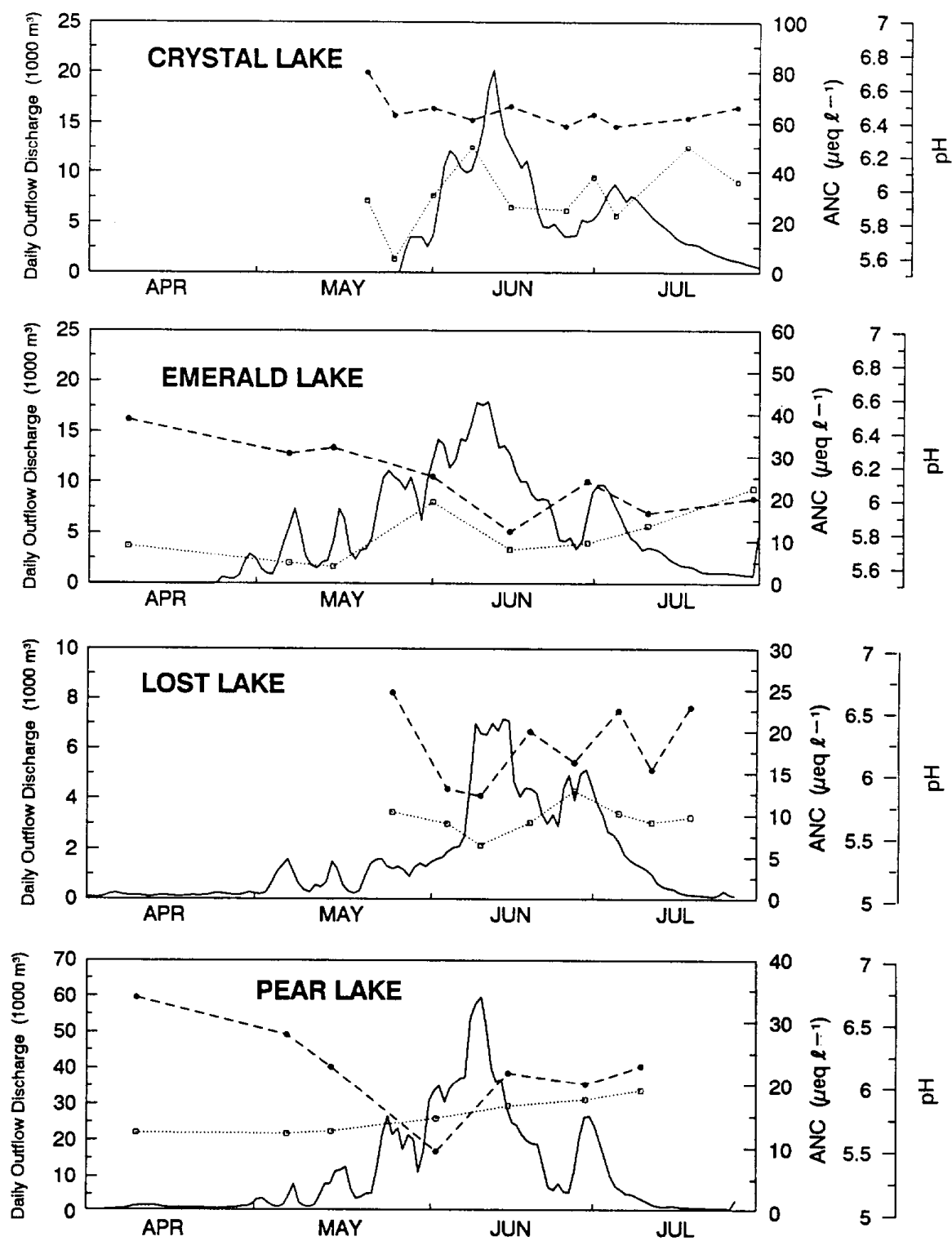
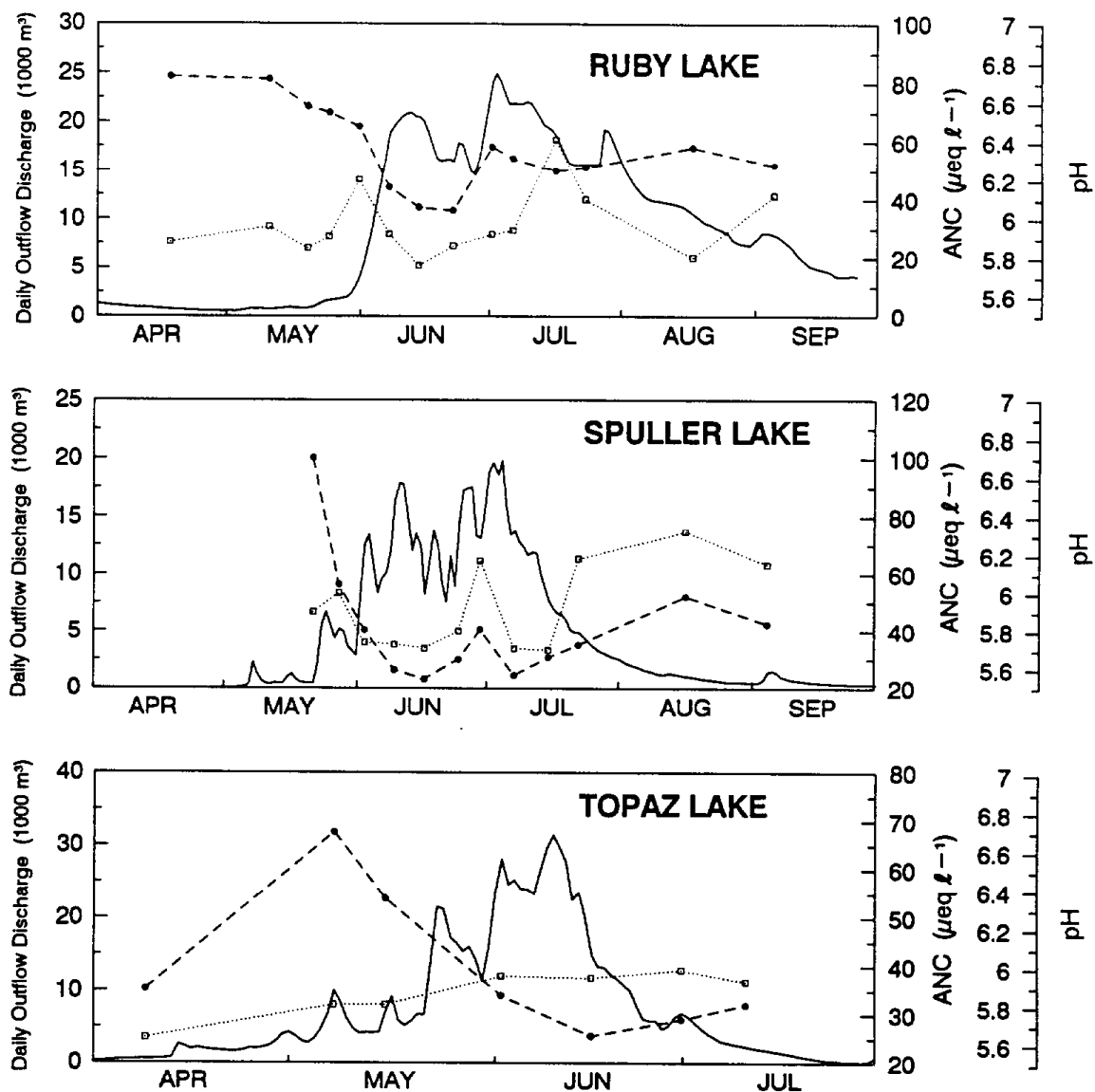


Fig. 25

Fig. 26





Outflow Chemistry Snowmelt 1991

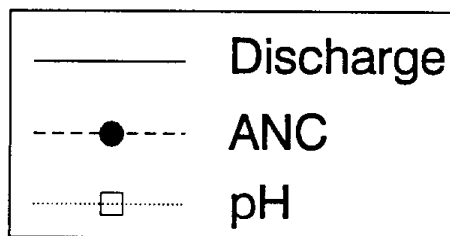
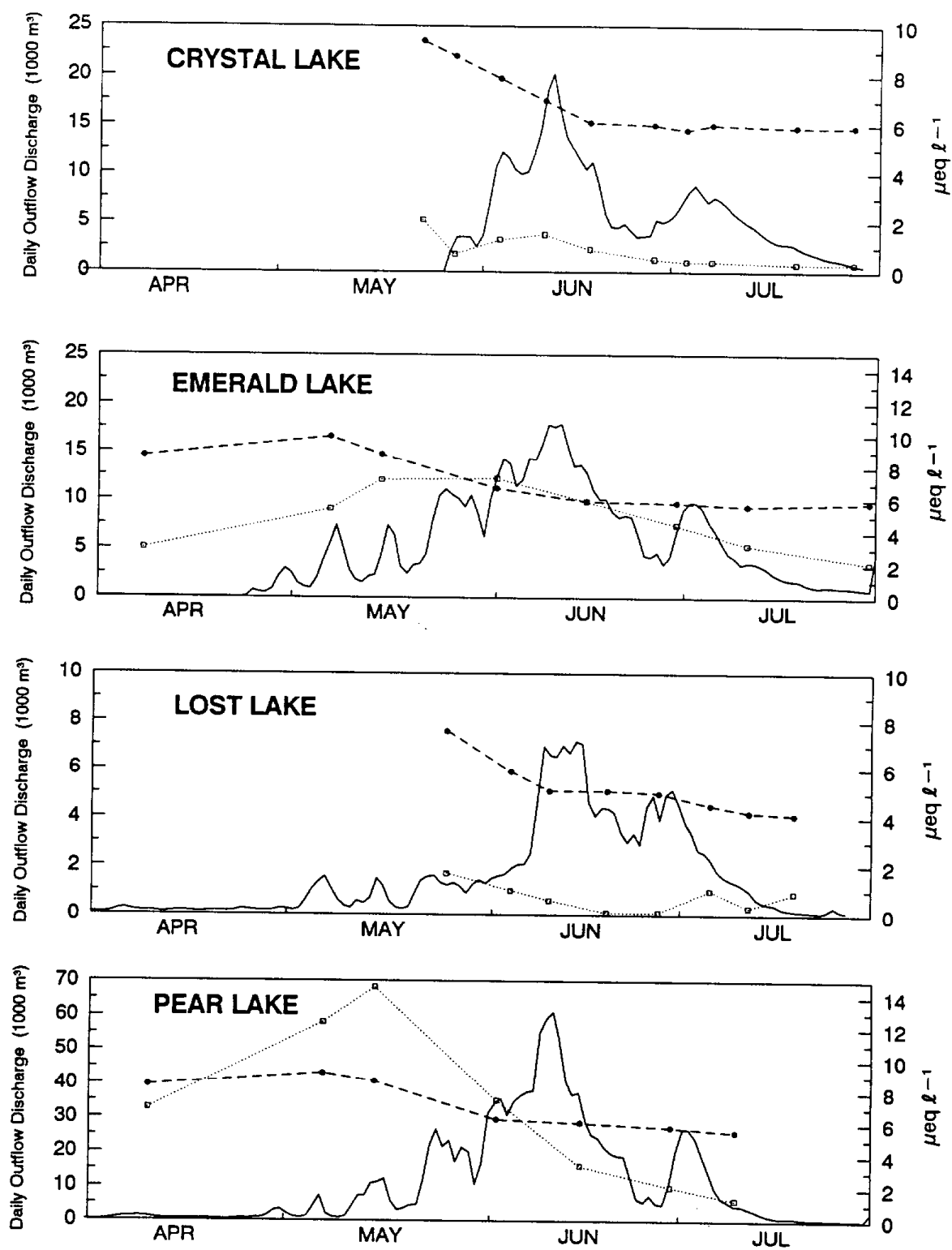
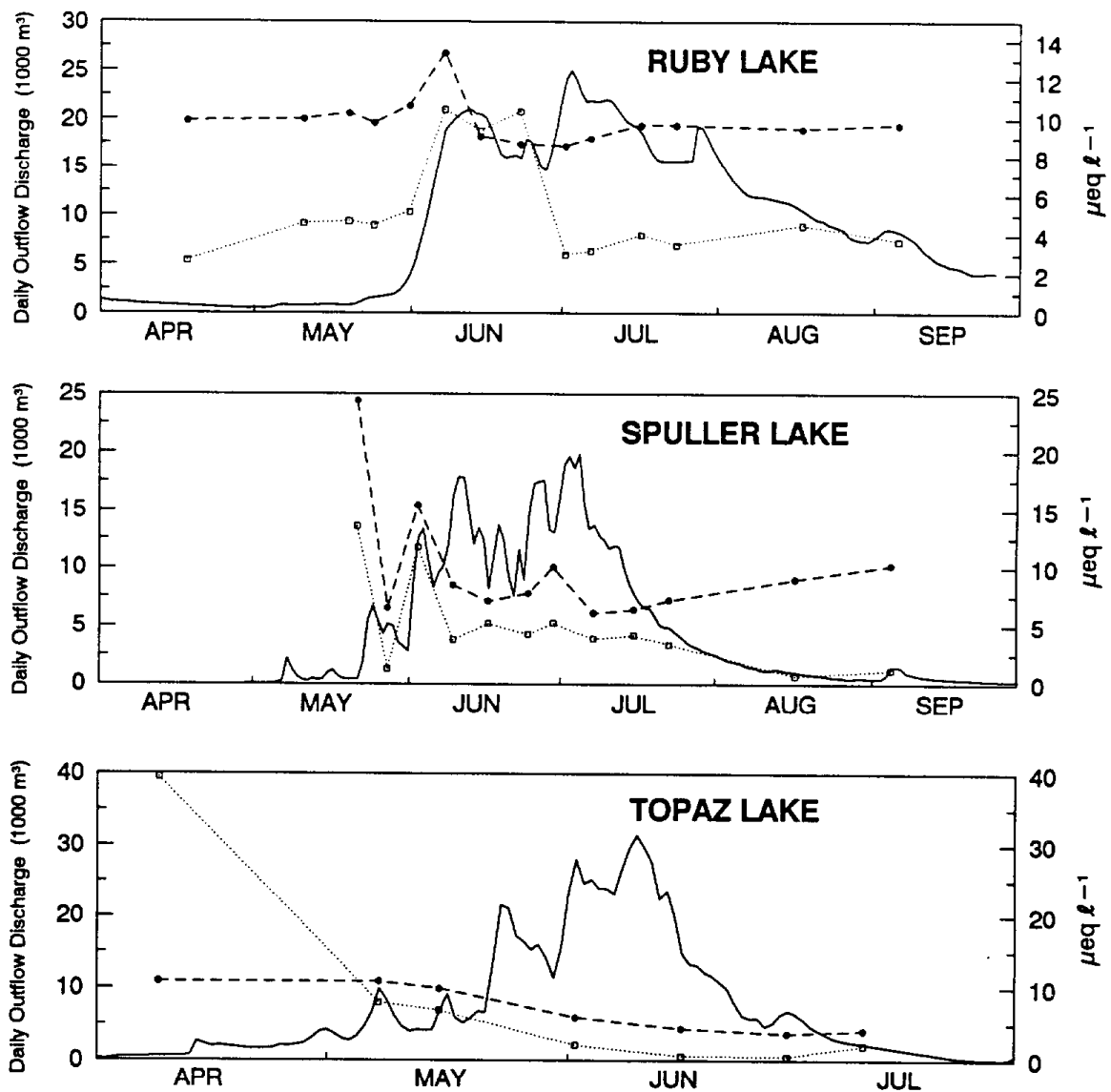


Fig. 26

Fig. 27





Outflow Chemistry Snowmelt 1991

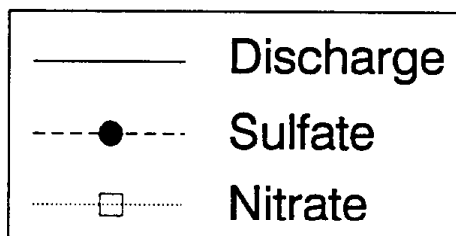
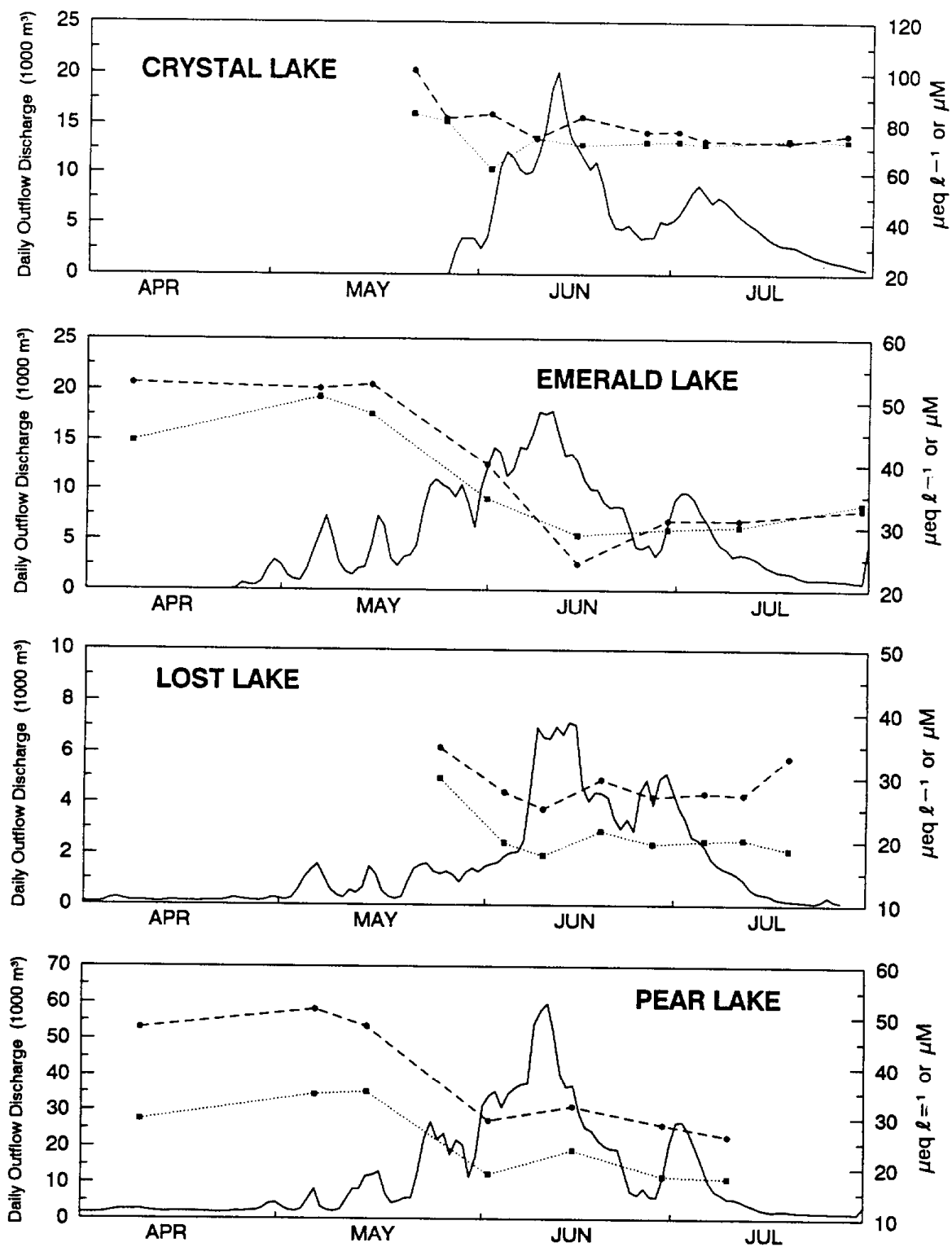
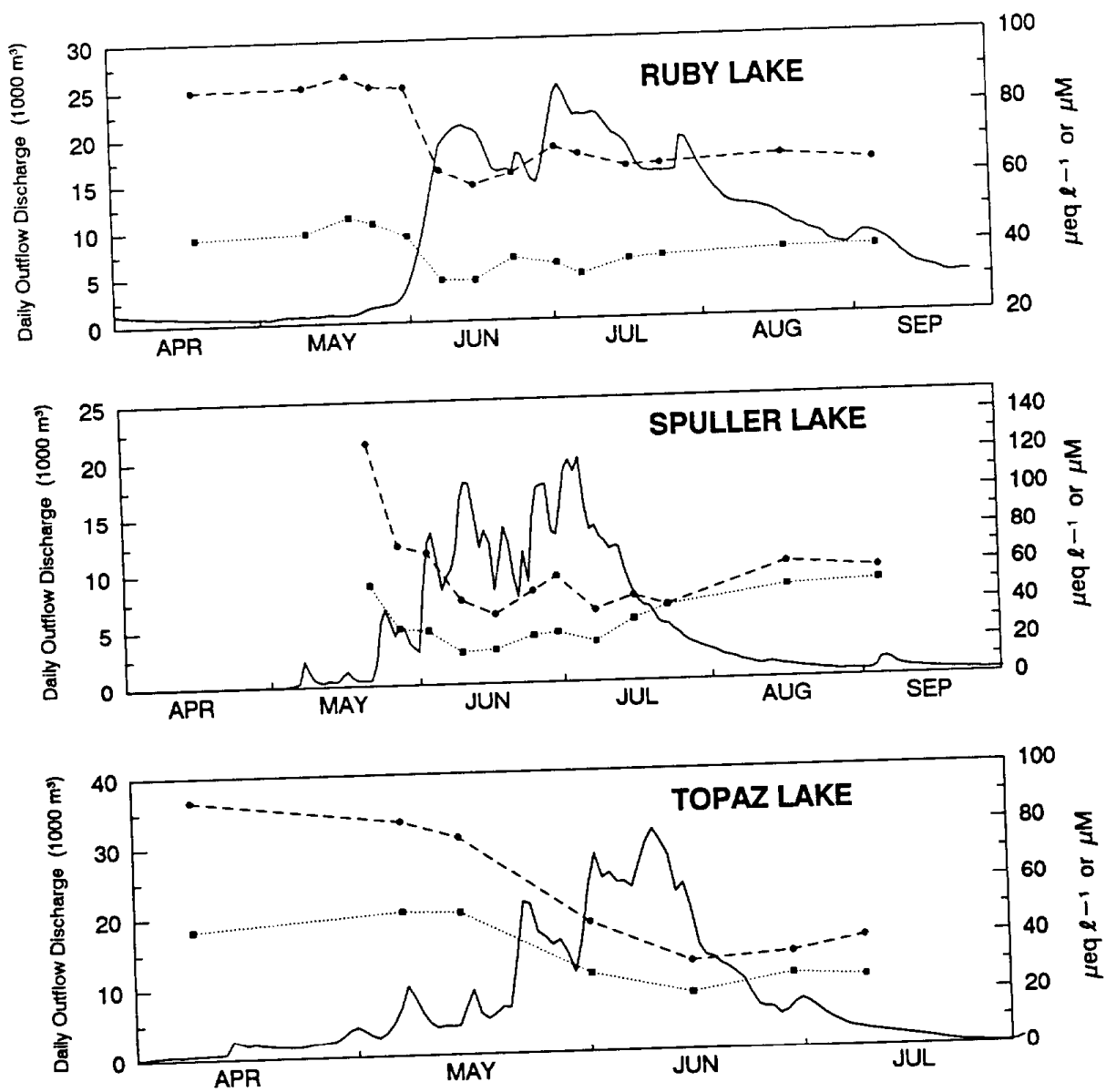


Fig. 27

Fig. 28





Outflow Chemistry Snowmelt 1991

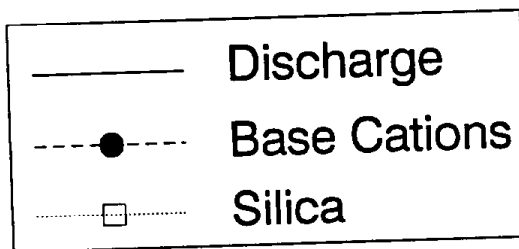


Fig. 28

Monthly Outflow Flux of Solutes

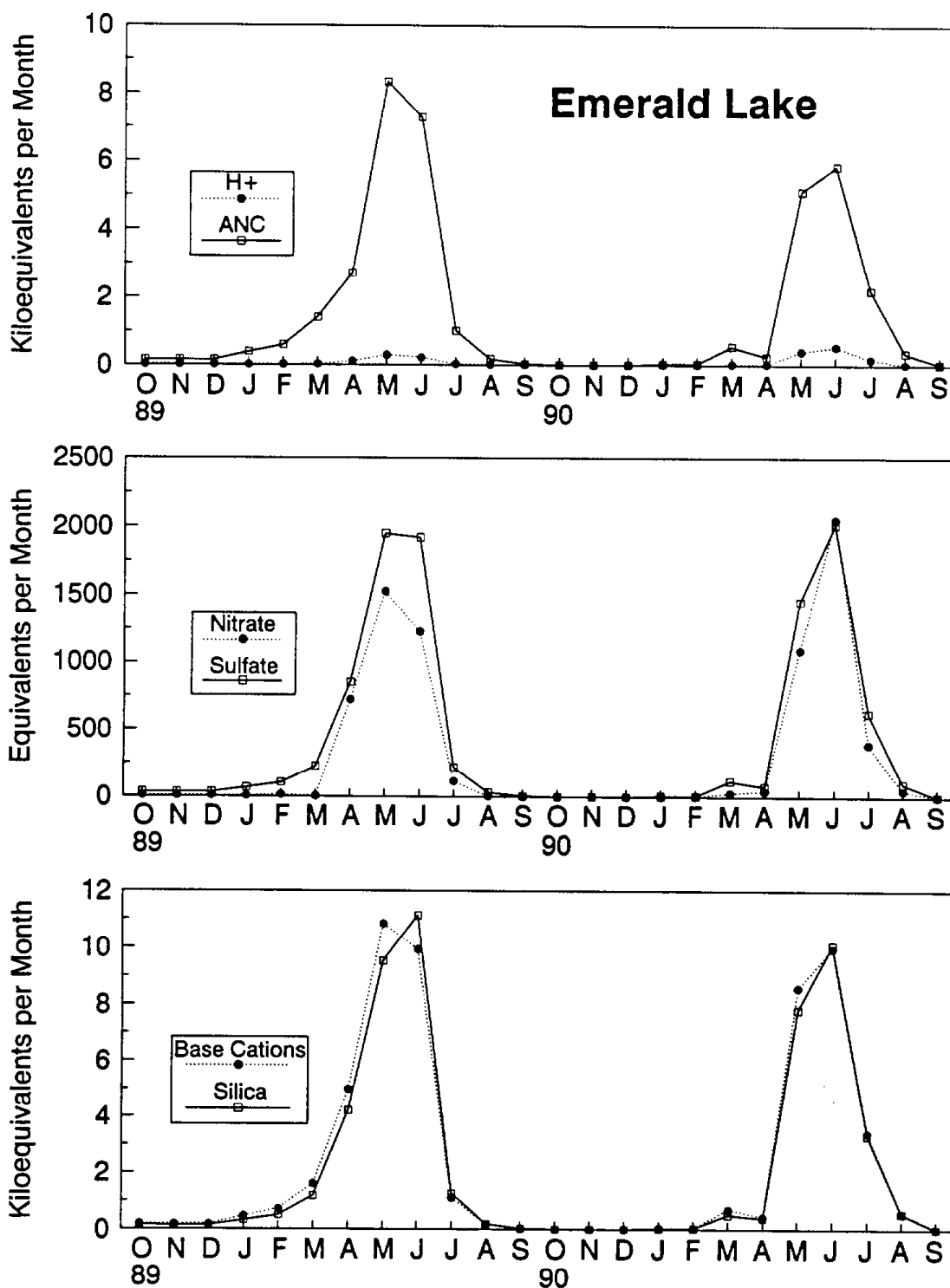
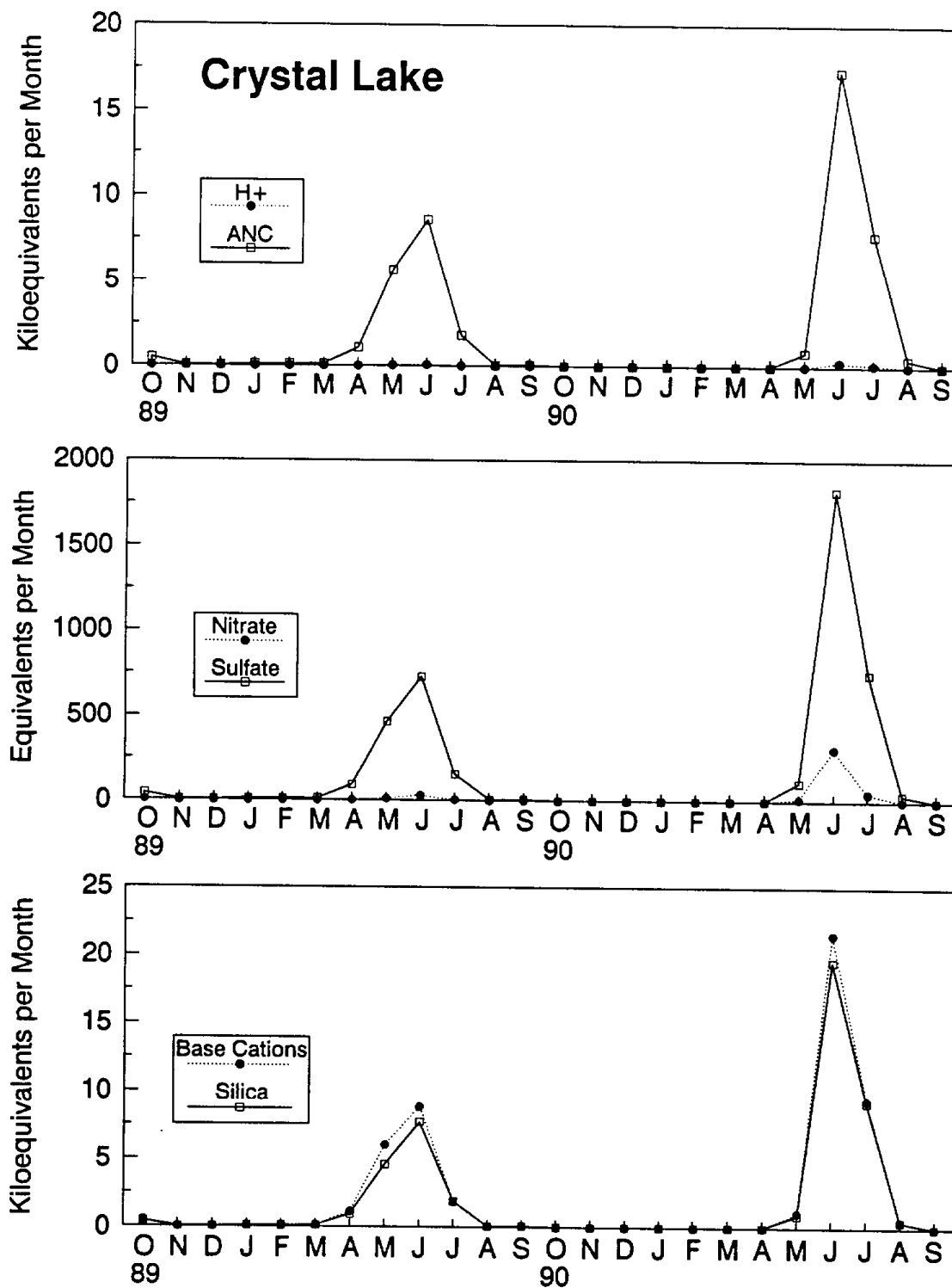


Fig. 29

Monthly Outflow Flux of Solutes



Monthly Outflow Flux of Solutes

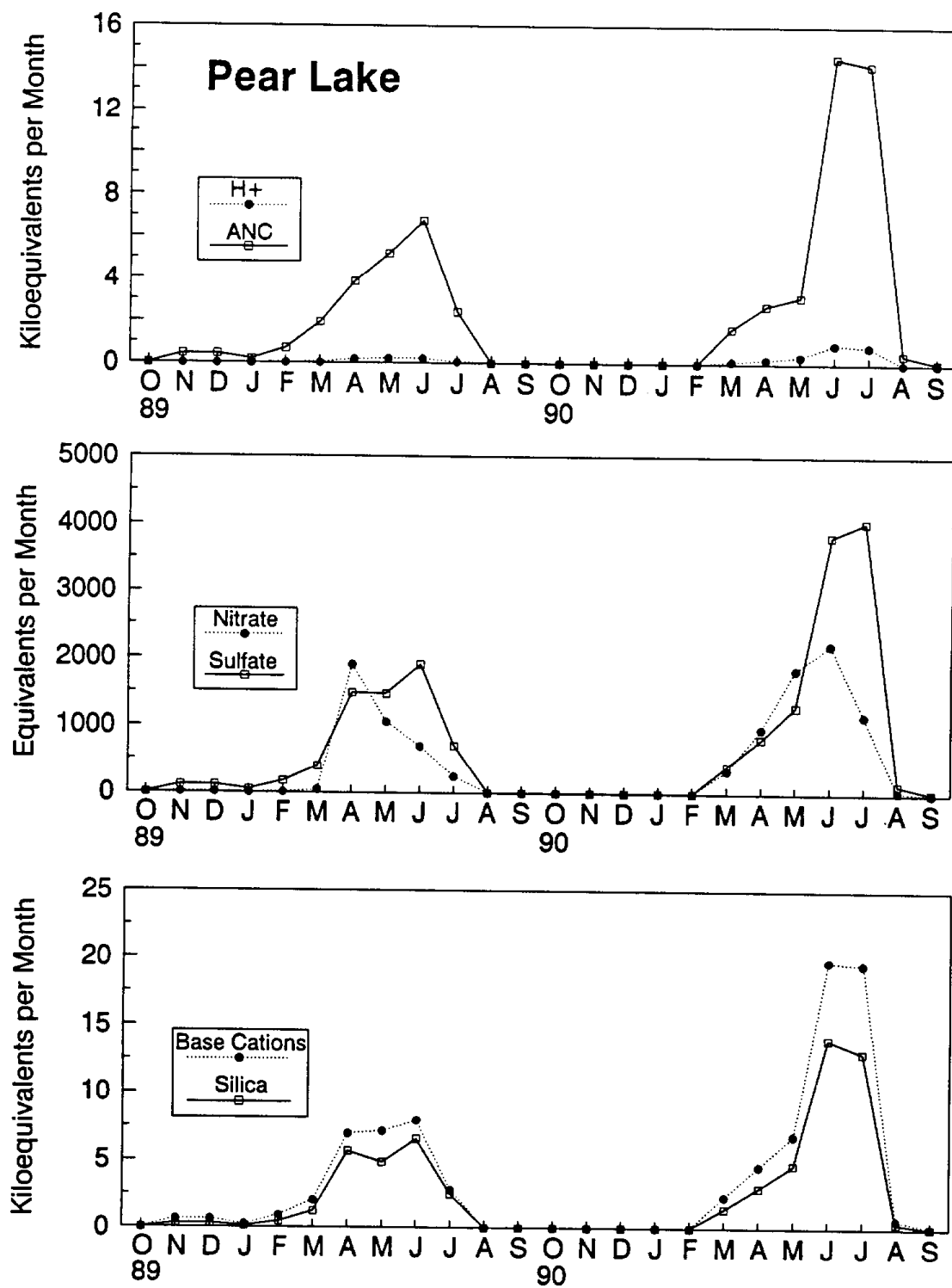
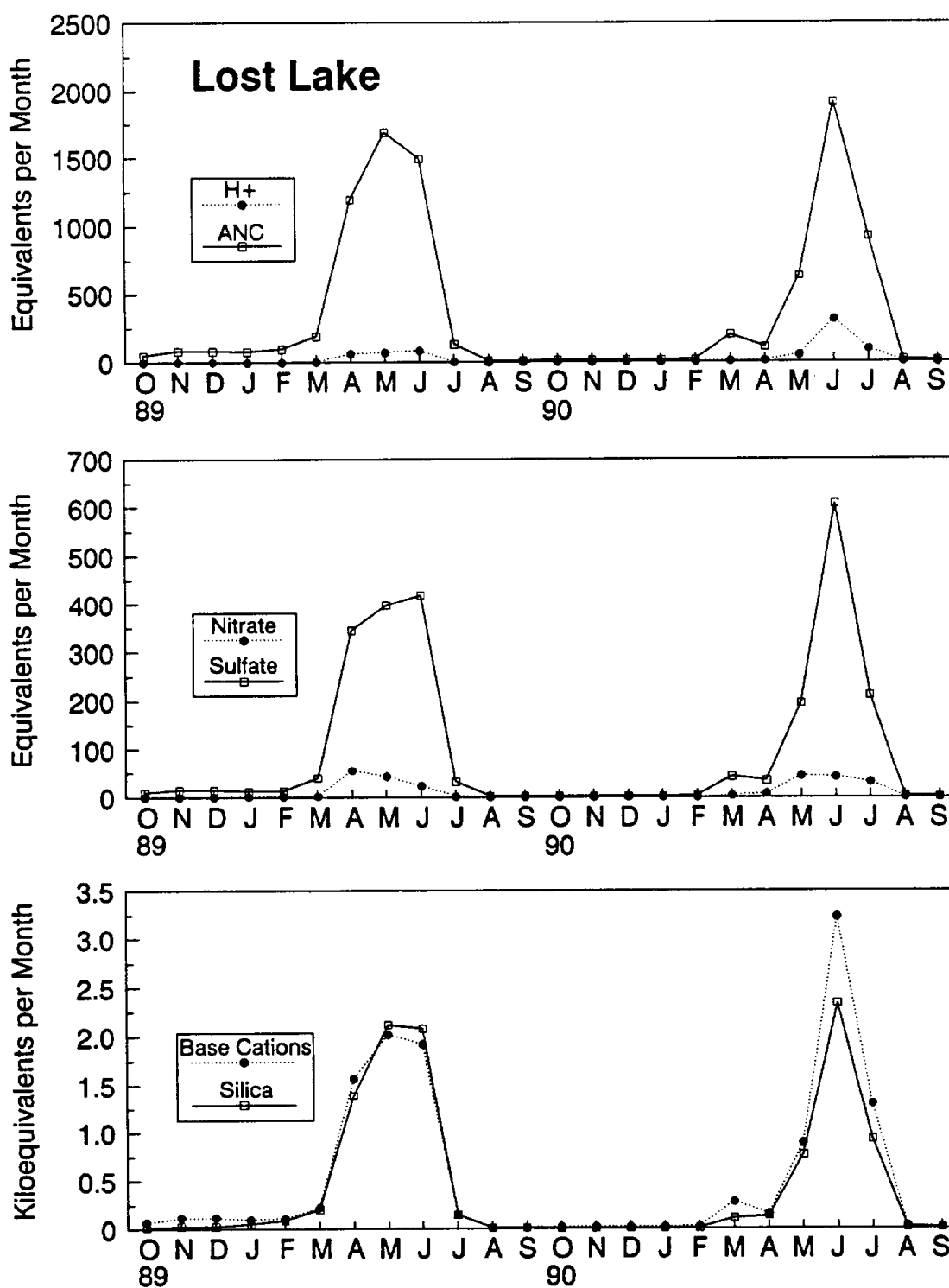


Fig. 31

Monthly Outflow Flux of Solutes



Monthly Outflow Flux of Solutes

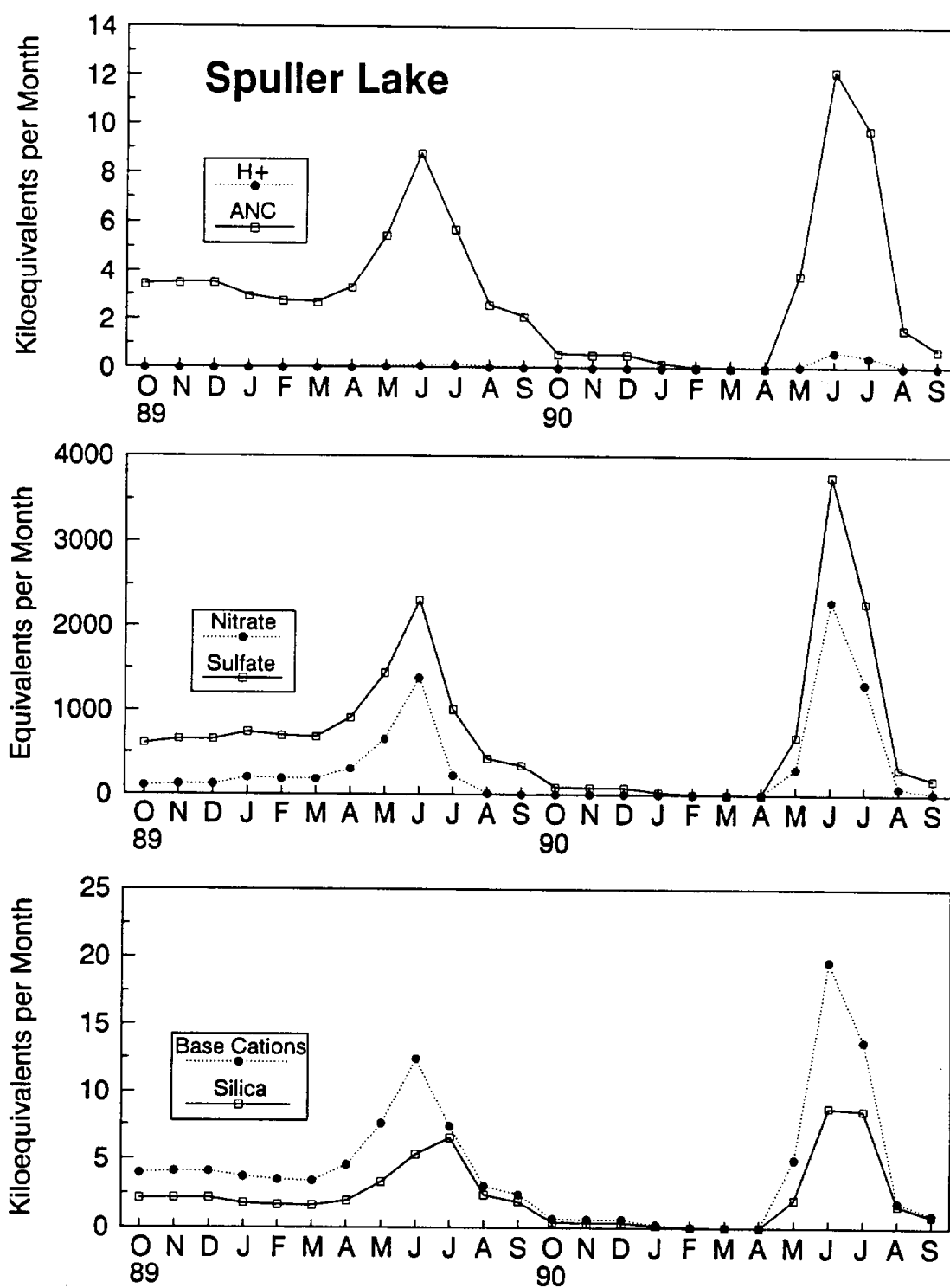
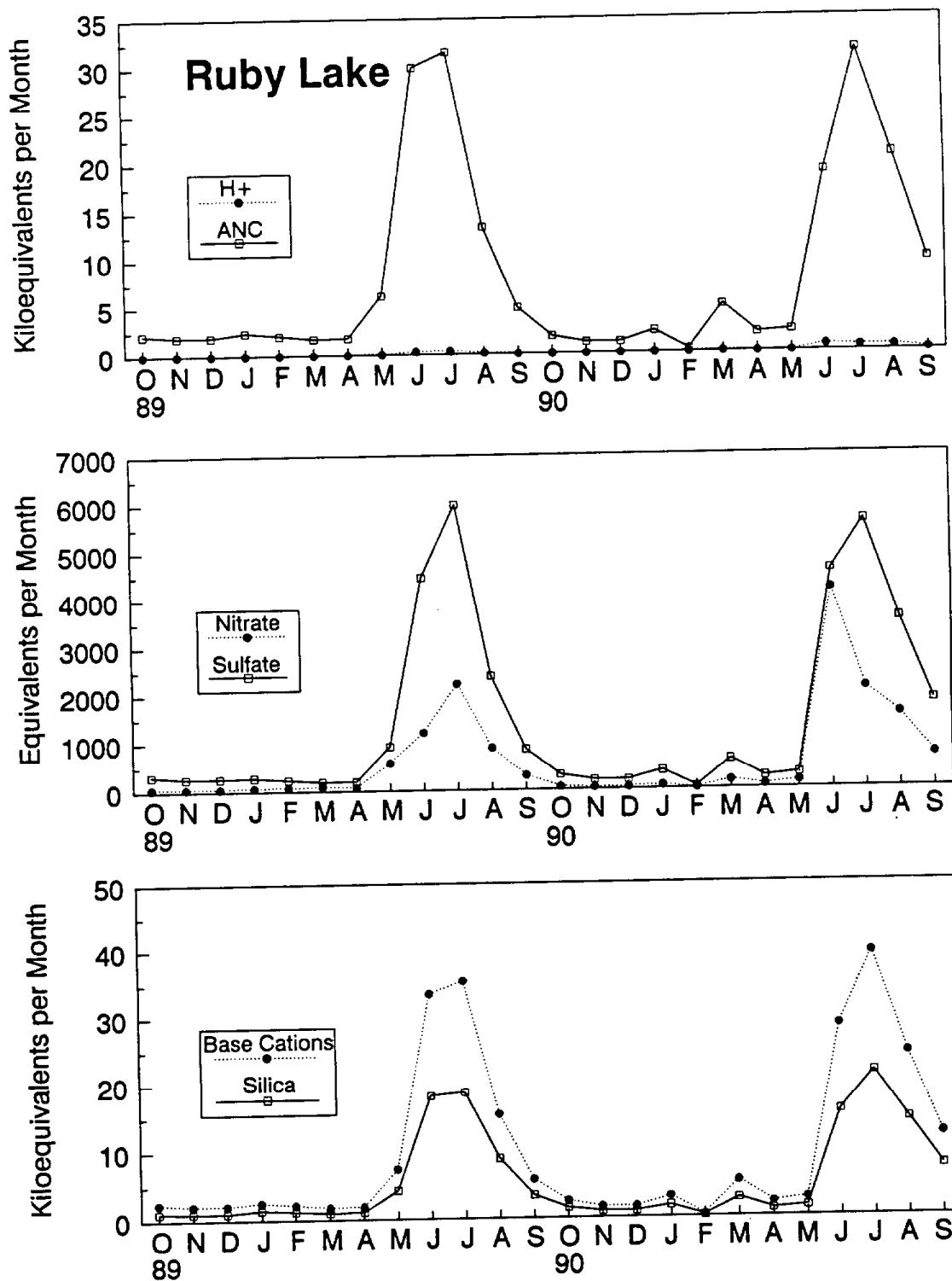


Fig. 33

Monthly Outflow Flux of Solutes



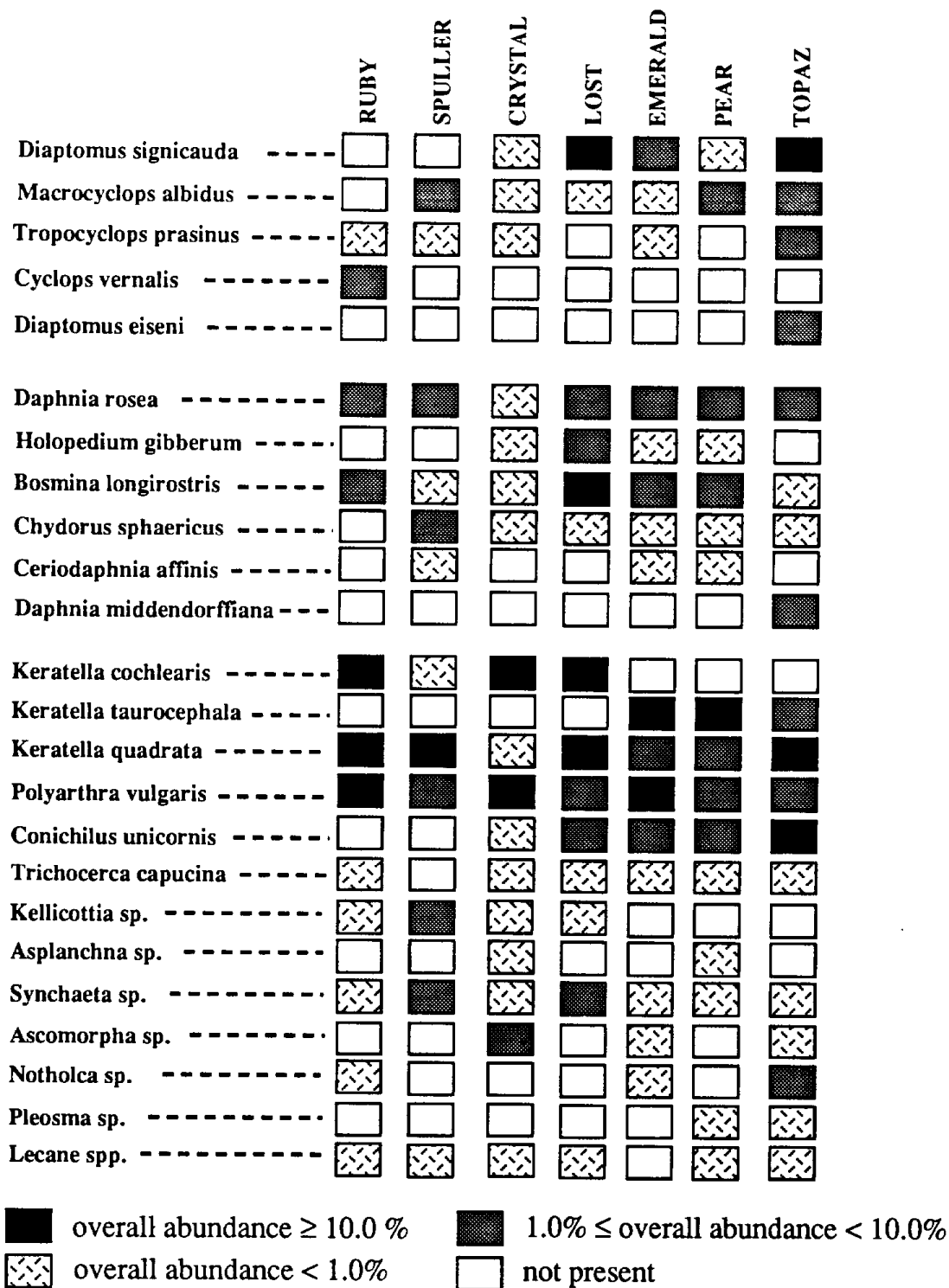
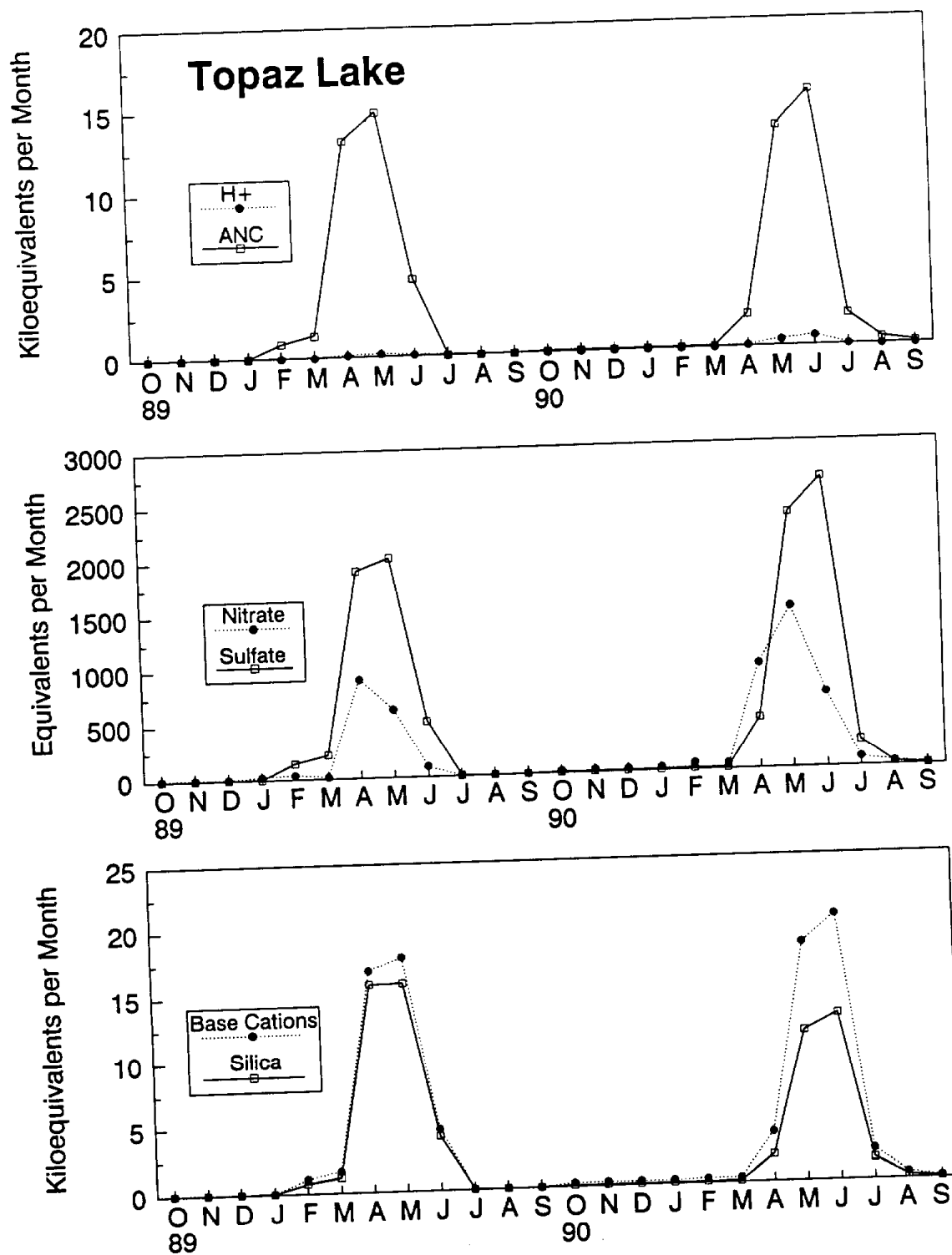


FIGURE 36 Zooplankton community composition for the seven survey lakes. Only species which comprised $> 0.10\%$ of overall abundance (for all sampling dates pooled) in at least one lake were included.

Monthly Outflow Flux of Solutes



CRYSTAL LAKE: MAJOR CLADOCERA SPECIES

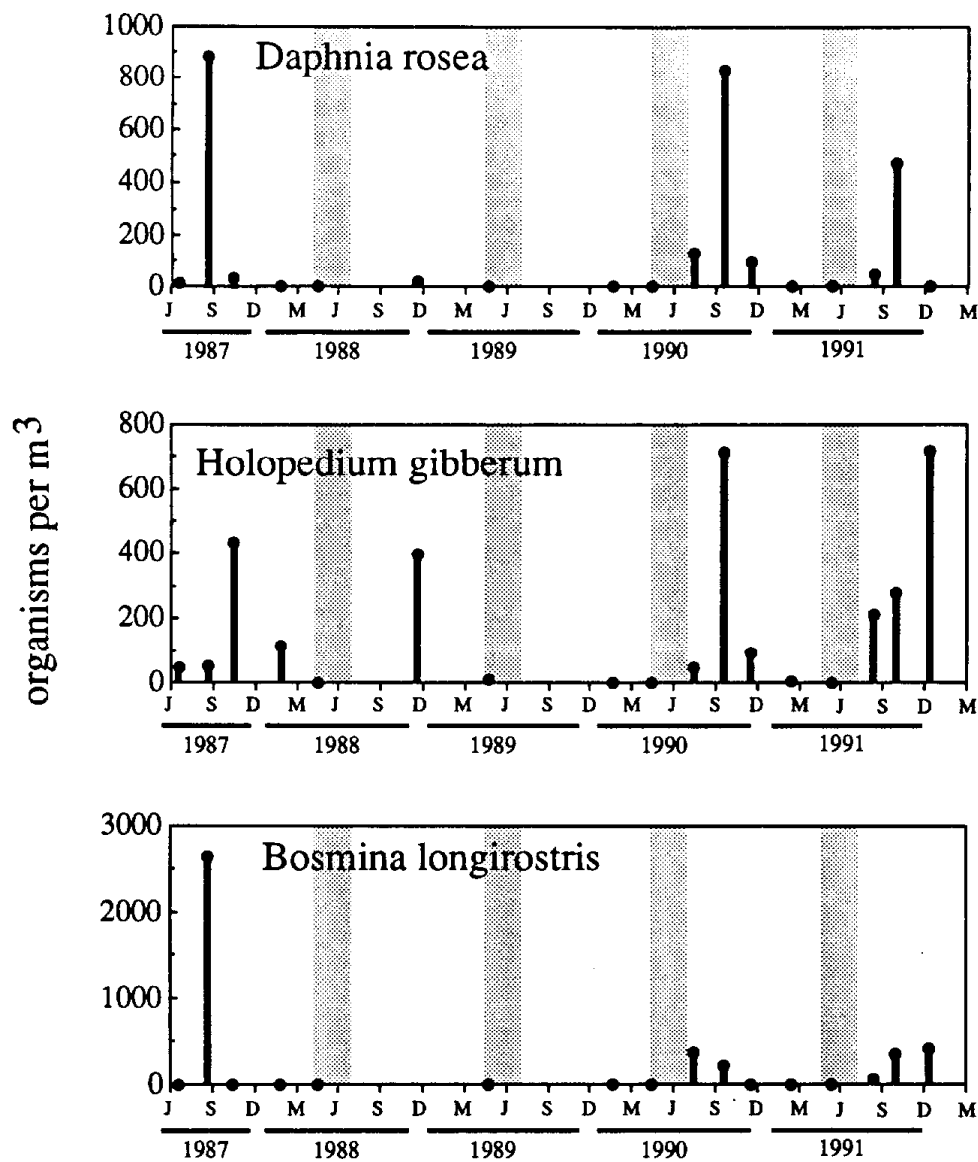


Figure 37 continued

CRYSTAL LAKE: MAJOR COPEPOD SPECIES

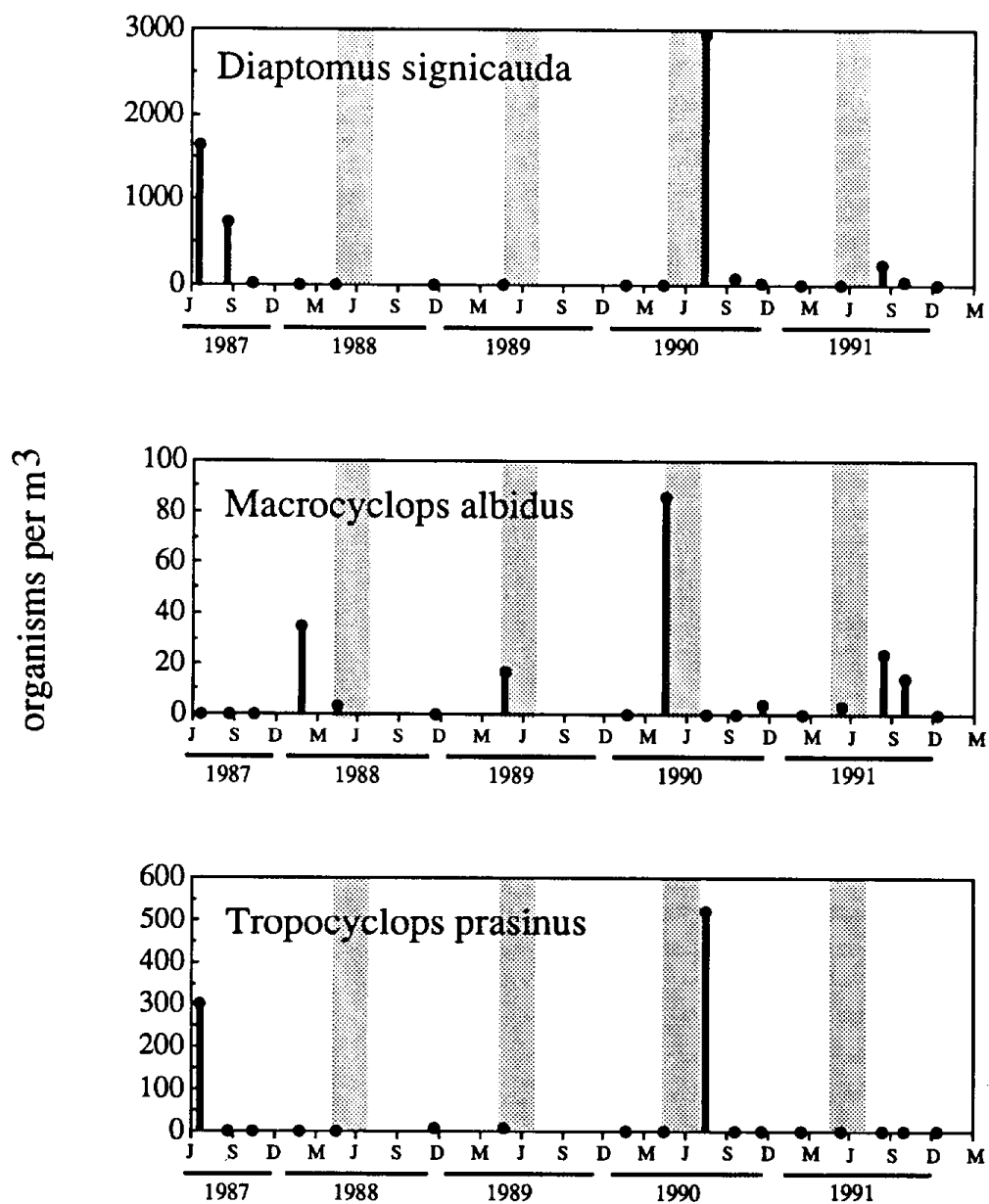


Figure 37 Mean abundance of major zooplankton species in Crystal Lake. Shaded regions indicate snow melt periods.

CRYSTAL LAKE: MAJOR ROTIFER SPECIES

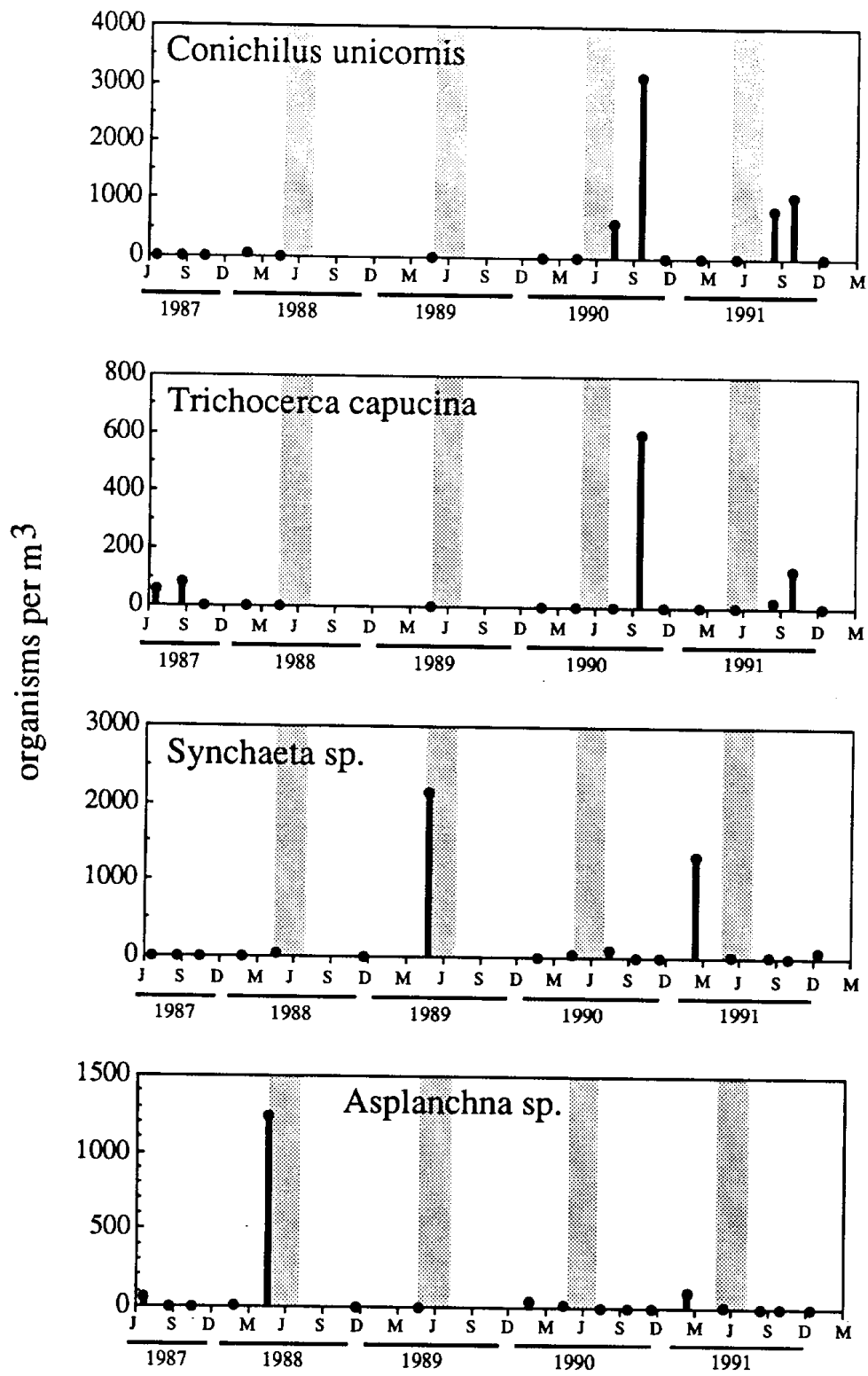


Figure 37 continued

CRYSTAL LAKE: MAJOR ROTIFER SPECIES

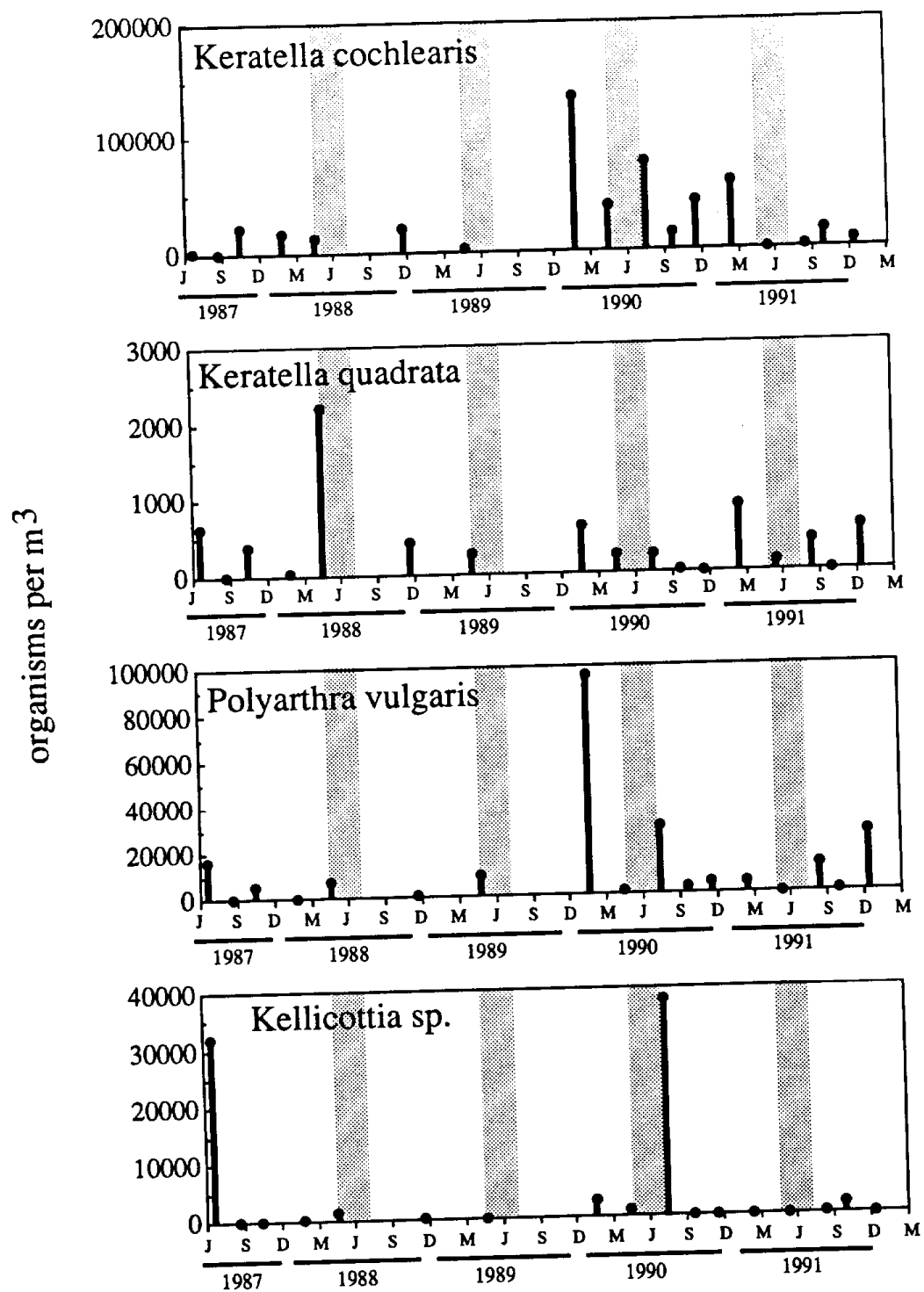


Figure 37 continued

EMERALD LAKE: MAJOR CLADOCERAN SPECIES

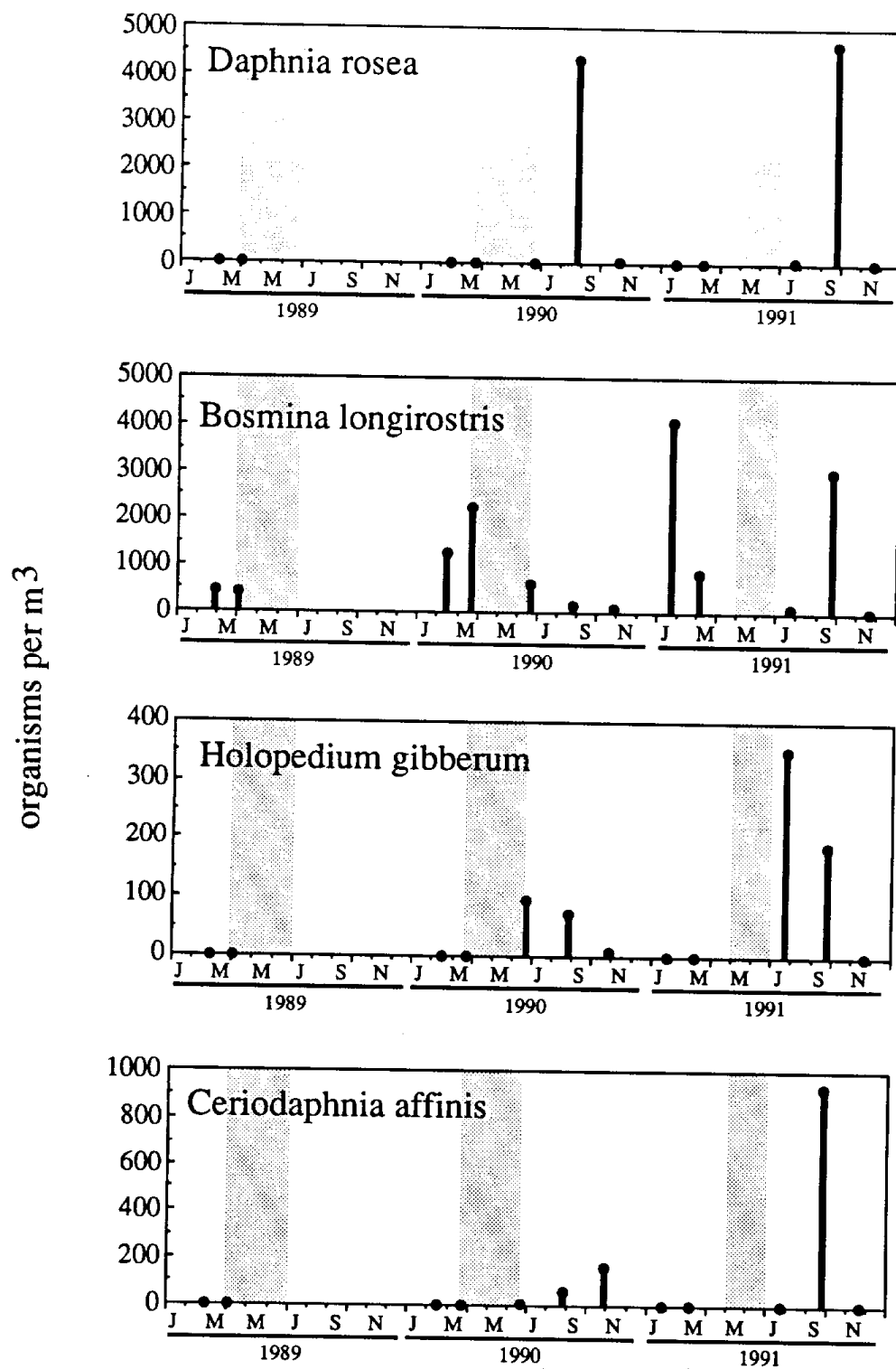


Figure 38 continued

EMERALD LAKE: MAJOR COPEPOD SPECIES

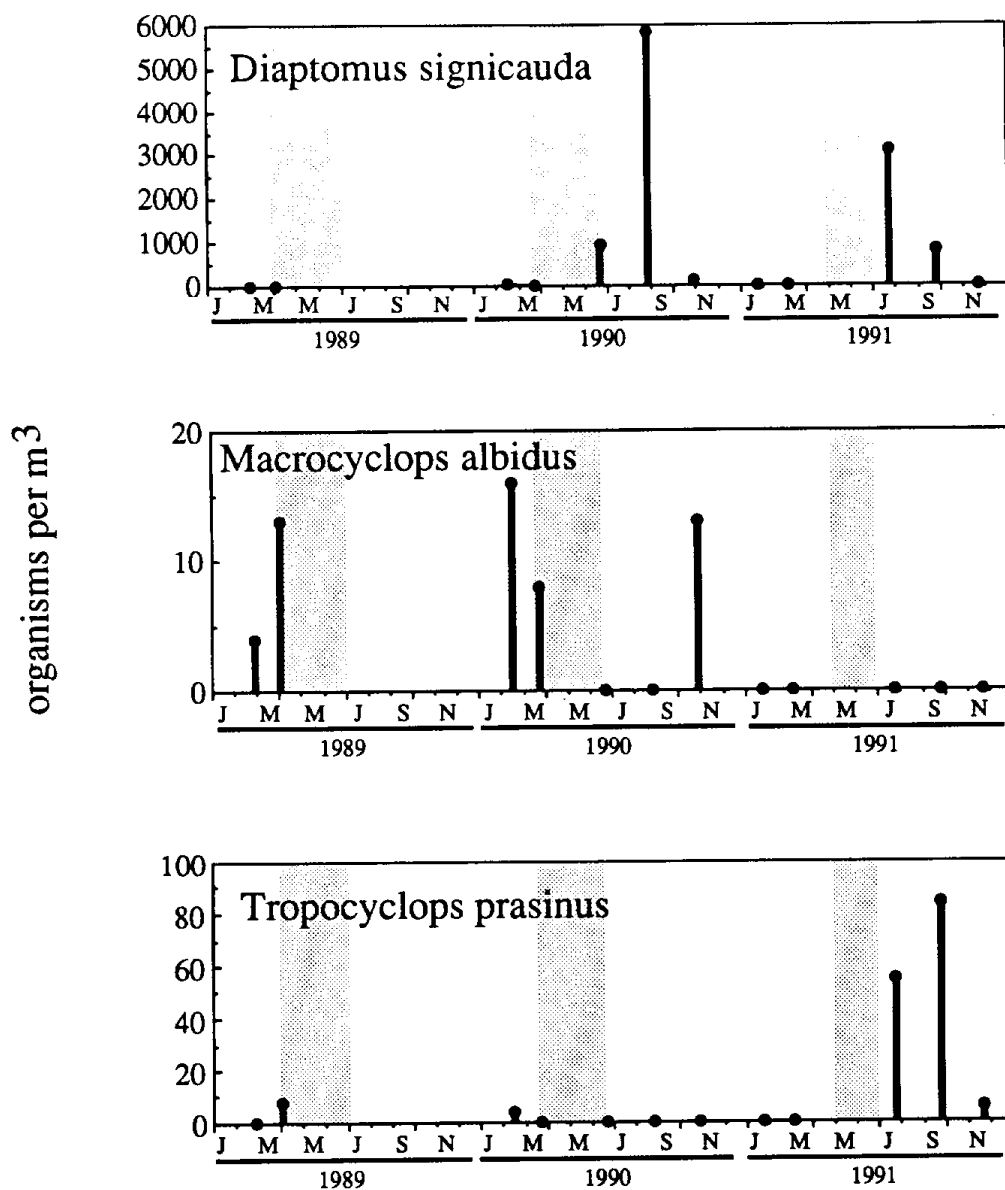


Figure 38. Mean abundance of major zooplankton species in Emerald Lake. Shaded regions indicate snow melt periods.

EMERALD LAKE: MINOR ROTIFER SPECIES

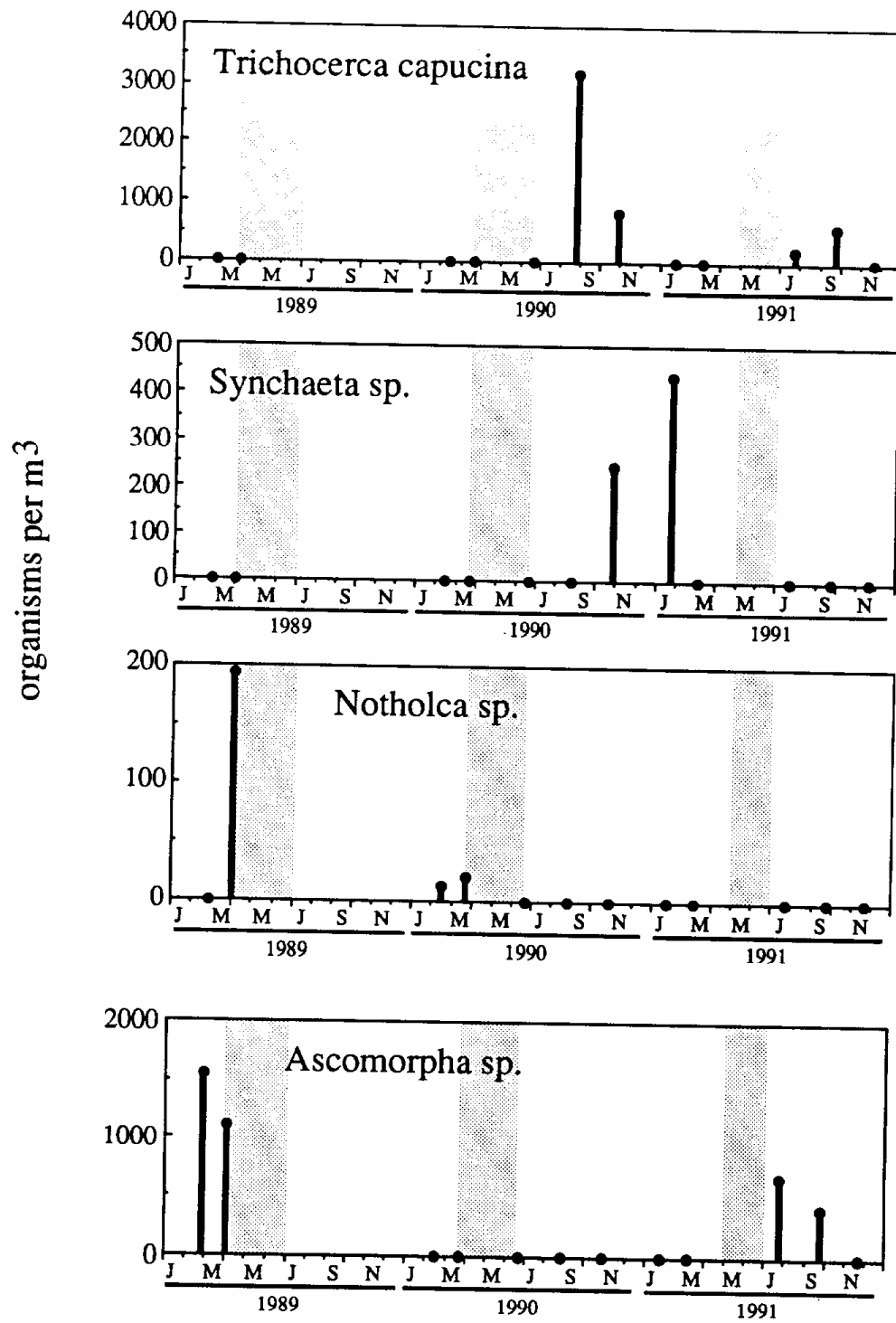


Figure 38 continued

EMERALD LAKE: MAJOR ROTIFER SPECIES

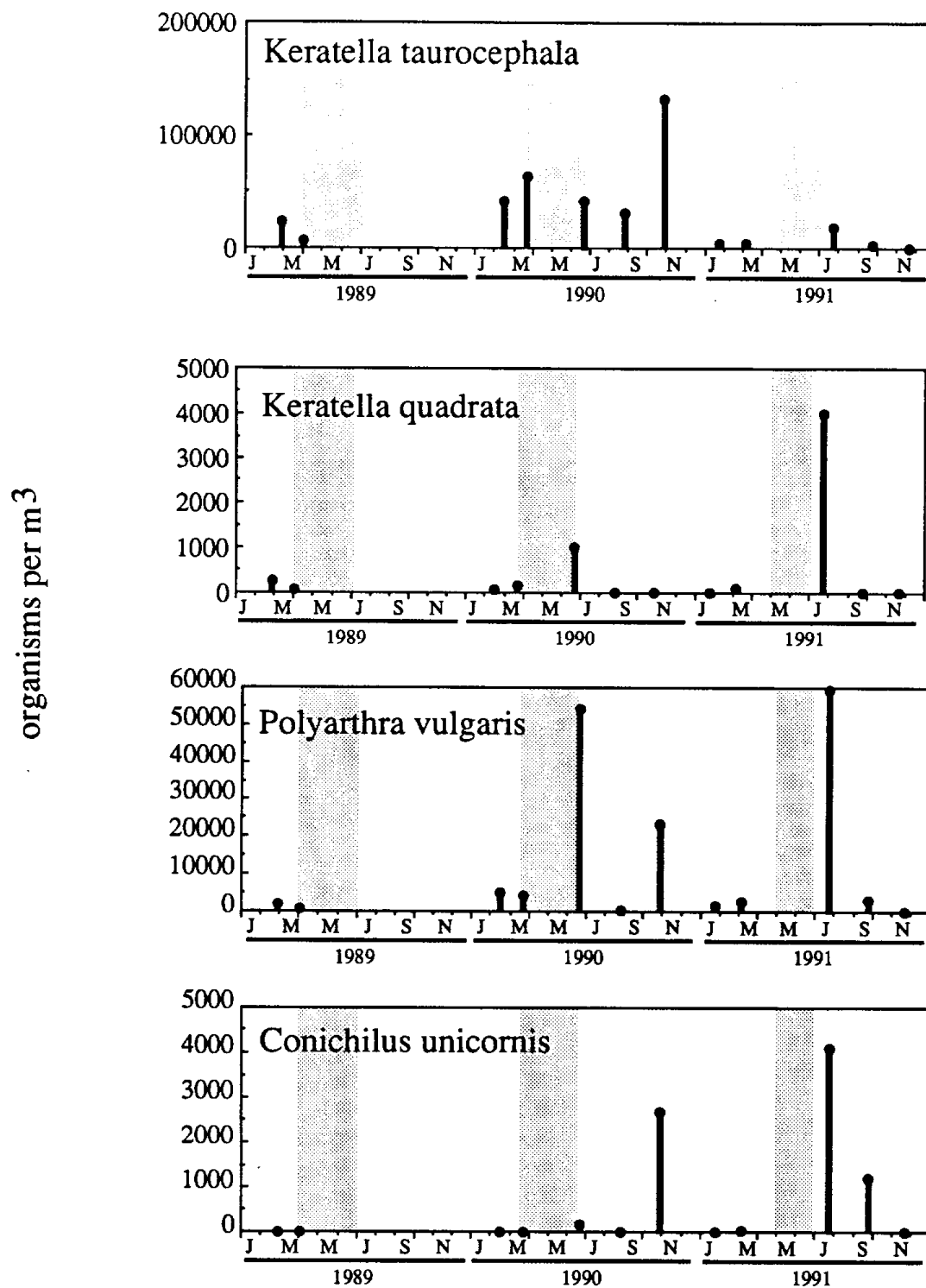


Figure 38 continued

LOST LAKE: MAJOR CLADOCERAN SPECIES

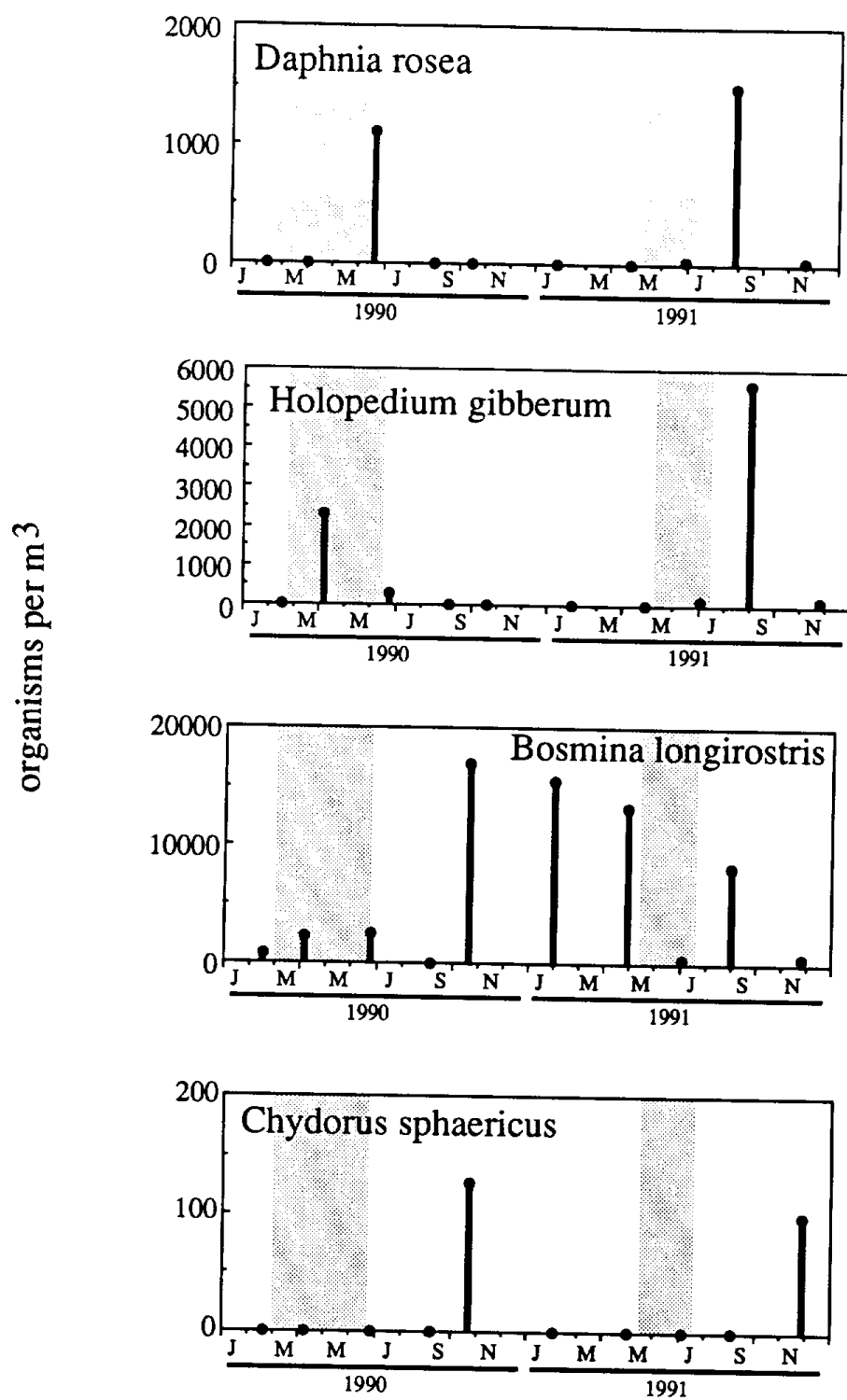


Figure 39 continued

LOST LAKE: MAJOR COPEPOD SPECIES

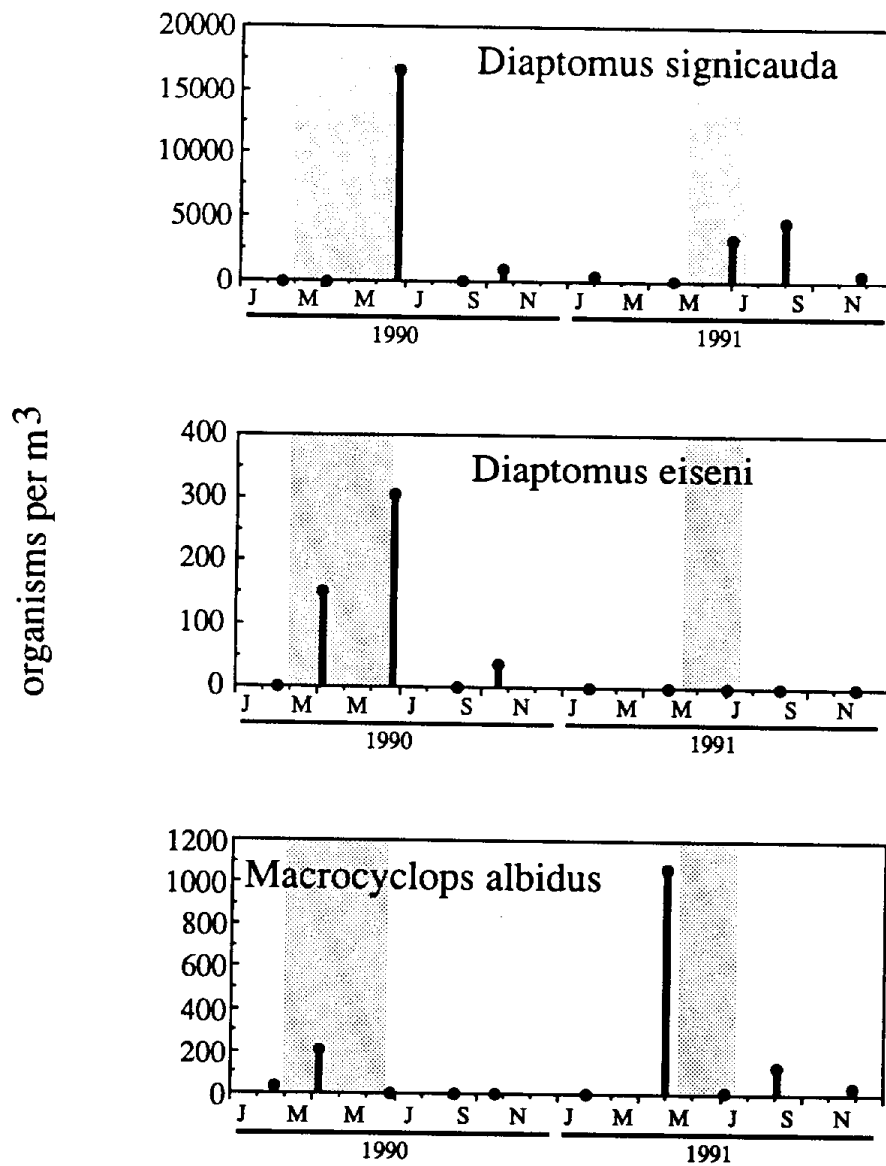


Figure 39 Mean abundance of major zooplankton species in Lost Lake. Shaded regions indicate snow melt periods.

LOST LAKE: MINOR ROTIFER SPECIES

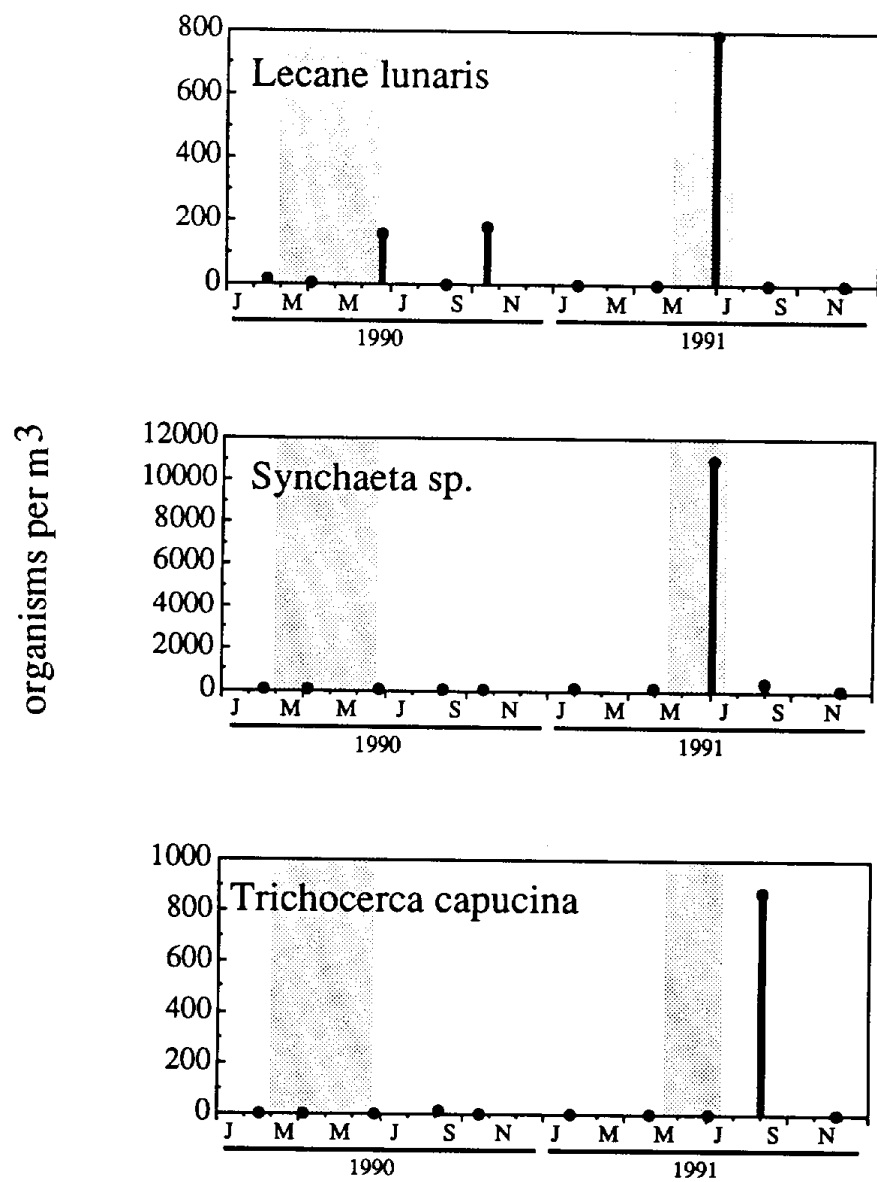


Figure 39 continued

LOST LAKE: MAJOR ROTIFER SPECIES

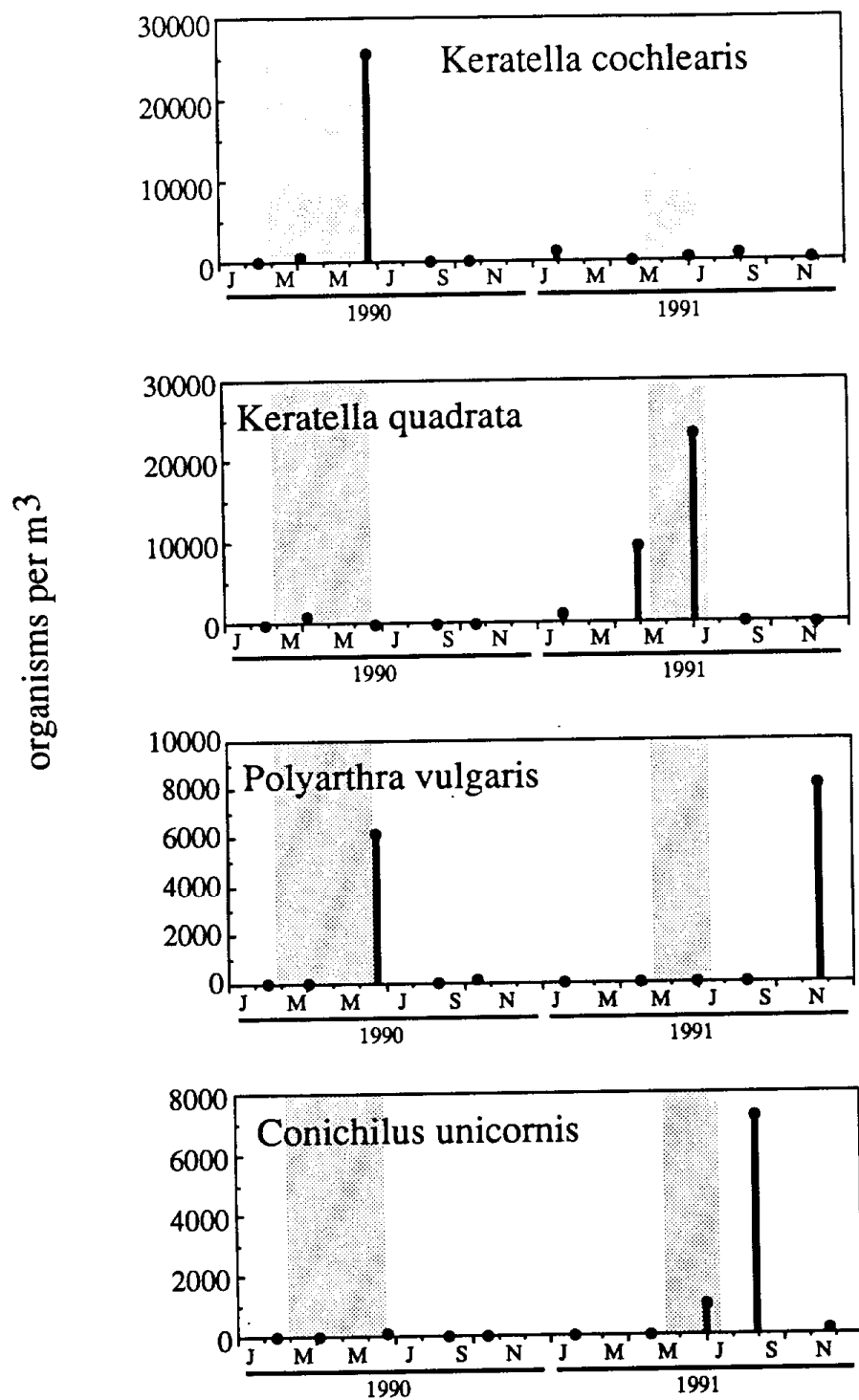


Figure 39 continued

PEAR LAKE: MAJOR CLADOCERAN SPECIES

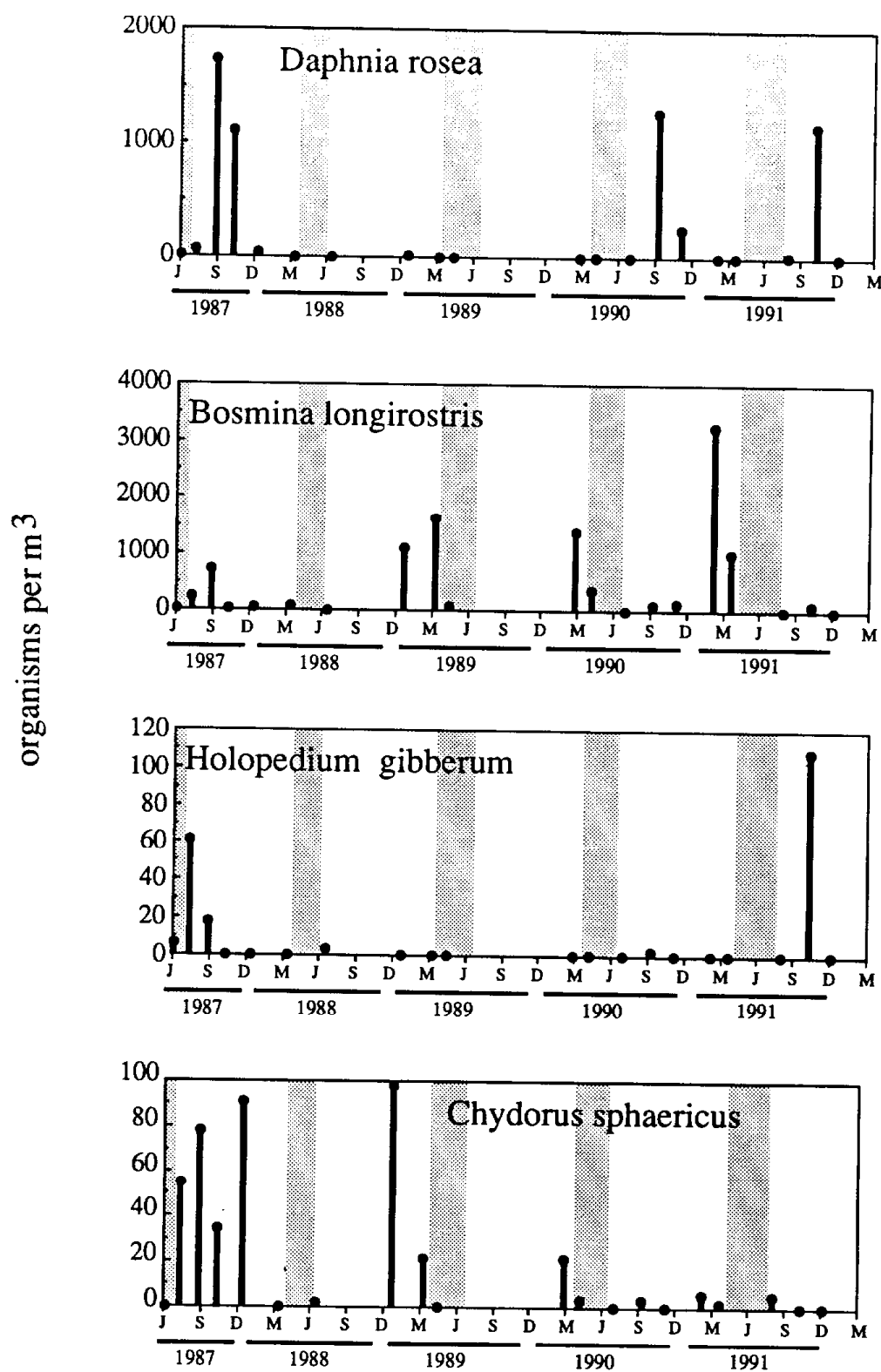


Figure 40 continued

PEAR LAKE: MAJOR COPEPOD SPECIES

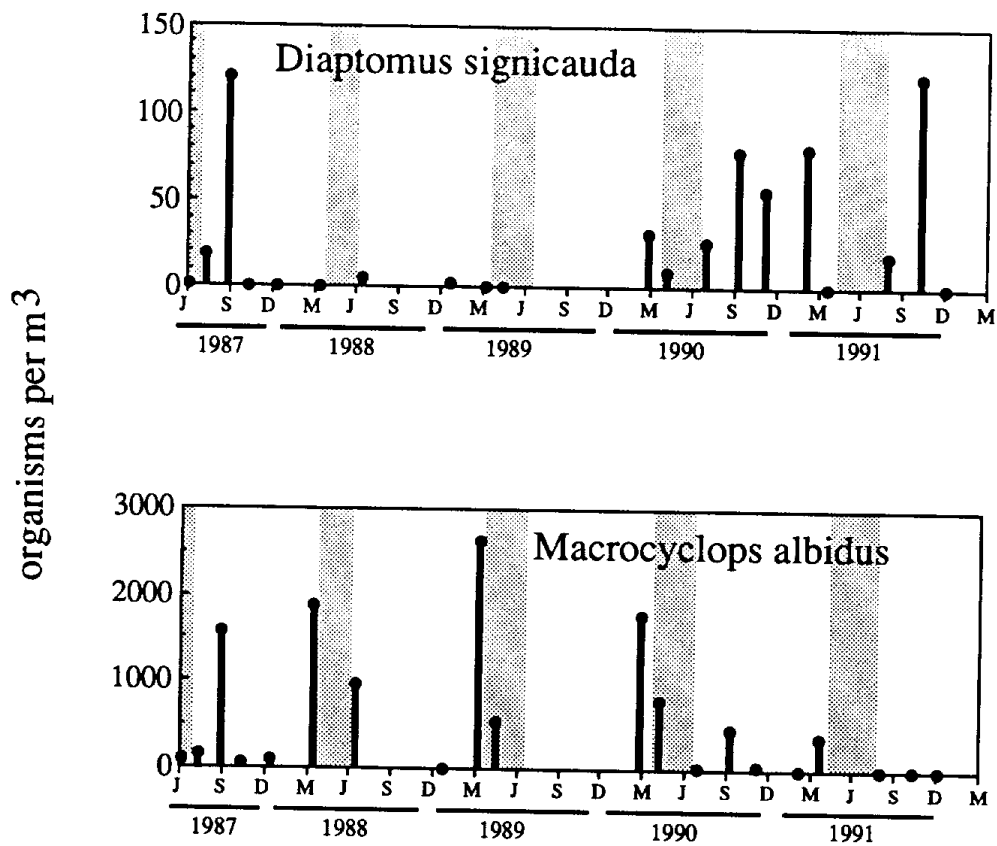


Figure 40 Mean abundance of major zooplankton species in Pear Lake. Shaded regions indicate snow melt periods.

PEAR LAKE: MINOR ROTIFER SPECIES

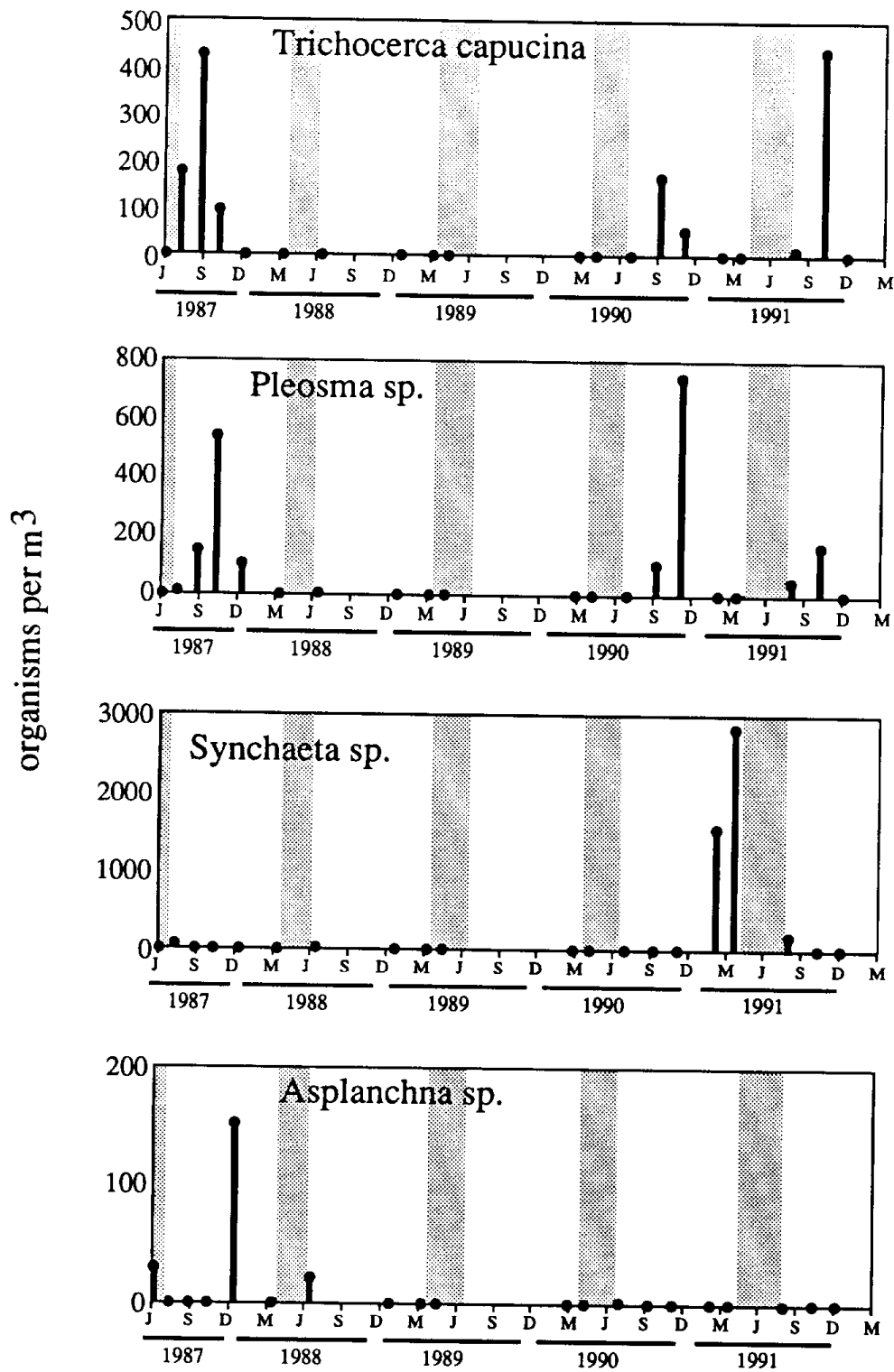


Figure 40 continued

PEAR LAKE: MAJOR ROTIFER SPECIES

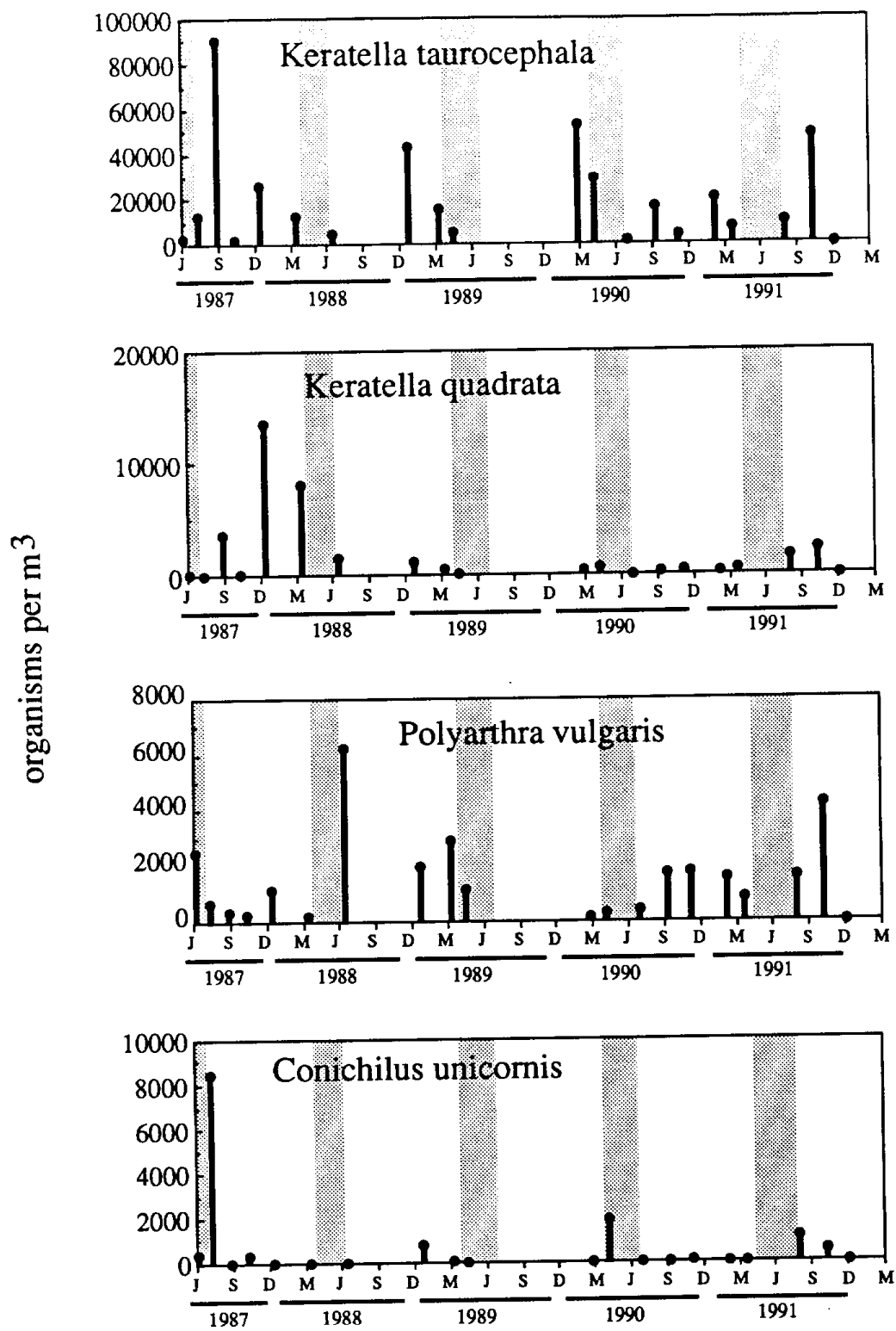


Figure 40 continued

RUBY LAKE: MAJOR ROTIFER SPECIES

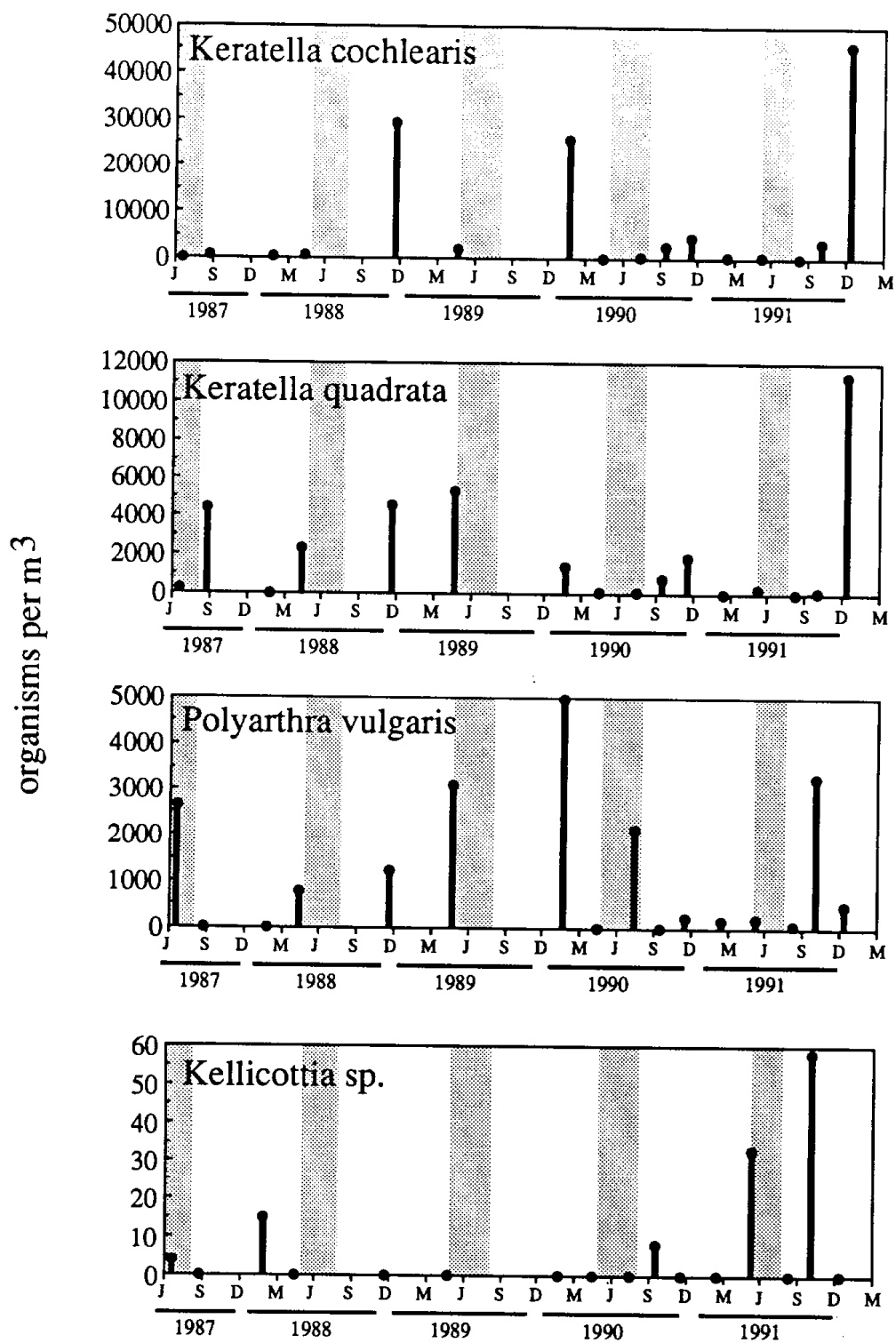


Figure 41 continued

RUBY LAKE: MAJOR CRUSTACEAN SPECIES

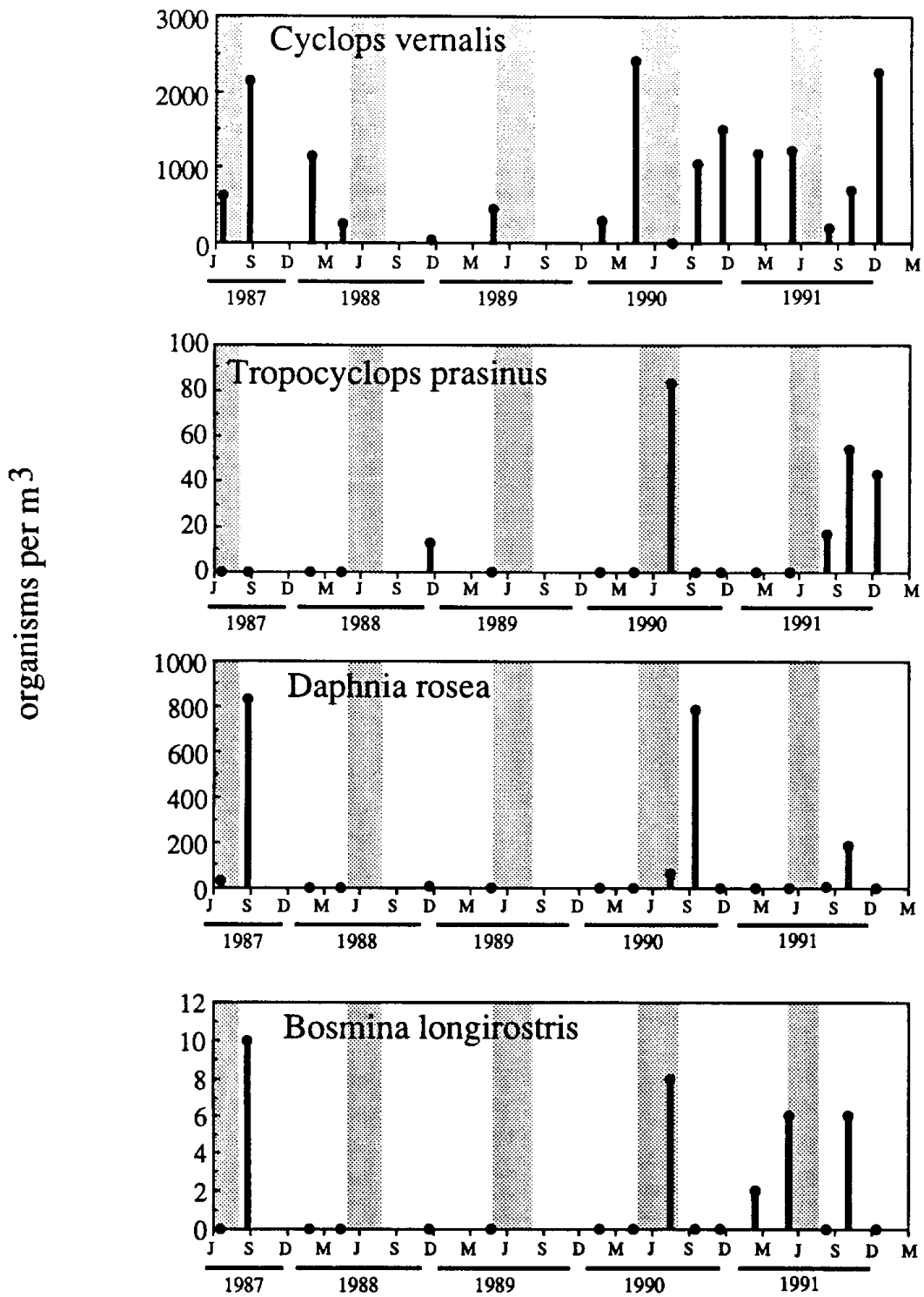


Figure 41 Mean abundance of major zooplankton species in Ruby Lake. Shaded regions indicate snow melt periods.

SPULLER LAKE: MAJOR ROTIFER SPECIES

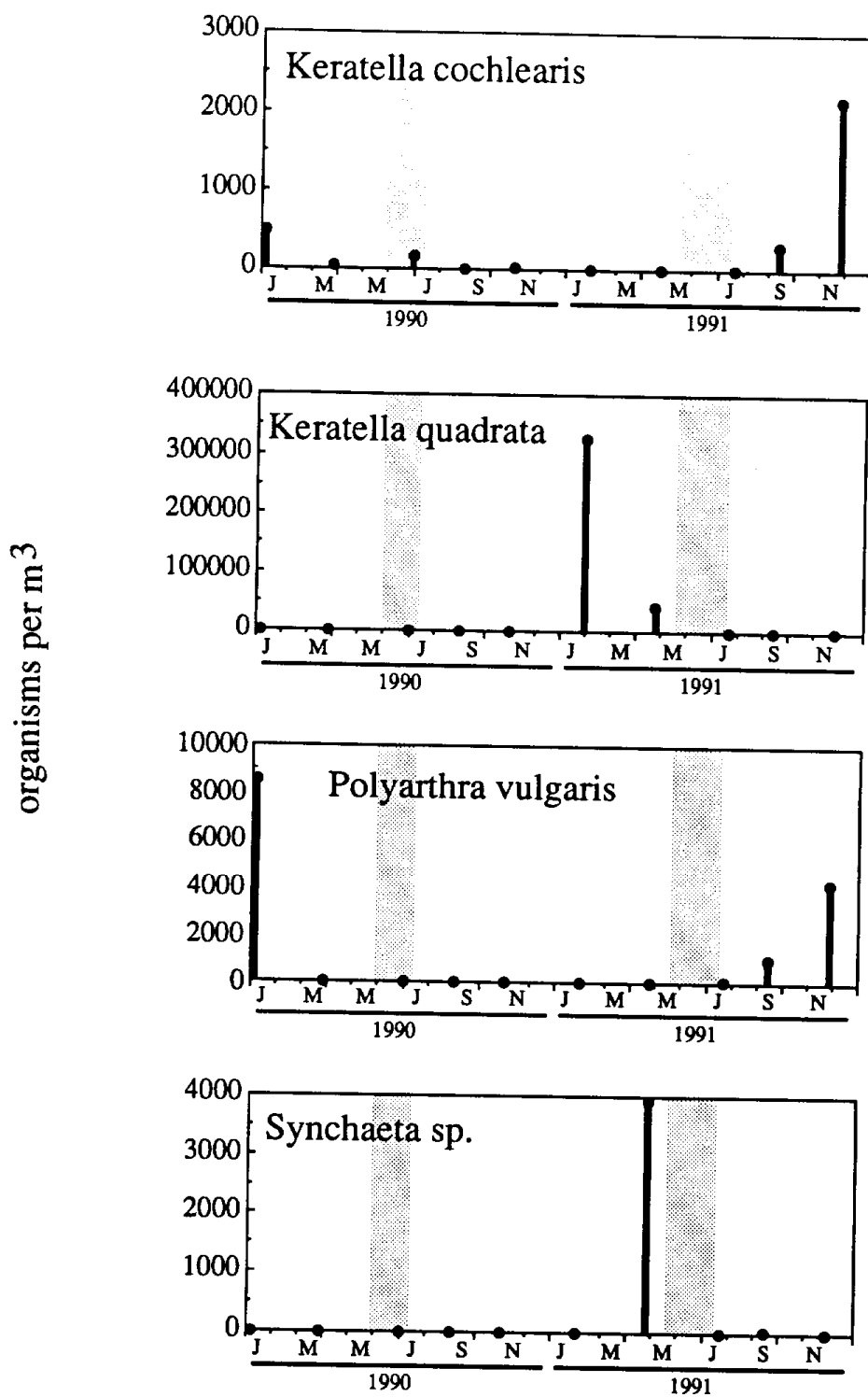


Figure 42 continued

SPULLER LAKE: MAJOR CRUSTACEAN SPECIES

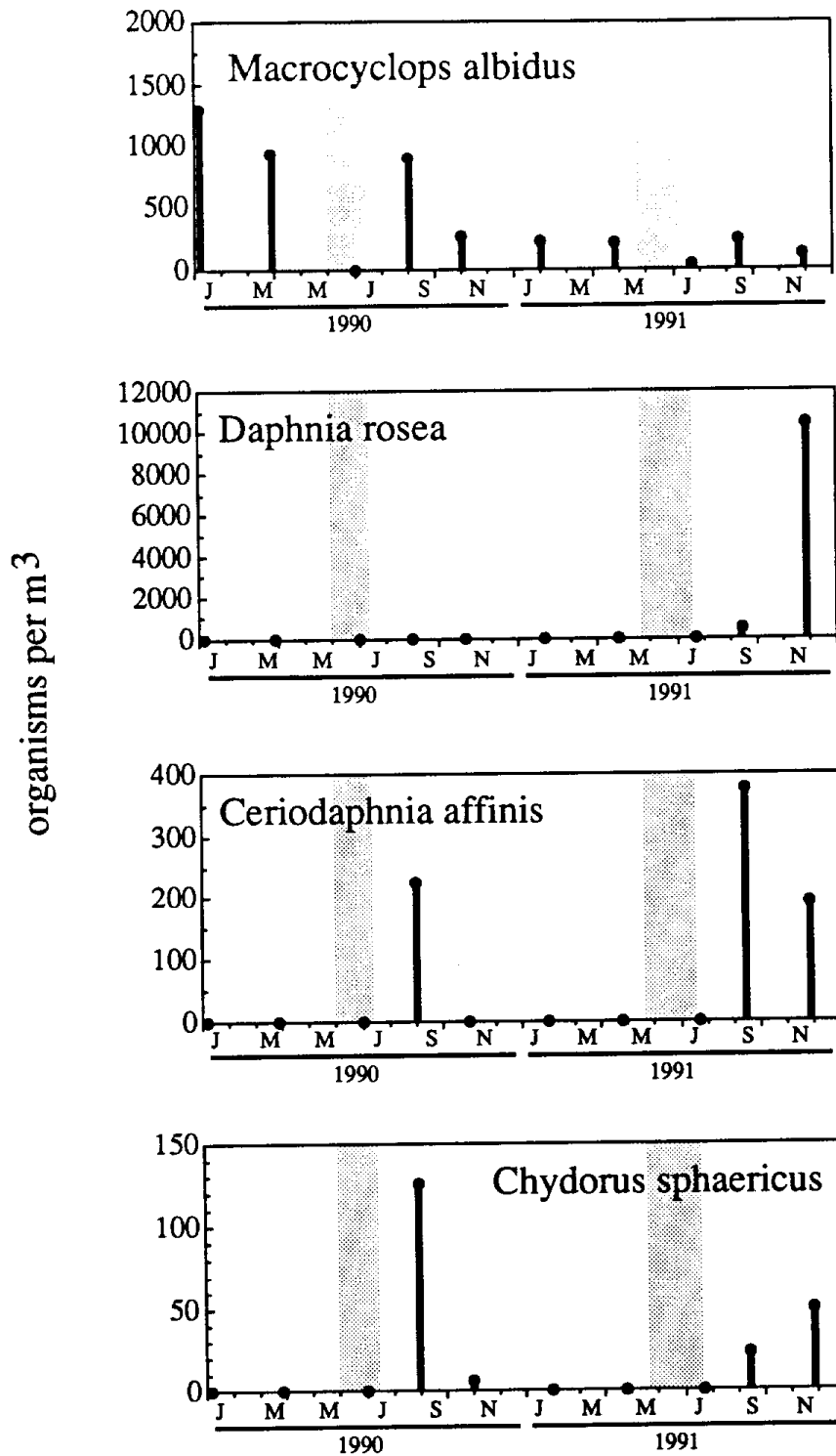


Figure 42 Mean abundance of major zooplankton species in Spuller Lake. Shaded regions indicate snow melt periods.

TOPAZ LAKE: MAJOR CLADOCERAN SPECIES

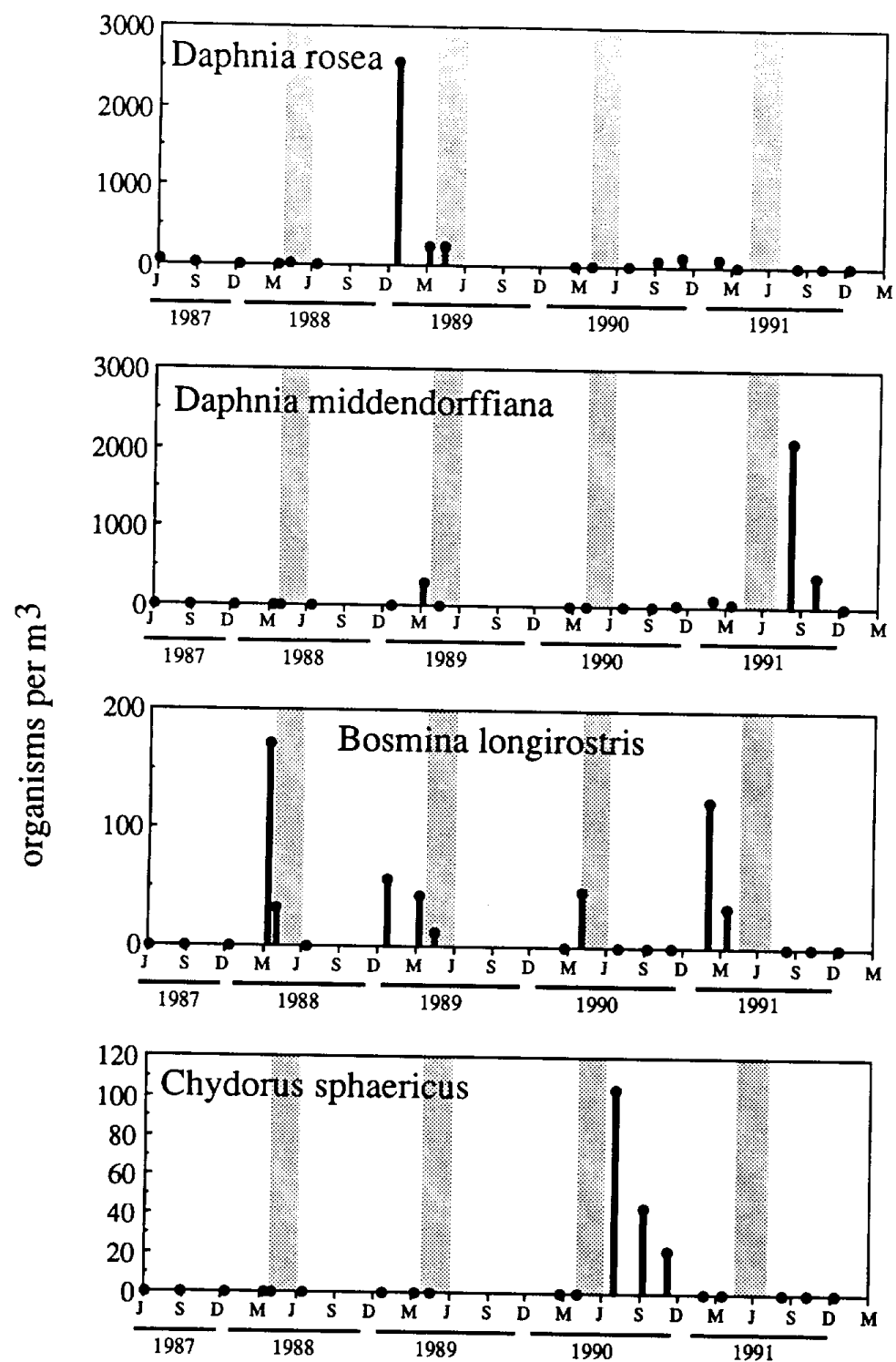


Figure 43 continued

TOPAZ LAKE: MAJOR COPEPOD SPECIES

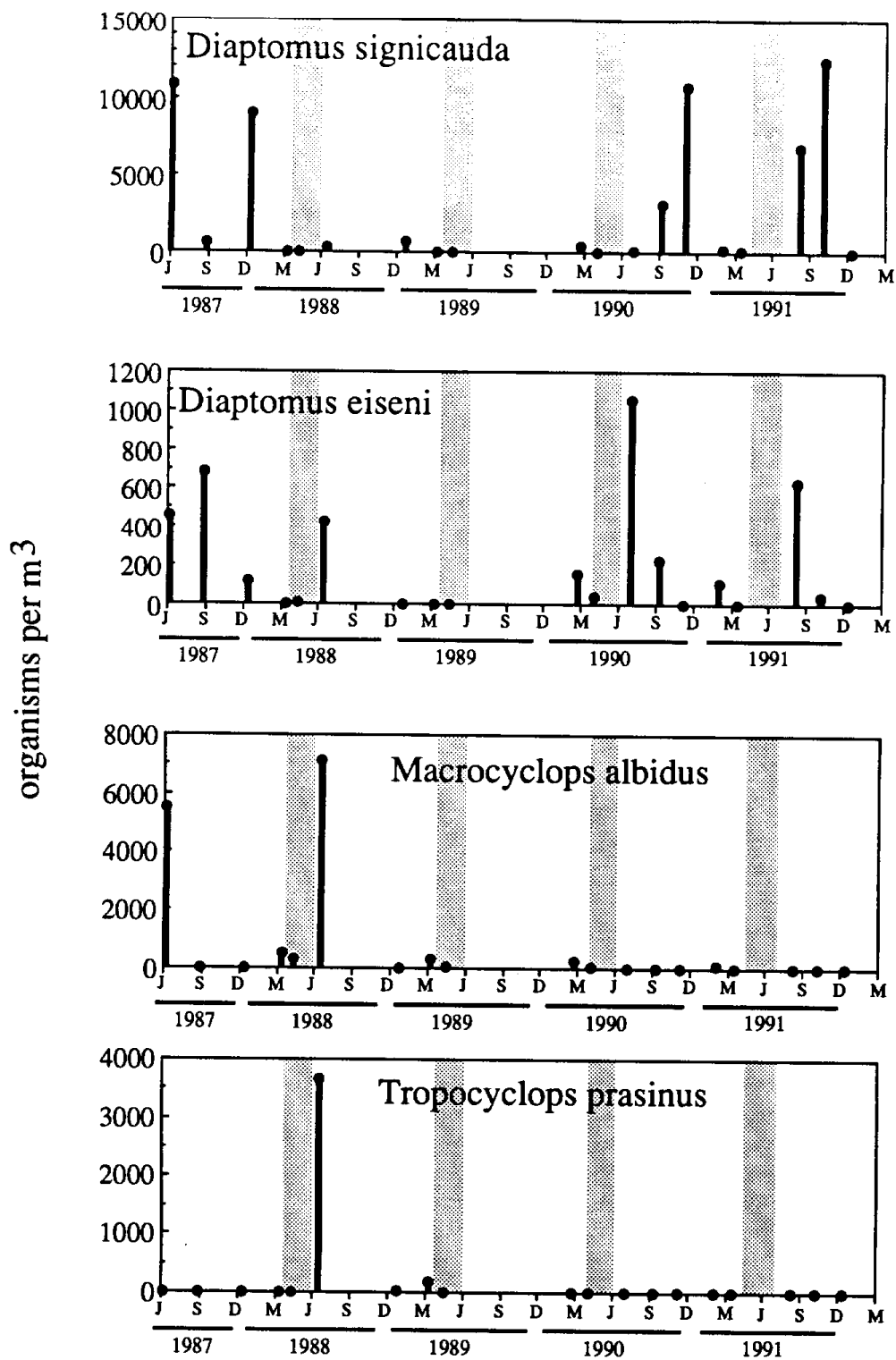


Figure 43 Mean abundance of major zooplankton species in Topaz Lake. Shaded regions indicate snow melt periods.

TOPAZ LAKE: MINOR ROTIFER SPECIES

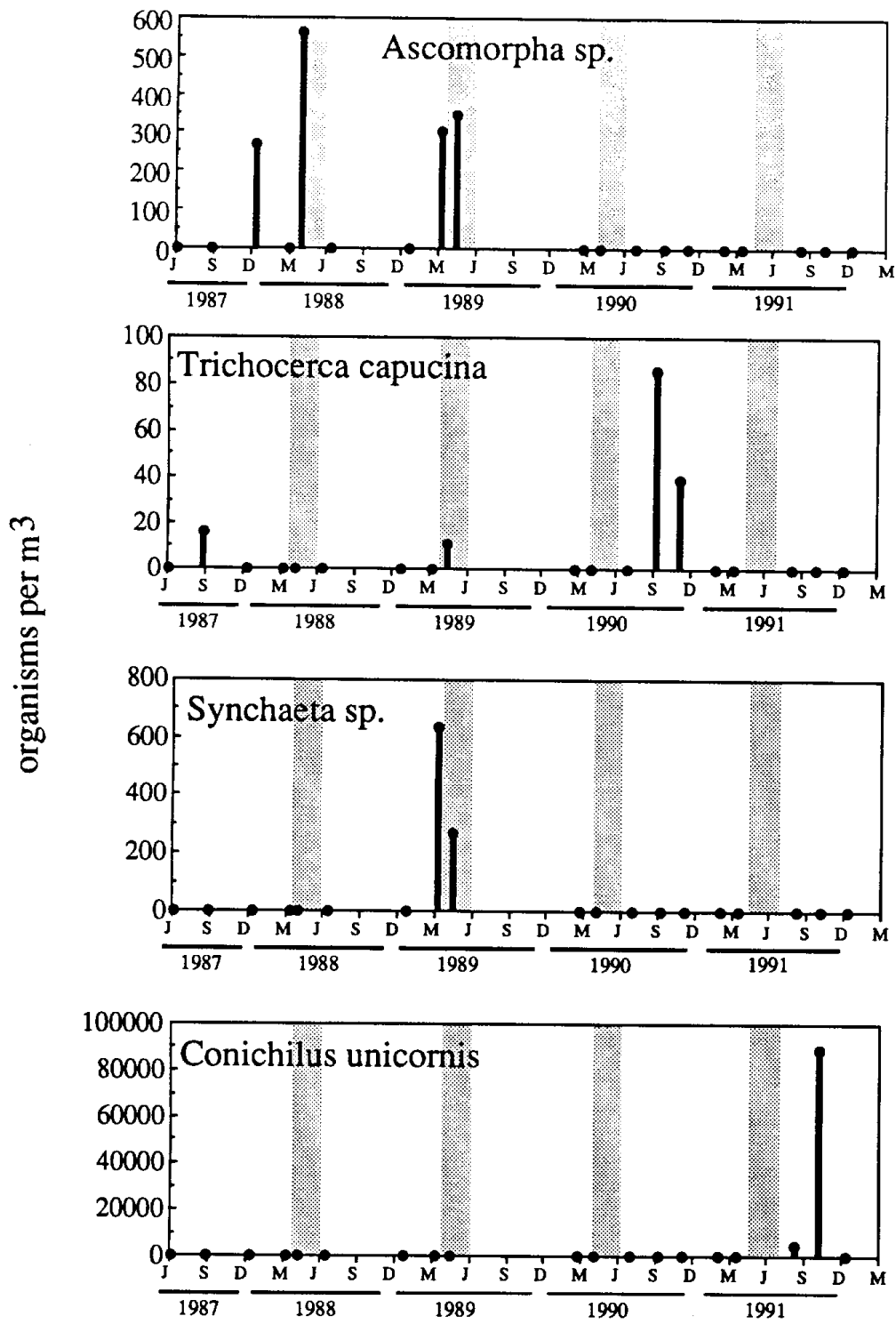


Figure 43 continued

TOPAZ LAKE: MAJOR ROTIFER SPECIES

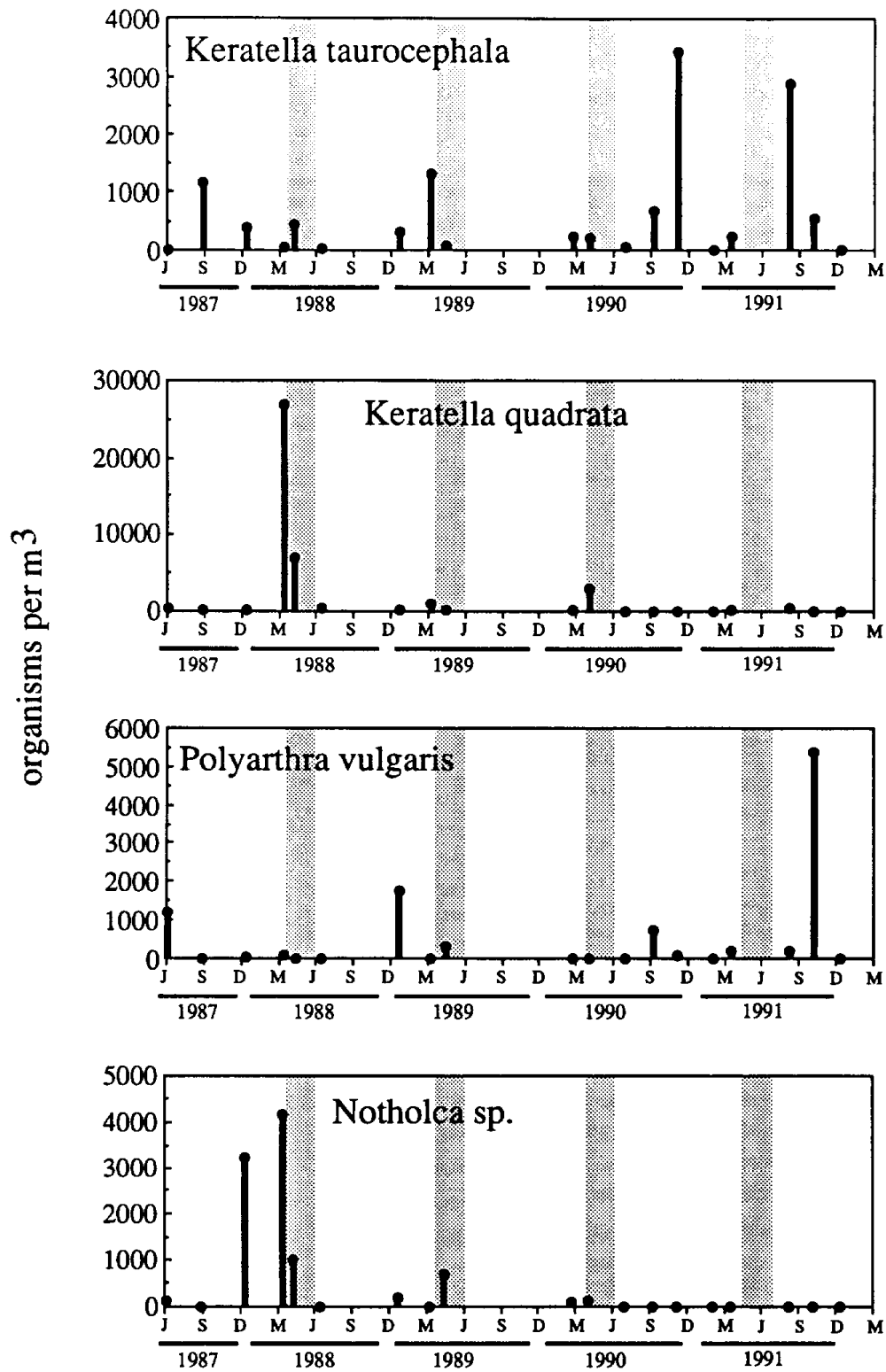


Figure 43 continued

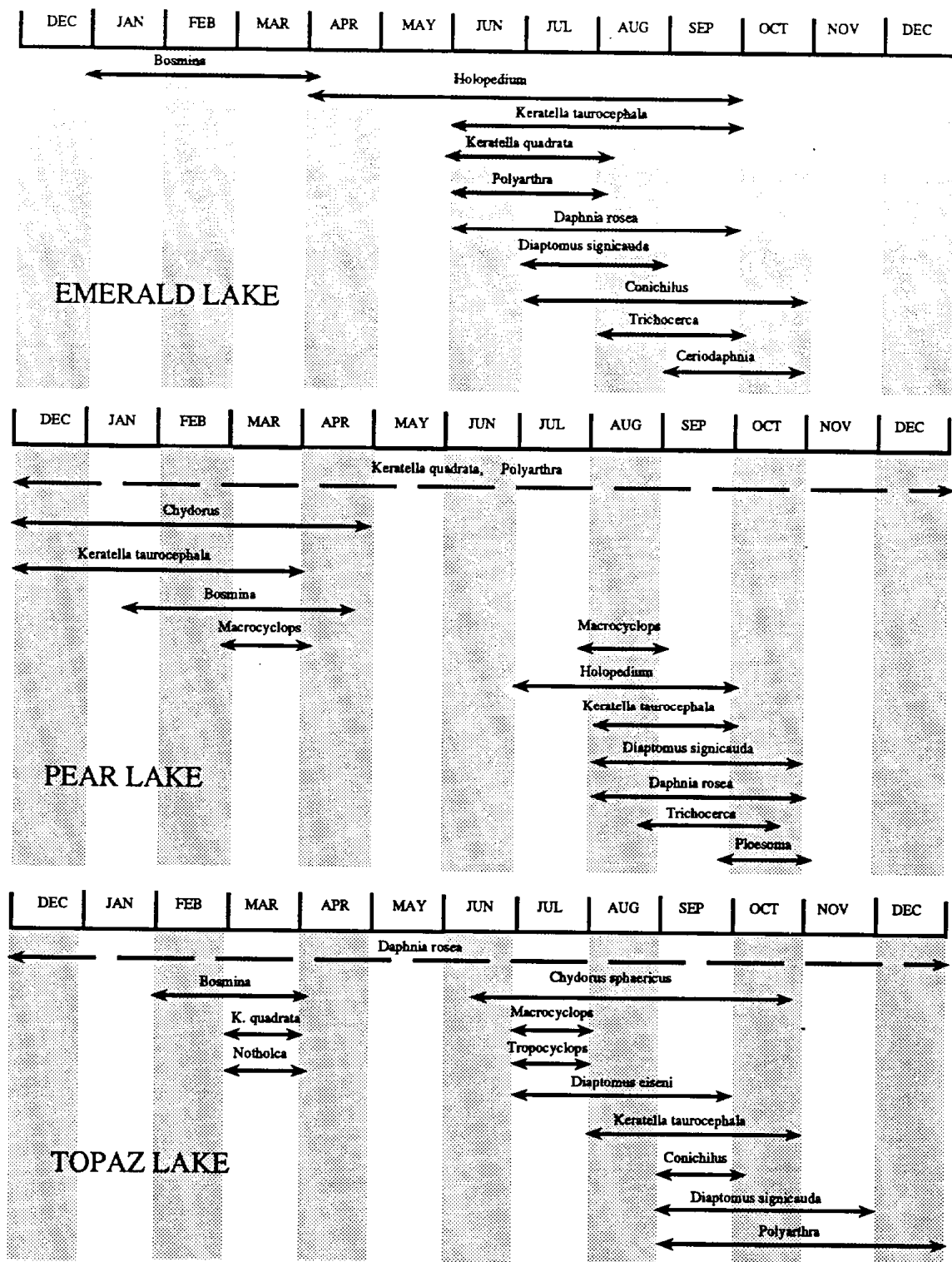
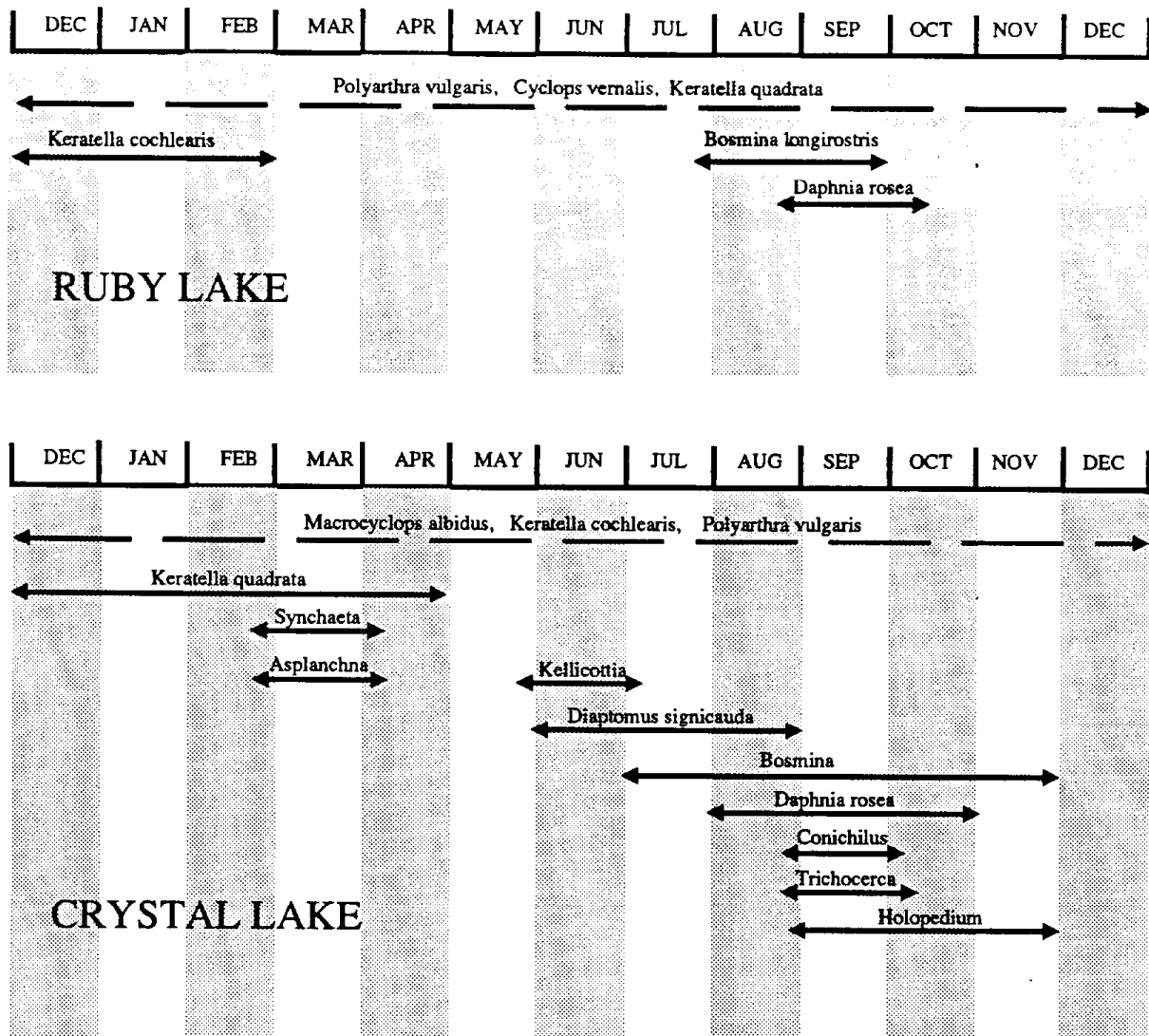


Figure 45 Seasonal abundance patterns in survey lakes from the Emerald Lake basin. Lines indicate periods in which annual population peaks are normally observed. Species appearing above dotted lines may occur at high abundances in any season. All species may occur in samples outside of the periods indicated.



Figure⁴⁴ Seasonal abundance patterns in Ruby and Crystal Lakes. Lines indicate periods in which annual population peaks are normally observed. Species appearing above dotted lines may occur at high abundances in any season. All species may occur in samples outside of the periods indicated.

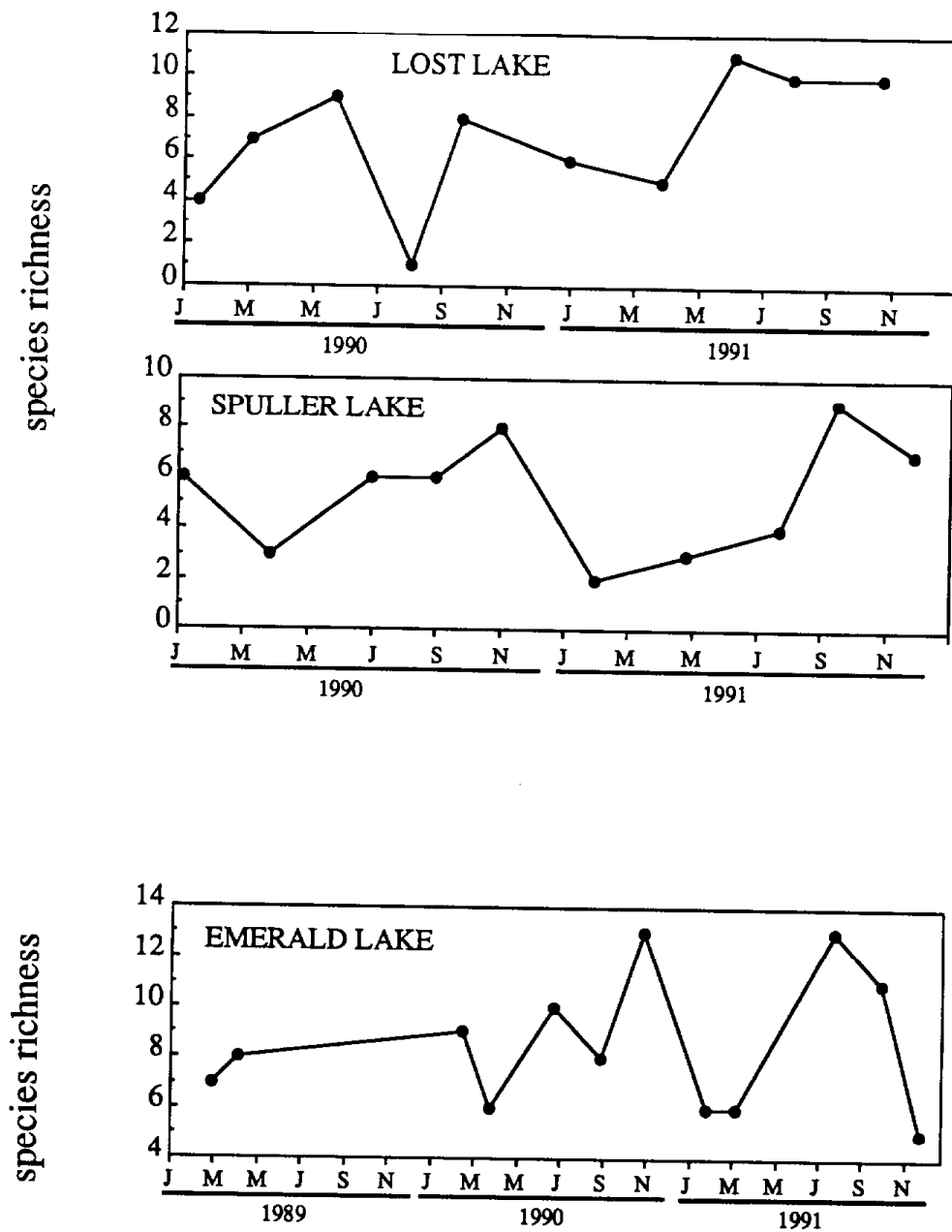


Figure 47 Species richness over time in Lost, Spuller and Emerald Lakes. Species richness was obtained by summing all crustacean and rotifer species observed on a given date without respect to relative abundance.

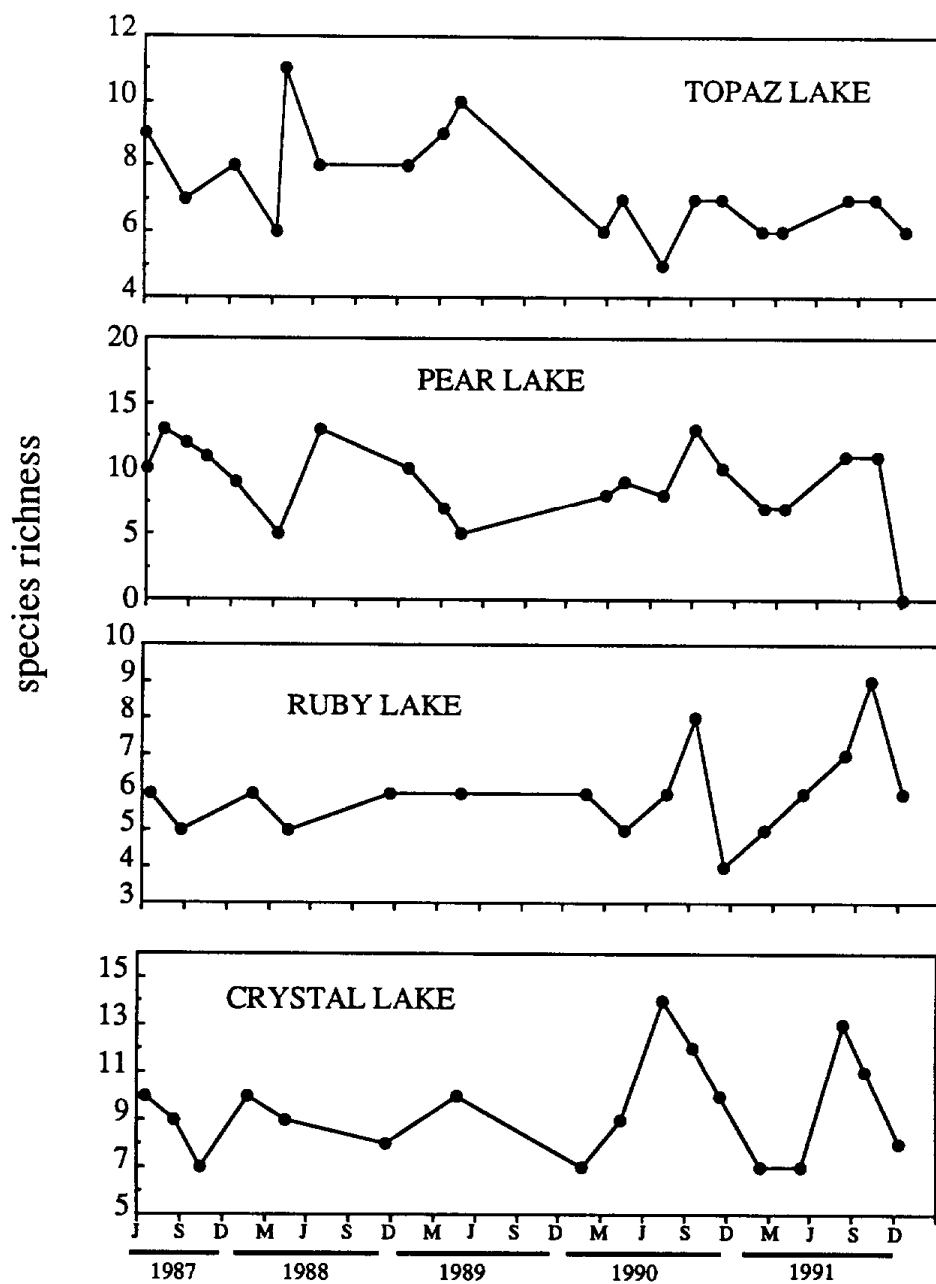


Figure 46 Species richness over time in Topaz, Pear, Ruby and Crystal Lakes. Species richness was obtained by summing all crustacean and rotifer species observed on a given date without respect to relative abundance.

Table 1. Summary of basin and lake characteristics.

Lake	Basin Area (ha)	Basin Relief (m)	Lake Area (ha)	Lake Elev. (m)	Lake Max. Depth (m)	Lake Mean Depth (m)	Lake Vol. (m ³)
Emerald	120	616	2.7	2,800	10	6.0	162,000
Topaz	142	244	5.2	3,219	5	1.5	76,900
Pear	136	471	8.0	2,904	27	7.4	591,000
Crystal	129	293	5.0	2,951	14	6.5	324,000
Ruby	424	754	12.6	3,426	35	16.4	2,080,000
Spuller	84	537	2.2	3,121	5.5	1.6	34,700
Lost	18.5	160	0.7	2,475	5.5	1.9	12,500

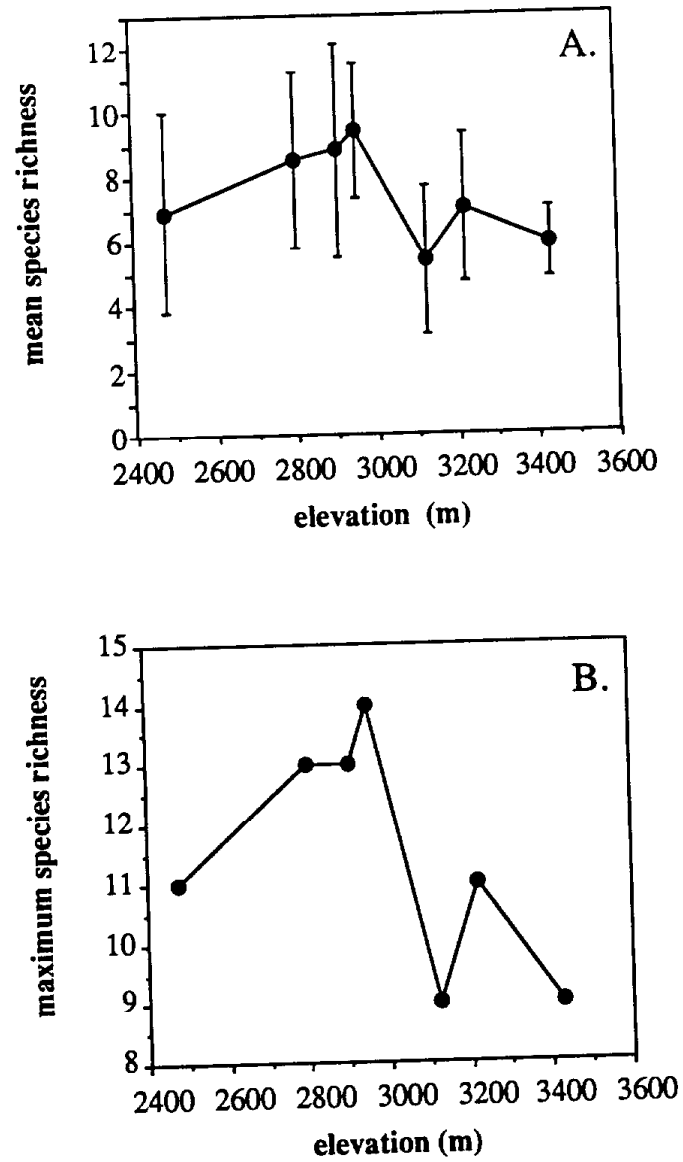


Figure 48 A. Mean species richness for each lake plotted against its elevation. Means were calculated by pooling values from all available sampling dates. Error bars show standard errors. B. Maximum species richness value observed over time for each lake.

Table 3. Summary of meteorologic and hydrologic measurements and instrumentation.

Parameter	Instrument	Model	Precision
Air Temperature	Thermistor	Omnidata ES060	$\pm 0.1^{\circ}\text{C}$
Relative Humidity	Capacitor	Vaisala HMP 35A	$\pm 2\%$
Wind Speed	Prop. Anemometer	RM Young 05103	$\pm 0.6 \text{ ms}^{-1}$
Wind Direction	Vane	RM Young 05103	$\pm 0.25\%$
Solar Radiation	Pyranometer	Eppley PSP WG7	$\pm 10 \text{ Wm}^{-2}$
Longwave Radiation	Pyrgeometer	Eppley PIR	$\pm 10 \text{ Wm}^{-2}$
Rainfall Quantity	Tipping Bucket	Qualimetrics 6011b	$\pm 0.1 \text{ mm}$
Stream Stage	Pressure Transducer	Montedero Whitney Wdm-1	$\pm 2\%$
Stream Temperature	Thermistor	Omnidata ES060	$\pm 0.1^{\circ}\text{C}$

Table 2. Summary of rating curves for the period 1987 through 1991. The equations take the general form of :

$$Q = 10[(\text{Log } V) - B] + M$$

Where: V = transducer voltage
B = y-intercept of Log:Log regression
M = slope of Log:Log regression

In the table, N is the number of data points in the regression, R^2 is the regression coefficient and Type refers to the full scale range of the pressure transducer. For Emerald and Spuller lakes the weir equations were used in 1991 to calculate discharge. 1 and 2 after dash indicate transducer number if more than one were used.

Lake	Years	M	B	N	R^2	Type
Crystal	1987-1989	0.1012	0.6231	51	0.94	1 psi
	1990	0.2188	0.7683	61	0.89	1 psi
	1991-1	0.1244	0.6516	42	0.89	1 psi
	1991-2	0.1249	0.6930	42	0.92	1 psi
Emerald	1990	0.2171	0.6928	12	0.99	1 psi
Lost	1990-1991-1	0.0982	0.3641	50	0.80	1 psi
	1990-1991-2	0.1259	0.5142	50	0.85	1 psi
Pear	1987-1989	0.1417	0.4665	53	0.90	1 psi
	1990-1991-1	0.1078	0.3896	27	0.85	1 psi
	1990-1991-2	0.1020	0.3667	27	0.85	1 psi
Ruby	1987-1990	0.0550	0.1584	113	0.95	5 psi
	1991-1	0.0721	0.2035	46	0.92	5 psi
	1991-2	0.2442	0.6282	46	0.87	1 psi
Spuller	1990-1	0.2828	0.6451	51	0.63	1 psi
	1990-2	0.4107	0.7981	51	0.78	1 psi
Topaz	1987-1990	0.0642	0.3002	48	0.94	5 psi
	1991-1	0.1053	0.3503	21	0.95	5 psi
	1991-2	0.2146	0.8181	21	0.87	1 psi

Table 5. Accuracy of analyses of anions by ion chromatography (Dionex 2010i, 200µl sample loop, attenuation = 3 µS) for lake and stream water at UCSB during 1990-1991. Accuracy was assessed by (1) comparing measured values with the certified values for 15-fold diluted NBS 2694-II simulated rain water control (Cl, NO₃, SO₄: 1.9, 7.6 ± 0.2, 15.1 ± 0.3 µeq·L⁻¹, respectively), and (2) by recovery after known additions to laboratory duplicates of randomly selected samples. Results are reported as mean percent spike recovery (R) at the mean, measured, final concentration (µeq·L⁻¹). Dash indicates no data.

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
<u>4 May 90</u>				
NBS		3.5	8.0	16.5
R82	R (final conc.)	80 (5.2)	103 (4.1)	118 (13.8)
C72	R (final conc.)	87 (5.9)	—	122 (7.4)
<u>8 May 90</u>				
NBS		2.3	7.8	16.6
S11	R (final conc.)	107 (5.3)	90 (5.6)	110 (22.5)
E8	R (final conc.)	123 (9.7)	107 (3.8)	107 (13.8)
<u>28 November 90</u>				
NBS		2.0	7.6	15.5
C96	R (final conc.)	83 (5.3)	100 (9.1)	108 (12.3)
<u>13 December 90</u>				
NBS		1.8	7.5	16.3
R88	R (final conc.)	87 (4.3)	97 (4.1)	113 (14.7)
<u>17 December 90</u>				
NBS		2.1	7.5	16.3
T79	R (final conc.)	110 (6.0)	87 (2.8)	102 (11.5)
L17	R (final conc.)	80 (5.2)	87 (2.8)	105 (15.0)

Table 4. Codes used to identify the sampling sites for the long-term study of lakes and watersheds, 1990-1991.

<u>Lake sites</u>	<u>Code</u>
Topaz Lake	T
Pear Lake	P
Emerald Lake	E
Crystal Lake	C
Ruby Lake	R
Lost Lake	L
Spuller Lake	S
 <u>Snow sites</u>	
Alpine Meadows	AM
Mammoth Mountain	MM
Kirkwood Meadows	KM
Sonora Pass	SN
Spuller Lake	SP
Lost Lake	LL
Emerald Lake	EM
Tioga Pass	TP
South Lake	SL
Onion Valley	OV
Eastern Brook Lake	EBL

Table 5 (cont'd)

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
C181	R (final conc.)	97 (4.9)	87 (2.9)	113 (9.3)
<u>16 September 91</u>				
S-65	R (final conc.)	77 (4.8)	110 (8.6)	120 (13.7)
T101	R (final conc.)	93 (7.9)	113 (6.5)	140 12.9
<u>18 September 91</u>				
NBS		2.0	7.6	16.1
L64	R (final conc.)	83 (5.0)	93 (2.8)	87 (7.8)

Table 5 (cont'd)

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
<u>20 December 90</u>				
NBS		2.2	7.5	16.7
S26	R (final conc.)	53 (4.5)	107 (5.3)	117 (15.2)
E24	R (final conc.)	113 (6.3)	103 (14.3)	118 (13.2)
<u>13 March 91</u>				
NBS		2.1	7.4	15.4
S45	R (final conc.)	93 (5.1)	103 (3.1)	107 (18.0)
E46	R (final conc.)	73 (5.2)	100 (3.0)	100 (13.1)
<u>20 March 91</u>				
NBS		2.1	7.3	15.3
H1	R (final conc.)	87 (8.5)	97 (2.9)	100 (11.0)
<u>7 September 91</u>				
NBS		2.0	7.7	16.5
E-67	R (final conc.)	103 (6.6)	113 (9.8)	97 (11.7)
E-81	R (final conc.)	90 (4.4)	117 (8.0)	93 (8.6)
<u>9 September 91</u>				
NBS		2.3	7.3	16.6
P127	R (final conc.)	97 (7.5)	107 (10.4)	100 (11.5)
P145	R (final conc.)	80 (4.7)	87 (4.4)	90 (8.6)
<u>13 September 91</u>				
NBS		2.4	7.6	16.8
C151	R (final conc.)	120 (7.6)	90 (4.3)	93 (10.3)
C166	R (final conc.)	97 (4.9)	83 (4.6)	83 (9.0)

Table 6 (continued)

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
<u>22 September 90</u>				
NBS		2.0	7.4	16.1
R005	R	100	107	107
	(final conc.)	3.4	(4.2)	(7.5)
P007	R	87	100	107
	(final conc.)	(5.0)	(4.5)	(8.8)
<u>24 September 90</u>				
NBS		2.1	7.3	16.1
EM003	R	73	110	103
	(final conc.)	(3.9)	(7.8)	(9.8)
EM013	R	70	100	110
	(final conc.)	(6.3)	(4.7)	(9.1)
<u>26 September 90</u>				
NBS		2.0	7.3	15.0
TP002	R	93	103	95
	(final conc.)	(4.0)	(5.8)	(7.7)
TP010	R	67	90	88
	(final conc.)	(3.7)	(4.6)	(7.2)
<u>29 September 90</u>				
NBS		2.3	7.4	13.8
MK010	R	97	103	97
	(final conc.)	(5.8)	(8.0)	(9.2)
<u>28 October 91</u>				
NBS		2.2	8.0	17.3
AM041	R	90	90	100
	(final conc.)	(4.0)	(4.8)	(4.6)
AM049	R	87	87	100
	(final conc.)	(4.1)	(5.2)	(4.9)
MM054	R	90	90	100
	(final conc.)	(3.7)	(7.6)	(4.9)

Table 6. Accuracy of analyses of anions by ion chromatography (Dionex 2010i, 200 μ L sample loop, attenuation = 3 μ S) for snow. Accuracy was assessed by (1) comparing measured values with the certified values for 15-fold diluted NBS 2694-II simulated rain water control (Cl, NO₃, SO₄: 1.9, 7.6 \pm 0.2, 15.1 \pm 0.3 μ eq•L⁻¹, respectively), and (2) by recovery after known additions to laboratory duplicates of randomly selected samples. Results are reported as mean percent spike recovery (R) at the mean, measured, final concentration (μ eq•L⁻¹).

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
<u>13 September 90</u>				
NBS		2.1	7.8	15.9
AM005	R	100	103	102
	(final conc.)	(7.4)	(10.8)	(14.1)
AM019	R	92	102	99
	(final conc.)	(6.5)	(7.3)	(12.7)
<u>17 September 90</u>				
NBS		1.9	7.4	15.5
MM033	R	113	107	103
	(final conc.)	(5.1)	(5.3)	(8.5)
MM044	R	117	113	103
	(final conc.)	(4.3)	(6.6)	(7.8)
KM006	R	100	103	103
	(final conc.)	(3.7)	(5.7)	(7.9)
<u>18 September 90</u>				
NBS		2.2	7.4	15.2
KM017	R	90	100	100
	(final conc.)	(3.5)	(5.0)	(7.4)
SN001	R	97	93	97
	(final conc.)	(3.2)	(5.5)	(7.4)
SP001	R	70	103	103
	(final conc.)	(2.9)	(3.1)	(8.2)
<u>20 September 90</u>				
NBS		2.0	7.4	15.3
SP016	R	107	97	97
	(final conc.)	(3.2)	(3.7)	(6.5)
LL006	R	77	97	98
	(final conc.)	(4.8)	(7.2)	(8.8)

Table 6 (continued)

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
<u>12 November 91</u>				
NBS		1.8	7.8	15.0
E041	R (final conc.)	116 (3.6)	110 (4.8)	110 (4.4)
E045	R (final conc.)	93 (4.4)	110 (8.9)	107 (5.1)
<u>14 November 91</u>				
NBS		1.7	8.1	16.2
T024	R (final conc.)	113 (4.2)	116 (4.2)	117 (3.5)
T044	R (final conc.)	133 (4.7)	117 (3.9)	123 (4.3)

Table 6 (continued)

<u>Run/Sample</u>		<u>Cl</u>	<u>NO₃</u>	<u>SO₄</u>
<u>29 October 91</u>				
NBS		2.0	8.2	16.2
MM068	R (final conc.)	80 (4.1)	100 (5.7)	100 (4.6)
MM080	R (final conc.)	87 (4.2)	120 (8.8)	100 (6.1)
MM091	R (final conc.)	83 (3.6)	87 (3.9)	100 (4.0)
<u>31 October 91</u>				
NBS		1.9	7.5	16.6
MM108	R (final conc.)	87 (5.3)	97 (13.7)	93 (6.6)
EBL016	R (final conc.)	110 (4.8)	90 (4.0)	107 (4.3)
OV029	R (final conc.)	83 (4.0)	87 (6.4)	100 (5.3)
<u>1 November 91</u>				
NBS		1.9	7.3	15.6
SL014	R (final conc.)	83 (3.2)	90 (3.9)	100 (4.3)
SN016	R (final conc.)	76 (3.5)	90 (4.6)	103 (5.3)
<u>8 November 91</u>				
NBS		2.2	7.8	15.6
SP034	R (final conc.)	93 (5.4)	100 (4.0)	100 (4.6)
SP047	R (final conc.)	100 (3.7)	103 (5.3)	100 (3.0)
L028	R (final conc.)	100 (3.0)	103 (4.2)	100 (4.4)

Table 7 (cont'd)

E37	R (final conc.)	95 (29.7)	104 (18.1)	99 (26.9)	- -
<u>27 March 91</u>					
S47	R (final conc.)	90 (63.3)	106 (12.4)	98 (24.8)	96 (9.1)
E49	R (final conc.)	114 (24.8)	104 (8.7)	142 (20.5)	122 (8.3)
R127	R (final conc.)	106 59.8	104 (10.0)	104 (18.5)	98 (9.4)
<u>21 October 91</u>					
NBS	Meas: Cert:	2.8 2.5 ± 0.6	4.3 4.2 ± 0.3	18.3 18.2 ± 0.7	2.8 2.7 ± 0.2
E73	R (final conc.)	106 (26.0)	102 (8.9)	110 (18.0)	102 (8.3)
E1	R (final conc.)	94 (7.1)	98 (5.6)	110 (8.8)	102 (5.9)
P137	R (final conc.)	92 (19.5)	94 (7.5)	104 (13.3)	102 (7.9)
R149	R (final conc.)	92 (28.2)	94 (7.4)	98 (12.9)	96 (9.5)
R169	R (final conc.)	90 (48.5)	98 (8.6)	96 (16.8)	100 (9.4)
C151	R (final conc.)	90 (31.4)	92 (11.0)	108 (22.3)	96 (11.5)
C170	R (final conc.)	74 (39.9)	98 (16.9)	86 (27.3)	98 (11.2)
S75	R (final conc.)	90 (34.7)	100 (8.8)	100 (17.5)	100 (8.0)

Table 7. Accuracy of analysis of cations in lake and stream water by atomic absorption spectrophotometry at UCSB during 1990-1991. Accuracy was assessed by (1) comparing measured values with certified values for NBS 2964-II simulated rainwater and (2) recovery after known additions to laboratory duplicates of randomly selected samples. The spike was $15.0 \mu\text{eq}\cdot\text{L}^{-1}$ in 1990 and $5.0 \mu\text{eq}\cdot\text{L}^{-1}$ in 1991. Results are reported as mean percent spike recovery (R) at the mean, measured, final concentration ($\mu\text{eq}\cdot\text{L}^{-1}$). Dash indicates no data.

<u>Run/Sample</u>		<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>
<u>22 April 90</u>					
NBS	Meas:	4.0	4.2	18.0	2.3
	Cert:	2.5 ± 0.6	4.2 ± 0.3	18.2 ± 0.7	2.7 ± 0.2
R83	R (final conc.)	100 (65.2)	103 (18.5)	107 (28.9)	103 (20.0)
P84	R (final conc.)	120 (31.7)	107 (19.0)	100 (27.0)	100 (19.3)
S3	R (final conc.)	107 (69.1)	105 (21.5)	100 (32.8)	100 (18.9)
L3	R (final conc.)	104 (35.0)	106 (19.9)	104 (28.3)	105 (19.2)
T67	R (final conc.)	105 (41.2)	107 (20.9)	105 (34.3)	113 (24.8)
<u>5 September 90</u>					
NBS	Meas:	3.6	3.8	18.0	3.0
	Cert:	2.5 ± 0.6	4.2 ± 0.3	18.2 ± 0.7	2.7 ± 0.2
C110	R (final conc.)	95 (46.8)	99 (25.8)	110 (35.9)	107 (21.8)
R108	R (final conc.)	103 (50.1)	102 (18.7)	101 (23.9)	96 (18.1)
T70	R (final conc.)	95 (50.9)	101 (22.0)	105 (34.3)	106 (34.4)
L21	R (final conc.)	98 (29.3)	101 (17.8)	109 (24.1)	94 (16.3)
S14	R (final conc.)	73 (104)	113 (24.0)	273 (24.6)	95 (18.1)
E14	R (final conc.)	101 (41.1)	105 (20.1)	96 (31.0)	-

Table 8 (cont'd)

<u>Run/Sample</u>		<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>
<u>July 1991</u>					
NBS	Meas:	1.9	3.8	16.6	2.8
	Cert:	2.5 ± 0.6	4.2 ± 0.3	18.2 ± 0.7	2.7 ± 0.2
MM049	R (final conc.)	108 (5.0)	116 (3.1)	108 (3.4)	108 (3.2)
MM076	R (final conc.)	108 (3.5)	116 (3.3)	108 (3.4)	108 (2.7)
EBL009	R (final conc.)	108 (4.0)	108 (3.1)	108 (3.3)	108 (2.9)
SN013	R (final conc.)	— —	108 (3.1)	124 (4.1)	108 (2.9)
SP056	R (final conc.)	96 (3.5)	108 (2.9)	128 (4.1)	108 (2.8)
<u>November 1991</u>					
NBS	Meas:	2.0	4.0	17.0	2.8
	Cert:	2.5 ± 0.6	4.2 ± 0.3	18.2 ± 0.7	2.7 ± 0.2
OV032	R (final conc.)	100 (3.5)	108 (2.7)	128 (4.2)	108 (3.1)
R043	R (final conc.)	88 (4.6)	104 (3.1)	104 (3.4)	108 (2.9)
T050	R (final conc.)	100 (7.9)	110 (3.2)	100 (3.7)	100 (3.3)

Table 8. Accuracy for analysis of cations in snow by atomic absorption spectrophotometry. Accuracy was assessed by (1) comparing measured values with certified values for NBS 2964-II simulated rainwater and (2) recovery after known additions to laboratory duplicates of randomly selected samples. Results are reported as mean percent spike recovery (R) at the mean, measured, final concentration ($\mu\text{eq}\cdot\text{L}^{-1}$). Dash indicates no data.

<u>Run/Sample</u>		<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>
<u>June 1990</u>					
NBS	Meas:	1.9	3.8	16.6	2.8
	Cert:	2.5 ± 0.6	4.2 ± 0.3	18.2 ± 0.7	2.7 ± 0.2
AM005	R (final conc.)	106 (8.0)	96 (5.3)	124 (9.7)	92 (6.2)
AM006	R (final conc.)	100 (6.0)	96 (5.1)	112 (8.1)	96 (5.1)
<u>Nov. 1990</u>					
NBS	Meas:	1.8	4.6	17.8	2.7
	Cert:	2.5 ± 0.6	4.2 ± 0.3	18.2 ± 0.7	2.7 ± 0.2
SP002	R (final conc.)	120 (3.3)	112 (3.0)	120 (3.3)	100 (2.6)
OV001	R (final conc.)	112 (5.5)	100 (3.1)	100 (3.6)	104 (2.9)
L011	R (final conc.)	100 (5.1)	88 (3.0)	112 (5.1)	96 (3.4)
R043	R (final conc.)	84 (4.6)	104 (3.1)	120 (3.9)	104 (2.9)
<u>Dec. 1990</u>					
E051	R (final conc.)	96 (3.9)	100 (2.9)	104 (3.4)	104 (2.9)
T050	R (final conc.)	100 (7.9)	112 (3.2)	120 (3.7)	120 (3.3)

Table 10. Snow water equivalence and rain for water year 1990.

SITE	SNOW WATER EQUIV. (m)	RAIN (m)
CRYSTAL	0.591	0.059
EMERALD	0.601	0.096
LOST	0.952	0.086
PEAR	0.784	0.096
RUBY	0.648	0.076
SPULLER	0.729	0.094
TOPAZ	0.548	0.096

Table 9.

Summary of quality assurance data for chemical analysis of lake samples and for snow samples. The overall precision and overall accuracy data for 1990-1991 are computed as the mean percent relative standard deviation (% RSD) and the mean percent spike recovery, respectively. Measured values (mean \pm S.D.) and certified values (mean \pm S.D.) for the NBS standard reference material (SRM) are tabulated in $\mu\text{eq}\cdot\text{L}^{-1}$. The values for Cl was not certified by NBS.

Element	Overall Precision % RSD	Overall Accuracy % Recovery	Measured SRM Concentration	Certified SRM Concentration
Lake and stream				
Calcium	1.1	97	3.4 ± 0.6	2.5 ± 0.6
Magnesium	1.0	102	4.1 ± 0.3	4.2 ± 0.3
Sodium	1.1	105	18.2 ± 0.2	18.2 ± 0.7
Potassium	1.7	102	2.7 ± 0.4	2.7 ± 0.2
Chloride	4.1	93	2.2 ± 0.4	1.9
Nitrate	2.9	99	7.6 ± 0.2	7.6 ± 0.2
Sulfate	2.8	109	16.2 ± 0.5	15.1 ± 0.3
Snow				
Calcium	1.2	102	1.9 ± 0.1	2.5 ± 0.6
Magnesium	1.1	105	4.1 ± 0.4	4.2 ± 0.3
Sodium	1.5	114	17.0 ± 0.6	18.2 ± 0.7
Potassium	1.8	106	2.8 ± 0.1	2.7 ± 0.2
Chloride	8.0	93	2.2 ± 0.2	1.9
Nitrate	1.8	102	7.5 ± 0.3	7.6 ± 0.2
Sulfate	2.5	99	15.6 ± 0.8	15.1 ± 0.3

Table 12. Snow water equivalence and rain for water year 1987.

SITE	SNOW WATER EQUIV. (m)	RAIN (m)
CRYSTAL	0.669	0.087
EMERALD	0.600	0.206
PEAR	0.463	0.206
RUBY	0.462	0.106
TOPAZ	0.570	0.266

Table 11. Snow water equivalence and rain for water year 1991.

SITE	SNOW WATER EQUIV. (m)	RAIN (m)
CRYSTAL	0.790	0.071
EMERALD	0.996	0.082
LOST	0.973	0.106
PEAR	0.903	0.084
RUBY	0.601	0.066
SPULLER	0.866	0.068
TOPAZ	0.820	0.082

Table 14. Volume-weighted mean concentrations of rain, snow and outflow of Emerald Lake for water-years 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others.

	H	(pH)	ANC	NH ₄	Cl	NO ₃	SO ₄	Ca	Mg	Na	K	SiO ₄	HCOOH	CH ₃ CO ₂
<u>1990:</u>														
RAIN	5.1	(5.29)	0.0	12.0	4.1	17.8	13.1	10.2	2.7	6.7	6.1	0.0	1.3	1.3
SNOW	4.7	(5.33)	0.0	4.6	2.1	2.6	2.6	1.3	0.6	1.8	0.5	0.0	1.3	0.4
RAIN+ SNOW	4.8	(5.32)	0.0	5.7	2.4	4.9	4.2	2.6	0.9	2.5	1.3	0.0	1.0	0.5
OUTFLOW	0.8	(6.10)	28.1	0.3	4.1	4.6	6.9	19.4	3.4	12.7	2.8	36.2	0.0	0.0
<u>1991:</u>														
RAIN	9.0	(5.05)	0.0	48.4	3.7	24.4	16.6	11.5	3.8	3.0	3.8	0.0	8.6	15.5
SNOW	3.3	(5.48)	0.0	2.9	1.2	1.7	1.2	1.1	0.4	1.0	0.3	0.0	0.2	0.3
RAIN+ SNOW	3.8	(5.42)	0.0	6.7	1.4	3.6	2.5	2.0	0.7	1.2	0.6	0.0	0.9	1.6
trans.1 OUTFLOW	1.8	(5.74)	22.7	0.3	3.7	5.7	6.9	17.5	3.6	13.3	3.0	35.7	0.0	0.0
trans.2 OUTFLOW	1.8	(5.74)	22.4	0.3	3.6	5.8	6.9	17.3	3.6	13.2	3.0	35.6	0.0	0.0

Table 13. Volume-weighted mean concentrations of rain, snow and outflow of Crystal Lake for water-years 1987, 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others. Formate and acetate were not determined in 1987.

	H	(pH)	ANC	NH ₄	Cl	NO ₃	SO ₄	Ca	Mg	Na	K	SiO ₄	HCOOH	CH ₃ CO ₂
<u>1987:</u>														
RAIN	3.2	(5.49)	0.0	15.3	2.3	12.0	10.4	5.8	1.3	2.6	0.8	0.0	NA	NA
SNOW	4.0	(5.40)	0.0	2.3	1.0	2.8	1.9	2.1	0.5	1.2	0.9	0.0	NA	NA
RAIN+ SNOW	3.9	(5.41)	0.0	4.0	1.2	4.0	3.0	2.6	0.6	1.4	0.9	0.0	NA	NA
OUTFLOW	0.3	(6.52)	72.0	0.2	2.0	0.1	7.0	36.3	11.8	20.0	6.8	58.1	0.0	0.0
<u>1990:</u>														
RAIN	22.2	(4.65)	0.0	26.9	5.3	30.1	16.4	10.5	2.3	5.5	2.1	0.0	17.0	18.2
SNOW	4.6	(5.34)	0.0	3.0	1.9	3.2	2.4	2.1	0.6	2.3	1.0	0.0	1.0	1.3
RAIN+ SNOW	6.3	(5.20)	0.0	5.4	2.2	5.9	3.8	2.9	0.8	2.6	1.1	0.0	2.6	3.0
OUTFLOW	0.6	(6.22)	73.3	0.1	3.5	0.2	6.2	35.6	12.5	21.5	6.2	64.3	0.0	0.0
<u>1991:</u>														
RAIN	16.9	(4.78)	0.0	28.2	4.7	25.2	20.7	15.5	2.0	9.2	1.8	0.0	9.5	12.7
SNOW	3.3	(5.48)	0.0	5.5	2.0	4.5	2.3	4.2	0.9	2.0	1.0	0.0	0.8	0.9
RAIN+ SNOW	4.5	(5.35)	0.0	7.6	2.2	6.4	4.0	5.2	1.0	2.7	1.1	0.0	1.6	2.0
Trans.1 OUTFLOW	1.0	(6.00)	62.8	0.0	3.0	0.9	6.5	35.2	12.4	22.2	7.6	71.8	0.0	0.0
Trans.2 OUTFLOW	1.0	(6.00)	62.6	0.0	3.0	0.9	6.5	35.2	12.4	22.2	7.6	71.8	0.0	0.0

Table 16. Volume-weighted mean concentrations of rain, snow and outflow of Pear Lake for water-years 1987, 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others. Formate and acetate were not determined in 1987.

	H	(pH)	ANC	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	SiO_4	HCOOH	CH_3CO_2
<u>1987:</u>														
RAIN	10.6	(4.97)	0.0	69.8	10.3	48.7	41.3	25.5	5.3	10.7	3.9	0.0	NA	NA
SNOW	5.0	(5.30)	0.0	2.5	1.0	3.6	2.6	2.0	0.4	1.7	0.3	0.0	NA	NA
RAIN+ SNOW	6.7	(5.17)	0.0	23.2	3.9	17.5	14.5	9.2	1.9	4.5	1.4	0.0	NA	NA
OUTFLOW	0.7	(6.15)	19.7	0.5	2.3	3.5	6.2	14.4	2.9	6.8	2.5	15.9	0.0	0.0
<u>1990:</u>														
RAIN	5.1	(5.29)	0.0	12.0	4.1	17.8	13.1	10.2	2.7	6.7	6.1	0.0	1.3	1.3
SNOW	4.3	(5.37)	0.0	4.1	2.2	2.2	2.7	1.0	0.5	1.7	0.3	0.0	0.5	0.6
RAIN+ SNOW	4.4	(5.36)	0.0	5.0	2.4	4.1	3.9	2.1	0.8	2.3	1.0	0.0	0.6	0.7
OUTFLOW	0.8	(6.10)	23.1	0.5	4.3	4.2	6.7	16.0	2.6	9.1	3.1	23.1	0.0	0.0
<u>1991:</u>														
RAIN	9.0	(5.05)	0.0	48.4	3.7	24.4	16.6	11.5	3.8	3.0	3.8	0.0	0.6	15.5
SNOW	3.6	(5.44)	0.0	4.0	1.1	2.6	1.7	1.4	0.5	1.0	0.3	0.0	0.5	1.1
RAIN+ SNOW	4.1	(5.39)	0.0	8.1	1.3	4.6	3.1	2.3	0.8	1.2	0.6	0.0	1.3	2.4
ins.1 OUTFLOW	1.5	(5.82)	21.9	0.2	3.0	3.9	6.3	16.6	3.1	9.2	3.2	21.8	0.0	0.0

Table 15. Volume-weighted mean concentrations of rain, snow and outflow of Lost Lake for water-years 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others.

	H	(pH)	ANC	NH ₄	Cl	NO ₃	SO ₄	Ca	Mg	Na	K	SiO ₄	HCOOH	CH ₃ CO ₂
<u>1990:</u>														
RAIN	13.7	(4.86)	0.0	13.0	5.4	23.6	17.2	13.4	4.0	7.2	4.6	0.0	19.3	17.2
SNOW	4.3	(5.37)	0.0	2.4	2.1	2.9	2.1	1.1	0.5	1.7	0.4	0.0	0.8	0.1
RAIN+ SNOW	5.1	(5.29)	0.0	3.3	2.4	4.7	3.4	2.2	0.8	2.2	0.8	0.0	2.4	1.6
Trans.1 OUTFLOW	1.2	(5.92)	26.1	0.2	3.4	0.7	6.7	18.0	3.2	8.7	2.8	31.6	0.0	0.0
Trans.2 OUTFLOW	1.1	(5.96)	27.9	0.2	3.7	0.6	6.6	19.0	3.5	9.5	3.0	30.0	0.0	0.0
<u>1991:</u>														
RAIN	13.5	(4.87)	0.0	20.1	4.7	19.0	13.2	7.2	2.5	7.0	1.9	0.0	12.0	11.2
SNOW	3.3	(5.48)	0.0	3.3	2.1	2.5	1.9	1.4	0.7	1.4	0.3	0.0	0.6	1.0
RAIN+ SNOW	4.3	(5.37)	0.0	5.0	2.4	4.2	3.1	2.0	0.9	2.0	0.5	0.0	1.8	2.0
Trans.1 OUTFLOW	2.4	(5.62)	19.0	0.0	2.8	0.6	5.4	15.2	3.4	8.3	2.4	21.1	0.0	0.0
Trans.2 OUTFLOW	2.2	(5.66)	20.7	0.1	3.0	0.9	6.0	16.3	3.6	8.9	2.5	22.5	0.0	0.0

Table 18. Volume-weighted mean concentrations of rain, snow and outflow of Spuller Lake for water-years 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others.

	H	(pH)	ANC	NH ₄	Cl	NO ₃	SO ₄	Ca	Mg	Na	K	SiO ₄	HCOOH	CH ₃ CO ₂
<u>1990:</u>														
RAIN	20.4	(4.69)	0.0	24.7	4.2	22.5	15.2	14.5	2.7	7.6	4.6	0.0	22.1	20.5
SNOW	5.6	(5.25)	0.0	1.6	1.3	1.5	1.3	0.9	0.3	0.7	0.4	0.0	0.3	0.2
RAIN+ SNOW	7.4	(5.13)	0.0	4.4	1.6	4.0	3.0	2.5	0.6	1.5	0.9	0.0	2.9	2.6
Trans.1														
OUTFLOW	0.5	(6.30)	55.4	0.1	2.9	4.2	12.4	48.8	5.0	14.1	3.3	39.9	0.0	0.0
Trans.2														
OUTFLOW	0.5	(6.30)	58.3	0.1	2.9	4.5	13.3	51.5	5.3	14.8	3.4	40.8	0.0	0.0
<u>1991:</u>														
RAIN	23.4	(4.63)	0.0	32.6	6.0	30.5	22.7	23.7	3.4	6.7	2.3	0.0	9.4	13.0
SNOW	3.9	(5.41)	0.0	2.2	1.1	2.1	1.7	2.0	0.4	1.0	0.7	0.0	0.5	0.7
RAIN+ SNOW	5.4	(5.27)	0.0	4.5	1.5	4.3	3.3	3.7	0.6	1.4	0.8	0.0	1.2	1.6
Trans.1														
OUTFLOW	1.5	(5.82)	35.7	0.1	2.6	4.8	8.9	33.7	4.2	9.9	3.6	27.4	0.0	0.0
Trans.2														
OUTFLOW	1.5	(5.82)	35.7	0.1	2.6	4.8	8.9	33.7	4.2	9.9	3.7	27.5	0.0	0.0

Table 17. Volume-weighted mean concentrations of rain, snow and outflow of Ruby Lake for water-years 1987, 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others. Formate and acetate were not determined in 1987.

	H	(pH)	ANC	NH ₄	Cl	NO ₃	SO ₄	Ca	Mg	Na	K	SiO ₄	HCOOH	CH ₃ CO
<u>1987:</u>														
RAIN	10.9	(4.96)	0.0	46.9	7.4	37.6	32.3	18.1	4.0	8.6	2.5	0.0	NA	NA
SNOW	5.0	(5.30)	0.0	0.9	1.8	3.0	2.0	2.1	0.5	1.9	0.5	0.0	NA	NA
RAIN+ SNOW	6.4	(5.19)	0.0	11.5	3.1	10.9	8.9	5.8	1.3	3.4	0.9	0.0	NA	NA
OUTFLOW	0.4	(6.40)	54.4	0.2	2.0	2.5	7.5	41.2	4.0	13.3	3.8	33.1	0.0	0.0
<u>1990:</u>														
RAIN	18.5	(4.73)	0.0	21.8	5.2	23.7	15.3	22.6	3.3	5.0	5.0	0.0	10.9	10.8
SNOW	5.2	(5.28)	0.0	1.9	1.0	2.8	2.3	2.0	0.5	1.1	0.3	0.0	1.0	0.7
RAIN+ SNOW	6.9	(5.16)	0.0	4.5	1.5	5.5	4.0	4.6	0.9	1.6	0.9	0.0	2.3	2.0
OUTFLOW	0.5	(6.30)	57.2	0.1	3.0	3.2	9.3	45.8	3.1	11.2	4.1	35.0	0.0	0.0
<u>1991:</u>														
RAIN	22.1	(4.66)	0.0	34.6	4.4	28.3	19.8	11.5	2.1	3.1	1.6	0.0	9.8	13.8
SNOW	2.7	(5.57)	0.0	2.7	0.6	1.7	1.4	2.4	0.3	0.5	0.2	0.0	0.4	1.4
RAIN+ SNOW	5.0	(5.30)	0.0	6.5	1.1	4.9	3.6	3.5	0.5	0.8	0.4	0.0	1.5	2.9
Trans.1 OUTFLOW	1.1	(5.96)	51.8	0.2	2.5	5.2	9.6	44.7	4.3	12.3	5.1	36.7	0.0	0.0
Trans.2 OUTFLOW	1.1	(5.96)	52.2	0.2	2.4	4.9	9.6	44.5	4.4	12.3	5.2	37.1	0.0	0.0

Table 20. Comparison of watershed yield of solutes vs atmospheric loading of solutes for the study lakes for water year 1990. The units are equivalents per hectare per year ($\text{eq ha}^{-1} \text{yr}^{-1}$). NM means the solute was undetectable or absent in precipitation samples.

Lake	H	ANC	NH ₄	Cl	NO ₃	SO ₄	Base Cations
Crystal Lake							
Loading	37	NM	32	13	35	22	44
Yield	-36	141	-32	-7	-34	-11	102
Emerald Lake							
Loading	30	NM	36	15	31	27	48
Yield	-25	186	-34	12	-1	19	207
Lost Lake (Transducer 1)							
Loading	51	NM	33	24	46	34	59
Yield	-38	275	-31	12	-39	36	286
Lost Lake (Transducer 2)							
Loading	51	NM	33	24	46	34	59
Yield	-34	412	-29	31	-37	64	458
Pear Lake							
Loading	35	NM	40	19	33	32	49
Yield	-29	160	-37	10	-4	15	163
Ruby Lake							
Loading	41	NM	26	9	33	24	48
Yield	-39	239	-26	3	-19	15	221
Spuller Lake (Transducer 1)							
Loading	58	NM	34	13	31	23	44
Yield	-53	484	-33	13	5	85	579
Spuller Lake (Transducer 2)							
Loading	58	NM	34	13	31	23	44
Yield	-53	552	-33	15	11	103	667
Topaz Lake							
Loading	26	NM	28	14	30	25	40
Yield	-23	246	-28	13	-18	9	256

Table 19. Volume-weighted mean concentrations of rain, snow and outflow of Topaz Lake for water-years 1987, 1990 and 1991. The units for concentration are μM for silica and $\mu\text{eq L}^{-1}$ for all others. Formate and acetate were not determined in 1987.

	H	(pH)	ANC	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	SiO_4	HCOOH	CH_3CO_2
<u>1987:</u>														
RAIN	10.7	(4.97)	0.0	75.5	11.5	50.5	42.2	27.2	5.6	11.3	4.2	0.0	NA	NA
SNOW	5.0	(5.30)	0.0	2.5	1.0	3.6	2.3	2.1	0.3	1.2	0.1	0.0	NA	NA
RAIN+ SNOW	7.1	(5.15)	0.0	29.4	4.9	20.9	17.0	11.4	2.3	4.9	1.6	0.0	NA	NA
OUTFLOW	1.0	(6.00)	32.9	0.2	2.8	2.8	6.6	30.7	4.4	9.7	3.1	23.6	0.0	0.0
<u>1990:</u>														
RAIN	5.1	(5.29)	0.0	12.0	4.1	17.8	13.1	10.2	2.7	6.7	6.1	0.0	1.3	1.3
SNOW	4.0	(5.40)	0.0	3.2	2.0	2.4	2.3	0.7	0.4	1.5	0.5	0.0	1.3	0.6
RAIN+ SNOW	4.2	(5.38)	0.0	4.6	2.3	4.8	4.0	2.2	0.8	2.3	1.4	0.0	1.3	0.7
OUTFLOW	0.5	(6.30)	42.7	0.1	4.7	2.1	5.9	30.3	4.4	11.8	4.9	46.1	0.0	0.0
<u>1991:</u>														
RAIN	9.0	(5.05)	0.0	48.4	3.7	24.4	16.6	11.5	3.8	3.0	3.8	0.0	8.6	15.5
SNOW	3.9	(5.41)	0.0	2.0	0.6	1.7	1.2	3.0	0.3	0.9	0.2	0.0	0.6	0.8
RAIN+ SNOW	4.4	(5.36)	0.0	6.4	0.9	3.9	2.7	3.8	0.6	1.1	0.5	0.0	1.4	2.2
OUTFLOW	1.3	(5.89)	37.2	0.3	3.5	5.5	6.3	29.6	5.2	11.4	5.0	31.4	0.0	0.0

Table 21
continued

Spuller Lake (Transducer 2)

Loading	48	NM	40	13	38	29	59
Yield	-34	332	-39	11	7	53	419

Topaz Lake (Transducer 1)

Loading	38	NM	5	8	33	23	52
Yield	-30	239	-54	15	2	18	277

Table 21. Comparison of watershed yield of solutes vs atmospheric loading of solutes for the study lakes for water year 1991. The units are equivalents per hectare per year ($\text{eq ha}^{-1} \text{yr}^{-1}$). NM means the solute was undetectable or absent in precipitation samples.

Lake	H	ANC	NH ₄	Cl	NO ₃	SO ₄	Base Cations
Crystal Lake (Transducer 1)							
Loading	36	NM	59	18	50	31	78
Yield	-32	204	-59	-8	-47	-10	172
Crystal Lake (Transducer 2)							
Loading	36	NM	59	18	50	31	78
Yield	-32	188	-59	-9	-47	-12	153
Emerald Lake (Transducer 1)							
Loading	37	NM	66	14	35	24	43
Yield	-27	121	-64	6	-5	12	156
Emerald Lake (Transducer 2)							
Loading	37	NM	66	14	35	24	43
Yield	-28	115	-65	5	-6	11	147
Lost Lake (Transducer 1)							
Loading	45	NM	52	24	43	32	55
Yield	-19	210	-51	6	-36	29	269
Lost Lake (Transducer 2)							
Loading	45	NM	52	24	43	32	55
Yield	-16	268	-51	14	-32	46	351
Pear Lake (Transducer 1)							
Loading	37	NM	73	12	42	28	45
Yield	-19	271	-70	25	6	50	351
Ruby Lake (Transducer 1)							
Loading	28	NM	36	6	27	20	28
Yield	-23	196	-35	4	-7	17	222
Ruby Lake (Transducer 2)							
Loading	28	NM	36	6	27	20	28
Yield	-23	227	-35	5	-5	22	259
Spuller Lake (Transducer 1)							
Loading	48	NM	40	13	38	29	59
Yield	-34	355	-39	13	10	59	453

Table 21
continued

Table 23. Ion enrichment analysis, units are $\mu\text{eq L}^{-1}$. Atmospheric input is the volume-weighted mean H concentration for water year 1991 adjusted for evapotranspiration. Biogeochemical reactions are calculated as the measured late summer concentrations in lakes minus evapotranspiration adjusted annual volume-weighted mean concentrations in rain plus snow. Lakewater ANC is the volume-weighted mean lakewater ANC determined from Gran titrations done during August or September 1991.

	Atmospheric Input	Biogeochemical Reactions				Lake Water ANC
		Σ Base Cations	NH_4	NO_3	SO_4	
CRYSTAL	-6.3	56.8	-10.4	-8.8	0.3	56.1
EMERALD	-8.8	27.4	-15.7	-6.5	0.7	25.1
LOST	-5.1	27.8	-5.9	-4.8	0.6	24.7
PEAR	-6.4	23.0	-12.7	-6.4	-0.2	24.3
RUBY	-10.5	61.7	-13.6	-8.1	2.0	60.0
SPULLER	-7.3	57.4	-6.1	-5.1	5.7	54.0
TOPAZ	-8.3	26.2	-12.2	-6.4	0.0	26.3

Table 22. Comparison of watershed yield of solutes vs atmospheric loading of solutes for Topaz, Pear, Crystal, Ruby and Emerald Lakes for water year 1987. The units are equivalents per hectare per year ($\text{eq ha}^{-1} \text{yr}^{-1}$). NM means the solute was undetectable or absent in precipitation samples. Data for Emerald Lake are from Dozier et al. 1989.

Lake	H	ANC	NH_4	Cl	NO_3	SO_4	Base Cations
<i>Crystal Lake</i>							
Loading	25	NM	26	8	26	20	36
Yield	-25	212	-26	-2	-26	1	185
<i>Emerald Lake</i>							
Loading	58	NM	138	27	114	94	112
Yield	-51	195	-136	-1	-59	-45	211
<i>Pear Lake</i>							
Loading	45	NM	155	26	117	97	114
Yield	-41	127	-152	-11	-94	-57	57
<i>Ruby Lake</i>							
Loading	29	NM	53	14	50	41	53
Yield	-27	283	-52	-4	-37	-2	271
<i>Topaz Lake</i>							
Loading	51	NM	212	35	151	123	146
Yield	-45	205	-211	-18	-134	-82	153

Table 2.5 Mean abundance of zooplankton in Emerald Lake (organisms/cubic meter).

Species	27-Feb-89	03-Apr-89	09-Feb-90	19-Mar-90	15-Jun-90	20-Aug-90	19-Oct-90	14-Jan-91	25-Feb-91	11-Jul-91	13-Sep-91	8-Nov-91
<i>Diaptomus signicauda</i>	4	0	20	0	937	5855	101	9	0	3084	825	0
<i>Macrocyclus albidus</i>	4	13	16	8	0	0	13	0	0	0	0	0
<i>Tropocyclops prasinus</i>	0	8	4	0	0	0	0	0	0	0	0	0
<i>Daphnia rosea</i>	0	0	0	0	4	4322	25	0	0	0	84	6
<i>Ceriodaphnia affinis</i>	0	0	0	0	4	60	163	0	0	24	4635	0
<i>Holopedium gibberum</i>	0	0	0	0	95	71	8	0	0	0	929	0
<i>Bosmina longirostris</i>	448	410	1258	2240	615	156	101	4065	825	350	188	0
<i>Chydorus sphaericus</i>	0	0	32	0	24	0	42	31	0	85	2986	28
<i>Alona sp.</i>	0	0	0	0	0	0	4	0	0	37	0	11
<i>Keratella taurocephala</i>	23264	6679	41570	63003	41557	30999	132302	3553	3440	18633	2223	0
<i>Keratella quadrata</i>	250	80	66	147	1012	0	0	0	109	4004	0	17
<i>Polyarthra vulgaris</i>	1978	829	5224	4271	54153	198	23109	1713	2541	59402	3108	0
<i>Conichilus unicomis</i>	0	0	0	0	159	0	2687	0	17	4083	1190	11
<i>Trichocerca capucina</i>	0	0	0	0	0	3198	831	0	0	208	582	0
<i>Ascomorpha sp.</i>	1544	1110	0	0	0	0	0	0	0	674	408	0
<i>Notholca sp.</i>	0	193	13	21	0	0	0	0	0	0	0	0
<i>Synchaeta sp.</i>	0	0	0	0	0	0	244	435	0	0	0	0
<i>Gastropus sp.</i>	0	0	0	0	0	0	0	0	71	0	0	0

Table 24 Mean abundance of zooplankton in Crystal Lake (organisms/cubic meter).

Species	-----1987-----				-----1988-----				1989				-----1990-----				-----1991-----			
	19-Jun	20-Aug	13-Oct	20-Jan	9-Apr	9-Nov	12-Apr	3-Jan	28-Mar	28-Jun	31-Aug	30-Oct	24-Jan	20-Apr	18-Jul	6-Sep	18-Nov			
<i>Diaptomus signicauda</i>	1641	733	26	3	0	0	0	0	0	2944	85	16	0	0	239	35	6			
<i>Macrocylops albidus</i>	0	0	0	35	3	0	17	0	86	0	0	4	0	3	24	14	0			
<i>Tropocyclops prasinus</i>	300	0	0	0	1	6	8	0	0	523	0	0	0	0	0	0	0			
<i>Harpacticoid sp.</i>	0	0	0	0	0	0	0	0	45	998	13	8	11	0	0	0	0			
<i>Daphnia rosea</i>	12	885	31	0	0	18	0	0	0	131	835	99	0	0	46	474	0			
<i>Diaphanosoma brachyurum</i>	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0			
<i>Holopedium gibberum</i>	46	51	434	115	0	398	8	0	0	49	713	91	4	0	213	279	716			
<i>Bosmina longirostris</i>	0	2625	0	6	1	0	0	4	0	360	207	8	0	0	52	348	401			
<i>Chydorus sphaericus</i>	0	0	0	0	0	3	4	0	3	131	0	0	0	0	0	0	14			
<i>Keratella cochlearis</i>	982	570	22043	16634	12403	21019	2402	133796	38828	77832	14188	40967	58274	79	1045	15313	7084			
<i>Keratella quadrata</i>	635	1	394	44	2199	429	280	628	223	229	15	0	877	134	415	0	584			
<i>Polyarthra vulgaris</i>	16176	0	5121	84	7366	351	8825	95828	1413	29575	2330	4263	4550	120	12376	625	26667			
<i>Conichilus unicornis</i>	0	0	0	64	0	0	0	0	0	589	3151	0	0	0	819	1068	0			
<i>Trichocerca capucina</i>	58	82	0	0	0	0	0	0	0	0	601	0	0	0	20	130	0			
<i>Kellicottia sp.</i>	32006	1	63	202	1430	143	119	2722	1028	37820	15	33	0	4	131	1901	0			
<i>Asplanchna sp.</i>	58	0	0	6	1235	0	0	34	23	0	0	4	92	14	0	0	0			
<i>Synchaeta sp.</i>	0	0	0	0	32	0	2140	0	34	98	0	0	1316	11	24	0	84			
<i>Lepadella sp.</i>	0	0	0	0	0	0	16	0	0	0	0	0	0	0	0	0	0			
<i>Ascomorpha sp.</i>	0	0	0	0	0	0	0	0	0	8637	0	0	0	0	0	703	0			
<i>Lecane subtilis</i>	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
<i>Hexarthra sp.</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0	36	0	0			

Table 27 Mean abundance of zooplankton in Pear Lake (organisms/cubic meter).

Species	-----1987-----					-----1988-----					--1989--					-----1990-----					-----1991-----				
	4-Jun	10-Jul	25-Aug	7-Oct	8-Dec	8-Mar	8-Jun	14-Dec	28-Feb	5-Apr	9-Feb	21-Mar	14-Jun	20-Aug	19-Oct	16-Jan	27-Feb	10-Jul	15-Sep	8-Nov					
<i>Diaptomus signicauda</i>	1	18	120	0	0	0	5	2	0	0	31	9	26	78	56	80	0	18	121	0					
<i>Macrocyclus albidus</i>	90	149	1576	63	97	1872	959	4	2626	550	1758	796	22	470	47	0	373	2	4	0					
<i>Daphnia rosea</i>	9	62	1723	1106	36	0	6	19	0	0	0	0	0	1281	243	0	0	9	1159	0					
<i>Ceriodaphnia affinis</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	112	0	0	0	0	0	0					
<i>Holopedium gibberum</i>	6	61	18	0	0	0	2	0	0	0	0	0	0	2	0	0	0	0	0	0					
<i>Bosmina longirostris</i>	16	239	729	15	41	80	11	1106	1622	78	1396	357	0	93	136	3258	1017	0	108	0					
<i>Chydorus sphaericus</i>	0	55	78	34	91	0	2	98	21	0	21	3	0	3	0	6	2	5	0	0					
<i>Keratella taurocephala</i>	2326	12050	90449	1623	25909	12486	4267	43272	15166	4881	53057	28960	1497	15814	4187	20096	7237	9583	48288	0					
<i>Keratella quadrata</i>	100	19	3642	135	13512	8156	1520	1178	552	170	359	623	64	226	448	235	480	1659	2337	0					
<i>Polyarthra vulgaris</i>	2483	692	355	261	1133	218	6222	1979	2868	1144	169	329	402	1692	1733	1544	821	1585	4212	0					
<i>Conichilus unicornis</i>	412	8443	0	298	0	0	6	754	34	0	0	1840	6	0	62	0	0	1066	544	0					
<i>Trichocerca capucina</i>	0	175	427	95	0	0	0	0	0	0	0	0	0	164	51	0	0	10	435	0					
<i>Ploesoma sp.</i>	0	10	150	544	101	0	6	0	0	0	0	0	0	102	741	0	0	45	163	0					
<i>Asplanchna sp.</i>	30	0	0	0	152	0	22	0	0	0	0	0	1	0	0	0	0	0	0	0					
<i>Lecane sp.</i>	0	0	50	2	0	0	0	0	0	0	0	0	0	6	0	0	0	0	0	0					
<i>Monostyla sp.</i>	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0					
<i>Synchaeta sp.</i>	0	49	0	0	0	0	24	0	0	0	0	0	0	0	0	1526	2822	172	0	0					

Table 29 Mean abundance of zooplankton in Spuller Lake (organisms/cubic meter).

Species	5-Jan-90	26-Mar-90	29-Jun-90	28-Aug-90	28-Oct-90	24-Jan-91	19-Apr-91	16-Jul-91	6-Sep-91	18-Nov-91
<i>Macrocyclus albidus</i>	1304	942	6	905	264	225	218	34	233	125
<i>Tropocyclops prasinus</i>	8	0	0	0	0	0	0	0	0	0
<i>Daphnia rosea</i>	0	0	0	13	13	0	0	0	444	10374
<i>Bosmina longirostris</i>	0	0	0	0	0	0	0	27	0	0
<i>Ceriodaphnia affinis</i>	0	0	0	226	0	0	0	0	376	194
<i>Chydorus sphaericus</i>	0	0	0	126	6	0	0	0	23	50
<i>Alona</i> sp.	0	0	0	63	38	0	0	0	0	0
<i>Keratella cochlearis</i>	482	38	163	0	12	0	0	0	293	2157
<i>Keratella quadrata</i>	460	107	82	0	0	326528	43381	21	414	1094
<i>Polyarthra vulgaris</i>	8548	0	19	0	25	0	0	41	970	4163
<i>Kellicottia</i> sp.	0	0	195	0	0	0	0	0	0	0
<i>Monostyla</i> sp.	0	0	6	0	0	0	0	0	0	0
<i>Lecane</i> sp.	0	0	0	0	6	0	0	0	8	0
<i>Pompholyx</i> sp.	256	0	0	0	0	0	0	0	0	0
<i>Lecane subtilis</i>	0	0	0	63	6	0	0	0	0	0
<i>Synchaeta</i> sp.	0	0	0	0	0	0	3910	0	23	0

Table 31. Species richness by season for the seven survey lakes. Means were calculated by pooling all sampling dates available for each lake for the periods Oct. - Mar. (winter) and April - Sept. (for summer). Asterisks mark cases in which differences between seasons were significant (T-tests, $p < 0.05$).

Lake	Season	N	Species richness	
			mean	SD
Crystal	winter	8	8.3	1.3 *
	summer	9	10.4	2.1
Emerald	winter	7	7.4	2.8
	summer	5	10.0	2.1
Lost	winter	4	6.8	2.5
	summer	6	7.0	3.7
Pear	winter	11	7.3	2.9 *
	summer	9	10.7	2.7
Ruby	winter	7	5.4	0.8
	summer	9	6.3	1.2
Spuller	winter	5	5.2	2.6
	summer	5	5.6	2.3
Topaz	winter	12	7.0	2.8
	summer	7	7.0	1.3

Table 33. Frequency of occurrence of species in samples from Emerald Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Diaptomus signicauda</i>	50	50	100
<i>Macrocyclus albidus</i>	50	50	25
<i>Tropocyclops prasinus</i>	33	50	50
<i>Daphnia rosea</i>	0	50	100
<i>Ceriodaphnia affinis</i>	0	50	75
<i>Holopedium gibberum</i>	0	50	100
<i>Bosmina longirostris</i>	100	100	100
<i>Chydorus sphaericus</i>	50	50	50
<i>Keratella taurocephala</i>	100	100	100
<i>Keratella quadrata</i>	67	100	25
<i>Polyarthra vulgaris</i>	100	100	100
<i>Conichilus unicornis</i>	17	50	75
<i>Trichocerca capucina</i>	0	0	100
<i>Ascomorpha</i> sp.	17	50	50
<i>Notholca</i> sp.	33	50	0

Table 32. Frequency of occurrence of species in samples from Crystal Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Diaptomus signicauda</i>	33	40	100
<i>Macrocylops albidus</i>	33	60	50
<i>Tropocyclops prasinus</i>	17	80	0
<i>Harpacticoid</i> sp.	33	20	33
<i>Daphnia rosea</i>	17	40	100
<i>Holopedium gibberum</i>	67	60	100
<i>Bomina longirostris</i>	50	40	83
<i>Chydorus sphaericus</i>	50	40	0
<i>Keratella cochlearis</i>	100	100	100
<i>Keratella quadrata</i>	100	100	67
<i>Polyarthra vulgaris</i>	100	100	83
<i>Conichilus unicornis</i>	17	20	50
<i>Trichocerca capucina</i>	0	20	67
<i>Kellicottia</i> sp.	67	100	100
<i>Asplanchna</i> sp.	67	60	17
<i>Synchaeta</i> sp.	50	80	17

Table 35. Frequency of occurrence of species in samples from Pear Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Diaptomus signicauda</i>	44	75	86
<i>Macrocyclus albidus</i>	78	100	100
<i>Daphnia rosea</i>	22	50	100
<i>Holopedium gibberum</i>	0	50	57
<i>Bosmina longirostris</i>	89	75	86
<i>Chydorus sphaericus</i>	78	25	71
<i>Keratella taurocephala</i>	89	100	100
<i>Keratella quadrata</i>	89	100	100
<i>Polyarthra vulgaris</i>	89	100	100
<i>Conichilus unicornis</i>	33	75	71
<i>Trichocerca capucina</i>	0	0	100
<i>Pleosoma</i> sp.	11	25	100
<i>Asplanchna</i> sp.	11	75	0
<i>Lecane</i> sp.	0	0	43
<i>Synchaeta</i> sp.	22	25	29

Table 34. Frequency of occurrence of species in samples from Lost Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Diaptomus signicauda</i>	67	50	67
<i>Macrocyclus albidus</i>	67	75	33
<i>Daphnia rosea</i>	33	50	33
<i>Holopedium gibberum</i>	33	75	33
<i>Bosmina longirostris</i>	100	100	67
<i>Keratella cochlearis</i>	100	100	67
<i>Keratella quadrata</i>	67	75	33
<i>Polyarthra vulgaris</i>	33	25	33
<i>Conichilus unicornis</i>	33	50	33
<i>Trichocerca capucina</i>	0	0	67
<i>Lecane lunaris</i>	33	75	33
<i>Synchaeta</i> sp.	33	50	33

Table 37. Frequency of occurrence of species in samples from Spuller Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Macrocyclus albidus</i>	100	100	100
<i>Daphnia rosea</i>	25	0	75
<i>Bosmina longirostris</i>	0	0	25
<i>Ceriodaphnia affinis</i>	25	0	50
<i>Chydorus sphaericus</i>	25	0	75
<i>Alona</i> sp.	0	0	50
<i>Keratella cochlearis</i>	75	50	50
<i>Keratella quadrata</i>	100	100	50
<i>Polyarthra vulgaris</i>	50	50	75
<i>Kellicottia</i> sp.	0	50	0
<i>Lecane</i> sp.	0	0	50
<i>Pompholyx</i> sp.	25	0	0
<i>Lecane subtilus</i>	0	0	50
<i>Synchaeta</i> sp.	0	50	25

Table 36. Frequency of occurrence of species in samples from Ruby Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Cyclops vernalis</i>	83	80	100
<i>Tropocyclops prasinus</i>	33	20	40
<i>Daphnia rosea</i>	83	40	80
<i>Bosmina longirostris</i>	17	40	40
<i>Keratella cochlearis</i>	100	100	100
<i>Keratella quadrata</i>	100	100	100
<i>Polyarthra vulgaris</i>	83	100	80
<i>Kellicottia</i> sp.	17	40	40
<i>Notholca</i> sp.	17	40	20

Table 39 Crustacean zooplankton sampled during snow melt periods*.

Species	Years	Lake
<i>Diaptomus signicauda</i>	87	Crystal
	90	Crystal, Emerald, Lost
	91	Lost
<i>Diaptomus eiseni</i>	87	Topaz
	88	Topaz
	90	Topaz
<i>Macrocyclus albidus</i>	87	Topaz
	88	Pear, Topaz
	89	Crystal, Emerald, Pear
	90	Crystal, Emerald, Pear, Lost
	91	Lost
<i>Tropocyclops prasinus</i>	87	Crystal
	88	Topaz
	90	Crystal, Ruby
<i>Cyclops vernalis</i>	89	Ruby
	90	Ruby
	91	Ruby
<i>Daphnia rosea</i>	89	Topaz
	90	Lost, Ruby
<i>Holopedium gibberum</i>	87	Pear
	90	Emerald, Lost
<i>Bosmina longirostris</i>	88	Topaz
	89	Emerald, Pear
	90	Emerald, Lost, Ruby, Topaz
	91	Ruby

*Snow melt period for each lake in each year determined as described in text using time series data on lake outflow discharge and ANC.

Table 38. Frequency of occurrence of species in samples from Topaz Lake.

SPECIES	PERCENT OCCURRENCE IN ALL SAMPLES FROM:		
	WINTER	SPRING	SUMMER
<i>Diaptomus signicauda</i>	70	75	100
<i>Diaptomus eiseni</i>	50	75	80
<i>Macrocylops albidus</i>	70	75	0
<i>Tropocyclops prasinus</i>	20	25	0
<i>Daphnia rosea</i>	40	75	60
<i>Daphnia middendorffiana</i>	30	0	60
<i>Bosmina longirostris</i>	70	25	0
<i>Chydorus sphaericus</i>	0	25	40
<i>Keratella taurocephala</i>	80	75	80
<i>Keratella quadrata</i>	80	100	40
<i>Polyarthra vulgaris</i>	40	50	80
<i>Conichilus unicornis</i>	10	0	40
<i>Trichocerca capucina</i>	0	25	60
<i>Ascomorpha</i> sp.	30	25	0
<i>Notholca</i> sp.	60	50	0
<i>Synchaeta</i> sp.	10	25	0

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16. Abstract (Limit: 200 words)

The tunable diode laser absorption spectrometer was used during the Southern California Air Quality Study to continuously measure the concentration of gas-phase nitric acid at Claremont, California. The measurements were made from June 15 through July 24, 1987. The detection limit was less than 0.1 ppbv for 1 minute averaging times. The data are presented in 1-minute, 15-minute, and 1-hour averages. Data recovery was better than 90%.

The diurnal behavior of nitric acid was quite regular. The maximum concentrations occurred between 1200 and 1800 each day. The daily maximum varied considerably during the study from a low of 5 ppbv on July 21 to a high of 24 ppbv on June 25. Nighttime minima occurred between 2200 and 0600 and were generally in the range 0.5 to 1 ppbv.

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