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Final Report

Characterization of Year-round Sensitivity of California's Montane Lakes to Acidic Deposition

by
J.O. Sickman and J.M. Melack
Marine Science Institute
and
Department of Biological Sciences
University of California
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June 1, 1989

California Air Resources Board Contract A5-203-32
Prepared for California Air Resources Board

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ABSTRACT

Surface-water chemistry in four watersheds in the Sierra Nevada, California was studied year-round during the period October 1986 through June 1988. The watersheds were located on both sides of the range and at altitudes greater than 2800 m. The basins were predominantly granitic, and the surface waters had acid neutralizing capacity (ANC) generally less than 100 µeq L^{-1}. Two lakes were situated on the eastern escarpment of the Sierra Nevada: Ruby Lake (37°24'50"N, 118°46'15"W) and Crystal Lake (37°35'36"N, 119°01'05"W). The western Sierran lakes were located in Sequoia National Park: Topaz Lake (36°37'30"N, 118°38'11"W) and Pear Lake (36°36'02"N, 118°40'00"W). The sampling program was designed to coincide with different seasonal conditions in the watersheds (*e.g.* snowmelt, summer and winter stratification, lake mixing and maximum snowpack accumulation).

All four lakes were found to be dimictic. They were ice-covered an average of 5 to 6 months of the year. The shallow lakes, Topaz (maximum depth, 5 m) and Crystal (maximum depth, 14 m), had weak thermal stratification during ice-free periods and stronger stratification under-ice. The deeper lakes, Ruby (maximum depth, 35 m) and Pear (maximum depth, 27 m), had strong temperature stratification during both winter and summer. These periods of stratification were associated with anoxia and large accumulations of ANC in the hypolimnion of Pear Lake. During February 1988 ANC reached 600 µeq L^{-1} in the bottom water of Pear Lake. More than 50% of the ANC at this time was contributed by ammonium; permanent ANC was on the order of 250 µeq L^{-1}. Ruby Lake had no hypolimnetic accumulation of ANC during winter anoxic periods. ANC was highest at a depth of 1 m and this was probably increased by inflowing stream water. Topaz and Crystal Lakes had slightly depressed dissolved oxygen concentrations in their hypolimnia but very little accumulation of ANC under ice.

The major solutes in the subsurface waters of the lakes reached their minima during the latter part of snowmelt and gradually increased through the remainder of the year. Lowest pH (5.7 - 6.0) was observed during snowmelt in these waters. Near-bottom concentrations of solutes generally had less seasonal variation and were higher than subsurface values. Lowest pH (5.8 to 6.0) was observed during periods of anoxia in the near-bottom waters.

Mean snow depth and snow chemistry were similar among watersheds and between years. Volume-weighted mean pH ranged from 5.3 to 5.5, and the dominant cations were hydrogen and ammonium. The order of anions based on concentration was acetate ≥ nitrate >

sulfate > formate ≥ chloride. Atmospheric, wet deposition of ammonium, basic cations and acidic anions can be greater during the period from May through October than during the period of snow accumulation. The majority of hydrogen loading occurred as snow.

Mass balance calculations indicate that the watersheds in Sequoia National Park (Topaz and Pear) produce less than half as much ANC (per hectare) as the Ruby and Crystal watersheds. Because of the coarse temporal spacing of the samples during snowmelt, ANC yield from the watersheds was probably overestimated. In addition, estimates of atmospheric loading to some watersheds were underestimated because of coarse spatial distribution of the snow surveys. After making conservative corrections of ANC yield and atmospheric loading, the ratio of ANC yield to atmospheric loading of hydrogen ion ranged from about 1 at Pear Lake to about 5 at Crystal Lake.

ACKNOWLEDGEMENTS

We thank Delores Lucero for assisting with all aspects of the field sampling and logistical planning. Delores performed virtually all the analyses for pH, ANC, conductance, chloride, nitrate, sulfate and organic acids. In addition she was responsible for drawing and digitizing the bathymetric maps of Topaz, Pear and Crystal Lakes. Delores also assisted in report preparation by making figures and tables and typing portions of the text.

We thank the many personnel from the National Park Service and the California Air Resource Board for logistical and financial support. We are especially grateful to David Parsons, Annie Esperanza and Kathy Tonnessen for all of their help and patience. We would like to thank the National Park Service, the Inyo National Forest and the Mammoth Ranger District for allowing us to conduct our research in their jurisdictions.

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We thank Kelly Elder, Rick Kattelmann, Danny Marks and Mike Zika for the valuable advice and help with the hydrological aspects of the study . In addition, we thank Mike Zika for designing and constructing the battery packs used to power the field stations, for programming field computers and for his expert assistance in getting the stations setup and running. We appreciate the morphometric map provided to us by Mark Whiting and the University of Indiana. We also thank Lance Lesack for the enormous amount of advice he provided.

Disclaimer

TABLE OF CONTENTS

Page

Abstract i

Acknowledgements iii

Table of Contents iv

List of Tables v

List of Figures vi

Summary and Conclusions 1

Recommendations 8

Introduction 12

Site Descriptions 13

Methods 15

Quality Control and Assurance Program 20

Results and Interpretation 22

Discussion 34

Tables and Figures 40

References 102

LIST OF TABLES

Page

Table 1 Summary of watershed and lake attributes. 40

Table 2 Summary of QA/QC statistics for major ions. 41

Table 3 Inflow chemistry for Pear and Ruby Lakes. 42

Table 4 Inflow chemistry for Topaz and Crystal Lakes. 43

Table 5 Outflow chemistry for Topaz and Crystal Lakes. 44

Table 6 Lake-ice chemistry for Emerald, Pear and Topaz Lakes. 45

Table 7 Snowpack characteristics for Topaz, Pear, Crystal and Ruby Lakes; 1987 and 1988. 46

Table 8 Snowpit chemistry for Topaz, Pear, Crystal and Ruby Lakes; 1987 and 1988. 47

Table 9 Ionic loading by snow for Topaz, Pear, Crystal and Ruby Lakes; 1987and 1988. 48

Table 10 Monthly precipitation totals for Topaz, Pear, Crystal and Ruby Lakes; June to October 1987. 49

Table 11 Summary of precipitation for June through October 1987. 49

Table 12 Monthly ionic loading during the ice-free period of 1987 at study lakes. 50

Table 13 Monthly ionic loading during water-year 1987 at Emerald Lake. 51

Table 14 Monthly outflow discharge; October 1986 through May 1988. 52

Table 15 Water balances for water-year 1987. 53

Table 16 Estimates of error in water balances. 54

Table 17 Comparison of ionic loading and watershed yield of solutes. 55

Table 18 Corrected ratios of watershed yield of ANC to atmospheric loading of H+. 56

Table 19 Median values of major ion chemistry for study lakes, Emerald Lake and two surveys of Sierran lakes. 57

List of Figures

			Page
Fig.	1	Location of study lakes in California.	58
Fig.	2	Map of Ruby Lake watershed.	59
Fig.	3	Map of Crystal Lake watershed.	60
Fig.	4	Map of Topaz Lake watershed.	61
Fig.	5	Map of Pear Lake watershed.	62
Fig.	6	Bathymetric map of Ruby Lake.	63
Fig.	7	Bathymetric map of Crystal Lake.	64
Fig.	8	Bathymetric map of Topaz Lake.	65
Fig.	9	Bathymetric map of Pear Lake.	66
Fig.	10	Histogram of frequency of charge imbalance and difference between calculated and measured conductance for water samples.	67
Fig.	11	Summary of sample storage test for pH, ANC and conductance.	68
Fig.	12	Summary of sample storage test for major ions.	69
Fig.	13	Lake time series of pH and ANC.	70
Fig.	14	Lake time series of chloride and conductance.	71
Fig.	15	Lake time series of nitrate and sulfate.	72
Fig.	16	Lake time series of calcium and magnesium.	73
Fig.	17	Lake time series of sodium and potassium.	74
Fig.	18	Lake time series of base cations and silica.	75
Fig.	19	Lake time series of temperature and oxygen.	76

Fig. 20 Lake time series of total dissolved nitrogen and phosphorus. 77
Fig. 21 Lake time series of ammonium. 78
Fig. 22 Lake time series of particulate nitrogen and phosphorus. 79
Fig. 23 Lake time series of chlorophyll and particulate carbon. 80
Fig. 24 Lake time series of dissolved aluminum and iron. 81
Fig. 25 Representative temperature profiles for Pear and Ruby Lakes. 82
Fig. 26 Representative temperature profiles for Topaz and Crystal Lakes. 83
Fig. 27 Representative oxygen profiles for Pear Lake. 84
Fig. 28 Representative oxygen profiles for Ruby Lake. 85
Fig. 29 Representative oxygen profiles for Topaz Lake. 86
Fig. 30 Representative oxygen profiles for Crystal Lake. 87
Fig. 31 Outflow time series for Pear and Ruby Lakes; pH, ANC, chloride andconductance. 88
Fig. 32 Outflow time series for Pear and Ruby Lakes; nitrate, sulfate and ammonium. 89
Fig. 33 Outflow time series for Pear and Ruby Lakes; calcium, magnesium, sodium and potassium. 90
Fig. 34 Outflow time series for Pear and Ruby Lakes; base cations, silica and total dissolved nitrogen and phosphorus. 91
Fig. 35 Representative chlorophyll profiles for Pear and Ruby Lakes. 92
Fig. 36 Rating curve and residuals for Pear Outflow. 93
Fig. 37 Rating curve and residuals for Topaz Outflow. 94

Fig. 38 Rating curve and residuals for Ruby Outflow. 95

Fig. 39 Rating curve and residuals for Crystal Outflow. 96

Fig. 40 Outflow hydrographs for Pear and Topaz Lakes for the period October 1986 through June 1988. 97

Fig. 41 Outflow hydrographs for Ruby and Crystal Lakes for the period October 1986 through June 1988. 98

Fig. 42 Outflow hydrographs for Pear and Topaz Lakes for the snowmelt period of 1987. 99

Fig. 43 Outflow hydrographs for Ruby and Crystal Lakes for the snowmelt period of 1987. 100

Fig. 44 Outflow discharge and times series of ANC for Emerald Lake outflow; snowmelt 1987. 101

SUMMARY AND CONCLUSIONS

Background

This project is an extension of the Emerald Lake integrated watershed study. It entailed a year-round examination of four watersheds in the Sierra Nevada to collect data with which to judge the generality of the intensive Emerald Lake study, and to characterize the year-round sensitivity of these lakes to acidification. The project had four major objectives:

1. To establish the year-round variability in pH, ANC and other major solutes in the lakes and their streams.

2. To identify those periods when ANC increases or those when it decreases and to offer hypotheses to explain these patterns.

3. To quantify the acidic deposition reaching these aquatic systems.

Answering these objectives allowed us to examine the year-round susceptibility of a variety of Sierran lakes to acid deposition and to formulate recommendations for a practical, scientifically-sound, long-term monitoring program to assess the status of California's inland waters with respect to acid deposition.

Study Sites

Four lakes were selected primarily on the basis of their low acid-neutralizing capacity (ANC), the extent of acid deposition in their vicinity, their geographic location and their year-round access. All four lakes were located in the subalpine-alpine region of the Sierra Nevada and had ANC less than 100 µeq L^{-1}. All but one occupy predominantly granitic basins.

Ruby Lake is situated on the eastern escarpment of the Sierra Nevada in the John Muir Wilderness of the Inyo National Forest. It is the largest (12.6 ha) and deepest (35 m) of the four lakes and lies at the highest altitude (3,426 m). It also has the largest watershed area (424 ha), greatest lake volume (2,156,000 m^3) and most watershed relief (754 m). The watershed contains a large amount of mineralized granite and a glacier in the uppermost cirque.

Crystal Lake, also situated in the eastern Sierra Nevada, is located about 10 km southwest of the town of Mammoth Lakes. The lake is the smallest of the four in surface area (5 ha) and second smallest in volume (320,000 m^3) and depth (14 m). The majority of the basin is composed of granitic rocks and talus and a small portion of ash and soils of volcanic origin. Soils are more common in this watershed than at the other 3 catchments.

Topaz Lake is in Sequoia National Park in a region known as the Tablelands, about 6 km north-northwest of Emerald Lake. The lake lies at an altitude of 3,219 m and covers an area of 5.2 ha. Vertical relief in the basin is the least of the four sites (244 m), and the entire watershed lies in the alpine zone. Topaz is the smallest of the four lakes both in depth (5 m) and volume (74,000 m^3). The basin is composed entirely of slowly weatherable granite.

Pear Lake is located in Sequoia National Park about 0.5 km from Emerald Lake at an altitude of 2,904 m. The lake's watershed drains an area of 136 ha, and the lake has a surface area of 8 ha. The lake has a maximum depth of 27 m and a volume of 578,000 m^3, placing it second in size to Ruby Lake. The basin has a relief of 471 m, and a relatively small area, 136 ha. The basin is composed, largely, of slowly weatherable granite.

General Approach

Pear, Topaz, Ruby and Crystal Lakes were sampled approximately bimonthly during the period from October 1986 through June 1988. Samples for chemical analyses were collected from four depths in Pear, Crystal, and Ruby Lakes and at three depths in Topaz Lake. A single sampling station, overlying the deepest portion of the lake was used. Outflow samples were collected when possible and some inflow samples were collected during snowmelt periods.

Samples of the snowpack were obtained during the period of maximum snow accumulation during the winters of 1986-87 and 1987-88. The sampling sites were located in portions of the watersheds with different exposures and altitudes. Snow density and snow-covered area were also determined in each basin. Snow-covered area for both winters was estimated from aerial photographs.

During the ice-free season in 1987, precipitation quantity was measured at each lake using a tipping-bucket rain-gauge connected to a solid-state data logger. Rain chemistry to estimate ionic loading was obtained from the ARB's precipitation monitoring network.

Stream stage was continuously monitored using micro-pressure transducers and the field computers. A thorough calibration of the transducers was done using salt dilution estimates of discharge.

Bathymetric maps of Pear, Topaz and Crystal Lakes were prepared from echo soundings done during August of 1987. The maps were drawn by hand and then digitized. The volumes of the lakes were estimated from their hypsographic curves. The map for Ruby Lake was prepared by Mark Whiting of the University of Indiana using the same techniques described above.

To ensure the quality of the chemical data, a rigorous and thorough QA/QC program was established. The program consisted of measurements of within-run precision and accuracy, participation in the USGS Analytical Evaluation Program, routine determination of NBS Standard Reference Materials and various statistical checks to ensure internal consistency and completeness.

Findings

The extent of vertical mixing varied among the lakes. Topaz Lake was stratified only during the winter, whereas the deep lakes, Pear and Ruby, showed pronounced stratification in both winter and summer. Crystal Lake was weakly stratified during the summer and winter and thoroughly mixed in the spring and autumn.

Summer stratification in Pear Lake was strong with surface temperatures being more than 12 °C higher than the temperature of near-bottom water. This strong persistent stratification led to oxygen depletion below about 18 m. Anoxic conditions persisted in the deeper portions of the lake throughout much of the year and were associated with large increases of ANC. Total ANC in the hypolimnion of Pear ranged from ~100 $\mu eq\ L^{-1}$ during the summer of 1987 to a maximum of ~600 $\mu eq\ L^{-1}$ during February 1988. During the winter of 1986-87, low dissolved oxygen values were measured in the hypolimnion of Pear Lake but no large increase in ANC was observed.

Ruby Lake had low dissolved oxygen concentrations in its deep waters throughout the year. However, little or no increase in ANC was observed. ANC was slightly higher at 35 m than in subsurface waters during the summer of 1987. During ice-cover (1986-87), the epilimnion of the lake had more ANC than the anoxic hypolimnetic waters. This was probably caused by streamwater entering Ruby Lake and pooling under the ice. At Ruby Lake, inflow waters often had greater ANC than lake water.

Topaz was sufficiently shallow and transparent that summer stratification did not occur and winter stratification was weak. ANC patterns in Topaz Lake were very regular, with minima every snowmelt and maxima under ice. There were no vertical differences of ANC in Topaz Lake.

Crystal Lake had slightly depressed dissolved oxygen concentrations in the winter but was well-oxygenated top to bottom in the summer. ANC concentrations were the same throughout the lake in the summer of 1987. In the winters of 1986-87 and 1987-88, near bottom values were about 25 μeq L^{-1} higher than surface values.

The other solutes generally followed patterns similar to ANC in each of the lakes. Subsurface pH, specific conductance, chloride, sulfate, silica, calcium, magnesium, potassium and ammonium ions all declined and reached minimum values during snowmelt and showed a gradual increase throughout the remainder of the year; maxima were recorded during the ice-covered season. Subsurface concentrations of nitrate were highest in all lakes during snowmelt; this pattern was also found in the outflow chemistry of Pear and Ruby Lakes. Nitrate and ammonium declined to the detection limit in all lakes during the remainder of the ice-free season.

Near-bottom concentrations of solutes generally showed less seasonal variations, were higher than subsurface values and reached maxima during the ice-covered season. They were also more variable between lakes. Lowest pH was observed during periods of oxygen depression (Pear, Ruby, Crystal) or during snowmelt (Topaz). Associated with periods of anoxia were increases in ammonium and total dissolved N and P in the hypolimnia of all four lakes.

Chlorophyll *a* and particulate carbon, nitrogen and phosphorus concentrations were low in the surface-waters of all the lakes and high in the hypolimnion of Pear Lake. Vertical heterogeneity of chlorophyll *a* was evident during the ice-free season of 1987 in both Pear and Ruby Lakes.

Inflow chemistry from samples collected during the spring of 1988 were very similar to subsurface lake chemistry (except at Ruby Lake). Generally, inflows had slightly less ANC and higher levels of nitrate.

Lake ice was sampled and found to occur in alternating layers of slush and hard ice. The chemistry of the slush-ice is like that of the subsurface lake chemistry. Hard-ice had slightly lower pH, specific conductance and ANC.

Snow chemistry was similar among watersheds and between years. pH ranged from 5.3 to 5.5. The order of ions was similar among the basins. The dominant cations were H^+ and NH_4^+. For anions in 1987 the order was: $NO_3^- > SO_4^{2-} > Cl^-$. In 1988 the organic anions, HCO_2^- (formate) and $CH_3CO_2^-$ (acetate) were assayed, and the order changed to: $CH_3CO_2^- \geq NO_3^- > SO_4^{2-} > HCO_2^- \geq Cl^-$. Using the snowpit chemistry and snow depths, ionic loadings to the watersheds by winter snow was calculated.

Using rain chemistry and volume, ionic loading by non-winter precipitation at each of the watersheds was estimated. The solute loading of winter snow *vs* spring-summer-autumn precipitation within an individual basin was compared. At all four watersheds, most H^+ deposition was by winter snow followed by spring rain/snow then summer and autumn rain. For chloride deposition, winter snow was the major source to Crystal and Ruby Lakes and spring rain/snow was the main source to Topaz and Pear Lakes. For all other ions the major supply was spring rain/snow followed by either winter snow or summer and autumn rain. Acidic anion loading (NO_3^- and So_4^{2-}) was 2 to 3 times higher in the summer/autumn period compared to winter at the Topaz and Pear watersheds because of the high concentration of these solutes in summer rain and autumn snow in the western Sierra Nevada. These findings suggest that non-winter loading can comprise a large proportion of the annual input of solutes to montane watersheds.

Outflow discharge hydrographs for Ruby and Crystal Lakes showed many differences when compared to hydrographs for Pear and Topaz Lakes. These differences consisted mainly in the timing of onset and the duration of snowmelt. Peak monthly discharge in 1987 was in June at Pear and Ruby Lakes and in May in the outflows of Topaz and Crystal Lakes. The melt at Ruby Lake lasted through October, through August at Pear and Crystal and through June at Topaz.

Mass balance calculations proved to be valuable in assessing watershed susceptibility to acidification and in identifying important watershed processes. Presently, all four watersheds are producing sufficient buffering to neutralize current levels of H^+ loading. Calculations show that the lakes in Sequoia National Park are more susceptible to acidification than the eastern Sierran lakes. This is due, in part, to higher levels of acid deposition and lower yields of ANC in the Sequoia watersheds. At Pear Lake, ANC yield from the watershed is unassociated with base cations yield; Pear Lake appears to be retaining these cations. Large amounts of ammonium ion and hydrogen sulfide in the hypolimnion of Pear Lake may be responsible for some of the decline in lake pH and ANC seen during spring-melt.

Major solute chemistry was similar among the four watersheds and Emerald Lake. Ions such as sulfate, chloride and pH varied little among the lakes. Other solutes like nitrate, basic cations and especially ANC were more different. Median values for near-surface ANC ranged from 22 $\mu eq\ L^{-1}$ at Pear to 27 $\mu eq\ L^{-1}$ at Emerald to 32 $\mu eq\ L^{-1}$ at Topaz. These lakes were more similar to one another than to the eastern Sierran lakes where median ANC ranged from 54 $\mu eq\ L^{-1}$ at Ruby Lake to 70 $\mu eq\ L^{-1}$ at Crystal Lake. Comparisons of chemistry from the Sequoia lakes and eastern slope lakes to a population of Sierran lakes shows them to have similar subsurface solute concentrations and ANC. This was also the case when comparing these lakes to Sierran lakes in the EPA's western lake survey. Based on lake chemistry, Emerald Lake and the four study lakes are representative of Sierran lakes.

Conclusions

1. The accumulation of ANC in Sierran lakes is closely related to water column stratification, the depletion of oxygen in their hypolimnia and high concentrations of ammonium, iron and reduced sulfur compounds.

2. The major loss of ANC in Sierran lakes occurs during snowmelt, and snowmelt is the time of year when these lakes are most susceptible to acidification.

3. Watershed geology and geographic location are important in determining lake chemistry and the susceptibility of lakes to acidification.

4. On an annual basis, Sierran watersheds produce sufficient ANC to neutralize current amounts of acid loading but reserves of ANC in some watersheds are small or absent. Based on one year of data, the ratio of watershed production of ANC to current H^+ ion loading ranges from about 1 to 3 at catchments in Sequoia National Park and from 4 to 5 at the watersheds in the eastern Sierra Nevada.

5. High altitude lakes in Sequoia National Park are more at risk to both episodic and chronic acidification than high altitude lakes along the eastern slope of the Sierra Nevada.

6. Deposition of H^+ ion by winter snow accounts for the majority of H^+ ion input to high-altitude watersheds in the Sierra Nevada.

7. During drought conditions, the greater part of acid anion, basic cation and ammonium deposition in the Sierra Nevada occurs during spring precipitation events.

8. Organic acids are a major component of snow deposition in the Sierra Nevada and probably comprise a large proportion of the solutes in non-winter deposition.

9. Montane lakes in the Sierra Nevada exhibit considerable seasonal and annual variation in chemistry and susceptibility to acidification.

10. Given the state of our knowledge about acid deposition in the Sierra Nevada, lake-chemistry surveys are of limited value in monitoring the status of these lakes. Year-round, long term studies offer the best assessment of the status of California's montane lakes because of large seasonal and interannual variation in lake chemistry and acidic deposition.

Recommendations

I. Research and Monitoring

To understand the influence and possible affects of acidic deposition on aquatic ecosystems in California requires both a long term and year-round sampling program. The prime focus for such a program should continue to be high altitude lakes of the Sierra Nevada. The four study lakes in this report and Emerald Lake represent a cross section of Sierran lakes. Their accessibility and our current knowledge of them makes these watersheds excellent choices for a long-term monitoring program. With this in mind we make the following recommendations:

1. Continue the current work at Emerald, Topaz, Pear, Crystal and Ruby Lakes.

2. Add additional study sites, preferably lakes in another region of the Sierra Nevada. The sites must be accessible year-round, should possess a gaugeable outflow stream and have ANC less than 100 μeq L^{-1}. It would be desirable to locate these sites in the Lake Tahoe and Yosemite regions.

3. Increase the sampling frequency during snowmelt, especially at its onset, in order to detect the ionic pulse and determine its impact on the lakes. Weekly or biweekly sampling is suggested. The bimonthly sampling schedule for the remainder of the year should include visits when the lakes are thermally stratified in the summer, after they mix in the autumn and prior to snowmelt in the winter. This schedule will allow detection of the peaks in ANC accumulation during the summer and winter periods. Sampling of outflow chemistry at this frequency would improve the accuracy of the solute mass balances.

4. We propose satellite telemetry of the data collected by our field computers. Real-time access to the data would allow timing sampling trips to coincide with the onset of snowmelt or other important, episodic events. Tipping bucket rain-gauge data would provide timing and intensity of rain storms and allow sampling of the lakes after particularly large events. Additional sensors such as a conductivity electrode could be added. This continuous monitoring of stream chemistry would indicate the timing and magnitude of the snowmelt ionic pulse or the impact of large storms on the lakes' chemistry. Prompt access to this data would allow timing lake sampling with these events. An added benefit of using satellite telemetry is that the operating condition of the sensors can be closely monitored. This would help minimize data loss due to instrument malfunction.

5. Improve rating curves at the outflows by doing more calibrations and making the installations more rugged. Placing thermistors in the outflow streams will enable correction of transducer voltages for temperature and indicate if the stream is frozen or flowing. The thermistor will improve discharge accuracy at low flows and the additional calibration and enhanced installations will improve accuracy at high flows. Refining outflow discharge measurements will increase the accuracy of the mass balance calculations and provide a better check of snow water equivalence estimates.

6. To reduce the uncertainty in our water balance at the catchments, monitoring of variables needed to calculate evaporation needs to be initiated. The total evaporation from a watershed (snow sublimation, lake evaporation and evapotranspiration) can account for 20 to 30% of total inputs of water to the basins. Since mass balance calculations are driven largely by water flux, improved water balance estimates would improve these calculations.

7. Continue testing for organic acids in the snowpack and extend this protocol to summer-autumn precipitation. We would also strongly suggest that ARB include this procedure in its statewide precipitation monitoring network. In addition, some attempt should be made to collect chemistry samples from non-winter precipitation within each watershed. Our data show that non-winter precipitation quantity differs considerably among watersheds. This may mean that precipitation chemistry also varies significantly among watersheds. These data are needed to better estimate acidic deposition to the catchments during the spring-summer-autumn period.

8. Include sampling of the biota in the monitoring program. Work done at Emerald has demonstrated the importance of plankton community structure as a sensitive indicator of acidification. These measurements should include vertical zooplankton tows and continued measurement of biomass indicators such as particulate carbon and nitrogen and chlorophyll.

Additional work is necessary to assess the possible impact of acidification on lake biota and to identify sensitive taxa. The results from limnocorral experiments at Emerald Lake have demonstrated a complex interaction of nutrients, phytoplankton productivity and zooplankton population dynamics during acidification and nutrient addition. The plankton of Emerald Lake are indicative of those found in lakes with fish but may not respond to acidification the same as taxa found in fishless lakes. Stoddard (1986) found that the presence of fish greatly altered the species composition of the zooplankton. Additionally, primary production in several Sierran lakes has been shown to be limited by nitrogen (Goldman and De Amezaga 1984) as are, most likely, several of our study lakes. These findings suggest that the plankton community structure and nutrient dynamics in Emerald Lake is not typical of all Sierran lakes. Additional acidification experiments are crucial in assessing the potential effects of acidification on Sierran lakes in general.

9. An attempt should be made to determine the cause of the large ANC buildup in Pear Lake and the absence of in-lake generation in Ruby Lake. Given that Pear and Ruby Lakes have similar hydraulic turnover-times and similar patterns of temperature and oxygen stratification, further understanding of the causes for this difference would increase our ability to model watershed and lake response to acidification. The sediments of the study lakes and the geology of the basins may hold the answer to this problem. We suggest lake sediments be collected and analyzed for mineral and organic composition. In addition, some quantitative, geological and soils mapping of the basins would be valuable. And finally, measurements of interstitial water chemistry would enhance knowledge of the influence of the sediment-water interface on lake chemistry.

10. Monitoring of lake stratification using thermistor strings should be initiated during representative periods. These thermistors can be connected to field computers, floated on rafts in the lakes. Stratification has been shown to be crucial to *in situ* production of ANC (this report and Melack *et al.* 1987). These data would also help assess the role of hypolimnetic solutes in mediating or exacerbating the pH and ANC declines observed during snowmelt and large rain events.

II. Use of Data in Policy Decisions

1. The data that have been collected should be used to validate the various computer simulations of the Emerald Lake watershed. Using this data would test the underlying assumptions of the models, assess the relative accuracy of their predictions and provide insight into watershed-processes or features which require more study in terms of acid deposition.

2. Projects similar to ours should be the next step in the evolution of acid-deposition research in the Sierra Nevada. It combines the best aspects of lake-surveys and intensive watershed studies while avoiding their drawbacks. Lake surveys in the Sierra Nevada have served their purpose (to identify sensitive habitats) and offer little to efforts monitoring the status of montane lakes. Large seasonal and interannual variation in lake chemistry and susceptibility to acidification occur in high-altitude watersheds. This precludes the use of once-yearly lake samples in identifying trends in surface water quality. However, the use of a single, intensely studied watershed to detect trends in water quality and susceptibility of

Sierran lakes to acidification has problems also. Our data have shown that, while Emerald Lake is representative of Sierran lakes chemically, other processes which affect a lake's susceptibility to acidification differ among these watersheds. The integrated watershed study has laid the foundation for studying acidification of Sierran watersheds in terms of biology, geochemistry and surface-water hydrology. In addition it was a proving ground for techniques and equipment necessary for acidification research. The next approach should involve many of the aspects of the watershed study: deposition monitoring, water balance measurements, mass balance estimates and in-lake process studies, but at a representative cross-section of Sierran watersheds.

3. Data such as was collected in this study could be used by the ARB to formulate deposition standards for the Sierran region. One of the best procedures in estimating lake sensitivity is the mass balance approach. This method integrates many individual biogeochemical processes which affect lake acidification. Moreover, these calculations take into consideration deposition of acidic components in the watersheds. Much improvement in methodology is needed before these data could be used in a policy-setting capacity but these improvements are tractable.

INTRODUCTION

Project Rationale and Objectives

Acid precipitation is falling on California's coast, inland valleys and montane regions (California Air Resources Board 1988). Such deposition has been shown to have major, adverse consequences to terrestrial and aquatic environments in areas such as Scandinavia and the northeastern United State (Almer et al. 1974; Geelen and Leuven 1986; Ravera 1986). Evaluating the harm posed by acid deposition in California requires an assessment of the current status of its aquatic resources and their possible responses to acidification. The California Air Resources Board (ARB) approached the problem in two ways. First, the ARB sought to determine the geographic extent of sensitive aquatic habitats by conducting state-wide surveys of lakes and streams. Second, an Integrated Watershed Study (IWS) of the Emerald Lake watershed in the Sierra Nevada was initiated in order to collect baseline data with which to detect acid induced damage and to conduct experiments to determine the possible consequences of acidification of California's montane lakes. Emerald Lake was selected because high elevation, granitic watersheds are the most susceptible to acidic inputs because of their limited capacity to neutralize acids. These areas may, therefore, be a harbinger of acidic deposition's impact on the state's lakes and streams.

Our project was formulated as an extension of the Emerald Lake IWS. It entailed a year-round study of other high-altitude watersheds in the Sierra Nevada designed to assess the generality of the intensive, Emerald Lake study and to characterize the year-round sensitivity of these lakes to acidification. Four lakes were selected, primarily on the basis of their acid neutralizing capacity, the extent of acid deposition in the vicinity of the lakes, their geographic location and the ease of access during all seasons. This last criteria was critical since we wanted to characterize the temporal variability in chemistry of these lakes. We had three major goals:

1. To establish the year-round variability in pH, ANC and other major solutes in the lakes and their streams.

2. To identify those periods when ANC increases or those when it decreases and to offer hypotheses to explain these patterns.

3. To quantify the acidic deposition reaching these habitats.

Answering these objectives will allow us to generalize about the year-round susceptibility to acid deposition of Sierran lakes and to design a practical, scientifically sound, long-term monitoring program to assess the status of California's inland waters with respect to acid deposition.

In this report we will describe the annual patterns of surface water chemistry in four montane watersheds in the Sierra Nevada. Using these data we will attempt to evaluate their susceptibility to acid deposition. Additionally, we will present data on solute deposition in the watersheds and discuss the seasonality of this deposition. Finally, we will discuss the successes and limitations of our present sampling protocols and make recommendations concerning a long-term monitoring program of montane watersheds and lakes in California.

Site Descriptions

Figure 1 shows the location of the four study sites in California. Topographic maps of the four watersheds are shown in Figures 2 through 5. Bathymetric maps of each lake are shown in Figures 6 through 9. The bathymetric maps show depth contours, any islands present and the position of major inflows and the outflow. A summary of the watershed and lake characteristics are contained in Table 1.

Ruby Lake is situated on the eastern slope of the Sierra Nevada in the John Muir Wilderness of the Inyo National Forest (37°24'50"N, 118°46'15"W) It is the largest and deepest of the four 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 of Mono recesses. This rock is typically coarse-grained and strongly porphyritic and contains minor amounts of hornblende and sphene (Lockwood and Lydon 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 made up primarily of 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.

Crystal Lake, also situated in the eastern Sierra Nevada, is located about 10 km southwest of Mammoth Lakes (37°35'36"N, 119°01'05"W). The lake is the smallest in area and ranks third in volume and depth. The watershed area is the smallest of the four lakes and 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 has a different geology. This area 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). During the spring of 1988 three major runoff channels were identified. Inflow #1 and the Main Inflow drain the eastern and southern portions of the basin (see Figure 7). 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.

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 . The lake ranks fourth in depth and volume. It is connected by a narrow channel to a small, shallow pond during high-water periods. This pond is very similar in chemical composition to Topaz Lake. Vertical relief in the basin is the least of the four sites and has a southern exposure. Portions of the upper basin have extensive meadows and short-lived ponds during snowmelt. There is also a small stand of Foxtail pines in the upper eastern portion of the watershed (~25 trees). The geology of the basin is dominated by fine-grained, porphyritic granodiorite containing abundant mafic inclusions. The phenocrysts include potassium feldspar, hornblende, biotite and plagioclase (Moore and Sisson 1987). Because of the gentle relief around the lake, it tends to expand during snowmelt and floods a small meadow, forming a large bay (see Figures 4 and 8). This bay comprises a substantial portion of the lake's area, although not its volume. As the summer progresses the lake level declines and the water retreats from this bay. Surface waters in the basin, other than the lake and the shallow pond, are short-lived and were present only until July during the two years of the study.

Pear Lake is located in Sequoia National Park (36°36'02"N, 118°40'00"W) about 0.5 km from Emerald Lake. The lake is second in depth and volume. 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 (Moore and Sisson 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 (see

Figure 5). The outflow to the lake is permanent, although it can drop to a trickle in the autumn.

METHODS

Lake and Stream Monitoring

Pear , Topaz , Ruby and Crystal Lakes were sampled approximately bimonthly during the period from October 1986 through June 1988. Pear and Topaz Lakes had a total of 12 sampling visits and Ruby and Crystal Lakes had 10. Samples for chemical analyses were collected from four depths in Pear, Crystal, and Ruby Lakes and from three depths in Topaz Lake. A single sampling station, overlying the deepest portion of each lake was used. Outflow samples were collected when possible, and some inflow samples were collected during snowmelt periods.

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. Samples for chlorophyll *a* and particulate carbon, nitrogen and phosphorus were collected on precombusted Gelman A/E filters. Vertical profiles of dissolved oxygen and temperature (meter intervals) were also measured, using a portable meter (YSI model 58) equipped with polarographic oxygen electrode and thermistor.

All apparatus and bottles used in sampling were rinsed with 10% HCl, rinsed 5 times with deionized water and then soaked in deionized water for several days. Trace metal bottles were cleaned as described by Tonnessen (1983) using a strong solution of nitric and sulfuric acid. Major solute and nutrient samples were filtered with either Gelman A/E filters which were rinsed with at least 1 liter of deionized water or Nuclepore polycarbonate filters (1.0 micron pore size). Our studies have shown that Gelman A/E filters can contribute sodium to samples unless they are rinsed thoroughly. Samples for trace metals were filtered through Nuclepore polycarbonate filters (0.1 micron pore size) using an all-plastic filter holder and a peristaltic pump. Trace metal samples were acidified with ultra-pure (Ultrex) nitric or sulfuric acid.

All samples were kept cool and in the dark during transport. For long-term storage, major solute and nutrient samples were held in a coldroom at 5 °C. Particulate samples and samples for total dissolved N and P were stored at -20 °C.

A Gran titration (Talling 1973) and pH measurement were done on unfiltered subsamples within 48 hours of collection using a Fisher Acumet meter and Ross (Orion) combination electrode. Specific conductance of unfiltered water was measured with a conductivity bridge (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 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. Samples for calcium and magnesium had lanthanum added to reduce chemical interferences. Iron and aluminum were analyzed by atomic absorption with the graphite-furnace technique. Total dissolved nitrogen and phosphorus and particulate phosphorus were determined after persulfate digestion using cadmium reduction and the molybdenum blue-ascorbate methods respectively (Valderrama 1981). Silica was determined on a filtered subsample using the silico-molybdate method (Strickland and Parsons 1972). Particulate carbon and nitrogen were determined by combustion in an elemental analyzer (CEC model 240XA). Chlorophyll *a* was measured after extraction with 90% acetone using a fluorometer (Wetzel and Likens 1979).

Precipitation Sampling

Samples of the snowpack were obtained by digging pits to the ground and collecting duplicate, contiguous, vertical sections every 40 cm using a PVC tube (5 cm diameter, 50 cm long, with a sharp, beveled cutting edge). The timing of the sampling coincided with the period of maximum snow accumulation during the winters of 1986-87 and 1987-88. In each basin three pits were sampled in 1987 and two in 1988. These pits were located in portions of the watersheds with different exposure and altitude.

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. A test was done to check for chloroform contamination of the organic anion samples and was negative. 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 72 hours of melting using filtered samples by the indophenol blue method (Strickland and Parsons 1972).

In order to estimate snow water equivalence, snow density and snow-covered area were determined in each basin. Snow density was determined in vertical 10 cm intervals in each sampling pit using a wedge shaped, stainless steel cutter (Dozier *et al.* 1987). The cutter was used in conjunction with a portable electronic balance. All cutters were calibrated and found to have less than 1% error in volume. Snow depth was determined along transects (using avalanche probes) from the lakes' edge to the boundaries of the watersheds; approximately 300 depth measurements were made at each basin. Snow-covered area for both winters was estimated from aerial photographs taken during April 1988. Since no photographs were available for 1987 and deposition for both winters similar, the snow-covered area from 1987-88 was used in the 1986-87 snow water equivalence calculation.

During the ice-free season in 1987, precipitation quantity was measured at each lake using a tipping-bucket rain-gauge (Qualimetrics model 6011-B) connected to a solid-state data logger (see next section). Because wind reduces the collection of precipitation by rain gauges, actual rainfall was estimated to exceed measured rainfall by 10 percent (Dozier *et al.* 1989). Rain chemistry from ARB's Emerald Lake site was used to estimate ionic loading at Pear and Topaz Lakes and at Crystal and Ruby Lakes during October 1986, November 1986 and May 1987. Other chemistry used for the eastern Sierra lakes was obtained from the ARB Mammoth Mt. site. No data were available for the Mammoth site for 1987; volume weighted mean concentrations had to be derived from 1984, 1985 and 1986 chemical data for the ionic loadings at Ruby and Crystal Lakes during June through October 1987.

Outflow Discharge

At each lake an automatic data collection station was established. The station consisted of an Easylogger field computer (Omnidata International) powered by a durable, weather-proof battery pack. The field computers were mounted in trees or under rock overhangs 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. The transducers at Pear and Ruby Lakes had a effective range of 0 to 350 cm and the ones at Topaz and Crystal Lakes had a 0 to 70 cm range. In addition, staff gauges were installed near each transducer as a benchmark to check for transducer movement.

In order to develop relationships between the pressure transducers and outflow discharge a lengthy calibration of the transducer 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 each sampling trip and intensively during the snowmelt periods of 1987 and 1988. For the outflows of Ruby and Crystal Lakes over 50 individual measurements were included in each rating curve; Topaz Lake had 39 and Pear Lake 18. The range of the calibration discharges spanned most of the range of observed discharges. There were, however, very brief (less than 48 hours) episodes at both Ruby and Crystal Lakes when the transducer readings were out of the calibration range. These transient episodes were probably due to avalanches or ponding at the transducer sites.

Water Balance

Water balances for each basin were constructed for water-year 1987. The water balance involved estimating all hydrologic inputs and losses to the basins. The inputs to the watersheds were rain and snow; the losses were lake outflow and evaporation. The evaporation term includes sublimation of snow, lake evaporation and evapotranspiration. The following equation was used:

Outflow + Residual = Snow + Rain - Evaporation

The residual term includes changes in basin water storage and error.

Outflow discharge was calculated by converting transducer voltage (time-step, 15 minutes) to discharge and then summing the flow from 1 October 1986 to 30 September 1987. The major input to the water balance was snow which was estimated to equal the amount of water present in the snowpack at or near peak accumulation (March and April 1987). This parameter was calculated from basin snow-water equivalence and basin area. Snow-water equivalence was in turn calculated from the snow-depth surveys and snow-density measurements. Rain input was estimated to equal all precipitation measured by the rain gauges from June through September 1987 plus additional precipitation during from the autumn of 1986 and spring of 1987. This additional rainfall was not measured at the watersheds but extrapolated from measurements made at Emerald Lake. For Topaz and Pear Lakes precipitation was estimated to equal Emerald Lake precipitation; at Crystal and Ruby Lakes precipitation was estimated to be half that at Emerald Lake. We felt it was reasonable to use the precipitation measurements at Emerald Lake without correction for Topaz and

Pear Lakes because of their close proximity. The correction of Emerald Lake data for Crystal and Ruby Lake was determined by comparing rainfall amounts in June 1987. During that month the western Sierran lakes (Topaz and Pear) received about twice as much precipitation as those on the eastern slope. We thought this correction was conservative, and it probably underestimates the actual precipitation at Crystal and Ruby watersheds. Precipitation which fell during May 1987 was a combination of rain and snow but was classified as rain in the water balance.

Evaporation estimates were also extrapolated from data collected at Emerald Lake during water-year 1987. This parameter was calculated by normalizing the monthly evaporation (sublimation, evapotranspiration and lake evaporation) at Emerald Lake to area (*i.e.* m^3 m^{-2} $month^{-1}$) and then multiplying this figure by the area of each watershed. The monthly evaporation estimates were then summed to determine the total evaporation for water-year 1987.

Evaporation from the Emerald watershed was distinguished as loss of water from snow, vegetation and soils, and open water (Dozier *et al.* 1989). Evaporation from open water and snow sublimation was calculated from continuous measurements of air temperature, surface-water temperature, relative humidity and windspeed. Of these physical parameters, air temperature and surface-water temperature were most similar between the four watersheds and Emerald Lake. Relative humidity and wind speed may have been comparable between Emerald Lake and the Sequoia lakes but these parameters were certainly different on the eastern slope of the Sierra Nevada. As such, we believe our estimates of lake evaporation at Topaz and Pear Lakes are probably good and not biased. However, the amount of evaporation at Crystal and Ruby Lakes has considerable uncertainty. By extrapolating from Emerald Lake we have probably underestimated both lake evaporation and snow sublimation since relative humidity is lower and windspeed probably greater on the eastern slope. Lower relative humidity and higher windspeed would increase evaporation despite slightly lower lake and air temperatures.

Evapotranspiration (ET; losses from soils and vegetation) was estimated at Emerald Lake with the Penman (1948) technique, a simplified energy balance combined with a mass-transfer term that accounts for wind movement and vapor-pressure gradient. Physical measurements for the calculation included temperature, vapor pressure, windspeed and net all-wave radiation. The fluxes from the above calculations were estimates of potential ET and required corrections for soil area, snow cover and vegetation cover and type. For a detailed explanation of these corrections see Dozier *et al.* (1989). Extrapolation of ET from

Emerald Lake to Topaz and Pear Lakes and especially Crystal and Ruby Lakes involves many sources of error. The physical parameters which drive ET, temperature, vapor pressure, windspeed and radiation may vary considerably between Emerald and the four study lakes. Moreover, the vegetation cover at these watersheds ranges from light forest (Crystal) to extensive meadows (Topaz) to primarily alpine conditions (Ruby). Thus, the degree and direction of the error in extrapolating these data are difficult to determine.

Lake Morphometry

Bathymetric maps of Pear, Topaz and Crystal Lakes were prepared from echo soundings done during August of 1987. 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 6 and 8 transects and a total of 300 to 400 individual measurements were made at each lake. The maps were drawn by hand and then digitized using a digitizing tablet and CAD software. Lake and depth contour areas were calculated using this software. The volumes of the lakes were estimated from their hypsographic curves. The map for Ruby Lake was prepared by Mark Whiting at the University of Indiana using the same techniques as described above.

Quality Control and Assurance

To ensure the quality of our chemical data, we have a rigorous and thorough QA/QC program. The program involves a variety of internal and external checks on the precision and accuracy of our data. The following is a summary of the internal checks used in each assay.

pH: Electrode calibration checks using dilute solutions of HCl (10^{-4} and 10^{-5} N).

ANC: Electrode checks as with pH. Titration checks prepared from NaOH (ANC, 30 µeq L^{-1}).

Specific Conductance: Comparison of measured conductance to theoretical conductance derived from major ion concentrations. Periodic analysis of conductivity standards.

Major Cations & Anions: Duplicate samples run at a 5% frequency in each assay session for within-run precision estimates. Known addition to sample duplicates at a 5% frequency in each assay session for within-run accuracy estimates.

In addition to the above procedures, the internal consistency of our chemical data is further checked by calculation of ionic charge balance and theoretical conductance. If measured ionic concentrations are accurate and all the major constituents measured, the sum of cations should equal the sum of anions. Furthermore, if actual conductance is the same as theoretical conductance, then our analytical protocol includes all the important ionic species and our measurements are not biased.

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 done. This material is synthetic rain-water with certified concentrations for major cations and anions. The second independent check on our chemical data is our participation in the U.S. Geological Survey's Analytical Evaluation Program. Twice yearly the USGS distributes a water sample to participants at labs and universities around the nation to be analyzed for major cations and anions. Participants return their results to the USGS who then tabulates the data. The USGS assigns a score to each lab based on how close their results come to the mean value obtain from all participants.

A summary of the results of the QA/QC procedures used in the chemical analyses is contained in Table 2. The results are based on 20 separate samples for cations and on 30 individual samples for anions. The percent agreement with the NBS control are based on 8 determinations for cations and 20 for anions. Lake and snow samples were lumped together for this exercise. Average precision for any ion was better than ± 6%, and the accuracy ranged from 99% to 117%. The precision values are the average standard error for samples analyzed in duplicate throughout each run. Values for accuracy are calculated as a percent spike recovery from known additions to natural water samples. We had good agreement with the standard reference material except for calcium, where the concentration was below our detection limit.

Figure 10 contains data on charge balance residuals and calculated conductance tests. The two samples from Pear Lake with high solute concentrations were not included in this exercise. For the lake samples, the mean charge balance ratio (cations ÷ anions) was 0.97 and charge error (cations - anions) -1.8 μeq L^{-1}. The average total charges for a sample (cation + anions) was 126 μeq L^{-1}. The histogram shows a negligible bias towards excessive negative charge. Calculated conductance *vs* measured showed no significant bias, and indicates we are measuring all the important ions. Also shown in Figure 10 are histograms of charge balance residuals for snow from 1987 and 1988. For 1987, the average charge imbalance was +3.9 μeq L^{-1} out of a total (cations + anions) of 19.2 μeq L^{-1}. The charge balances for 1988 were better; the average ratio was 1.05 and the average imbalance +0.2 μeq L^{-1} out of an average of 20.3 total charges. These data demonstrate the significant contribution of organic anions to the chemical composition of snow and rain in the Sierra Nevada (see Results below).

The results of the USGS analytical evaluation concurrent with this study are very good. For pH, specific conductance, chloride, sulfate, calcium, and magnesium our score was 4 (excellent; 0.00 to 0.50 standard deviation from the mean value) and for sodium and potassium a 3 (good; 0.51 to 1.00 standard deviation from the mean value). The scoring ranged from 0 (poor) to 4 (excellent).

Since delays between collection and analysis were unavoidable in this project, we sought to determine the chemical stability of these waters. Figures 11 and 12 are plots of the concentration of various solutes measured on two different dates. The horizontal axis is either on the day of collection or within two weeks of collection; the vertical axis is one week later or 10 months later, respectively. pH showed a change within one week of collection; values were lower. The two samples which showed pH increase were anoxic when collected. ANC showed no change after one week of storage; specific conductance increased. These samples were unfiltered. For chloride, silica, calcium, magnesium and sodium there was no change in concentration during the 10 month storage. These samples were filtered. Sulfate and potassium showed minor increases, but nitrate declined in virtually all the samples.

Based on these results we determined maximum, recommended storage times for each assay. pH and conductance should be measured within 48 hours, ANC determinations should be done within one week of collection and basic cations and major anions samples should be analyzed within two months. Since all chemical analyses performed during the present study were completed well within these limits we conclude that the small delays incurred in sample processing had no significant effect on our chemical data. Ammonium and phosphate were not included in this test because their concentrations are generally below our detection limit. These solutes are known to be capricious (Strickland and Parsons 1972) and should be determined as soon after collection as possible.

RESULTS AND INTERPRETATION

Surface Water Chemistry

For each lake, time series plots of subsurface and near-bottom chemistry (pH, ANC, specific conductance, chloride, nitrate, sulfate, calcium, magnesium, sodium, potassium, sum of basic cations, silica, ammonium, total dissolved nitrogen, total dissolved phosphorus, particulate nitrogen, phosphorus, carbon and chlorophyll *a* and dissolved aluminum and iron) and temperature and dissolved oxygen are presented to show the seasonal patterns of these constituents and the vertical differences that develop during stratification (Figures 13 through 25). These figures include a top panel which shows the yearly progression of ice cover on the lakes. Owing to the wide variation in lake chemistry, the vertical axes have different scales. Individual profiles of temperature for various seasons are presented in Figures 25 and 26 to illustrate the extent of vertical stratification found in the lakes. Dissolved oxygen profiles for both the ice-free and ice-covered season are shown in Figures 27 through 30. Time series of outflow chemistry for Pear and Ruby Lakes are presented in Figures 31 through 34; these figures also show ice-cover on lake and daily outflow discharge in a top panel. Due to the ephemeral nature of the outflows from Topaz and Crystal Lakes we did not make time series figures. Tables 3, 4 and 5 contain data on inflow chemistry in all four watersheds and outflow chemistry at Topaz and Crystal Lakes.

All four lakes were dimictic, although the extent of their mixing varied due to the wide range in depth. Topaz Lake (5 m deep) was stratified only during the winter, whereas the deeper lakes, Pear and Ruby, showed pronounced stratification in both winter and summer (Figure 19). Crystal Lake was weakly stratified during the summer and winter and thoroughly mixed in the spring and autumn.

The strength and longevity of a lakes' stratification can determine the extent of oxygen depletion and subsequent increase in ANC in the hypolimnion. Summer stratification in Pear Lake was strong with surface temperatures being more than 12 °C higher than the bottom (Figure 25). During this period of persistent stratification, oxygen depletion below about 18 m developed during the summer of 1987. Anoxic conditions persisted in the deeper portions of the lake throughout the winter and were associated with a large increase of ANC (Figure 13). Total ANC in the hypolimnion of Pear ranged from ~100 µeq L^{-1} during the summer of 1987 to a maximum of ~600 µeq L^{-1} during February 1988. During the winter of 1986-87 similar oxygen values were measured in the hypolimnion of Pear Lake but no large increase in ANC was observed (ANC, ~60 µeq L^{-1}). The difference between winters in Pear Lake suggests that deep, alpine lakes are not always completely mixed or flushed by snowmelt and that solute chemistry may not reset for several years. The ANC pattern in Pear Lake showed a carry-over from season to season which may be driven by accumulation and degradation of organic matter. Figures 22 and 23 show that concentrations of particulate C, N and P all reached peaks during February 1988. Deep water samples at this time were characterized by a strong smell of hydrogen sulfide and upon oxygenation, large amounts of iron precipitate formed.

Ruby Lake also showed depressed dissolved oxygen concentrations in both winter and summer. However, little increase in ANC was observed during these periods. Summer 1987 ANC was higher at 30 m depth (~80 µeq L^{-1}) compared to subsurface waters (~60 µeq L^{-1}), but winter ANC patterns and vertical differences was reversed. During ice-cover, the epilimnion of the lake had the same or more ANC than the anoxic hypolimnetic waters (winter 1986-87; Figure 13). This occurred despite the fact that dissolved oxygen was always lower or absent in the hypolimnion. Streamwater entering Ruby Lake often had greater ANC than lake water (see Table 3). This watershed input was contributing ANC to Ruby Lake and may explain the higher concentration of ANC just under the ice during winter periods. Groundwater or streamwater seeping into the lake during the winter months, being close to 0 °C, would tend to flow just under the ice to the outlet. Figure 31 shows that ANC peaks in the outflow during the winter of 1986-87; these lend support to the scenario.

Montane lakes like Topaz are so shallow (and transparent) that summer stratification does not occur and winter stratification is weak. Even small snowmelt volumes can flush and mix them thoroughly thereby resetting their chemistry every year. ANC patterns in Topaz Lake were regular: minima every snowmelt, maxima under ice. There were virtually no vertical differences of ANC in Topaz Lake.

Crystal Lake showed slightly depressed oxygen concentrations in the winter but was well-oxygenated top to bottom in the summer. ANC concentration were the same throughout the lake in the summer of 1987 (60-80 µeq L^{-1}). In the winters of 1986-87 and 1987-88 near-bottom values were about 25 µeq L^{-1} higher.

The other solutes generally followed patterns similar to ANC in each of the lakes. Subsurface pH, specific conductance, chloride, sulfate, silica, calcium, magnesium, potassium and ammonium all declined and reached minimum values during snowmelt and showed a gradual increase throughout the remainder of the year; maxima were recorded under ice. Sodium showed a similar pattern in Topaz Lake. In the other three lakes and the outflows of Pear and Ruby Lakes, an additional sodium peak was observed during August 1987 (Figures 17 and 33). This peak was, at first, believed to be caused by a large rain storm. However, after examining our rain gauge records we saw no events of sufficient size to explain the increases. We postulate that the sodium peak was caused by wind induced mixing of the sodium rich, hypolimnetic water with the surface waters.

Subsurface concentrations of nitrate were highest in all lakes during snowmelt (Figure 15). This pattern was also found in the outflow chemistry of Pear and Ruby Lakes

(Figure 32). Nitrate and ammonium declined to the detection limit in all lakes during the remainder of the ice-free season (Figures 15 and 21). Total dissolved phosphorus was low in the surface waters of Pear, Topaz and Ruby Lakes (Figure 20) and attained moderate concentrations in Crystal Lake.

Near-bottom concentrations of solutes generally showed lower seasonal variations (except in Topaz Lake), were higher than subsurface values and reached maxima under ice. Lowest pH was observed during periods of oxygen depression (Pear, Ruby, Crystal) or during snowmelt (Topaz). Associated with periods of anoxia were increases in ammonium and total dissolved N and P in the hypolimnia of all four lakes (Figures 20 and 21). These observations suggest that nutrient remineralization occurs in these deeper lakes and that it may be an important source of nutrients and ANC.

Chlorophyll *a* and particulate carbon, nitrogen and phosphorus concentrations (indices of biomass) are low in the surface waters of all the lakes. Time series plots of chlorophyll *a* show there was an increase in chlorophyll starting in the autumn which was associated with lake mixing (Figure 23). Vertical heterogeneity of chlorophyll was evident during the ice-free season of 1987 in both Pear and Ruby Lakes. A chlorophyll maximum in Pear Lake persisted throughout the summer at a depth of 10 meters (Figure 35). In Ruby Lake the maximum was not as persistent but was more pronounced. Associated with these chlorophyll maxima were peaks in oxygen concentration (see Figures 27 and 28).

Inflow chemistry from samples collected during the spring of 1988 was similar to subsurface lake chemistry (except at Ruby Lake). Generally, inflows had slightly less ANC (lowest values: Pear Lake, 17 μeq L^{-1}) and higher levels of nitrate. Table 6 contains data on lake-ice chemistry from Emerald, Pear and Topaz Lakes. An attempt was made to segregate slushy ice layers from harder ice lenses. The chemistry of the slush-ice is like that of the subsurface lake chemistry except that NH_4^+ is lower and acid anion concentrations greater in slush-ice. Hard-ice had a lower pH, specific conductance and ANC than slush-ice and lower ANC and NH_4^+ than subsurface-lake samples.

Precipitation

Physical parameters of the 1987 and 1988 snowpack at maximum accumulation are presented in Table 7. Included are estimates of mean density, mean depth, snow covered area (SCA), snow water equivalence (SWE) and the water volume of the snowpack. To complement our results and sampling protocols, data from the intensive snow studies at

Emerald Lake are included (Dozier et al. 1989). The density, depth and SWE data have been averaged over the entire watershed area.

In 1987 snow density was similar among the four watersheds and averaged 375 kg m^{-3}. In 1988 density was similar at Topaz, Pear and Crystal Lakes (mean, 464 kg m^{-3}) but lower at Ruby Lake (394 kg m^{-3}). Comparing these results to Emerald Lake indicates that density was higher at Emerald Lake in 1987 and generally lower in 1988. These differences were probably not analytical errors but rather a result of the timing of the snowpit sampling. At Emerald Lake, snow density was determined about 3 weeks later than at the four watersheds in 1987. This time-lag allowed the snowpack at Emerald to consolidate further and reach higher densities (Dozier et al. 1989). In 1988 the opposite occurred; the Emerald Lake snowpack was sampled about 3 weeks prior to the measurements at Topaz, Pear, Crystal and Ruby Lakes.

Differences in snow water equivalence were evident, both among watersheds and between years. In 1987 and 1988, SWE was lower at Topaz and Pear Lakes compared to Crystal and Ruby Lakes. Comparison to SWE at Emerald shows that the lakes on the eastern slope were similar but Topaz and Pear Lake had much lower deposition. The lack of agreement between SWE at Emerald and the two Sequoia lakes is troubling. Much of the discrepancy between Emerald and Topaz is probably explained by the lack of relief and southern exposure in the Topaz watershed. Furthermore, outflow discharge records (next section) reveal that snowmelt at Topaz started prior to our snow surveys, and therefore, we missed the maximum snowpack. However, the incongruity between Pear and Emerald Lakes cannot be as easily dismissed. These watersheds are adjacent and have similar altitude, relief and aspect (Table 1). As such, snow deposition should be very similar at these watersheds. Because of the steep terrain in the Pear Lake drainage, it is difficult and hazardous to reach the upper cirques of the basin. During both 1987 and 1988 we conducted snow-depth transects along south facing slopes, ignoring higher-elevation north-facing areas. Since these northern-aspect regions comprise the majority of the watershed, we must be under-estimating the average snow depth at Pear Lake and consequently the SWE.

The winter of 1987-88 deposited less water than the winter of 1986-87 at Topaz (see above) and Ruby Lakes, about the same at Crystal and Emerald Lakes and more at Pear Lake. A review of the snowfall records at Emerald Lake (Dozier et al. 1989) from 1985 through 1988 reveals that annual snowfall is quite variable and the differences between the 1987 and 1988 snowpacks are actually small.

Snowpack chemistry from both winters (1986-87, 1987-88) is presented in Table 8. These values are volume-weighted mean concentrations. Snow chemistry was very similar among watersheds and between years. pH ranged from 5.3 to 5.5. The order of ions based on concentration was also similar among the basins. The dominant cations were H^+ and NH_4^+. For anions in 1986-87 the order was: $NO_3^- > SO_4^{2-} > Cl^-$. In 1988 we began assaying for the organic anions, HCO_2^- (formate) and $CH_3CO_2^-$ (acetate), and the order changed to: $CH_3CO_2^- \geq NO_3^- > SO_4^{2-} > HCO_2^- \geq Cl^-$. In 1988 we also performed Gran titrations and found ANC absent or a slight positive acidity. Calcium was uniformly higher in 1987 compared to 1988 but, this difference is within the precision of the assay.

Using the snowpit chemistry and data from our snow depth surveys we calculated ionic loadings to the watersheds. These data are summarized in Table 9. In general, loadings were similar among lakes and between years with H^+, NH_4^+, NO_3^-, SO_4^{2-}, HCO_2^- and $CH_3CO_2^-$ comprising the majority of the deposition.

Table 10 presents monthly precipitation totals from the period June 1987 through October 1987 and during the spring of 1988. Generally, June received the most precipitation; July and August received the least. Spring (April-June) storms occurred both years and were composed of precipitation which fell as snow and rain (Dozier et al. 1989). The snow component of this precipitation is distinguished from winter snow because its chemical composition is more similar to summer rain than winter snow (Dozier et al. 1989).

There was much between lake variability in precipitation quantity. Sequoia lakes received more than twice as much non-snow precipitation as Crystal and Ruby Lakes during water year 1987. In addition, rainfall during the summer of 1987 was twice as large at Topaz Lake as at Pear Lake. These findings demonstrate the heterogeneous nature of non-snow precipitation in the Sierra Nevada both between western slope and eastern slope basins and between closely adjacent watersheds (*e.g.* Topaz and Pear).

Table 11 contains a summary of observed rainfall amounts and intensities during the summer of 1987. The largest daily total was observed in September 1987 at Topaz Lake where 2.9 cm fell in a single 24 hour period. This rain event also had the largest 15 minute total; 1.4 cm. Overall, the Topaz watershed received twice as much rain as Pear and the Ruby watershed twice as much as Crystal's.

In order to assess the impact of these summer storms on lake chemistry we examined the outflow discharge of the lakes to determine if any increases could be attributed to rainstorms. In no case did rainfall increase outflow discharge. This does not mean the lakes did not receive storm runoff but that the runoff was probably insufficient to alter lake chemistry in the manner which occurred at Emerald Lake during July 1984 (Melack et al. 1987).

Using rain chemistry supplied by ARB (California Air Resources Board 1988) we estimated ionic loading by rain at each of the watersheds (Table 12). Data for October 1986, November 1986, May 1987 were estimated from Dozier *et al.* (1989) (see Table 13). At Topaz and Pear Lakes deposition was assumed to equal that at Emerald Lake; at Crystal and Ruby deposition was estimated to be half that at Emerald Lake. The basis of these assumptions is examined in the Water Balance section of this report. Deposition was solely a function of precipitation amount on either the eastern or western slope since the same chemistry was used for Pear and Topaz and the same for Ruby and Crystal. Comparing deposition between watersheds is, therefore, useless. A more informative exercise is to compare the relative solute loading of winter snow *vs* spring rain-snow *vs* summer and autumn precipitation within an individual basin. At all four watersheds, most H^+ deposition was by winter snow followed by spring rain-snow and then by summer and autumn rain. For chloride deposition, winter snow was the major source to Crystal and Ruby Lakes and spring rain/snow was the main source to Topaz and Pear Lakes. For all other ions the major supply was spring rain/snow followed by either winter snow or summer and autumn rain. Acidic anion loading (NO_3^- and SO_4^{2-}) was 2 to 3 times higher in the summer/autumn period compared to snow at the Topaz and Pear watersheds because of the high concentration of these solutes in summer rain and autumn snow in the western Sierra Nevada. These findings suggest that non-winter loading can comprise a large proportion of the annual input of solutes to montane watersheds. Both winters included in our study had below normal precipitation.

Water Balance

Figures 36 through 39 are the rating curves from the four watersheds and an analysis of their accuracy. These plots show the relationship between outflow discharge (Q) and pressure-transducer voltage (V). Shown also are the 95% confidence limits for each of the curves and a depiction of discharge error as a function of discharge volume. For the Pear Lake outflow a log:log function ($Q = 10^{[(\log(V)-0.439)+0.131]}$) was fit to the transducer-discharge data (R^2, 0.98). Residuals for this curve are small, but it is the weakest of the four curves since it is based on only 18 points. The Topaz outflow has a rating curve based on a cubic function ($Q=[(2.72 \times 10^{-9}) \times (695(V)-878)^3]-.0046$; $R^2= 0.97$); the log:log fit yielded large residuals at high discharge and the fit was not as good. The Ruby outflow rating curve is founded on 61 calibration points ($Q=10^{[(\log(V)-0.157)+0.055]}$), and it is based on a log:log fit

(R^2, 0.97). The rating curve for the Crystal Lake outflow is also a log:log fit of the data ($Q=10^{[(\log(V)-0.627)+0.106]}$; R2, 0.96; n = 44). The residuals for this curve are small and balance one another well at high discharges.

Using these rating curves, the transducer voltages from the stream micro-transducer records were converted to discharges. Figures 40 and 41 are the 21-month hydrographs for the four watersheds. For the western Sierran watersheds, peak daily discharges during the 1987 snowmelt season were similar at Pear and Topaz Lakes (~22,000 m^3), but outflow from Pear Lake stayed consistently higher (Figure 42). In 1988 peak daily discharge during snowmelt was highest at Topaz (~21,000 m^3).

The Ruby and Crystal Lakes' hydrographs were different from those at Pear and Topaz Lakes. The majority of the Ruby watershed lies well above that of Crystal, and given its large size and northern aspect, the snowpack started melting later (Figure 43). Moreover, snowmelt lasted almost 3 months longer. Peak daily discharge at Ruby Lake (~35,000 m^3) was more than twice that at Crystal Lake (~16,000 m^3). An important difference between the hydrographs is the large variability of Crystal's compared to the smooth rise and fall of Ruby's.

There was one clear similarity among the hydrographs at Topaz, Pear, Crystal and Ruby Lakes. A large decrease in outflow discharge was observed in all four watersheds during the latter part of May 1987 and early part of June. This decline was associated with a late spring snowstorm and cold weather. The decline at Pear Lake occurred about one week later than the other lakes for unknown reasons.

Table 14 contains a summary of monthly discharge for snowmelt and the whole study period for each of the watersheds. Peak monthly discharge in 1987 was in June at Pear and Ruby Lakes and in May in the outflows from Topaz and Crystal Lakes. The melt at Ruby Lake lasted through October, through August at Pear and Crystal and through June at Topaz.

Table 15 contains a summary of the water balance for water-year 1987 at Topaz, Pear, Crystal and Ruby Lakes. Precipitation which fell in May 1987 as a combination of rain and snow was classified as rain in the water balance. At all four watersheds the major input was winter snow, comprising on average 64% of the precipitation at the Sequoia lakes and 87% of precipitation at the eastern-slope lakes. The water balances show that evaporation is an important loss in the water budget. Evaporation from lake surfaces, snow sublimation and evapotranspiration accounts for 21% of all inputs to Topaz Lake, 28% of inputs to Pear Lake, 24% of inputs to Crystal Lake and 20% of the inputs to Ruby Lake. Given the degree of uncertainty in the individual components, closure of the water balance was impossible. The residual term in the water budget integrates changes in basin water-storage and the sum of all errors in the water balance. In these lakes, changes in water storage is probably small (Dozier et al. 1989), thus the majority of the residual term represents error. The residual term equaled about 23% of the inputs to Topaz and Crystal Lake, 12% of inputs at Ruby Lake and 74% of inputs at Pear Lake. At three of the four lakes (Topaz, Crystal and Ruby) the residual component of the water balance was negative, indicating that inputs to the basins exceeded losses. At Pear Lake the residual was positive indicating that losses greatly exceeded inputs. This large positive residual and a comparison of snow water equivalence between Emerald and Pear Lakes (see Table 7 and Precipitation section) strongly suggests that snow deposition at Pear Lake was underestimated. If SWE calculated at Emerald Lake is applied to the Pear Lake watershed, the snow term in the budget increases to 813,000 m^3, the residual becomes +245,000 m^3 and the residual now comprises +32% of measured inputs. The residual is still positive which suggest, we are over estimating losses from the catchment assuming changes in water storage are small or that there is a significant groundwater supply to Pear Lake.

Another approach to estimating the error in the water balances is to combine the errors in the individual components. The procedure used here is identical to that used by Dozier et al. (1989). Estimated error bounds for each parameter were multiplied by the volume of the parameter during the water-year. The total error was calculated as the square root of the sum of squared errors. Table 16 contains the proportional error bounds (from Dozier et al. 1989), the absolute error bounds for each component and the total error in the water balances at the four watersheds. Proportionally, the largest error term in the water balance was evaporation followed by uncertainties in outflow discharge, rain deposition and snow deposition. In absolute terms, the largest source of error was in estimating outflow discharge, followed by uncertainties in evaporation estimates and then precipitation deposition. Total error as a percent of measured precipitation was about 18% at Topaz, Crystal and Ruby Lakes and 33% of inputs at Pear Lake. For comparison, the estimated uncertainty in the water balance for the same period at Emerald Lake was 12 to 18 percent of the year's precipitation.

Watershed Mass Balance

Table 17 contains data on mass balance calculations for the four watersheds. The table includes estimates of wet atmospheric loading of solutes and the watershed flux or consumption of those solutes. In this exercise watershed yield is defined as:

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

where Output equals the mass flux in the outflow of each lake and Input equals the sum of snow and rain ionic 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. A negative yield may be taken to mean that the ion of question was retained in the watershed by some biogeochemical process; a positive yield that the ion was produced by some biogeochemical process. 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 than 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. The snowmelt sample-chemistry would be extrapolated back to the beginning of melt. If there was an additional sample made at the end of snowmelt, the mid-snowmelt sample would be extrapolated to a date halfway to the late-snowmelt sample. Likewise, the late-snowmelt chemistry would be extrapolated backwards to this midpoint date.

The mass balance indicates that the annual yield of ANC produced in the Topaz and Pear watersheds is one to two times current H^+ deposition. The Crystal and Ruby Lake watersheds are yielding from 4 to 5 times more ANC than current H^+ deposition. These values are on an annual basis and may not be indicative of the status of the watershed at all times of the year. Additionally, these estimates integrate all the errors involved in the water balance and solute chemistry and are based on low sampling frequency of the outflows. These errors are discussed further, later in this section.

Another important finding in the mass balance is that at Crystal and Ruby Lakes, the yield of basic cations (calcium, magnesium, sodium and potassium) approximately equals the yield of ANC. This coupling of ANC and basic cations suggests that mineral weathering is mainly responsible for the ANC of the outflow waters at these lakes. For Topaz and especially Pear Lake, the yield of basic cations is less than the yield of ANC. This suggests that some other process than mineral weathering is a major source of ANC to these lakes. Based on lake chemistry, possible sources of ANC to Pear Lake could include reduction of iron, sulfur and nitrogen in the anoxic hypolimnion. Surprisingly, the yield of basic cations from Pear watershed is negative which indicates that the output of these cations from the basin is less than the input by precipitation. Possible explanations for the apparent retention of basic cations could include large groundwater inputs of solute rich water or the precipitation of these ions in the lake. During mixing events, large volumes of anoxic-hypolimnetic waters become oxygenated forming precipitates of iron thereby liberating OH^-.

Complexes are then formed with the liberated OH^- and the basic cations. Possible complexes could include $Ca(OH)_2$, $Mg(OH)_2$ and other hydroxide compounds. These solid complexes then sink, and are lost to the sediments.

The four watersheds effectively take up inputs of ammonium and nitrate. More than 95% of the ammonium loading and from 80% (Ruby Lake) to 100% (Crystal Lake) of the nitrate loading is consumed within the catchments. The chloride and sulfate mass balances also indicate a net loss to the basins but to lesser extent than ammonium, nitrate or H^+.

In order to interpret the results of the mass balance, the amount and nature of the uncertainty inherent in the calculation must be understood. This uncertainty integrates the errors of all the separate components. These include errors in estimating precipitation loading (snow + rain), in measuring outflow discharge and the large uncertainty involved in assigning chemistry to outflow discharge. The error involved in quantifying the inputs to the mass balance are probably only slightly larger than those in Table 16 except at Pear Lake. At Pear, the deposition of solutes by snow may be underestimated by as much as 40% due to inaccuracies in snow water equivalence measurements (see Water Balance section). At the other three watersheds, the error in precipitation loading is at most ± 20%. Moreover, dry deposition is largely ignored in the mass balance. Our snowpack sampling probably integrates any dry deposition which occurred during the winter, but summer dryfall is not estimated. These observations lead us to believe our estimates of ionic loadings are slightly lower than actual deposition at Topaz, Crystal and Ruby Lakes and much lower than actual loading at Pear Lake.

Outflow discharge errors are probably of the same magnitude as those for precipitation, ± 20%. However, assigning error bounds to the outflow mass-transfer is more difficult. Of primary concern is assigning chemistry to the outflow volume during snowmelt. Most of the water which enters the catchments is lost during the 4-5 month snowmelt period. Hence, outflow chemistry should be sampled frequently during this period. Due to logistical constraints, however, few samples were collected during snowmelt.

Analysis of outflow discharge and ANC at Emerald Lake during water year 1987 allowed us to assess the direction of the error introduced by the coarse sampling regime. Figure 44 contains time series plots of outflow discharge and ANC during the snowmelt period of water year 1987 (April through July). The general pattern that emerges is that the rise of the hydrograph is characterized by relatively high ANC, followed by low ANC during peak flows, followed by intermediate values during the fall of the hydrograph. The one major exception to the pattern is the sharp decline and recovery of ANC at the onset of melt. Using this pattern and outflow ANC data from 1988, we assessed the direction of the ANC flux error in the mass balances at the four watersheds.

At Topaz and Pear Lakes, the outflows were sampled three times during the snowmelt period of 1987 (see Figure 42). These samples were evenly spaced and should provide a reasonable estimate of ANC yield. At Crystal Lake one sample was collected at the onset of melt and one at the end of snowmelt, and none at peak discharge (*i.e.* low ANC). Therefore the ANC concentrations assigned to discharge during peak run-off were probably too high. Further evidence for this bias comes from comparing outflow ANC during the snowmelt periods of 1987 and 1988 (Table 5). In 1987 the minimum ANC in the outflow reached 67 µeq L^{-1} but in 1988 the minimum was lower, 57 µeq L^{-1}. During the snowmelt period of 1988 the outflow was sample more frequently and included samples during the peak of the melt hydrograph. Based on these observations, the actual ANC yield at Crystal Lake for water-year 1987 was less than our estimated yield.

At Ruby Lake, two chemistry samples were collected; one before peak discharge and one on the falling limb of the hydrograph. Neither of these samples accurately represented the low-ANC portion of the idealized hydrograph. Comparing ANC data from the snowmelt period of 1987 and 1988 (five samples) shows that ANC dropped as low as 33 µeq L^{-1} in 1988 but the minimum during 1987 was higher 53 µeq L^{-1}. Based on these observations, it is very probable that watershed yield estimates at Ruby Lake are overestimated.

Table 18 shows the ratio of catchment yield of ANC to H^+ loading as calculated in the mass balance and by assuming various errors for the input/output biases. The first scenario assumes that watershed ANC yield was overestimated by 20% or that H^+ loading was underestimated by 20%. The second scenario assumes that ANC yield was overestimated by 40% or H^+ loading underestimated by 40%. These scenarios assume that the errors in the mass balances are biased towards overestimates of ANC output and underestimates of acid loading. The most likely ratio of ANC yield to H^+ loading at Topaz Lake is the one calculated directly from the mass balance. No significant bias could be reasonably assumed in either ANC yield or acid deposition at this watershed. At the Pear Lake watershed, output of ANC had no bias but H^+ loading was underestimated by at least 40%. Therefore, the most likely scenario would be where ANC yield equals H+ loading. The mass balances for the Crystal and Ruby watersheds have no discernable bias in H^+ loading, but ANC flux from the outflows is probably overestimated because of infrequent sampling during snowmelt. The most likely ratio of ANC yield to H+ loading at these catchments is 4.3 at Crystal and 5.1 at Ruby.

DISCUSSION

Importance of In-Lake Processes

Recently there has been debate on the nature of ANC production in alpine lakes of the Sierra Nevada. In 1987 Stoddard published a paper on ANC dynamics in Gem Lake, an alpine lake located in the eastern Sierra Nevada near Ruby Lake (see Stoddard 1987). In his year-round study, Stoddard found that ANC in Gem Lake resulted primarily from mineral weathering within its watershed. ANC increased in the bottom-waters during ice-cover and the increase was attributed to inputs from groundwater. He concluded that in-lake processes (via bacterial mediated reduction reactions) were insignificant in the ANC dynamics of the lake. He suggested that Sierran lakes may be fundamentally different in terms of ANC sources from those in the Experimental Lakes Area (ELA) of Canada (Stoddard 1988). ELA researchers have since replied to this assertion (see Kelly 1988 and Schindler 1988). They suggest that in-lake generation of ANC is present in all lakes, and the reason it was not found in Gem Lake was because of the high hydraulic turnover rate of the lake. They assert that the ratio of watershed area to lake volume is the major determinant of the relative importance of in-lake ANC production vs mineral weathering. Results from our study are relevant to this debate.

In 1987, Topaz Lake was flushed over ten times (annual residence time, 34 days), Crystal Lake almost twice (annual residence time, 187 days) , Ruby Lake about once (annual residence time, 319 days) and Pear about 1.5 times (annual residence time, 241 days). Overall, Topaz Lake had the shortest residence time and, consistent with Schindler and Kelly's suggestion, the lake appears to generate little ANC during anytime of the year (see Figure 13). Similarly, Crystal Lake, with a residence time of about 6 months, shows only slight ANC increase during periods when the lake is not receiving inflow waters (see Figure 13; winters periods). This flux is probably not large in comparison to the annual input of ANC from the watershed.

Residence time fails to explain the observed patterns in some deeper lakes. Both Pear and Ruby Lakes have similar patterns of oxygen and temperature stratification and have similar residence times, but, the sources of ANC supply to the lakes appear to be different. ANC in Ruby Lake appears to be derived largely from mineral weathering within the watershed. We base this conclusion on the lack of ANC buildup in the hypolimnion despite the persistent state of anoxia (see Figures 19 and 28). Moreover, ANC at a depth of one meter is higher during winter because of high ANC streamwater entering the lake. Also, the mass balance for this watershed demonstrates a close coupling of ANC and basic cations; basic cation yield was equal to 91% of ANC yield. In Pear Lake, large accumulations of ANC do occur in the anoxic hypolimnion. This buildup is associated with reduction of iron, sulfur and probably nitrogen (see Figures 13, 15 and 24). Much of this ANC was not permanent (NH_4^+, 400 μM), but the net increase of carbonate alkalinity was still on the order of 250 μeq L^{-1}. In addition, the solute mass balance for this watershed (Table 17) shows that basic cation yield is low and unassociated with ANC yield. Clearly in-lake processes are an important source of ANC to Pear Lake and something other than the watershed area to lake volume ratio is determining the ANC dynamics. Furthermore, Stoddard's assertion of mineral weathering as the primary source for ANC in Sierran lakes must be qualified in light of the absence of basic cation yield from the Pear Lake basin.

We propose that factors such as plankton biomass and annual mean temperature, along with lake turnover time may determine the relative importance of in situ ANC generation and watershed weathering. Based on data from Pear Lake, large accumulations of ANC were associated with high concentrations of particulate carbon and nitrogen. Plankton biomass probably contributed most of this material. This detritus provided an abundant substrate for bacterial reduction and temperature controls the rate of these reactions. Lake productivity and temperature may explain the differences in ANC production at Ruby and Pear Lakes. Pear Lake remains consistently warmer than Ruby Lake and has higher concentrations of chlorophyll and particulate carbon, nitrogen and phosphorus (see Figures 19, 22 and 23).

It is clear that there is variation among lakes in the Sierra Nevada and that predicting the relative importance of ANC supply from catchment and in-lake sources is difficult. Projections based on simple morphological characteristics are unsuccessful. Not only are there between lake differences but, interannual variation within a single lake can be great. Furthermore, ignoring in situ processes because of their relatively minor role in the yearly ANC cycle fails to recognize their importance in protecting the lakes from acidification during intense summer rainstorms (see Melack et al. 1987) or from a snowmelt, acid pulse.

In-lake processes may also make the lakes more susceptible to anthropogenically induced acidification. An example is the possible impact of a large hypolimnetic ammonium and sulfide-pools on lake chemistry during mixing events. Prior to spring turnover at Pear Lake, ammonium concentrations are as high as 400 μM in a hypolimnion and large amounts of hydrogen-sulfide are present. When these waters are oxygenated during spring mixing several chemical reactions may occur. NH_4^+ is converted to NO_3^- and H_2S converted to SO_4^{2-} thereby liberating hydrogen ion and lowering pH. This supply of H^+ occurs when the lake is being rapidly flushed by snowmelt and could further depress lake pH.

Sensitivity of Sierran Lakes to Acidification

Lake sensitivity to acidification can be estimated in several ways. One way would be to measure the acid neutralizing capacity of the lakewater. Another approach would employ measuring the deposition or load of acidic components to the lake. The mass balance approach of estimating sensitivity used in this study integrates many different measures of acid-susceptibility. Mass balance calculations for the four lakes indicate that their watersheds and lakes are, on an annual basis, producing sufficient ANC to neutralize current wet deposition of H^+. However, reserves of ANC are small or absent. These calculations indicate that watersheds in the western Sierra Nevada may produce less ANC per hectare than those in the eastern Sierra. The numbers show that if H^+ deposition were to double, the buffering capacity within both Topaz and Pear watersheds could be exceeded. Crystal and Ruby Lake appear to be less sensitive and presently produce about five times more ANC than current H^+ loading.

Data from the four watersheds show that hydrogen and ammonium ion deposition from spring/summer/fall precipitation can be greater than deposition by winter snow. This non-winter deposition is more variable and is generally greater in the western Sierra Nevada. Snow deposition was similar in composition and amount, both among watersheds and between winters. Implications of these deposition patterns, observations of ANC dynamics and mass balance calculations, in terms of lake sensitivity to acidification, are as follows:

1. Lakes in the western Sierra Nevada may be at higher risk of acidification, compared to eastern Sierran lakes, because of greater deposition of acid and the lower yield of ANC in these watersheds.

2. In general, lakes along the western slope of the Sierra Nevada are at greater risk to episodic acidification than east slope lakes because of higher rates of H^+ deposition during ice-free periods.

3. Lakes with little *in situ* production of ANC may be at higher risk from summer/autumn, episodic acidification than lakes with large *in situ* ANC production.

4. Lakes with small ratios of watershed area-to-lake volume are more resistant to snowmelt-induced declines in ANC or those caused by large rain events. Because much of the ANC decline caused by snowmelt or rain-events is due to dilution, lakes with greater volumes will be more resistant to chemical changes.

5. The risk of episodic lake acidification may partially depend on the altitude of the watershed. This is because lakes at higher altitudes receive greater amounts of rain and the proportion of soils in the catchments is generally smaller (Melack et al. 1985).

While not presently acidified, the four study lakes are susceptible to this process. The portion of the year when this sensitivity is greatest is when the lakes are diluted by snowmelt runoff. Because of considerable year-to-year variation of lake chemistry (see also Melack et al. 1989), long-term monitoring of solute deposition and surface-water chemistry is needed to determine if the lakes are undergoing change. State-wide surveys of lake chemistry are of limited value in assessing the status of California's montane lakes. Previous studies (Melack et al. 1985, Melack and Setaro 1986, EPA 1987) have already identified sensitive habitats. Our goal now should be intensive, long-term monitoring of a variety of sensitive habitats. Additional research on episodic acidification (in particular snowmelt) and in-lake processes is necessary in order to fully understand and assess the susceptibility of these lakes to water quality degradation.

Comparisons to Emerald Lake

One of the purposes of this study was to collect data with which to judge the representiveness and generality of the intensive, Emerald Lake study. What follows will be a comparison between some of the features of Topaz, Pear, Crystal and Ruby Lakes and Emerald Lake along with some ramifications of their similarities and differences.

Seasonal patterns of surface-lake chemistry were similar between the four watersheds and Emerald Lake. The near-surface portions of all lakes had decreases in solute concentration during spring runoff and gradual increases through the remainder of the year. Table 18 contains data on subsurface chemistry during ice-free periods for the four study lakes, Emerald Lake and two surveys of lakes in the Sierra Nevada (Melack *et al.* 1985, Landers *et al.* 1987). There is much similarity in the data for Topaz, Pear, Crystal and Ruby Lakes and Emerald Lake. Certain solutes such as chloride and sulfate along with pH have similar concentrations. Others, like ANC, nitrate and the basic cations are more variable. ANC especially, shows some differences. Pear Lake has the lowest median ANC (22 μeq L^-

^{1}) closely followed Emerald Lake (27 μeq L^{-1}) and Topaz Lake (27 μeq L^{-1}). Median ANC in Crystal and Ruby Lakes is greater (70 μeq L^{-1} and 56 μeq L^{-1} respectively). Lakes in Sequoia are chemically more similar to one-another than to the lakes on the eastern slope. The same is true of the Crystal and Ruby Lakes. Examining the ratio of watershed yield of ANC to H^+ loading at the study lakes and Emerald Lake we see the same pattern emerge (Table 18). Using these ratios as an index of sensitivity to acidification, we see that the Sequoia lakes are more similar to one-another and more at risk than the eastern slope lakes. One could conclude, given the similarities in solute chemistry and mass balances of the Sequoia lakes, that geography and geology determine the generality of Emerald Lake. As evidenced in Table 19, Emerald and the study lakes represent a good cross-section of Sierra Nevada lakes. Quartile values in Melack's survey generally bracket the median values found at the above lakes. The same is true when comparing to data from the EPA's lake survey.

Dissimilarities between the study lakes and Emerald become evident when examining in-lake processes. During winter stratification, large ANC accumulation occurs in some lakes (*e.g.* Pear), moderate amounts in others (Emerald and Crystal) and appear to negligible in the rest (Topaz and Ruby). Temperature and oxygen stratification may explain some of these differences, but it is probable that bacterial processes, primary production and respiration vary widely between the lakes. Furthermore, these in-lake processes may alter the annual mass balance of solutes in these some watersheds. Assessment of lake sensitivity becomes more complicated than merely looking at deposition rates and surface-water ANC. Year-round study of a broad range of lake types is needed to adequately understand the susceptibility of Sierran lakes to acid deposition.

Assessment of Monitoring Program

Our primary objective in this study was to characterize the year-round sensitivity of California's montane lakes to acid deposition. Inasmuch as ANC determines this susceptibility we believe we have succeeded. Our sampling frequency and protocol allowed us to identify the periods of the year when ANC accumulates in these lakes (summer and winter stratified periods) and when it can be depleted (snowmelt). Our determinations of the water balance in the basins were fairly accurate and we were able to identify the major errors in the measurements. Other successes include quantifying the amount of deposition reaching the watersheds in various seasons and in identifying organic acids as major components of this deposition. Coupling our deposition monitoring with measures of outflow chemistry and discharge allowed us to calculate a mass balance for each watershed. This exercise integrated many different indices of lake sensitivity and allowed us to judge the current status of the lakes in terms of both current surface-water chemistry and current (and future) H^+ loading.

Furthermore, the mass balance was a tool that allowed us to evaluate the importance of in-lake processes in controlling lake chemistry.

Table 1. Summary of basin and lake characteristics for the present study and selected montane lakes of the Sierra Nevada, California. Data for Emerald Lake are from Melack *et al.* (1989). Data for Gem are from Stoddard (1987). Data for Eastern Brook Lakes are from Nodvin (1988).

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)
Topaz	142	244	5.2	3,219	5	1.4	74,000
Pear	136	471	8.0	2,904	27	7.3	578,000
Crystal	129	293	5.0	2,951	14	6.5	320,000
Ruby	424	754	12.6	3,426	35	17.1	2,156,000
Emerald	120	616	2.7	2,800	10	5.9	160,000
Gem	123	775	2.8	3,341	6	3.4	95,000
Eastern Brook	225	575	4.7	3,146	9	4.0	186,000

Table 2. Summary of quality assurance data for chemical analyses of lake and snow samples. The precision and accuracy data for cations are based on 20 individual determinations; for anions 30 individual determinations. Eight duplicate assays of the NBS standard reference material (SRM) were performed for cations and 20 for anions. The units for SRM concentration are μeq L^{-1}.

Element	Average Precision	Average Accuracy	Agreement NBS Control	NBS Reference Material Concentration
Calcium	4.4 %	99 %	74 %	0.7
Magnesium	1.3 %	103 %	96 %	2.0
Sodium	1.1 %	117 %	93 %	8.9
Potassium	4.8 %	110 %	84 %	1.3
Chloride	5.8 %	106 %	90 %	1.9
Nitrate	1.2 %	101 %	99 %	7.6
Sulfate	1.7 %	103 %	97 %	15.1

Table 3. Inflow chemistry for Pear and Ruby Lakes. Units are µM for SiO_4, µSiemens cm^{-1} for COND (specific conductance) and µeq L^{-1} for all others.

Lake Inflow (Date)	pH	ANC	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	SiO_4	COND
Pear Lake												
Main												
9-Jul-87	6.3	29	0.0	2.1	1.1	3.4	11	2.7	15.3	2.0	32	3.3
29-Mar-88	6.3	21	0.0	2.4	2.5	5.7	13	2.3	10.0	3.0	35	4.4
8-Jun-88	5.9	17	0.9	1.3	1.1	3.1	8	1.5	5.7	0.8	13	2.4
Ruby Lake												
Main												
24-May-88	6.2	32	0.1	2.8	14.4	12.6	37	4.0	9.4	4.3	42	7.5
4-Jun-88	6.1	32	0.2	2.2	16.4	10.0	34	2.9	8.8	3.9	39	7.3
10-Jun-88	6.2	19	0.1	2.7	17.8	10.6	35	3.3	9.8	3.8	42	7.7
10-Jul-88	6.5	41	1.5	3.3	4.0	8.4	37	2.5	9.3	3.8	30	7.3
Mono Pass												
8-Apr-88	7.2	153	0.3	2.8	6.1	6.6	108	6.0	33.7	7.6	90	16.5
24-May-88	6.7	106	0.1	3.5	10.6	5.7	89	2.7	20.4	4.2	71	13.6
4-Jun-88	6.8	96	0.2	3.1	10.8	5.9	87	2.7	20.7	4.3	71	13.5
10-Jun-88	7.0	135	0.1	2.5	8.4	7.1	107	5.3	34.9	7.6	106	16.8
Cirque												
24-May-88	6.5	46	0.0	2.8	15.0	7.1	51	3.2	9.6	4.5	41	8.8
4-Jun-88	6.2	54	0.5	2.5	6.4	7.1	42	2.9	10.0	5.9	37	8.4
10-Jun-88	6.2	45	0.0	2.6	14.3	6.9	45	2.5	9.5	3.8	41	8.0

Table 4. Inflow chemistry for Topaz and Crystal Lakes. Units are μM for SiO_4, μSiemens cm^{-1} for COND (specific conductance) and μeq L^{-1} for all others.

Lake Inflow (Date)	pH	ANC	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	SiO_4	COND
Topaz Lake												
Main												
5-Jun-87	6.4	44	0.3	1.3	0.1	4.3	35	3.8	9.2	2.8	39	5.9
8-Mar-88	6.0	81	0.7	4.3	1.8	8.2	63	6.8	21.8	4.1	64	10.5
29-Mar-88	6.4	62	0.0	4.3	4.8	7.4	54	5.6	15.8	4.7	56	8.8
9-Jun-88	6.4	50	0.4	2.3	0.5	6.1	31	3.1	12.7	3.2	50	5.8
Crystal Lake												
Main												
11-Oct-86	6.3	67	0.2	3.8	0.1	8.3	36	11.0	24.9	6.9	98	7.6
25-May-88	6.2	46	0.1	3.5	1.1	7.7	25	6.0	15.5	5.6	80	6.1
4-Jun-88	6.1	43	0.1	4.0	0.8	7.3	22	5.3	17.3	5.2	77	6.0
10-Jun-88	6.1	36	0.2	3.1	1.1	7.8	22	5.9	18.1	4.7	86	6.5
9-Jul-88	6.6	61	0.5	2.8	0.6	6.3	31	11.7	19.5	6.6	66	8.1
Inflow #1												
25-May-88	6.6	77	0.1	2.8	11.3	5.1	41	12.0	24.8	8.2	118	10.1
4-Jun-88	6.2	32	0.1	4.3	1.6	7.4	21	5.3	15.2	5.0	77	5.3
10-Jun-88	6.2	89	0.3	3.6	0.4	6.3	41	15.5	26.1	7.6	91	10.4
Inflow #2												
25-May-88	5.9	42	0.4	4.9	0.1	8.5	18	6.0	18.0	5.1	87	7.5
4-Jun-88	6.2	67	0.1	2.8	6.0	8.1	38	13.4	21.7	8.2	101	9.9
10-Jun-88	6.2	64	0.2	4.8	7.4	6.9	45	13.3	21.9	7.0	103	10.9

Table 5. Outflow chemistry for Topaz and Crystal Lakes. Units are μM for SiO_4, μSiemens cm^{-1} for COND (specific conductance) and μeq L^{-1} for all others.

Lake (Date)	pH	ANC	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	SiO_4	COND
Topaz Lake												
16-Dec-86	6.5	42	0.2	4.9	13.0	6.1	50	5.2	15.2	3.1	35	7.8
1-Apr-87	6.5	51	0.1	3.7	1.9	5.6	48	5.2	12.7	5.0	27	7.4
5-May-87	5.9	31	0.0	3.1	3.1	7.7	30	4.6	10.0	2.8	23	5.6
5-Jun-87	6.4	30	0.7	1.3	1.2	4.0	25	3.5	7.4	3.1	23	4.7
8-Mar-88	6.0	76	0.1	6.2	2.4	7.5	49	6.3	19.7	7.6	52	9.5
29-Mar-88	6.2	60	0.0	4.5	4.2	6.9	41	6.5	16.5	5.4	51	8.0
9-Jun-88	6.2	29	0.3	2.2	0.3	4.2	20	2.8	9.7	3.1	28	4.7
Crystal Lake												
11-Oct-86	6.5	71	0.1	2.4	0.1	7.1	36	11.0	19.7	5.9	62	10.1
19-Jun-87	6.5	67	0.3	1.9	0.1	6.2	33	11.0	20.8	6.5	56	8.8
25-May-88	5.9	61	0.3	3.9	0.2	10.7	41	10.5	19.2	6.6	81	10.5
4-Jun-88	6.5	57	0.4	3.0	0.7	6.4	33	12.9	19.7	7.2	58	9.0
10-Jun-88	6.2	98	0.6	4.7	1.3	8.1	49	17.2	32.5	9.1	90	12.7
9-Jul-88	6.6	60	0.3	2.9	0.6	6.2	31	11.4	19.5	6.7	66	8.8

Table 6. Lake-ice chemistry for Emerald (EML), Pear and Topaz Lakes. Subsurface lake chemistry is presented for comparison. Units are μSiemens cm^{-1} for COND (specific conductance) and μeq L^{-1} for all others. Slush ice is composed of liquid water and ice crystals; hard ice is composed of solid ice only.

Type (Date)	Lake	pH	ANC	NH_4	Cl	NO_3	SO_4	COND
Slush								
9-Mar-88	EML	5.7	24	0.2	6.5	7.4	11.2	9.5
9-Mar-88	EML	6.0	38	0.2	6.8	5.7	8.1	9.5
9-Mar-88	EML	6.0	42	0.3	8.2	7.7	12.5	9.5
29-Mar-88	Pear	6.3	27	0.9	5.3	4.6	5.7	8.0
Hard Ice								
9-Mar-88	EML	5.8	21	0.3	3.2	2.1	3.1	6.7
9-Mar-88	EML	5.8	19	0.3	3.2	1.7	3.0	2.9
29-Mar-88	Topaz	6.0	13	0.8	3.6	1.0	3.0	3.1
Lake-Subsurface								
9-Mar-88	EML	5.7	37	2.8	4.4	3.9	7.7	5.6
29-Mar-88	Pear	6.2	29	1.0	3.5	5.3	6.3	5.6
29-Mar-88	Topaz	5.9	59	2.9	4.2	1.7	7.5	6.4

Table 7. Summary of snowpack characteristics for Topaz, Pear, Crystal, Ruby and Emerald watersheds during maximum accumulation in 1987 and 1988. Data for Topaz and Pear Lakes were collected from 1-3 April 1987 and 29-30 March 1988. The sampling dates for Crystal and Ruby Lakes were 7-8 April 1987 and 8-9 April 1988. 1987 snowpack data at Emerald Lake were collected 18 April 1987 and in 1988 during 20-23 March. Data for Emerald Lake are from Dozier *et al.* (1987) and Dozier *et al.* (1989). The units for snow water equivalence (SWE) and mean depth are centimeters. Snow density units are kg m^{-3}. SCA % is the percent of each watershed covered with snow. The values for snow depth and SWE have been averaged over the entire watershed area. The units for water volume are m^3.

1987	*Emerald*	*Topaz*	*Pear*	*Crystal*	*Ruby*
Mean Density	427	373	368	386	372
Mean Depth	140	120	98	142	166
SCA %	~90%	80%	77%	85%	77%
SWE	60	45	36	55	62
Water Volume	718,000	636,000	491,000	707,000	2,630,000

1988	*Emerald*	*Topaz*	*Pear*	*Crystal*	*Ruby*
Mean Density	411	467	443	481	394
Mean Depth	153	71	93	116	135
SCA %	~90%	80%	77%	85%	78%
SWE	63	33	41	56	53
Water Volume	756,000	469,000	563,000	720,000	2,260,000

Table 8. Snowpit, volume-weighted mean chemistry during maximum accumulation in 1987 and 1988. All units are μeq L^{-1}. ND = not determined.

1987

Lake	pH	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	HCO_2	CH_3CO_2
Topaz	5.3	2.1	1.0	3.6	2.3	2.1	0.3	1.2	0.1	ND	ND
Pear	5.3	2.5	1.0	3.6	2.6	2.0	0.4	1.7	0.3	ND	ND
Crystal	5.4	2.3	1.0	2.8	1.9	2.1	0.5	1.2	0.9	ND	ND
Ruby	5.3	0.9	1.8	3.0	2.0	2.1	0.5	1.9	0.5	ND	ND

1988

Lake	pH	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	HCO_2	CH_3CO_2
Topaz	5.5	1.8	1.6	1.9	1.6	0.9	0.3	1.5	0.9	0.7	2.1
Pear	5.5	2.4	0.9	1.5	0.8	0.6	0.2	0.7	0.2	1.6	2.1
Crystal	5.4	5.2	1.7	3.5	2.2	0.9	0.4	1.3	0.7	1.6	3.7
Ruby	5.4	3.5	1.5	2.7	2.7	0.8	0.3	1.3	0.5	1.4	2.8

Table 9. Ionic loading during the winters of 1986-87 and 1987-88. All units are meq m^{-2}. ND = not determined.

1986-87

Lake	H	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	HCO_2	CH_3CO_2
Topaz	3.1	1.1	0.6	2.0	1.4	1.1	0.2	0.7	0.1	ND	ND
Pear	2.2	1.2	0.5	1.7	1.3	0.9	0.2	0.8	0.1	ND	ND
Crystal	2.9	1.5	0.6	1.9	1.2	1.4	0.2	0.7	0.5	ND	ND
Ruby	3.7	0.7	1.5	2.4	1.6	1.7	0.4	1.6	0.4	ND	ND

1987-88

Lake	H	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K	HCO_2	CH_3CO_2
Topaz	1.3	0.8	0.7	0.8	0.7	0.3	0.1	0.6	0.3	0.3	0.9
Pear	1.9	1.3	0.5	0.8	0.5	0.4	0.1	0.4	0.1	0.8	1.1
Crystal	2.8	3.4	1.1	2.3	1.5	0.6	0.3	0.9	0.5	0.9	2.3
Ruby	2.9	2.5	1.0	1.8	1.9	0.6	0.2	0.9	0.3	0.9	1.8

Table 10. Monthly precipitation for Topaz, Pear, Crystal and Ruby Lakes during the period June through October 1987 and April through June 1988. All units are centimeters. ND = not determined. Precipitation which fell during April and May 1988 was a combination of snow and rain.

Month	*Topaz*	*Pear*	*Crystal*	*Ruby*
Jun/87	4.4	2.3	1.4	1.8
Jul/87	2.9	1.0	0.0	0.7
Aug/87	0.9	1.2	0.2	0.1
Sep/87	5.6	2.6	0.1	1.3
Oct/87	0.0	trace	0.0	trace
Apr/88	1.6	5.3	ND	ND
May/88	1.6	3.4	ND	ND
Jun/88	1.3	ND	2.6	ND

Table 11. Rain summary; June through October 1987. All units are centimeters.

Lake	Largest 15 Min. Total	Largest Daily Total	Total Jun-Oct
Topaz	1.5	3.2	13.8
Pear	0.6	2.3	7.2
Crystal	0.4	1.3	1.8
Ruby	0.3	1.2	3.9

Table 12. Monthly ionic loading for Topaz, Pear, Crystal and Ruby Lakes during the period June through October 1987. All units are meq m^{-2}.

	H	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K
Topaz Lake									
June	0.42	3.85	0.63	2.28	1.84	1.34	0.25	0.55	0.22
July	0.28	2.50	0.41	1.49	1.20	0.87	0.17	0.35	0.14
August	0.09	0.78	0.13	0.46	0.37	0.28	0.06	0.11	0.04
September	0.53	4.87	0.80	2.89	2.32	1.69	0.33	0.69	0.28
October	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	1.32	12.00	1.97	7.12	5.73	4.18	0.81	1.70	0.68
Pear Lake									
June	0.22	2.06	0.34	1.22	0.99	0.72	0.13	0.30	0.12
July	0.09	0.84	0.13	0.50	0.40	0.29	0.06	0.12	0.04
August	0.11	1.03	0.17	0.61	0.50	0.36	0.07	0.14	0.06
September	0.25	2.33	0.39	1.38	1.11	0.81	0.15	0.33	0.13
October	0.00	0.02	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Total	0.67	6.28	1.03	3.72	3.01	2.19	0.41	0.89	0.35
Crystal Lake									
June	0.14	0.33	0.09	0.30	0.24	0.14	0.03	0.09	0.01
July	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
August	0.02	0.06	0.01	0.04	0.03	0.02	0.00	0.01	0.00
September	0.01	0.03	0.01	0.03	0.02	0.01	0.00	0.01	0.00
October	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	0.17	0.42	0.11	0.37	0.29	0.17	0.03	0.11	0.01
Ruby Lake									
June	0.18	0.41	0.10	0.36	0.30	0.17	0.04	0.11	0.01
July	0.07	0.17	0.04	0.14	0.12	0.07	0.01	0.04	0.01
August	0.01	0.02	0.01	0.02	0.02	0.01	0.00	0.01	0.00
September	0.13	0.31	0.08	0.29	0.23	0.13	0.03	0.09	0.01
October	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Total	0.39	0.92	0.23	0.82	0.67	0.38	0.08	0.25	0.03

Table 13. Monthly ionic loading for Emerald Lake during selected months of water-year 1987. Please note that precipitation fell as a combination of rain and snow in April and May 1987 and as snow in October 1986 and November 1986. All units are meq m^{-2}.

Month/Year	H	NH_4	Cl	NO_3	SO_4	Ca	Mg	Na	K
October/86	0.12	0.84	0.09	0.49	0.17	0.03	0.02	0.03	0.01
November/86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
April/87	0.27	0.20	0.05	0.35	0.31	0.23	0.04	0.05	0.03
May/87	1.12	7.05	0.96	5.47	5.02	2.81	0.62	1.24	0.41
June/87	0.49	1.00	0.12	0.75	0.66	0.20	0.05	1.17	0.04
July/87	0.01	0.03	0.04	0.03	0.03	0.04	0.01	0.04	0.01
August/87	0.05	0.72	0.16	0.42	0.45	0.27	0.06	0.15	0.05
September/87	0.13	0.99	0.09	0.62	0.40	0.32	0.06	0.08	0.04

Table 14. Monthly discharge for Topaz, Pear, Crystal and Ruby Lakes for the period October 1986 through May 1988. The units are cubic meters per month. NA = not available because of datalogger malfunction.

Month/Year	*Topaz*	*Pear*	*Crystal*	*Ruby*
Oct 86	2350	81,700	800	4,800
Nov 86	0	13,200	12,050	35,050
Dec 86	0	9,000	50	29,650
Jan 87	0	10,650	700	25,250
Feb 87	16,800	13,350	50	23,950
Mar 87	1,350	18,900	100	23,350
Apr 87	140,650	141,200	57,150	23,600
May 87	332,550	299,000	223,700	27,900
Jun 87	85,350	470,250	117,850	747,250
Jul 87	0	55,200	25,850	588,750
Aug 87	0	3,400	850	389,700
Sep 87	0	200	0	173,550
Oct 87	0	100	0	81,650
Nov 87	10,000	7,050	0	37,250
Dec 87	450	12,900	0	28,900
Jan 88	6,100	15,650	NA	52,800
Feb 88	3,650	7,450	NA	19,900
Mar 88	42,100	49,850	NA	16,950
Apr 88	150,000	233,900	15,300	21,250
May 88	291,500	255,400	202,050	75,800

Table 15. Water balances for Topaz, Pear, Crystal and Ruby Lakes during water-year 1987 (October 1986 to October 1987). Snow volume was calculated from snowpit data from April 1987. Rain volume was measured with tipping bucket rain gauges at each of the lakes during the period June through September 1987. For rain and snow volumes in the autumn of 1986 and the spring of 1987 data from Emerald Lake were used. Precipitation for these months was estimated to equal that measured at Emerald Lake for Topaz and Pear. At Crystal and Ruby Lakes rain was estimated to equal half that measured at Emerald Lake. Evaporation estimates are the sum of snow sublimation, lake evaporation and evapotranspiration. These numbers were extrapolated from Emerald Lake (Dozier *et al.* 1989). The residual component was calculated using the following equation: Resid = Outflow + Evap - Snow - Rain. The Residual % is the ratio of the residual to the total of measured inputs (snow + rain). All units are m^3 x 1000. Note that precipitation during the autumn of 1986 and spring of 1987 fell as both snow and rain and was classified as rain.

Flux	*Topaz*	*Pear*	*Crystal*	*Ruby*
Snow	636	491	707	2,630
Rain	378	280	112	449
Evap	210	218	193	611
Outflow	579	1,120	439	2,090
Residual	-225	+567	-187	-378
Residual %	-22%	+74%	-23%	-12%

Table 16. Estimated absolute error in the water balances for water-year 1987 at Topaz, Pear, Crystal and Ruby Lakes. Error bounds are from Dozier *et al.* (1989). The total error was calculated as the square root of the sum of the component squared-errors. Error % is the total error divided by the sum of measured inputs (snow + rain). All units are m^3 x 1000.

Flux	Error Bounds	*Topaz*	*Pear*	*Crystal*	*Ruby*
Snow	± 10%	63.6	49.1	70.7	262
Rain	± 20%	75.6	56.0	22.4	89.8
Evap	± 50%	105	109	96.5	306
Outflow	± 20%	116	220	87.8	420
Total Error		185	257	150	589
Error %		18%	33%	18%	19%

Table 17. 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 (eq ha^{-1} yr^{-1}). The watershed yield is defined as [(Output - Loading) ÷ Basin Area]. Atmospheric loading is for wet deposition (snow and rain) only. NM means the solute was undetectable or absent in precipitation samples. A negative yield indicates the solute was retained within the watershed. Data for Emerald Lake are from Dozier *et al.* 1989.

Lake	H	ANC	NH_4	Cl	NO_3	SO_4	Basic Cations
Topaz Lake							
Loading	58	NM	204	36	150	125	150
Yield	-54	133	-203	-25	-140	-100	41
Pear Lake							
Loading	44	NM	148	25	113	97	111
Yield	-41	74	-145	-17	-101	-75	-13
Crystal Lake							
Loading	38	NM	55	12	52	41	59
Yield	-37	202	-53	-8	-52	-23	157
Ruby Lake							
Loading	47	NM	53	22	62	50	75
Yield	-44	300	-52	-11	-49	-9	273
Emerald Lake							
Loading	58	NM	138	27	114	94	112
Yield	-51	195	-136	1	-59	-45	211

Table 18. Ratio of watershed ANC yield vs hydrogen ion loading for Topaz, Pear, Crystal, Ruby and Emerald Lakes during water-year 1987. In addition to a calculated scenario from Table 17 two other estimates are presented: one with ANC yield decreased by 20% or H^+ loading increased by 20% and one with ANC yield decreased by 40% or H^+ loading increased by 40%. Watershed yield is defined as [(Output - Loading) ÷ Basin Area]. Loading is the sum of H^+ deposition for snow and rain only. Underlined values are the most likely ratios for that lake.

Lake	Calculated Ratio	Yield minus 20% or Loading plus 20%	Yield minus 40% or Loading plus 40%
Topaz	2.3	1.8	1.4
Pear	1.7	1.3	1.0
Crystal	5.3	4.3	3.2
Ruby	6.4	5.1	3.8
Emerald	3.4		

Table 19. Median values (with first and third quartiles in parenthesis) of major ion chemistry for the lakes in the present study, for Emerald Lake, for a population of Sierran lakes (Melack *et al.* 1985) and for Sierran lakes in the Environmental Protection Agency's Western Lake Survey (Landers *et al.* 1987). All units are μeq L^{-1} except for pH. All data are from surface water samples taken during ice-free seasons. Data for Emerald are from the ice-free periods of 1983 through 1987. C_B is the sum of basic cations (calcium, magnesium, sodium and potassium).

Data Set	pH	ANC	SO_4	NO_3	Cl	C_B
Topaz	6.4	32	4.5	0.1	2.5	40
	(6.2-6.5)	(27-34)	(4.1-4.7)	(0.1-0.5)	(2.0-3.8)	(38-41)
Pear	6.3	22	6.0	2.2	2.5	29
	(6.1-6.4)	(15-26)	(4.6-6.3)	(0.1-3.9)	(2.4-5.0)	(27-35)
Crystal	6.5	70	6.3	0.1	2.9	73
	(6.5-6.6)	(60-77)	(6.0-7.0)	(0.1-0.7)	(2.4-3.0)	(68-95)
Ruby	6.4	54	7.5	2.5	2.1	60
	(6.3-6.5)	(47-58)	(6.7-7.5)	(2.0-4.3)	(1.7-2.6)	(57-64)
Emerald	6.3	27	6.0	2.8	2.5	39
	(6.2-6.4)	(23-32)	(5.4-6.8)	(2.0-4.2)	(2.0-3.0)	(34-42)
Sierran Survey	7.0	48	15.0	0.4	6.0	73
	(6.5-7.3)	(25-98)	(9.0- 31)	(0.1-1.5)	(4.0- 10)	(44-137)
Western Lake Survey	7.1	71	6.0	0.3	3.0	86
	(6.9-7.4)	(45-137)	(4.0- 11)	(0.1-1.2)	(2.0-6.0)	(58-164)

Figure 1. Map of California and location of Study Lakes.

Figure 2. Topographic map of Ruby Lake Watershed.

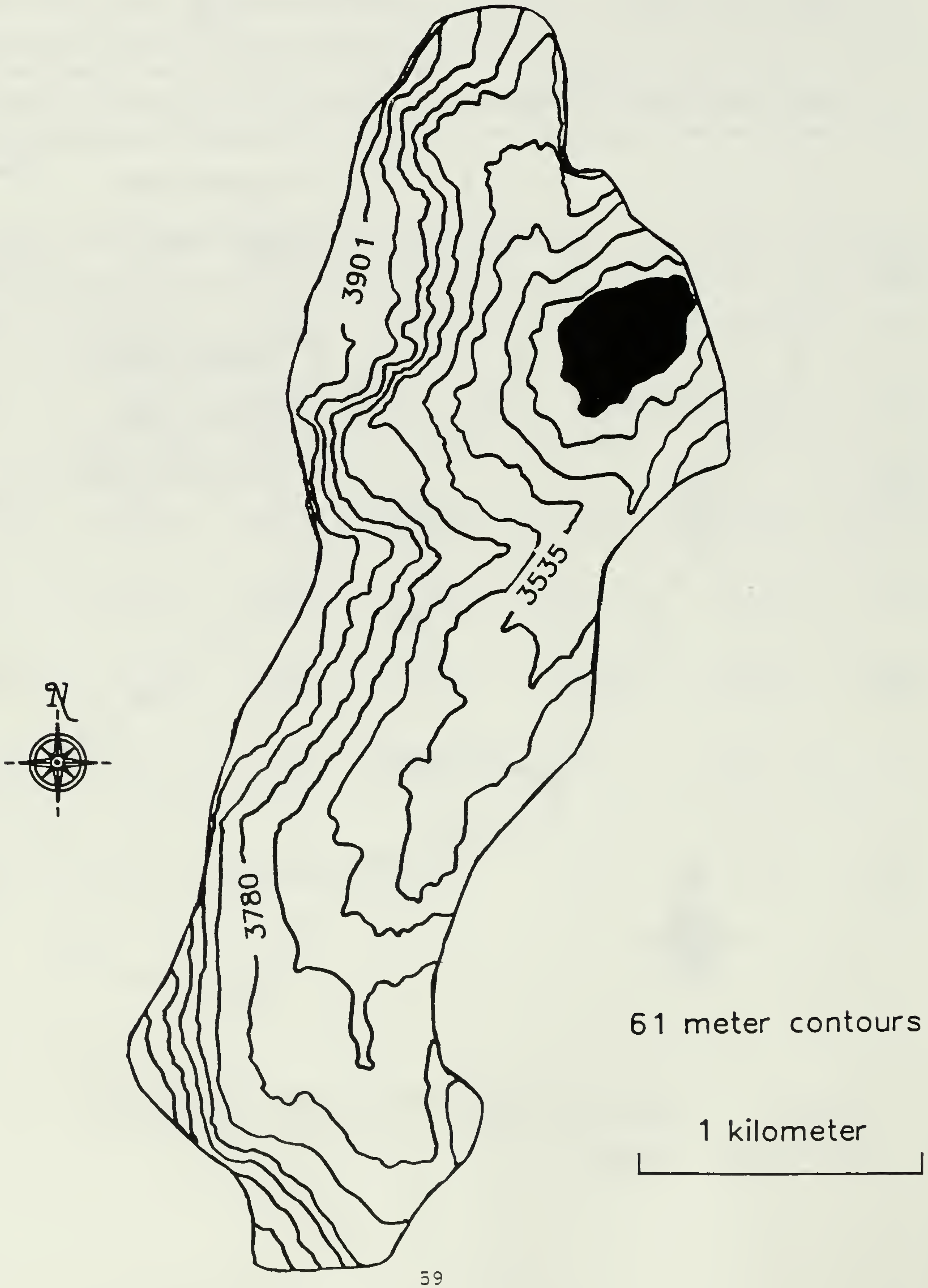


Figure 3. Topographic map of Crystal Lake Watershed.

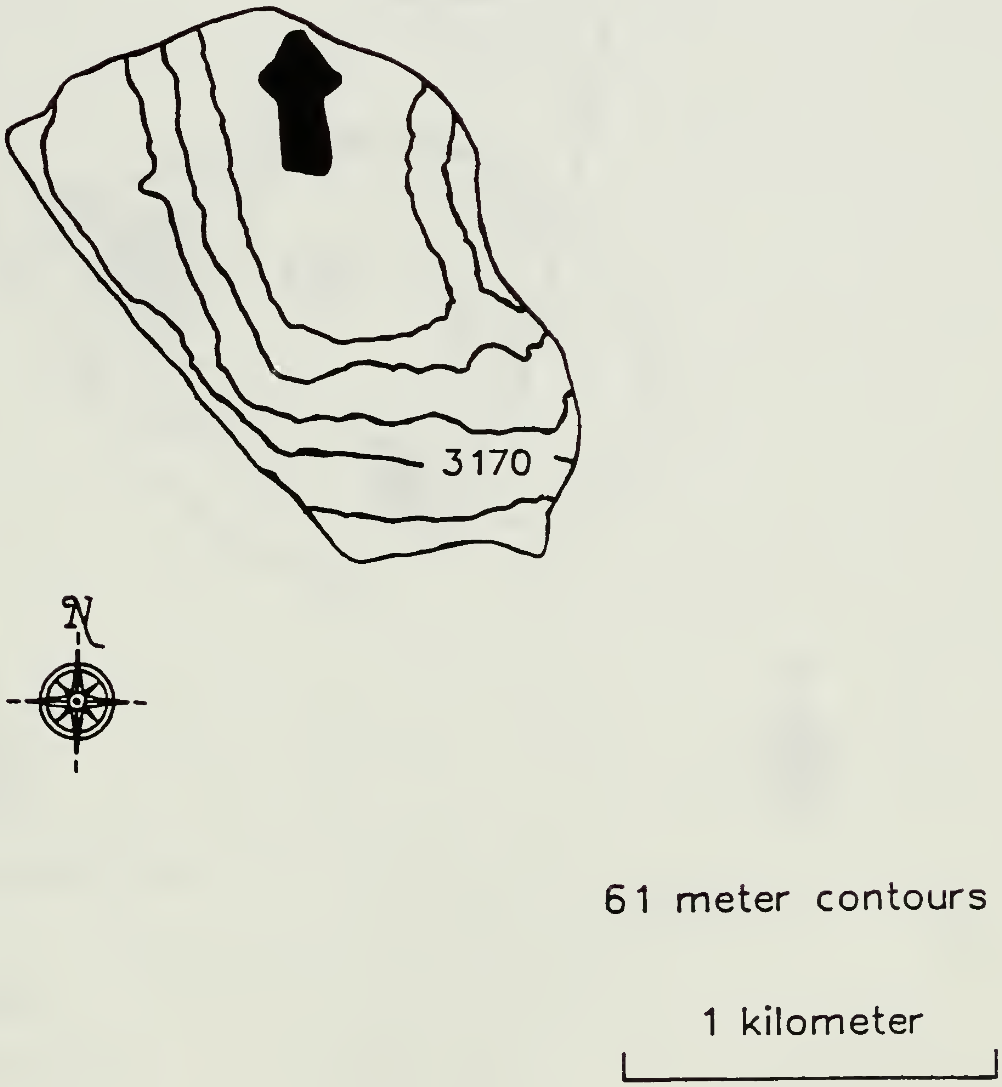


Figure 4. Topographic map of Topaz Lake Watershed.

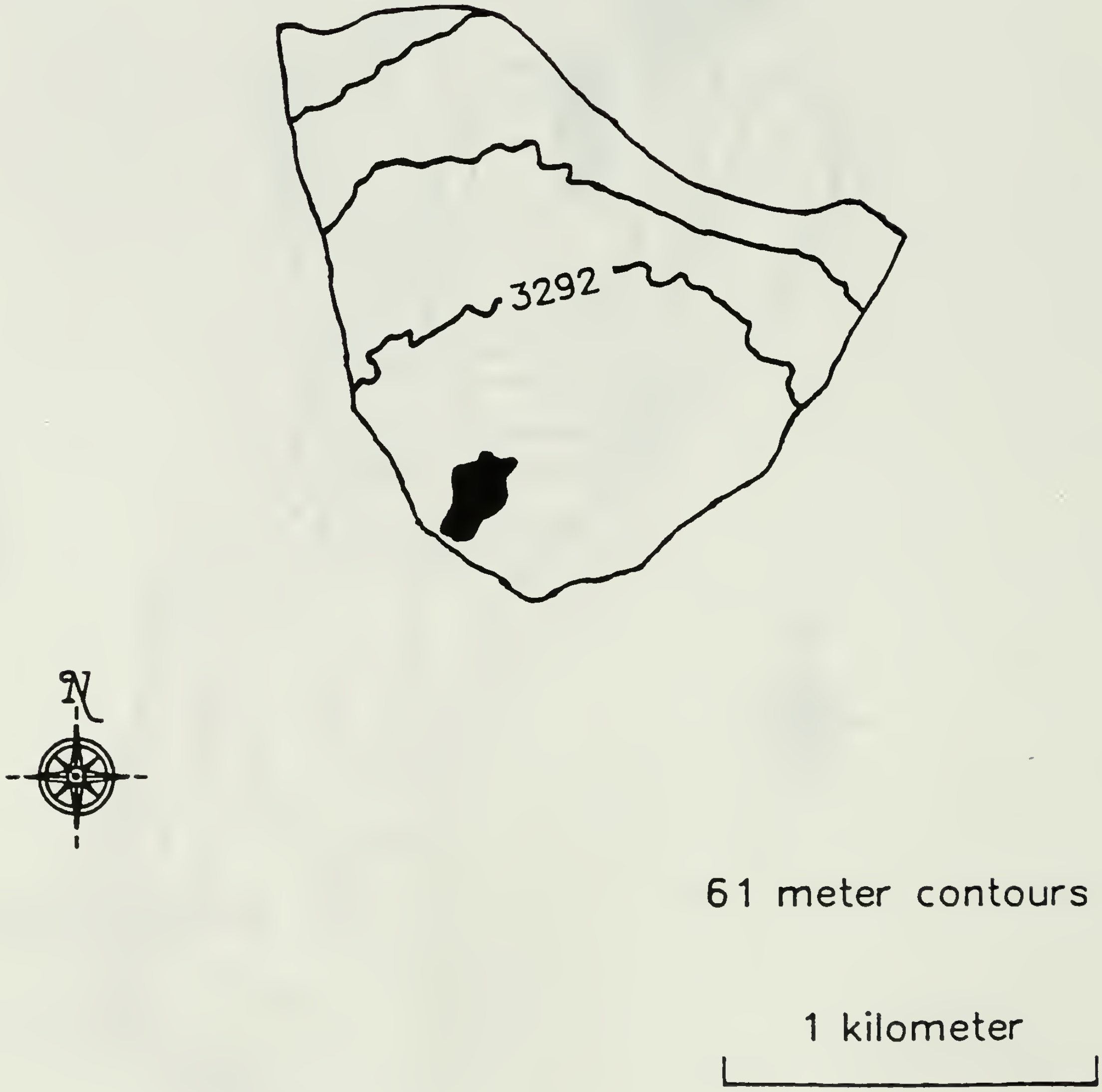
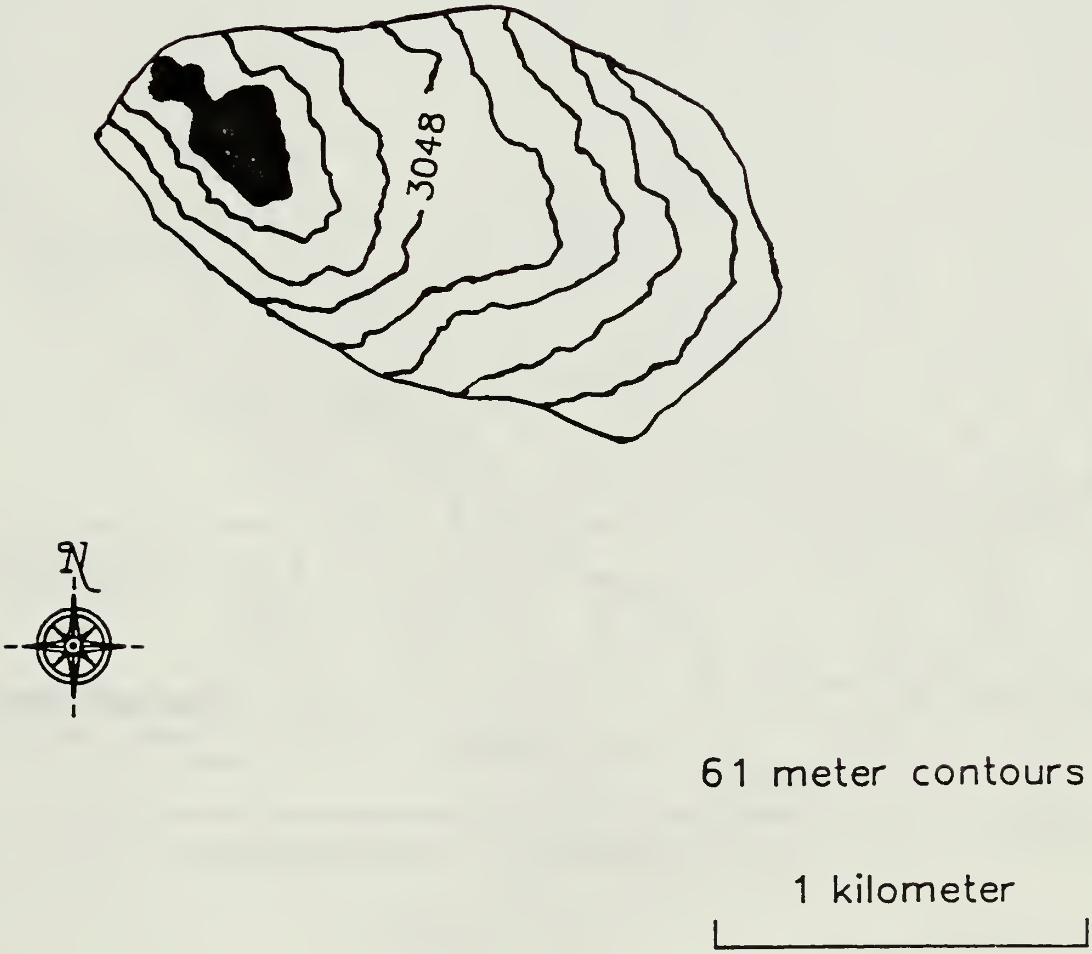


Figure 5. Topographic map of Pear Lake Watershed.



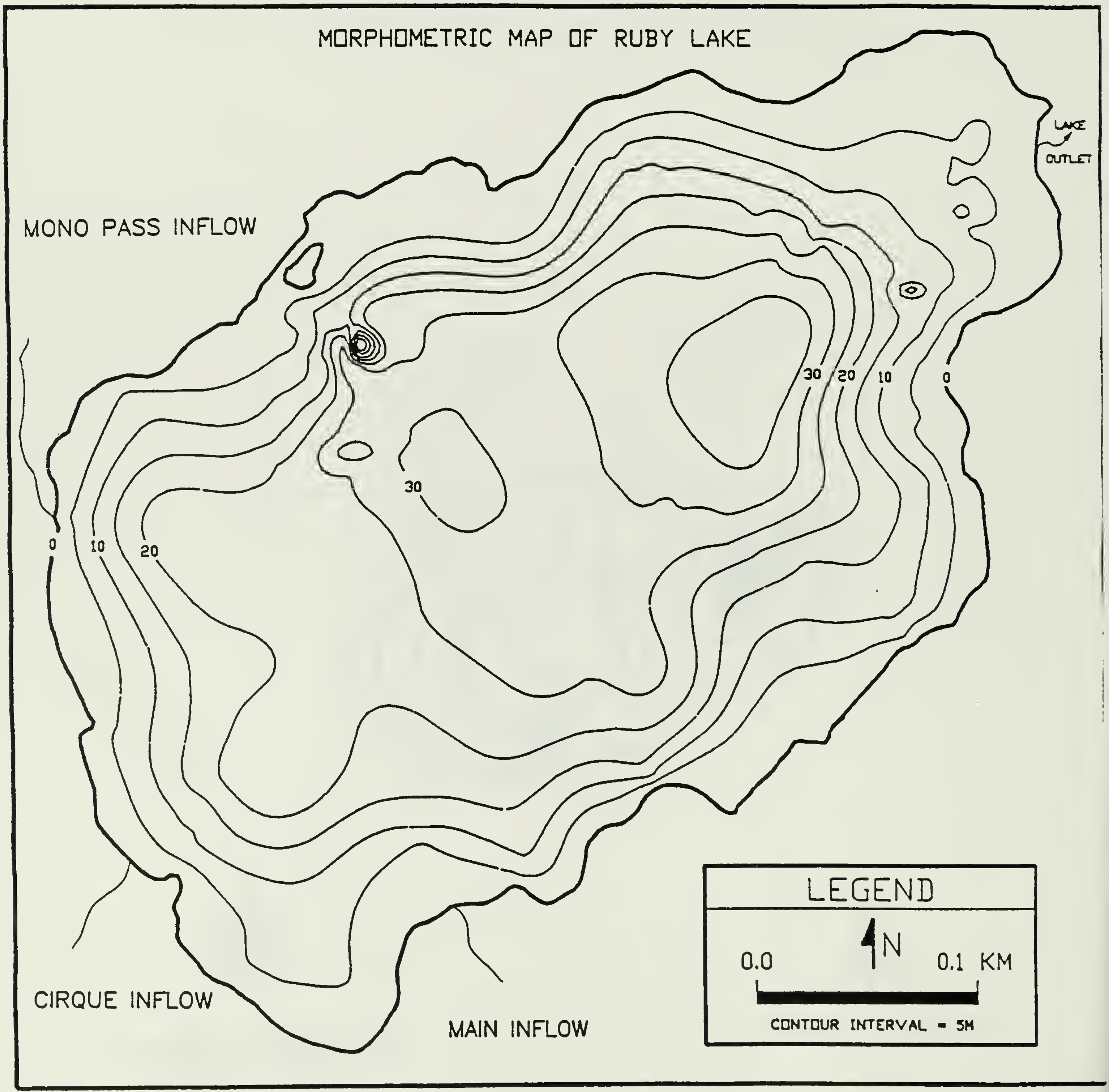
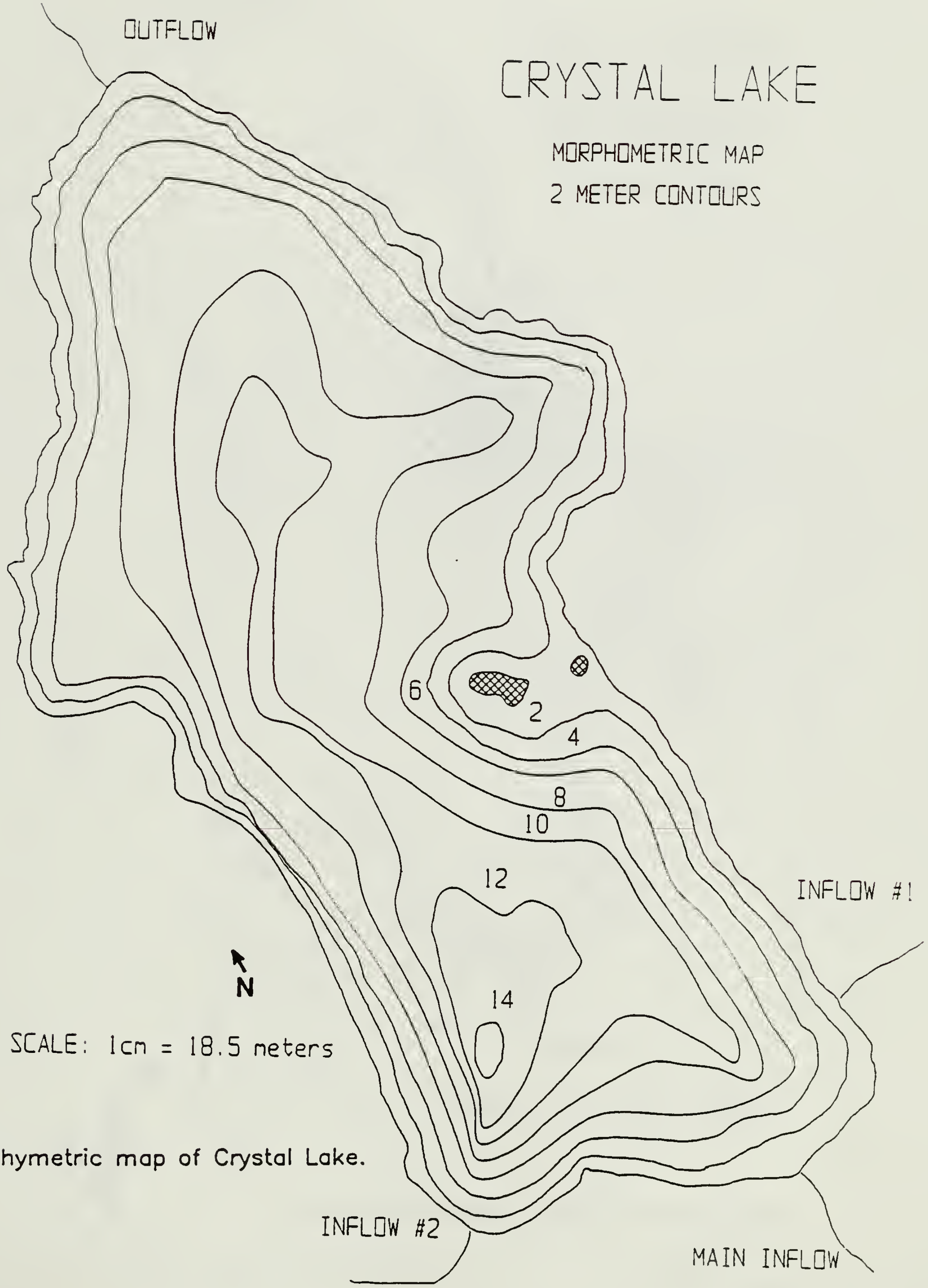


Figure 6. Bathymetric map of Ruby Lake.



gure 7. Bathymetric map of Crystal Lake.

Figure 8. Bathymetric map of Topaz Lake.

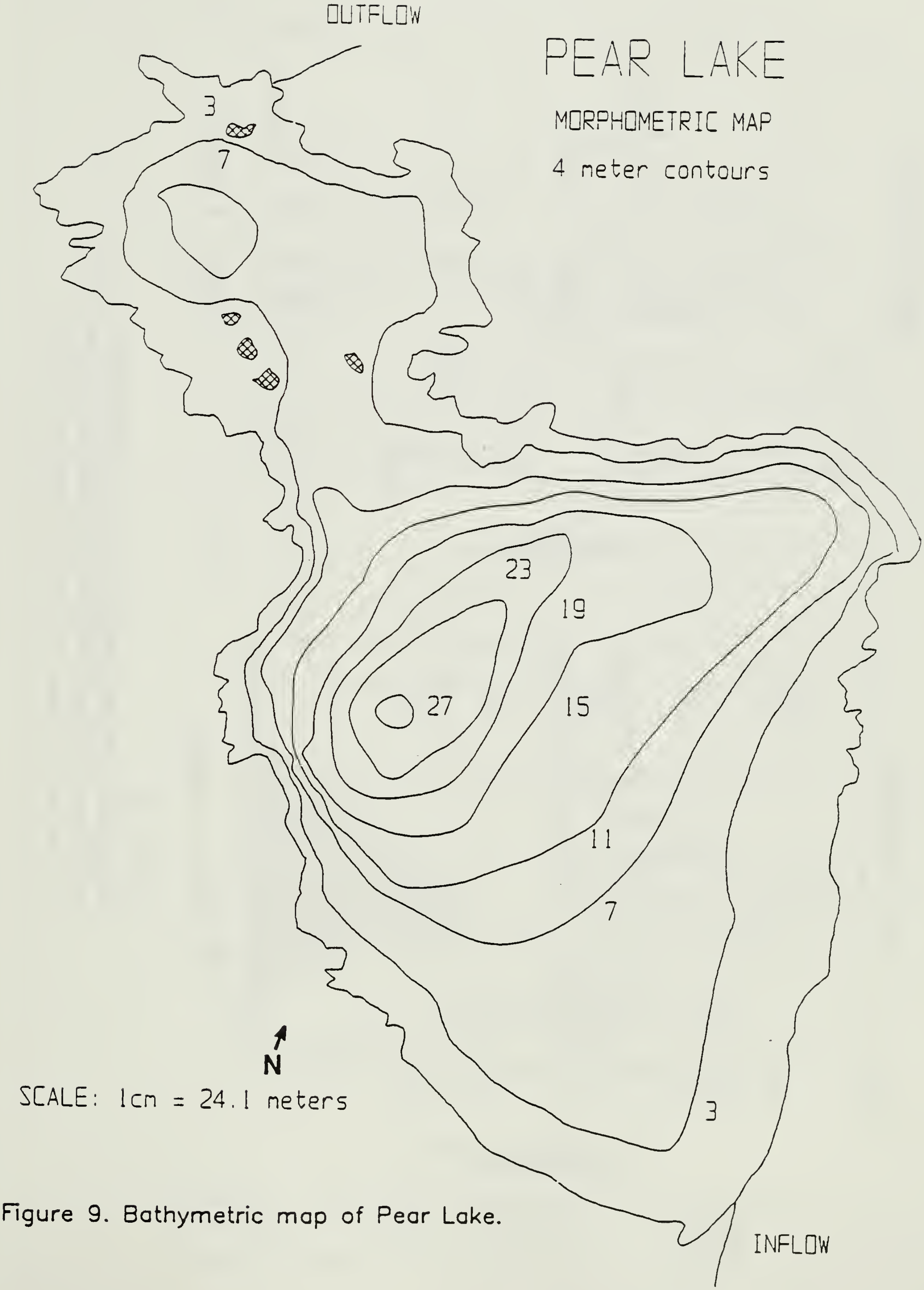


Figure 9. Bathymetric map of Pear Lake.

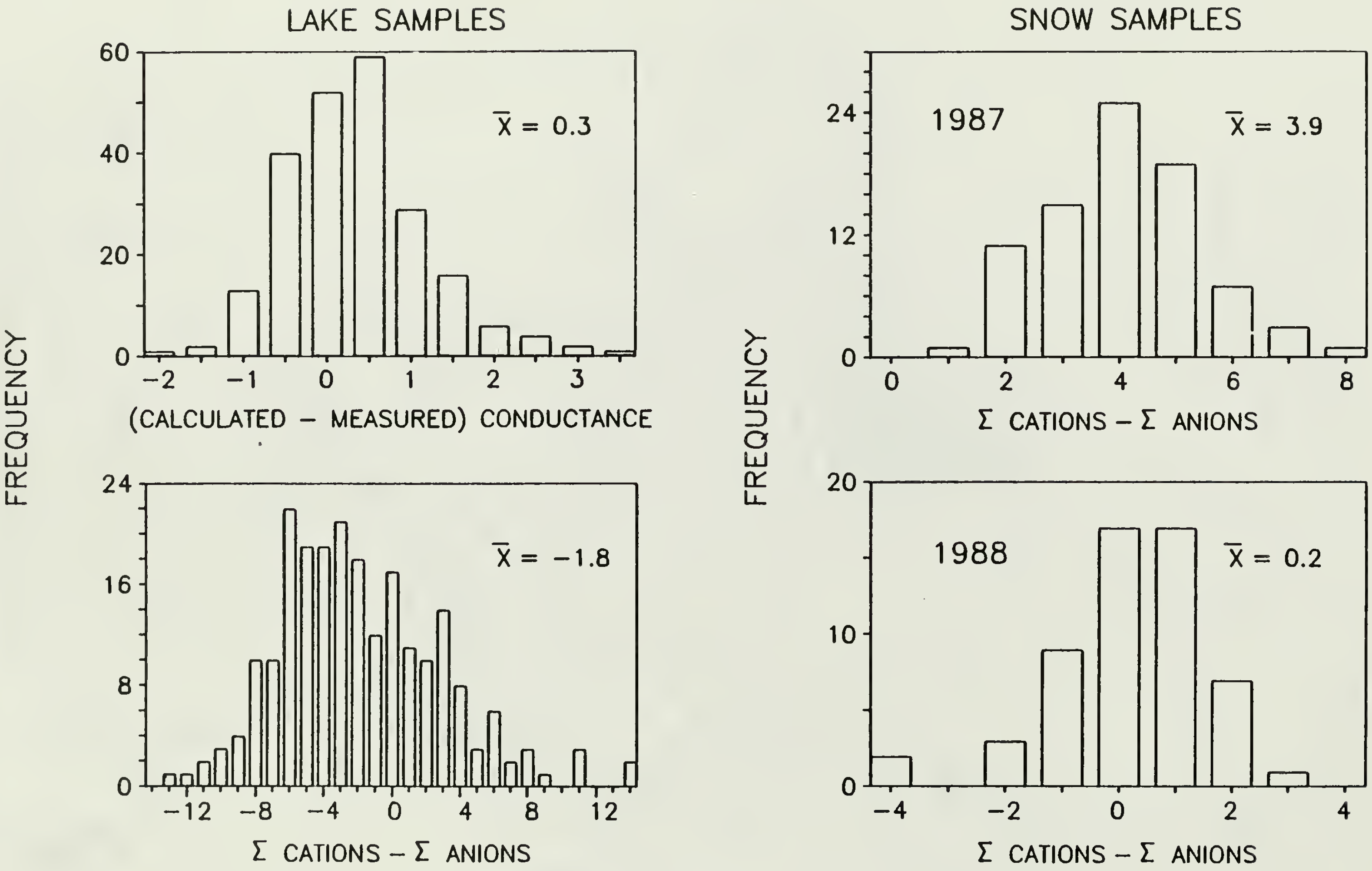


Figure 10.
Histograms of the frequency of charge imbalance and the difference between calculated and measured conductance for lake and snow samples. Note Y−axis scales are different.

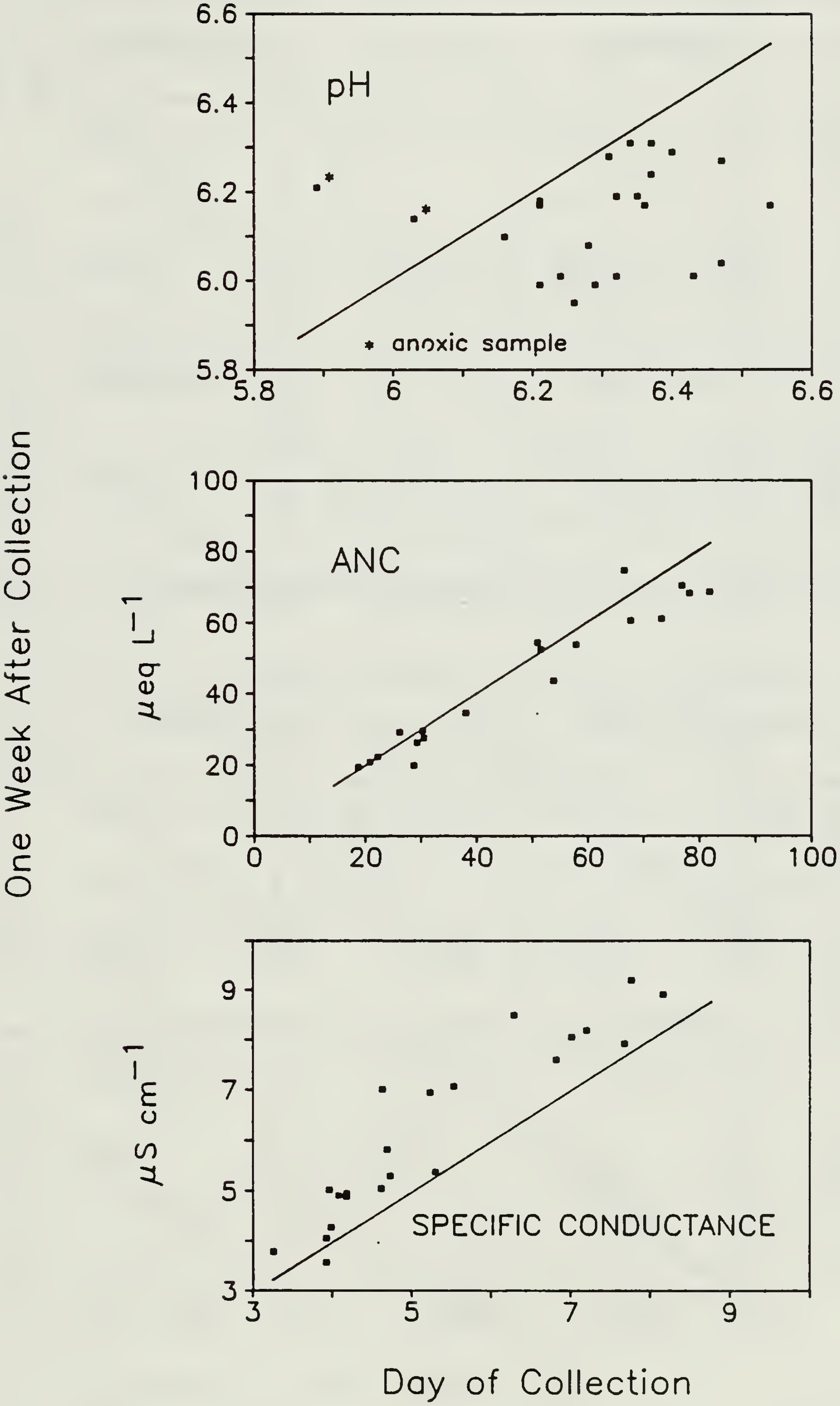


Figure 11. Summary of sample storage test for pH, ANC and specific conductance. Samples were unfiltered. Units are shown on Y–axis.

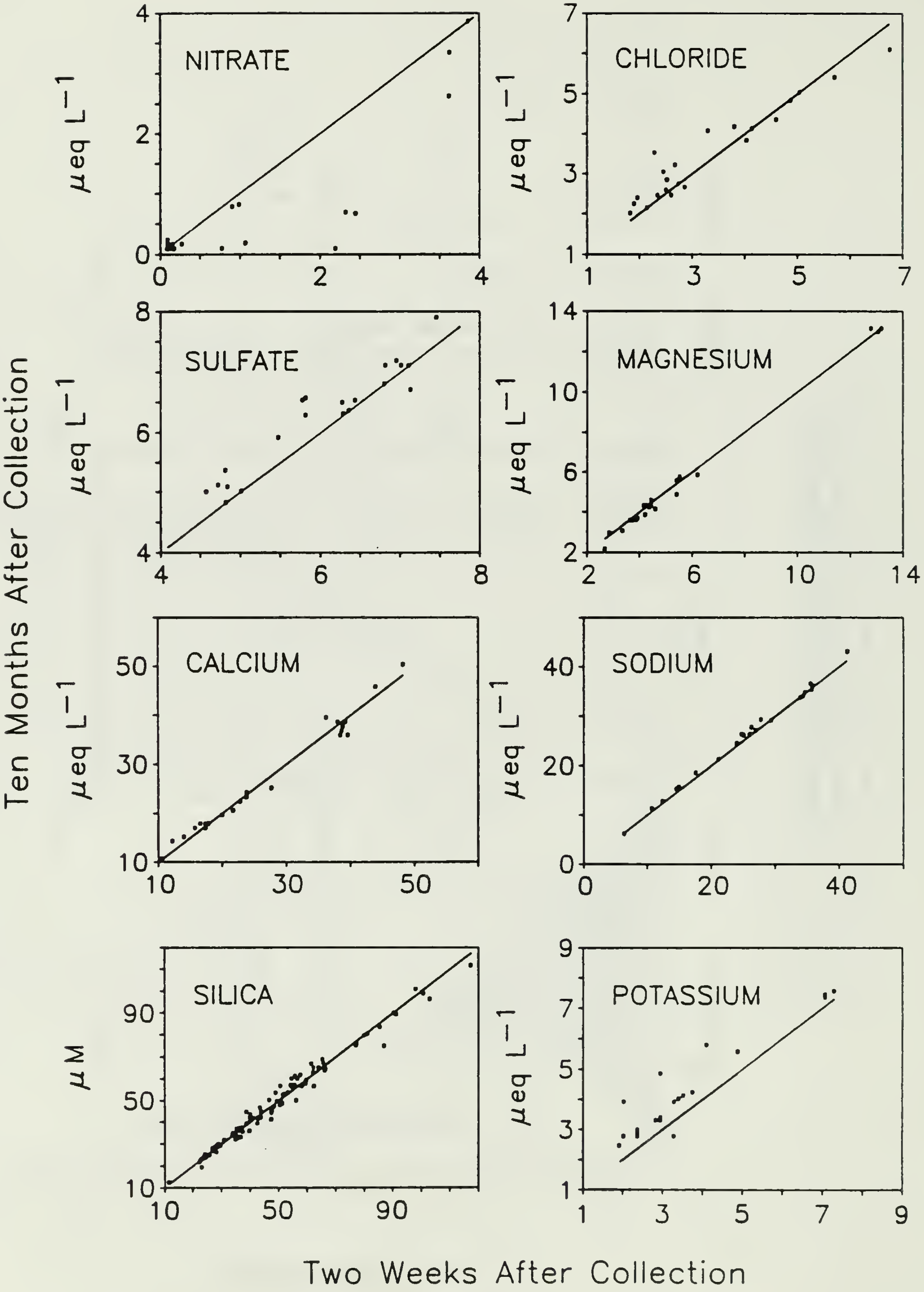


Figure 12. Summary of Storage test for major ions. Samples were filtered. Units are shown on Y-axis.

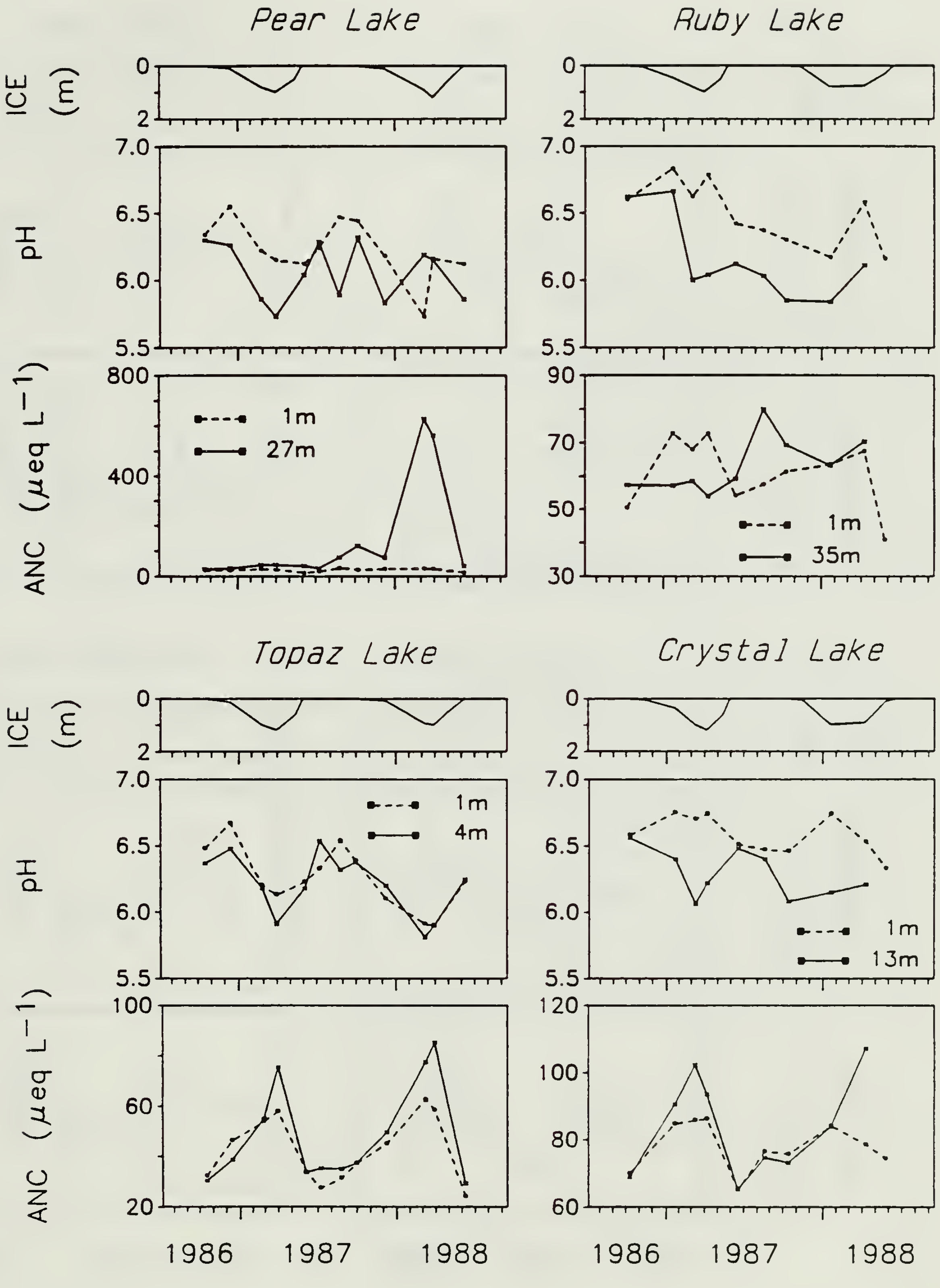


Figure13. Time series of pH and ANC.

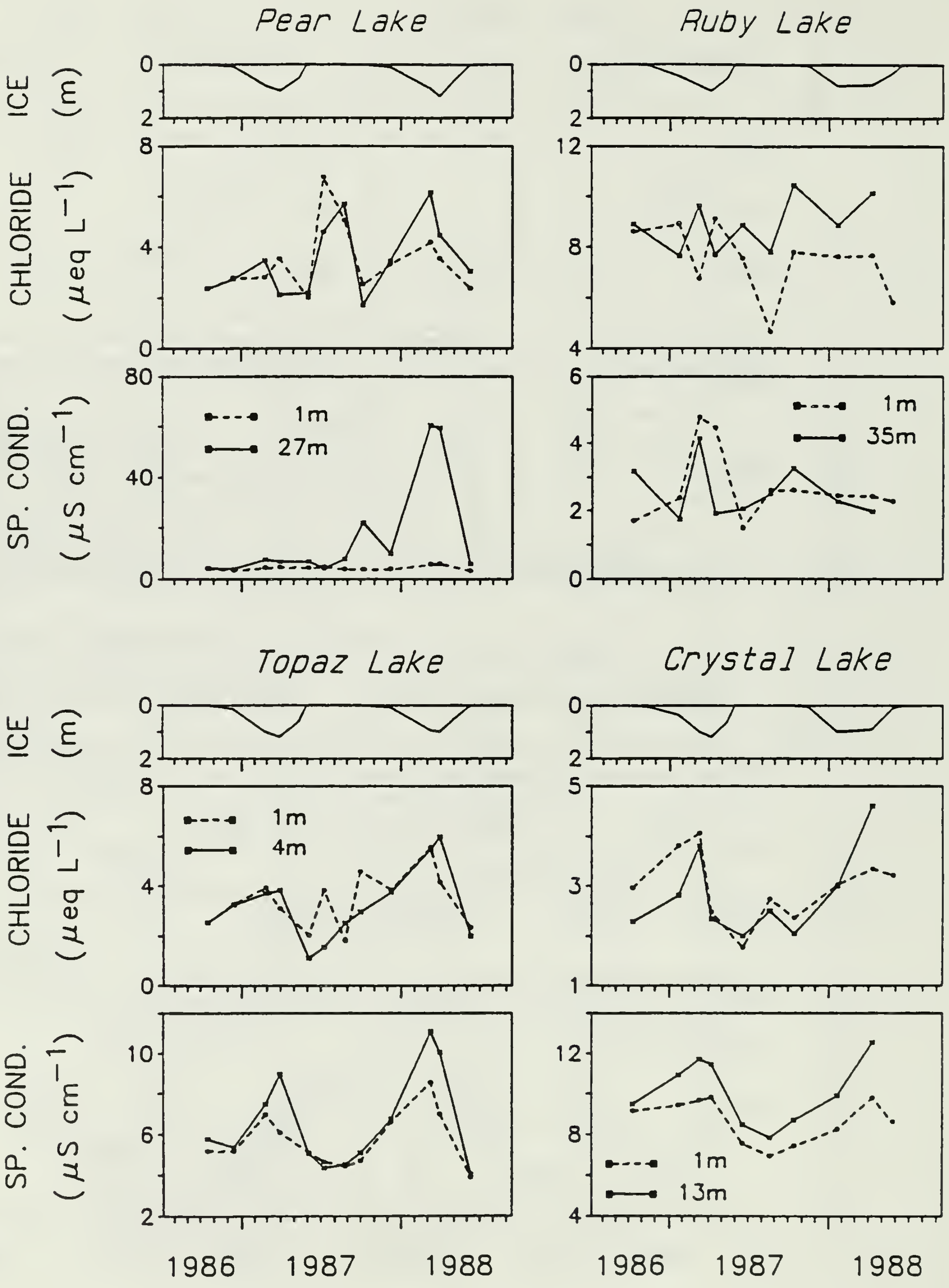


Figure 14. Time series of chloride and specific conductance.

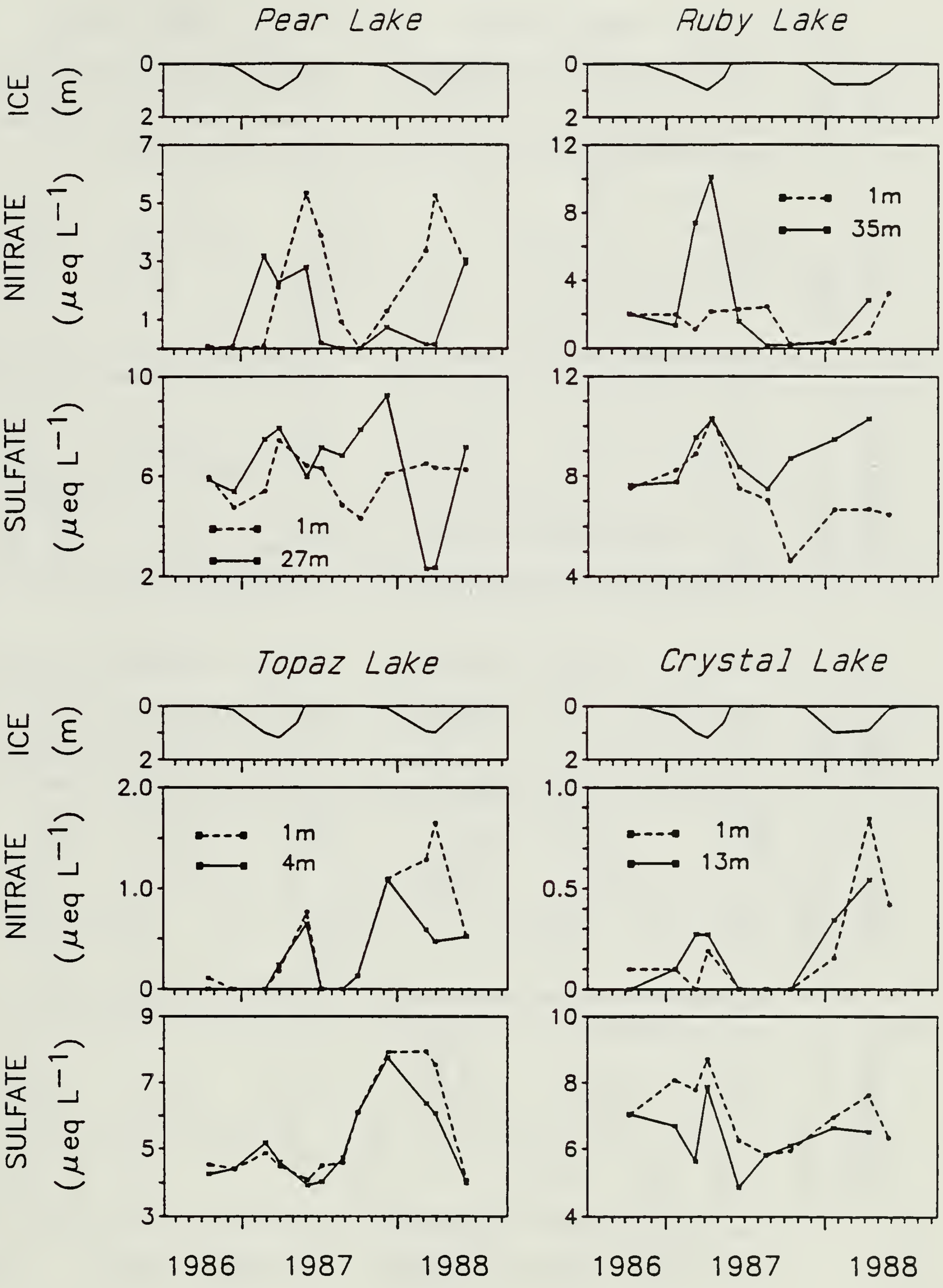


Figure 15. Time series of nitrate and sulfate.

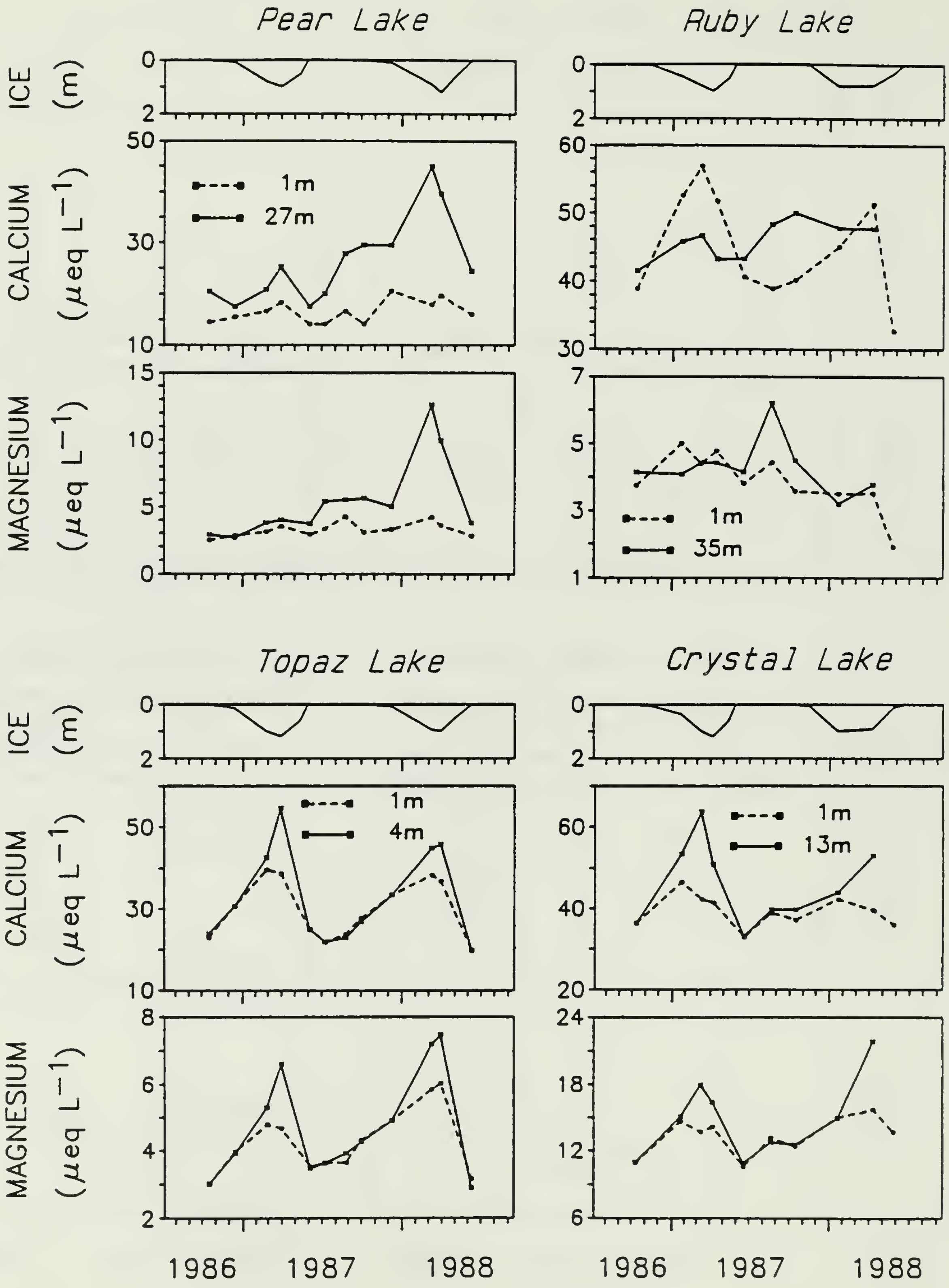


Figure16. Time series of calcium and magnesium.

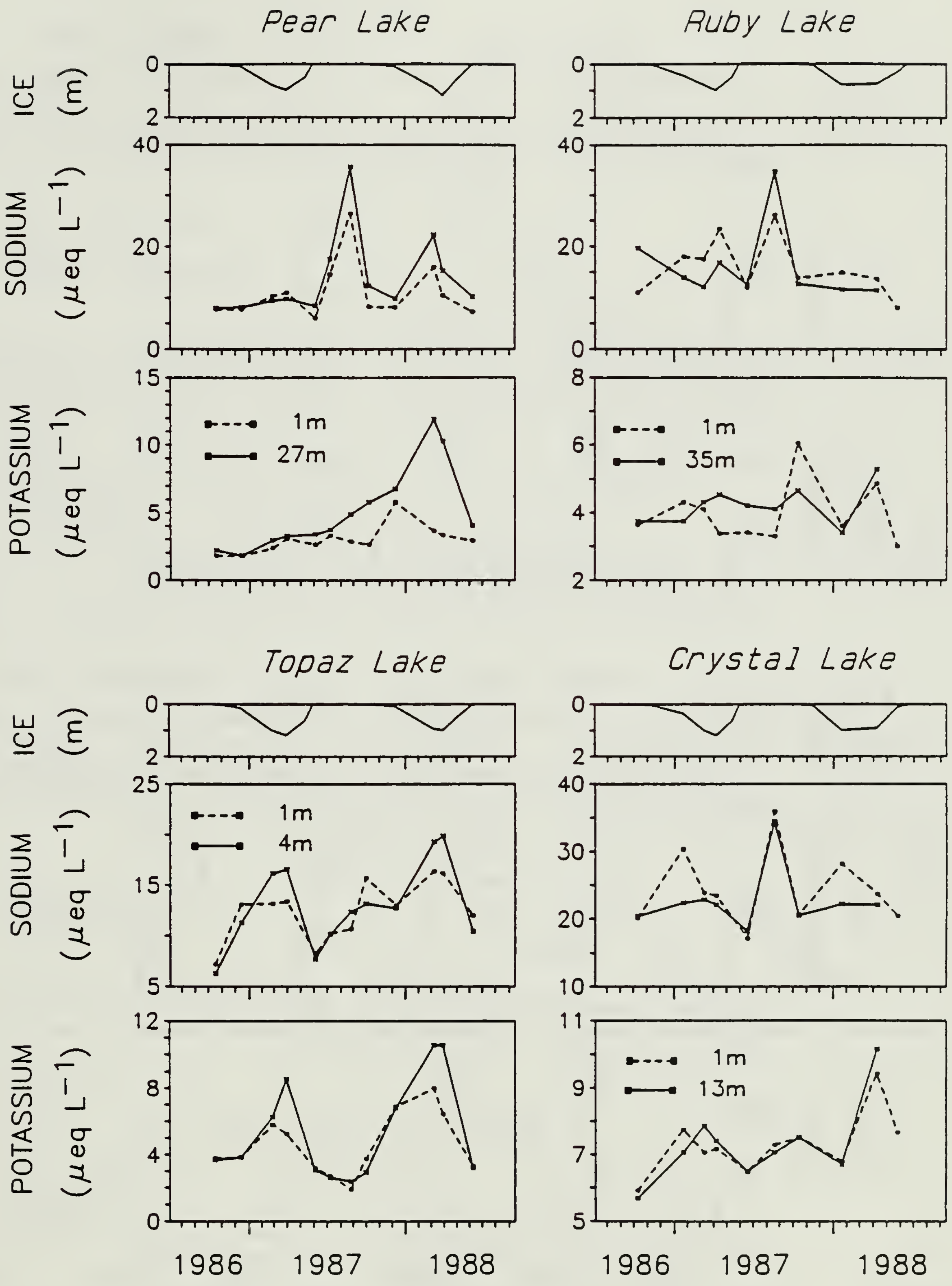


Figure 17. Time series of sodium and potassium.

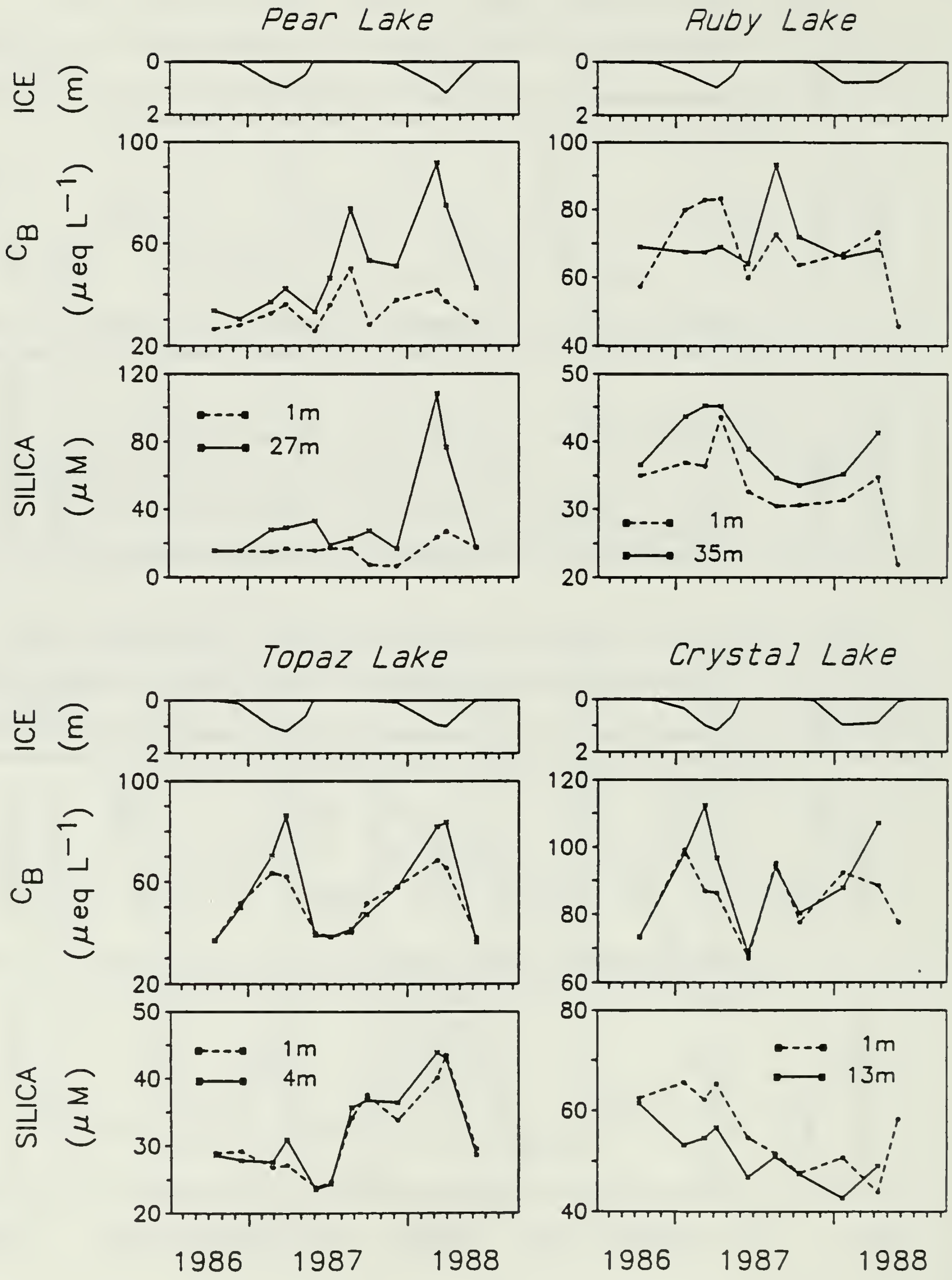


Figure18. Time series of sum of base cations and silica.

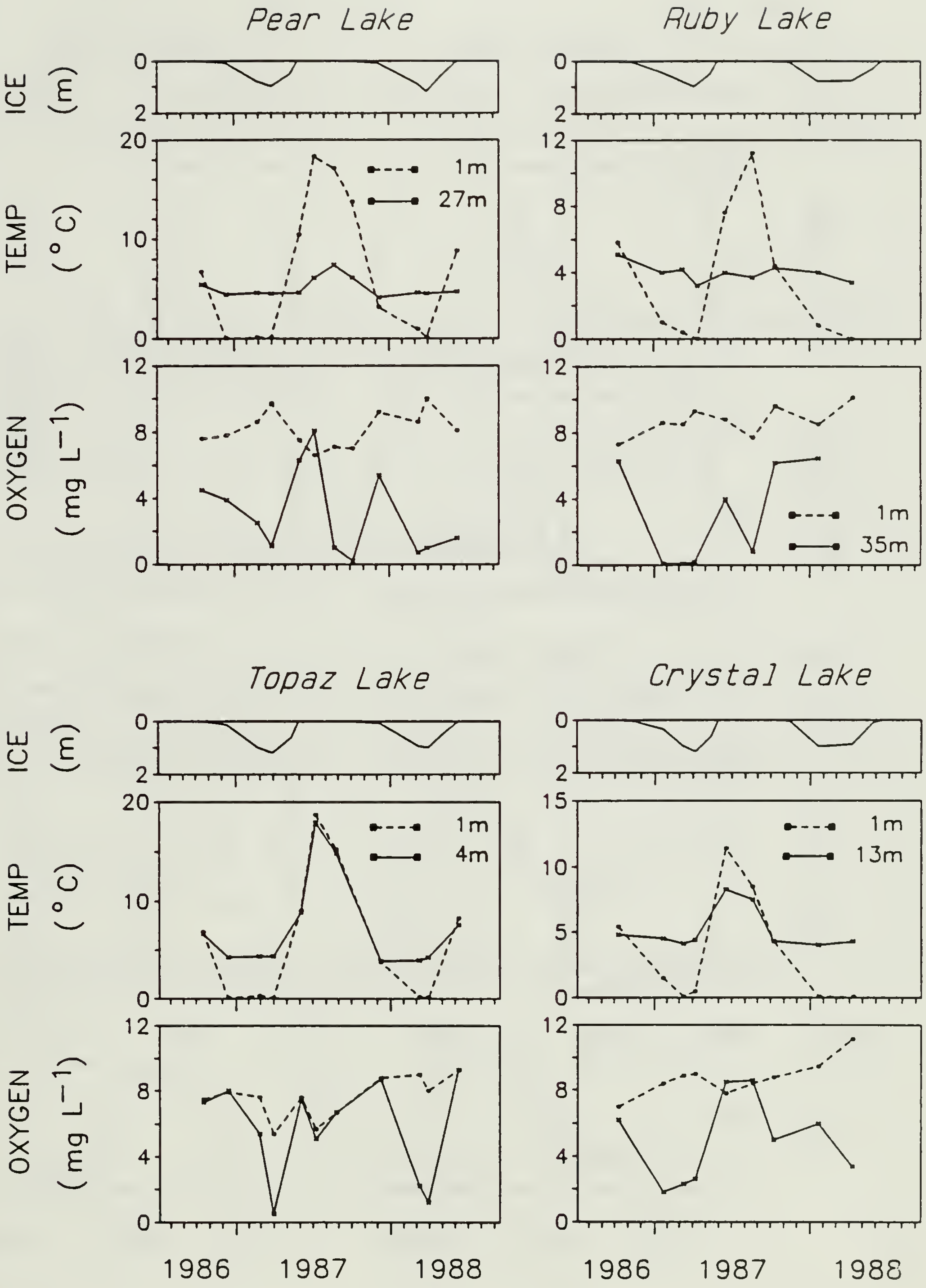


Figure 19. Time series of temperature and oxygen.

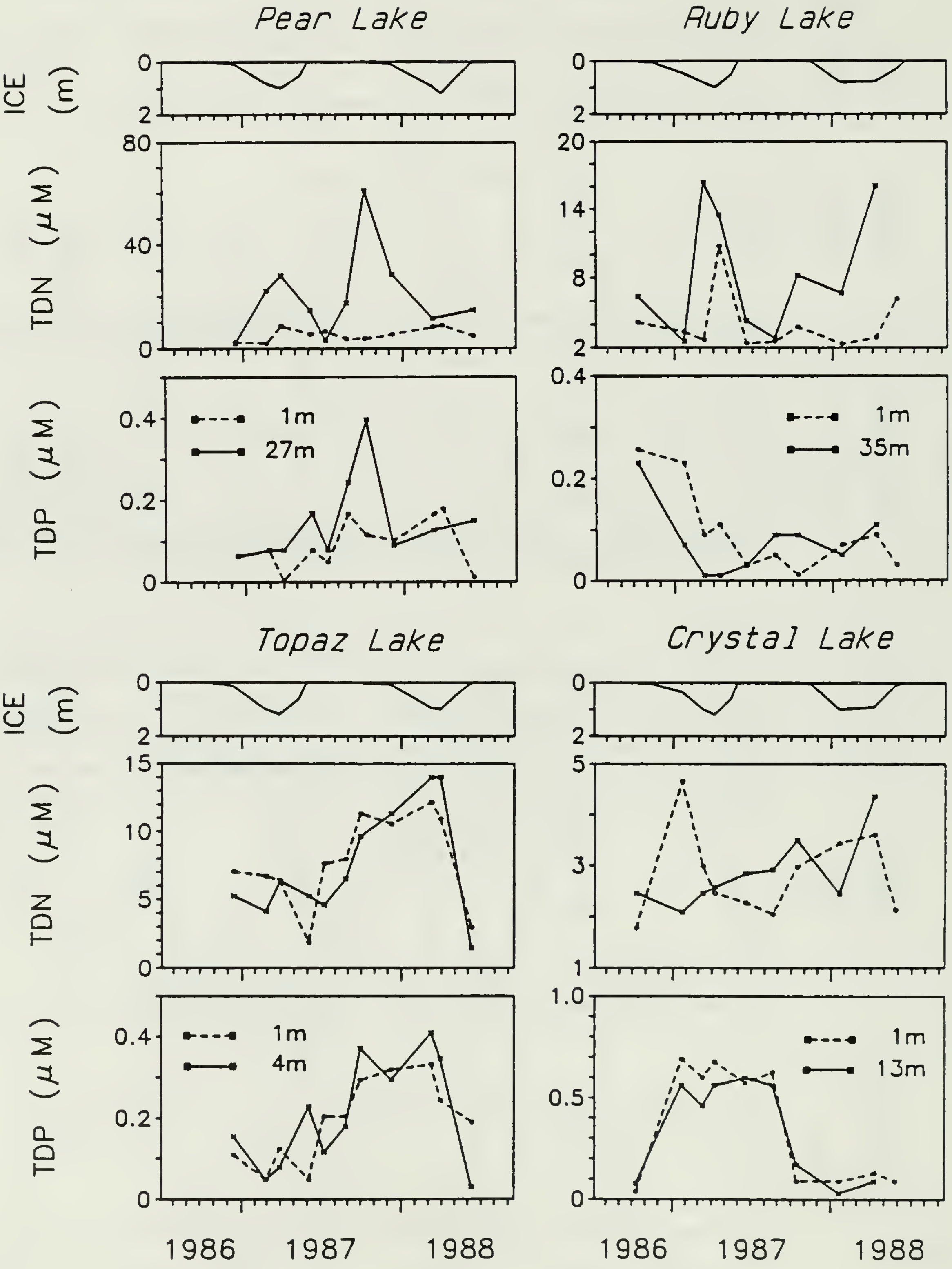


Figure 20. Time series of total dissolved nitrogen and phosphorus.

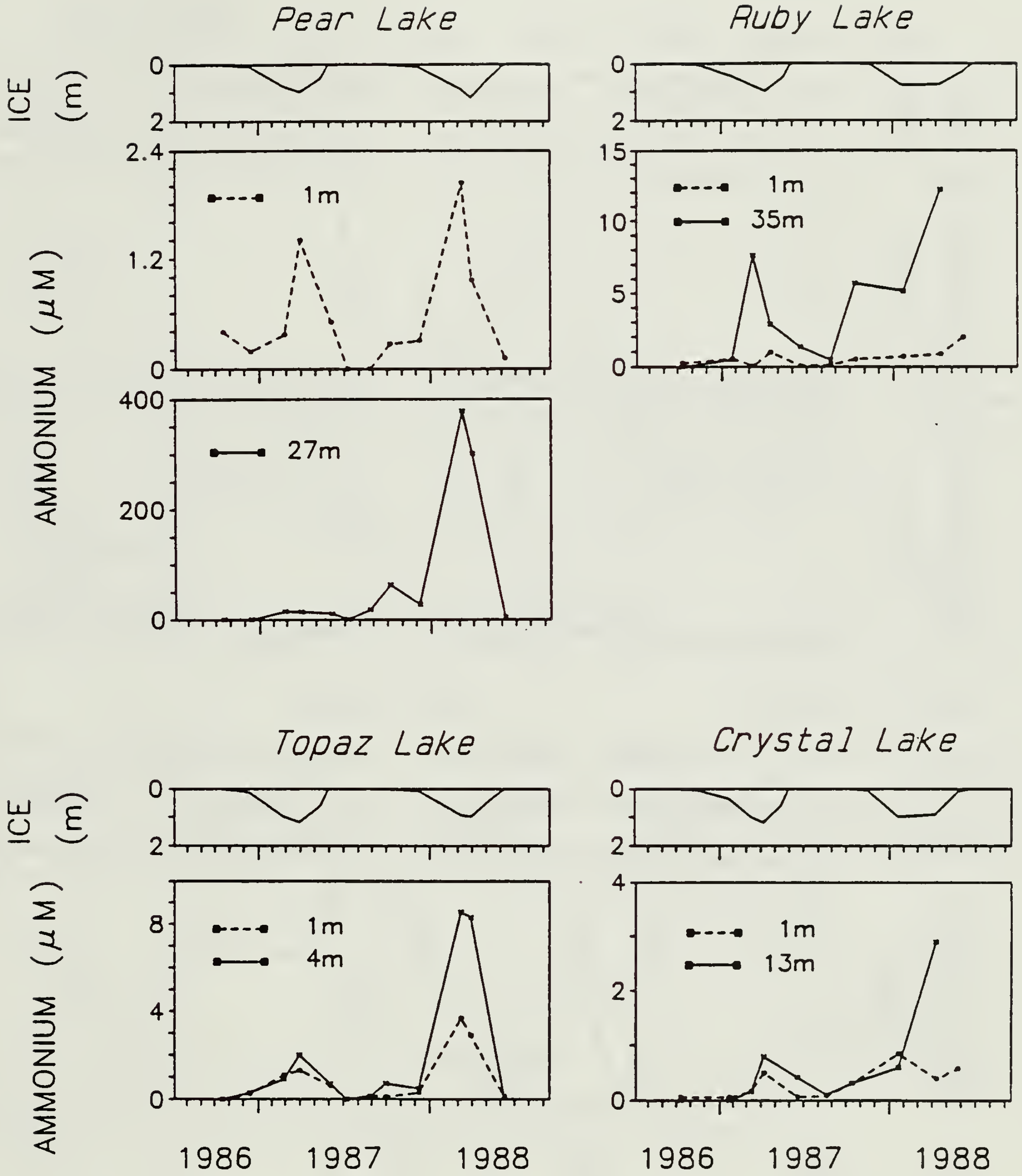


Figure 21. Time series of ammonium.

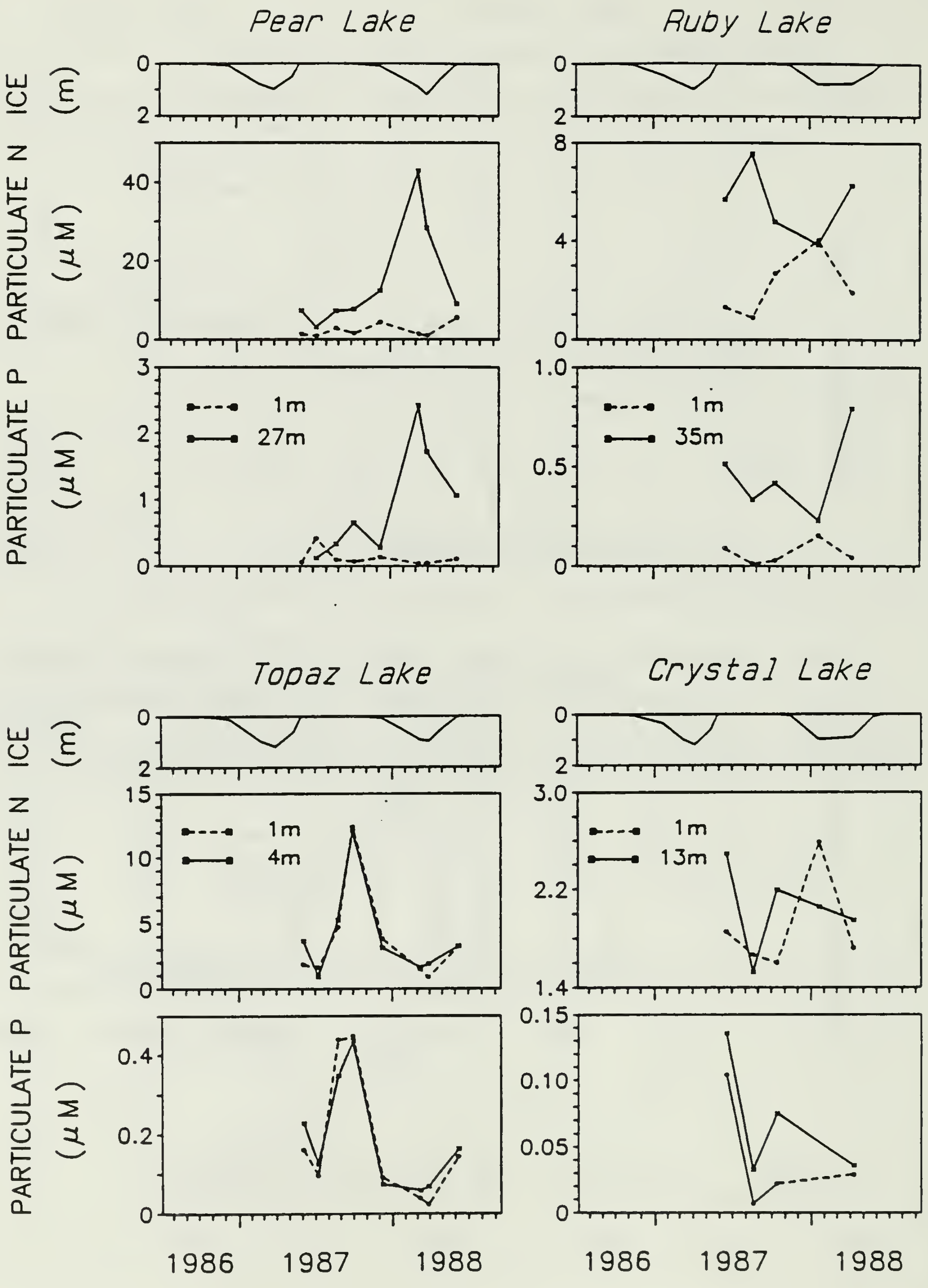


Figure 22. Time series of particulate nitrogen and phosphorus.

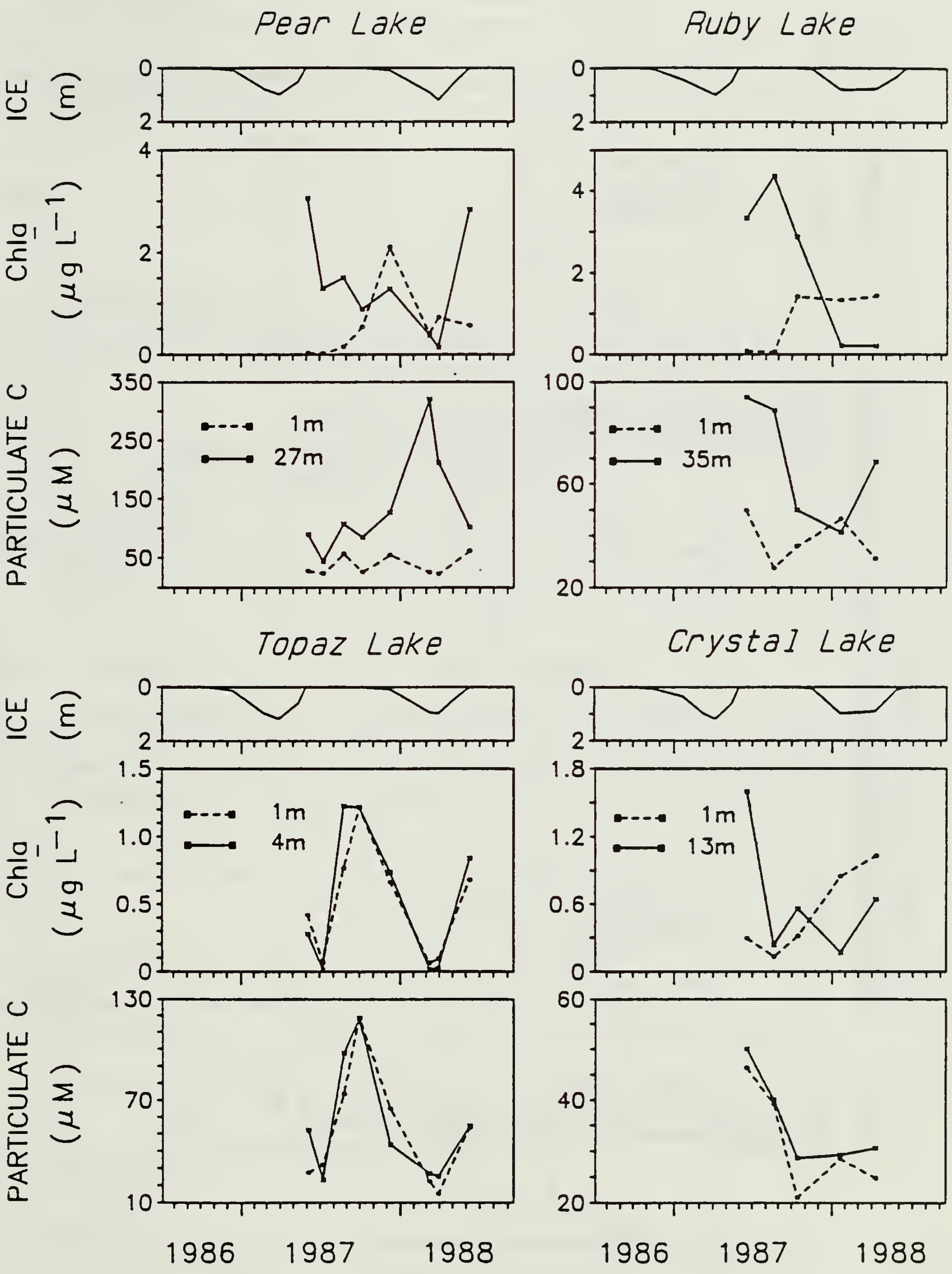


Figure 23. Time series of chlorophyll and particulate carbon.

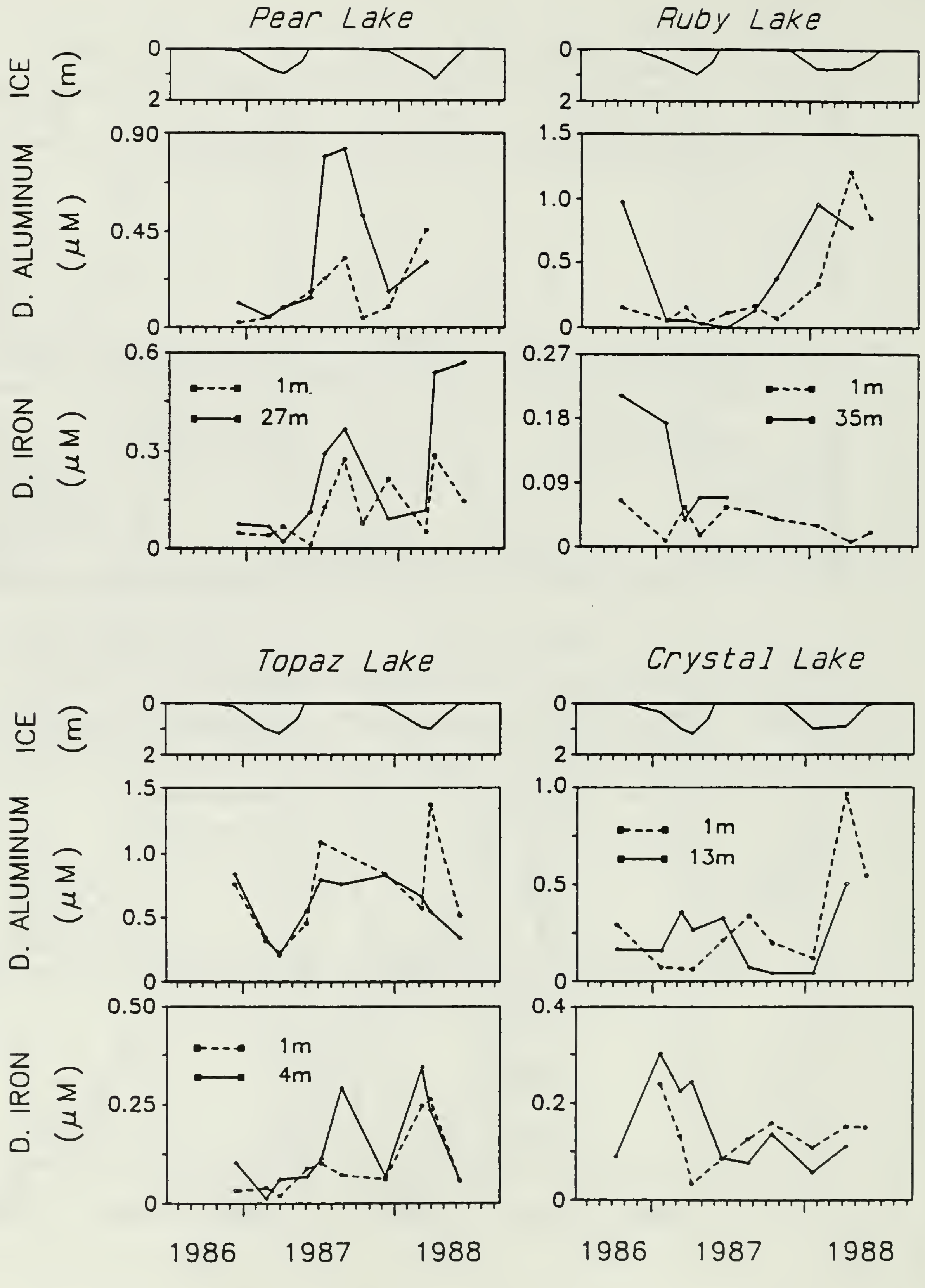


Figure 24. Time series of dissolved aluminum and iron.

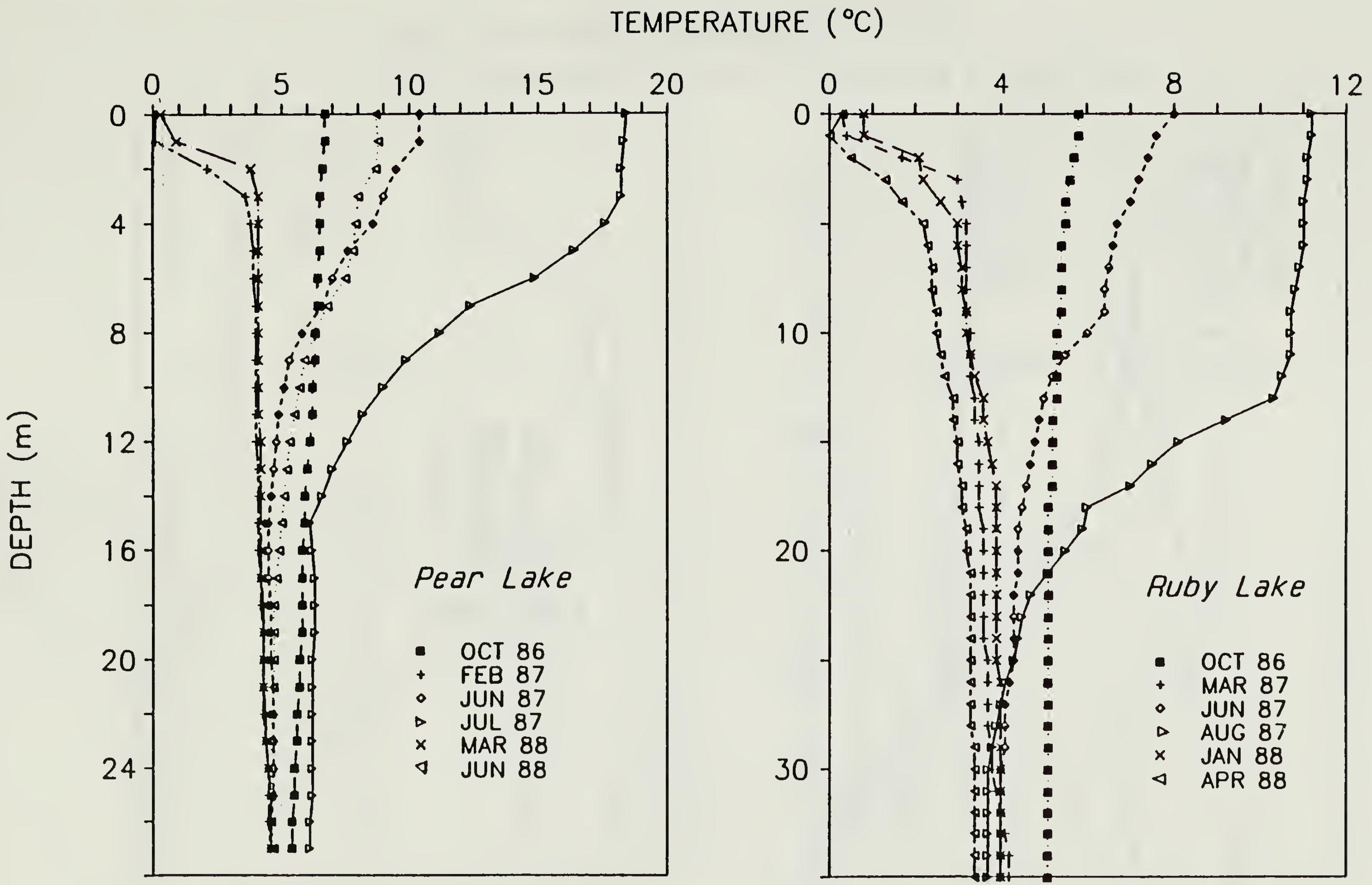


Figure 25. Representative temperature profiles for Pear Lake and Ruby Lake.

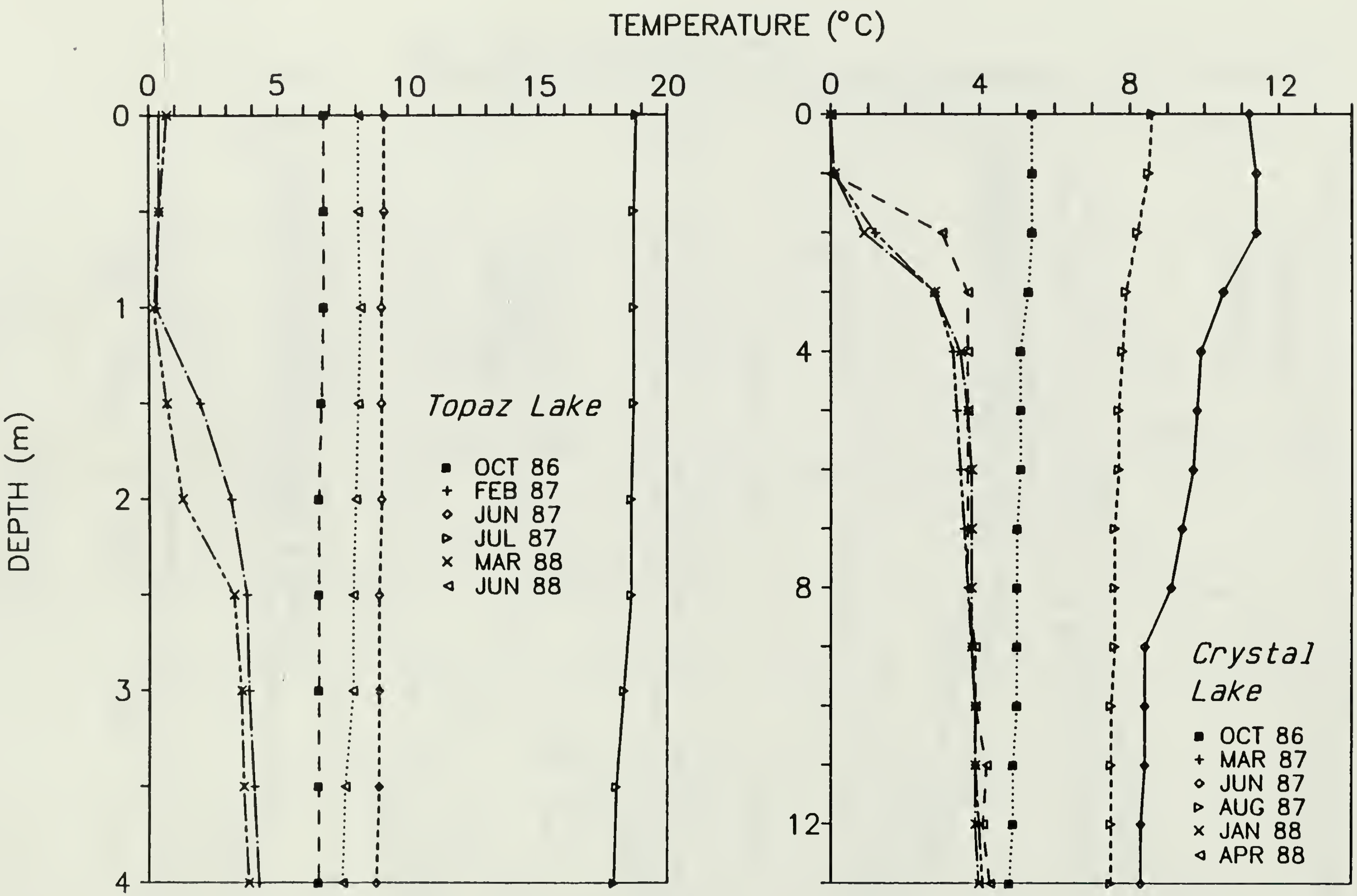


Figure 26. Representative temperature profiles for Topaz Lake and Crystal Lake.

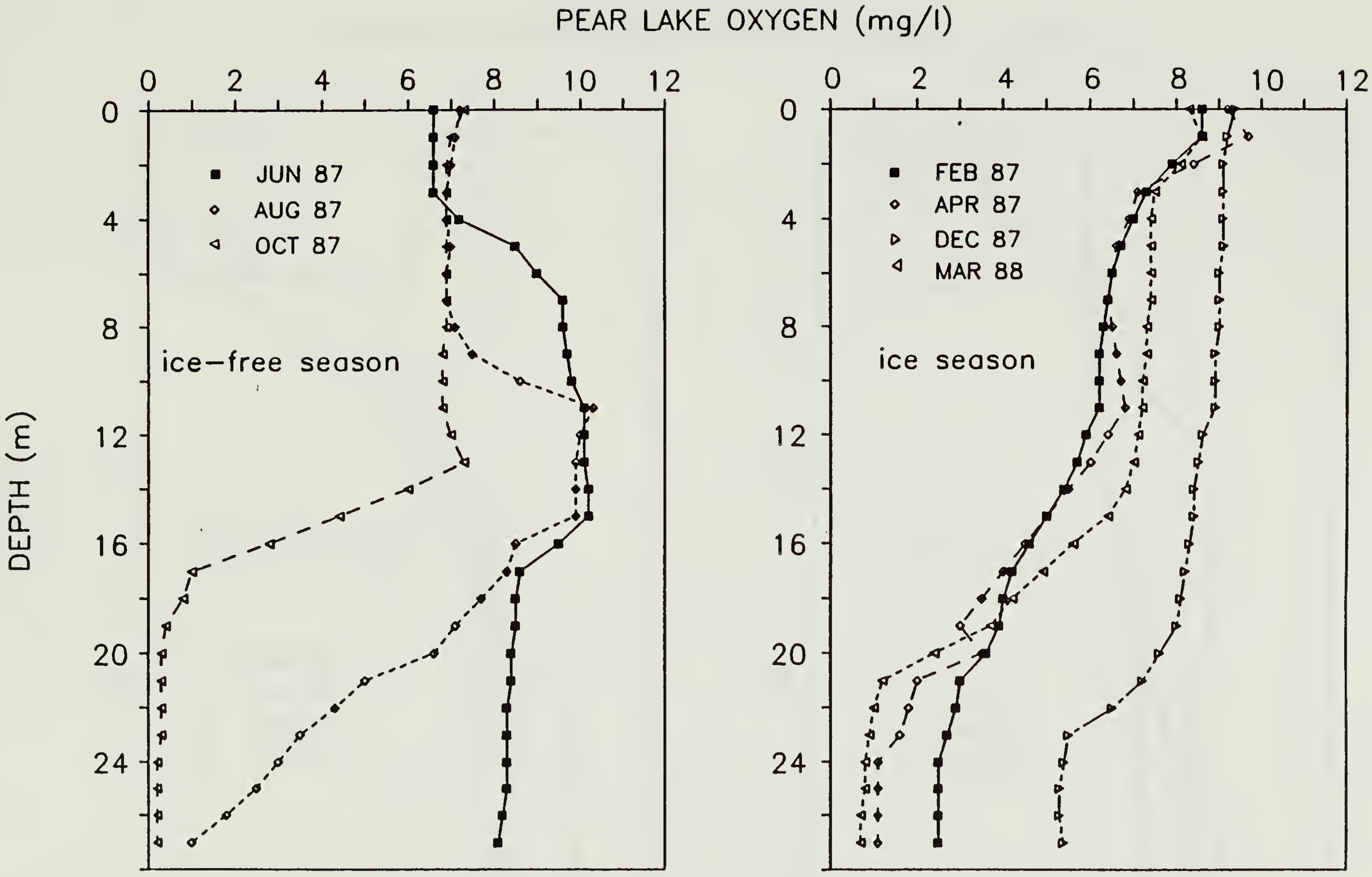


Figure 27. Representative oxygen profiles in Pear Lake.

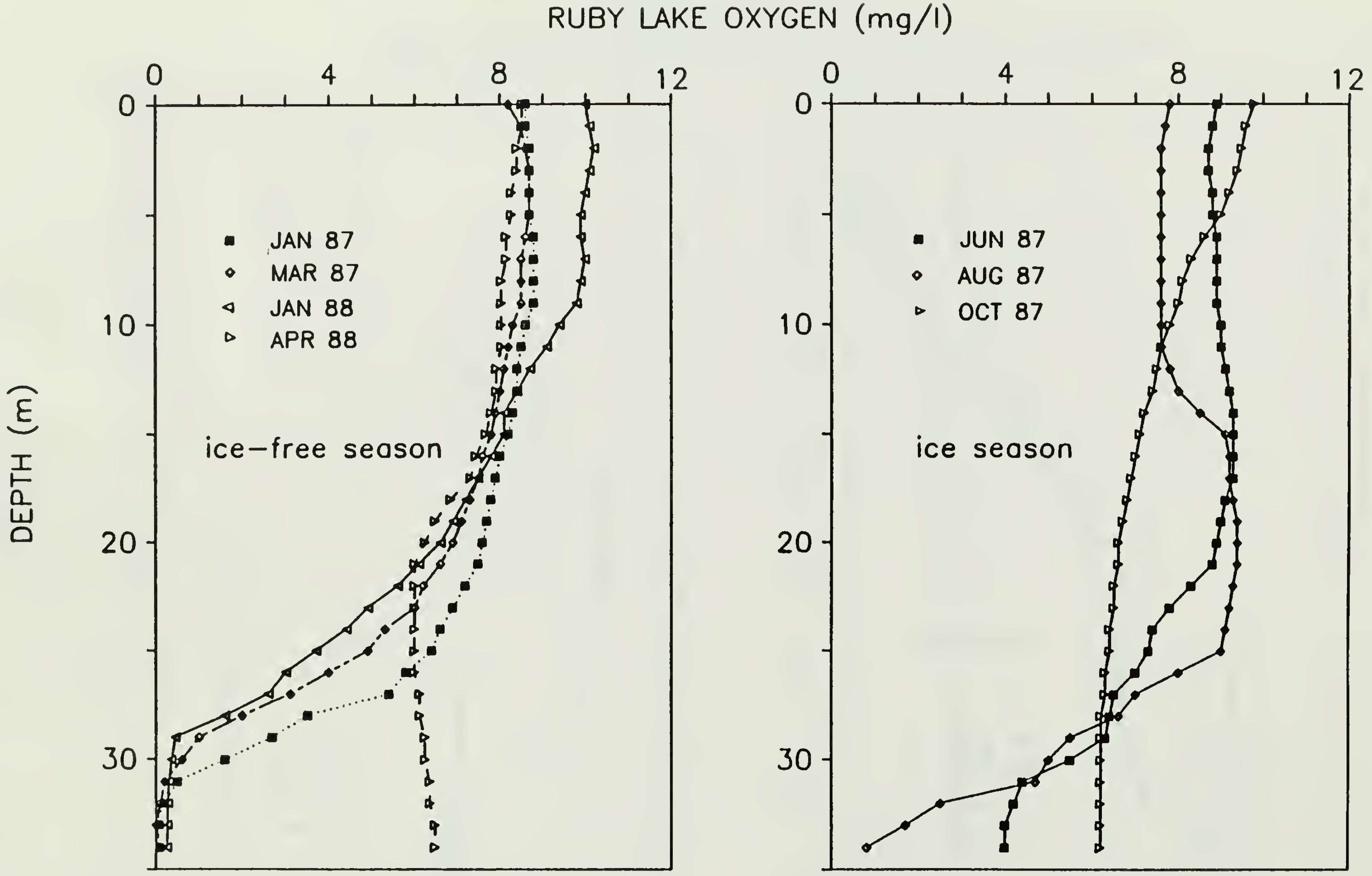


Figure 28. Representative oxygen profiles in Ruby Lake.

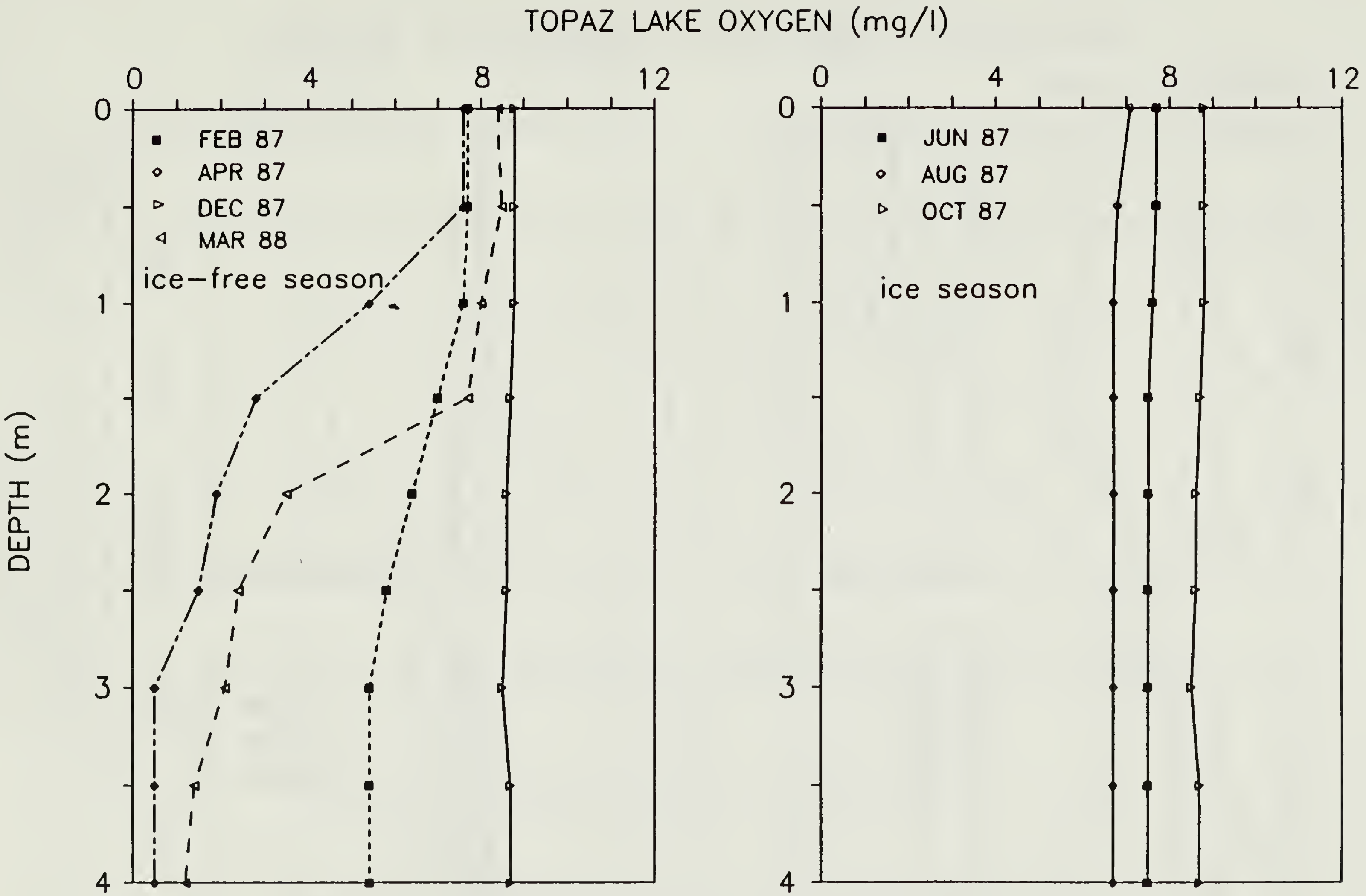


Figure 29. Representative oxygen profiles in Topaz Lake.

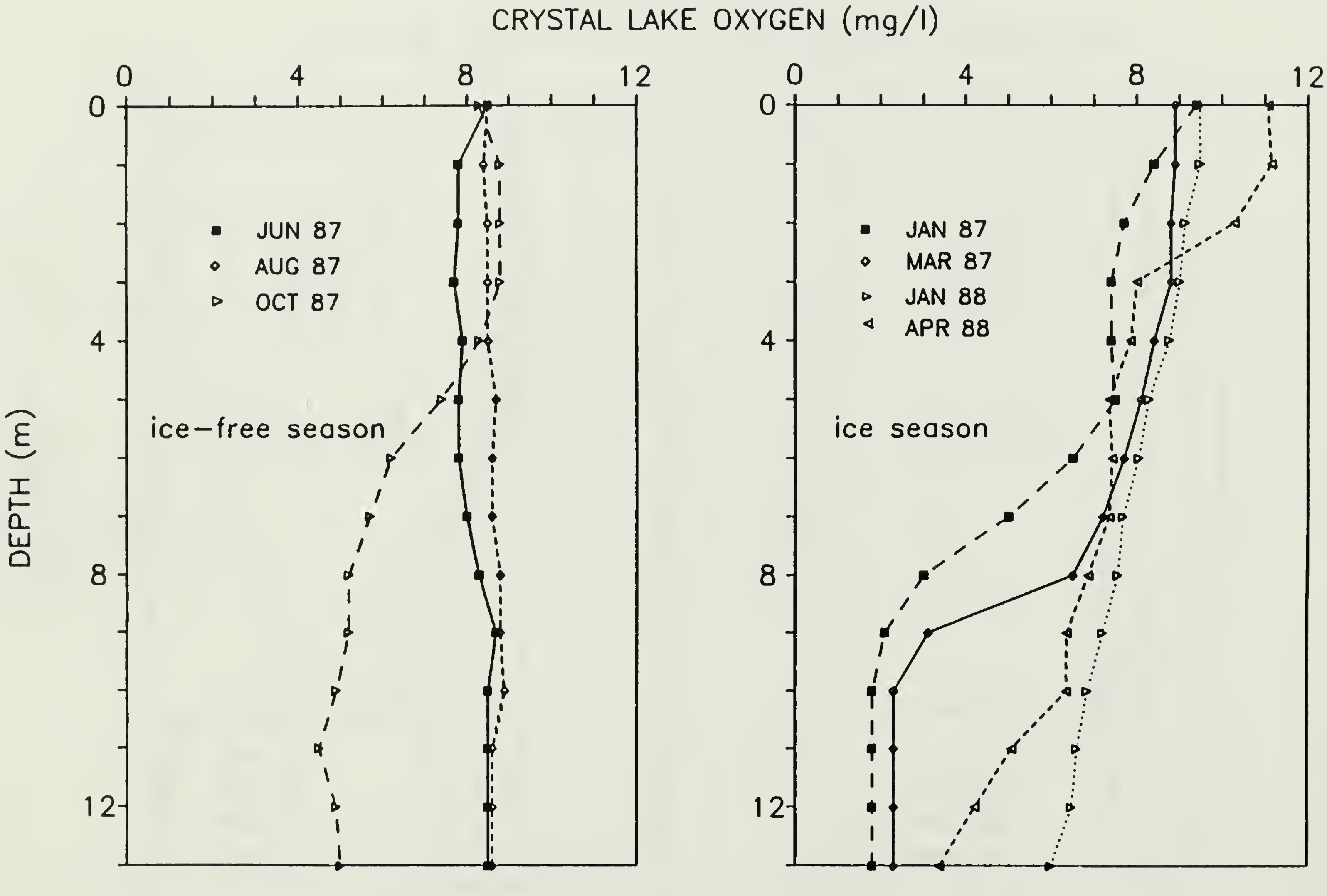


Figure 30. Representative oxygen profiles in Crystal Lake.

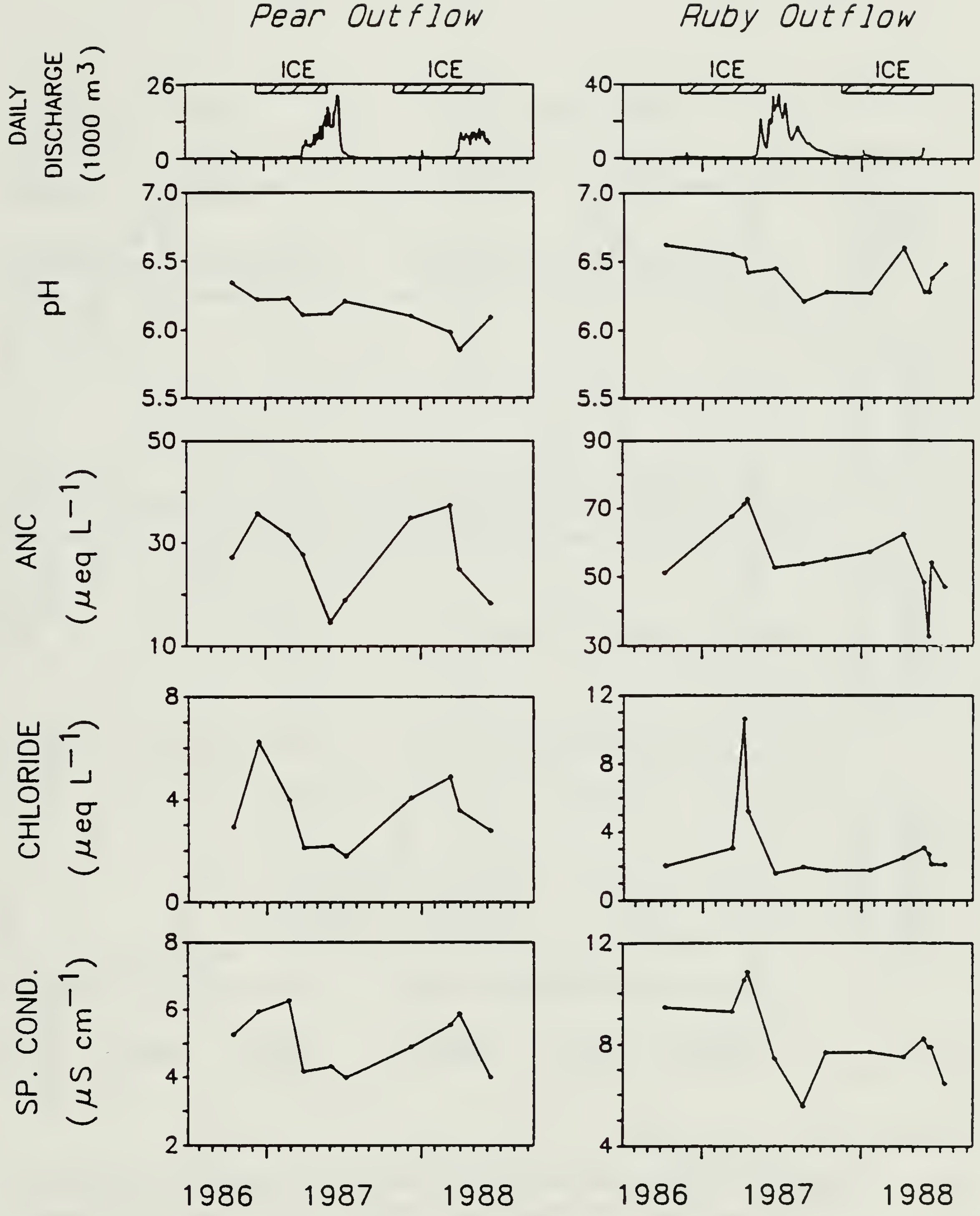


Figure 31. Time series of pH, ANC, chloride and specific conductance for the outflows of Pear and Ruby Lakes. Top panels show ice-cover and discharge.

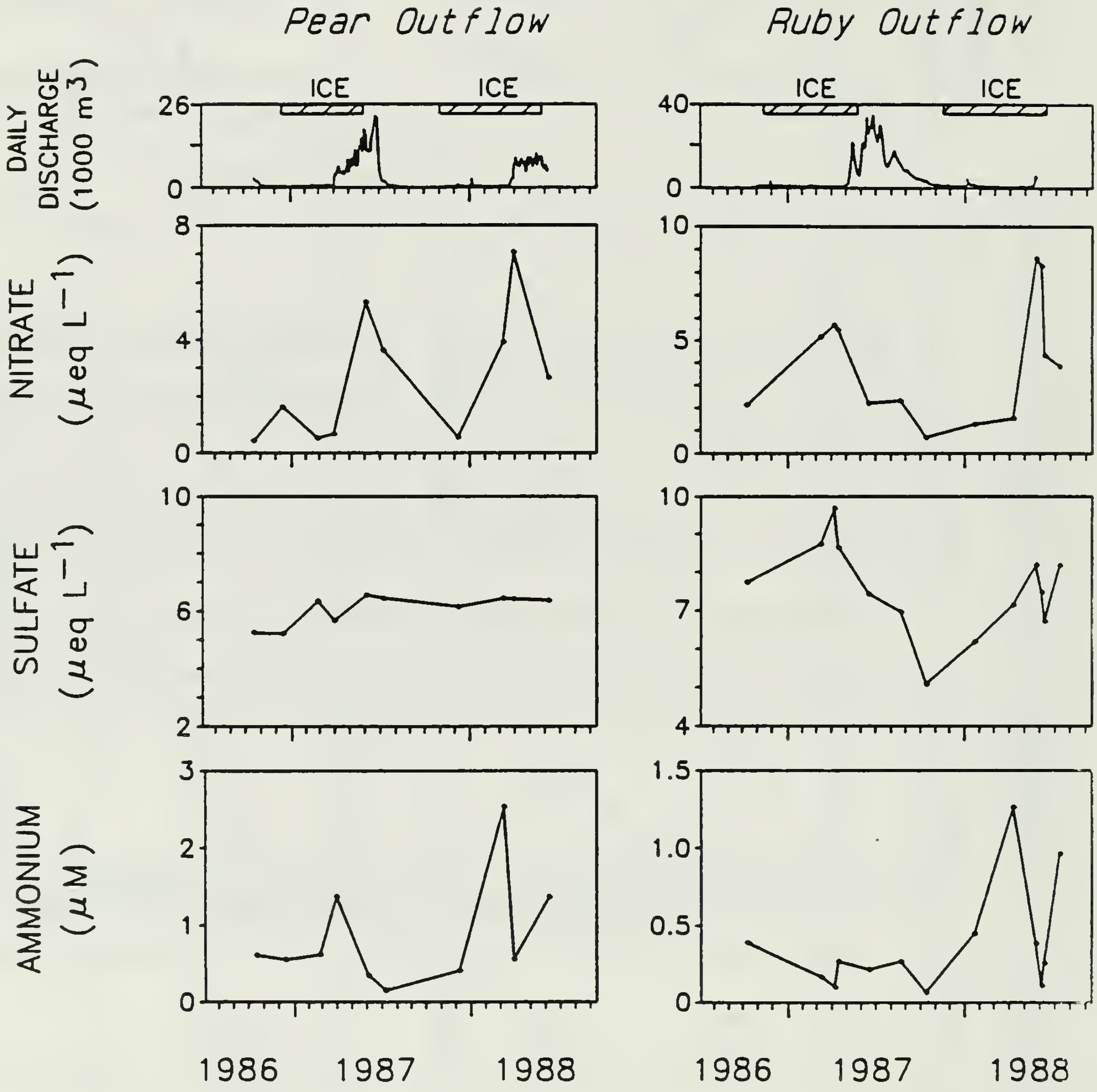


Figure 32. Time series of nitrate, sulfate and ammonium for the outflows of Pear and Ruby Lake. The top panels show ice–cover and discharge.

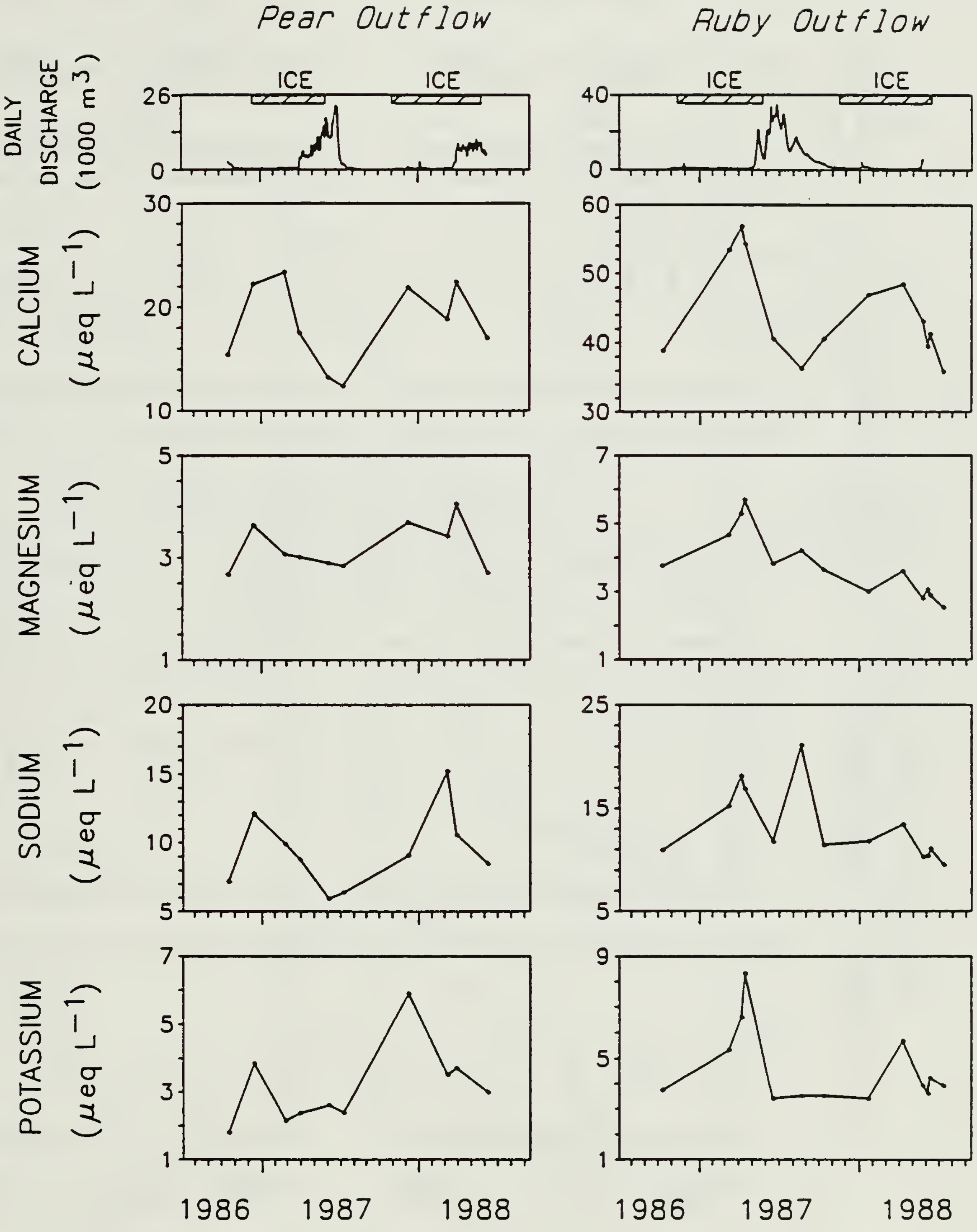


Figure 33. Time series of calcium, magnesium, sodium and potassium for the outflows of Pear and Ruby Lake. The top panels show ice-cover and discharge.

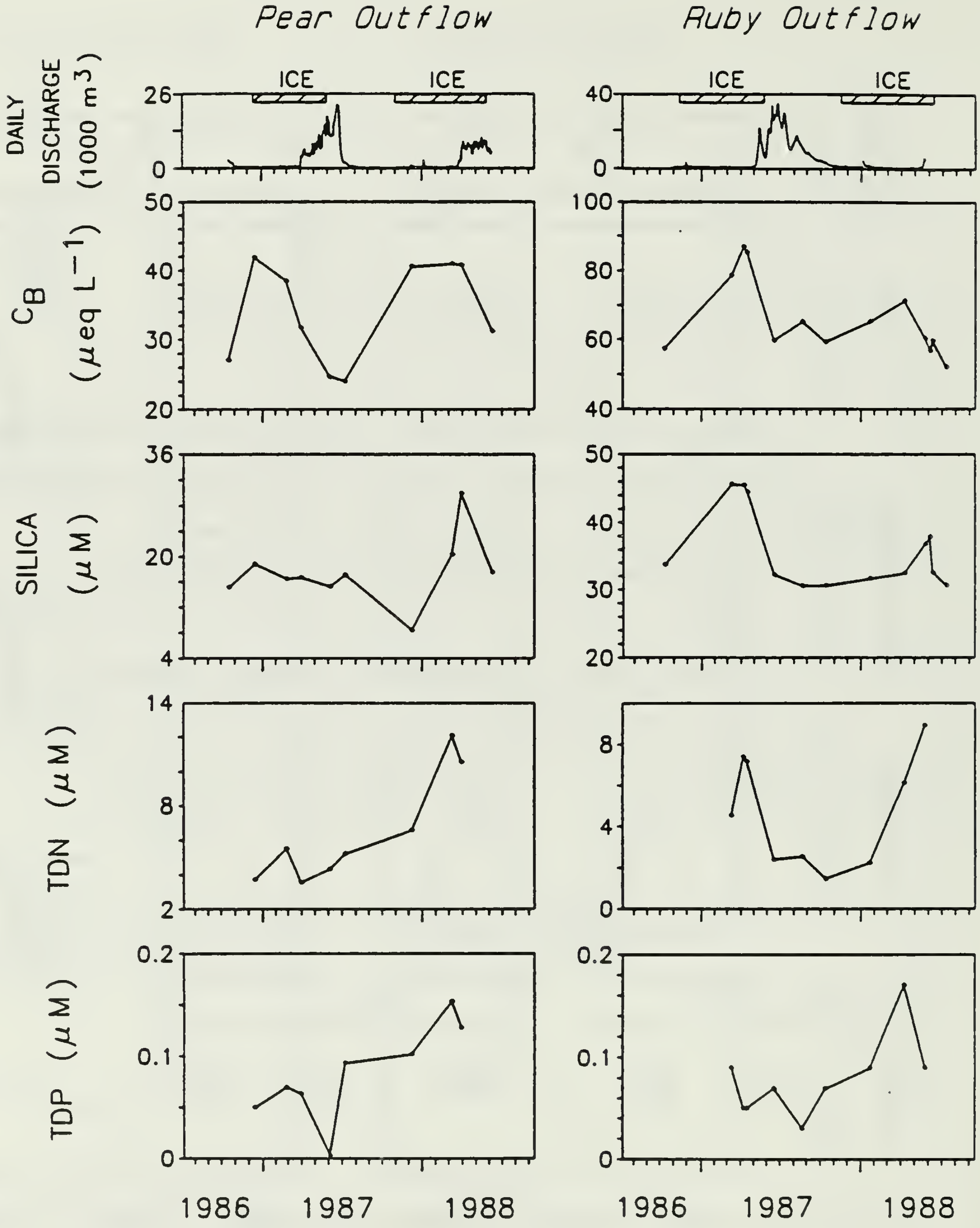


Figure 34. Time series of the sum of base cations, silica, and total dissolved nitrogen and phosphorus for the outflows of Pear and Ruby Lakes. The top panels show ice–cover and discharge.

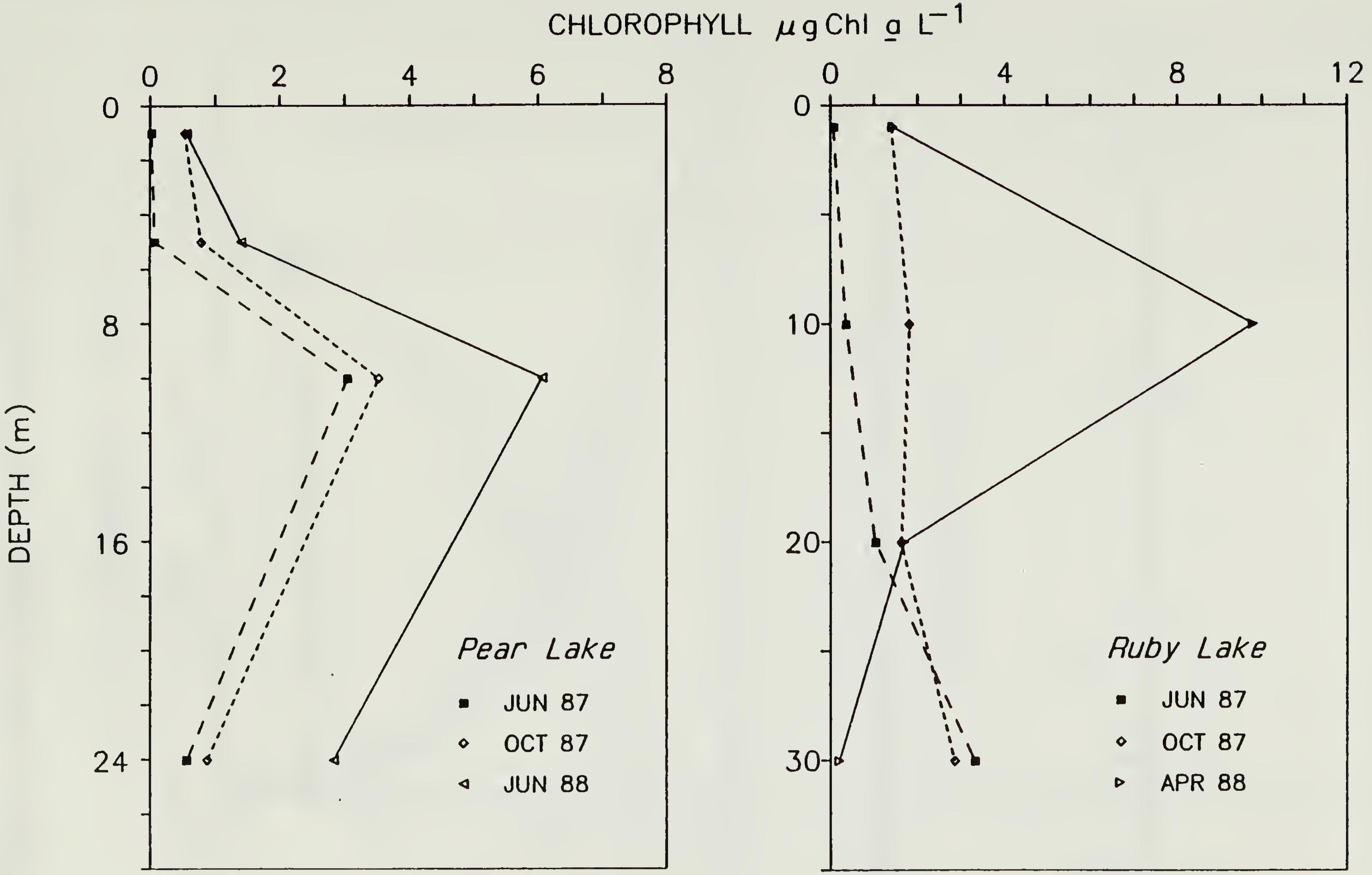


Figure 35. Representative chlorophyll profiles for Pear Lake and Ruby Lake.

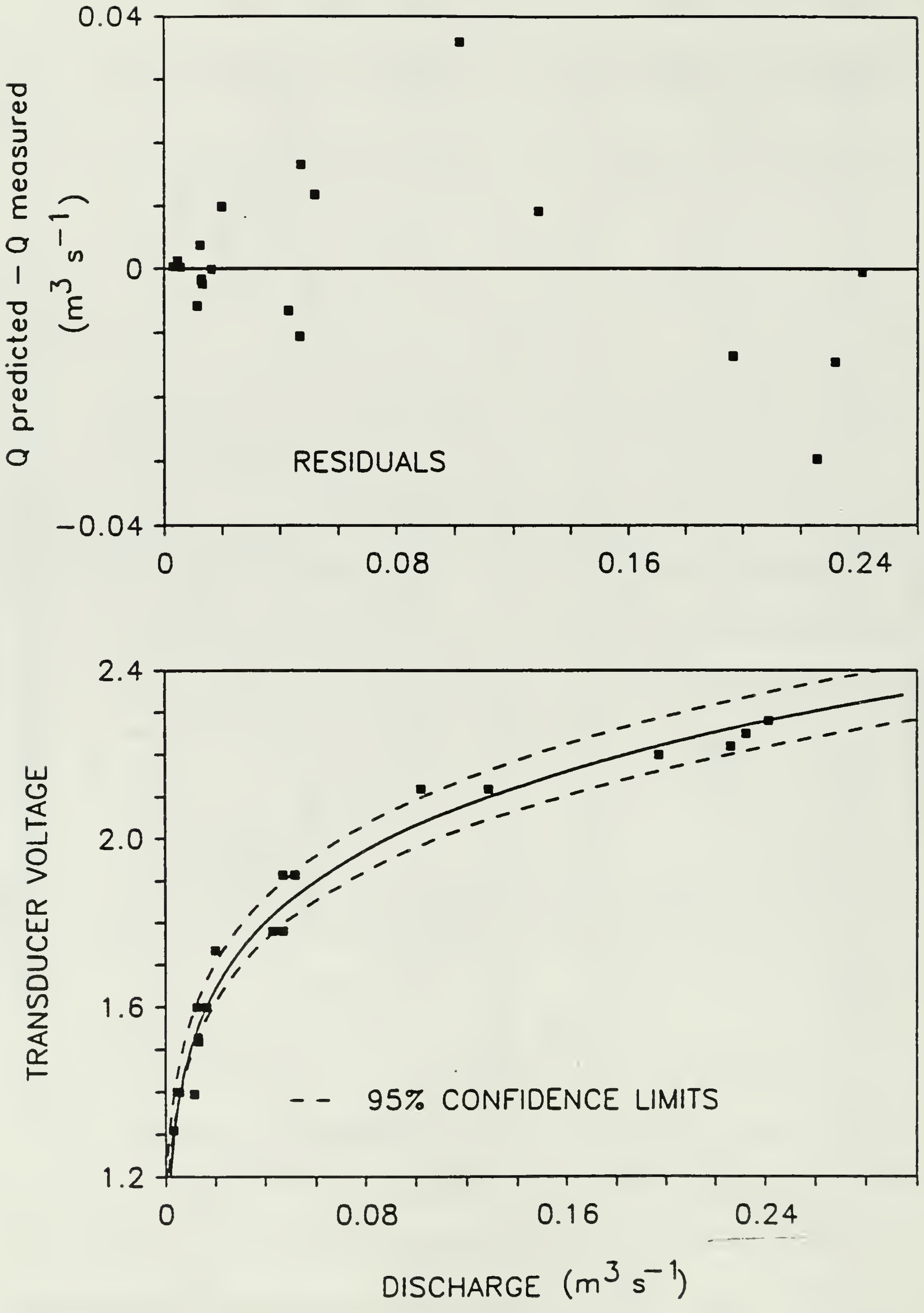


Figure 36. Pear Outflow rating curve and curve residuals. Dashed lines are 95% confidence limits.

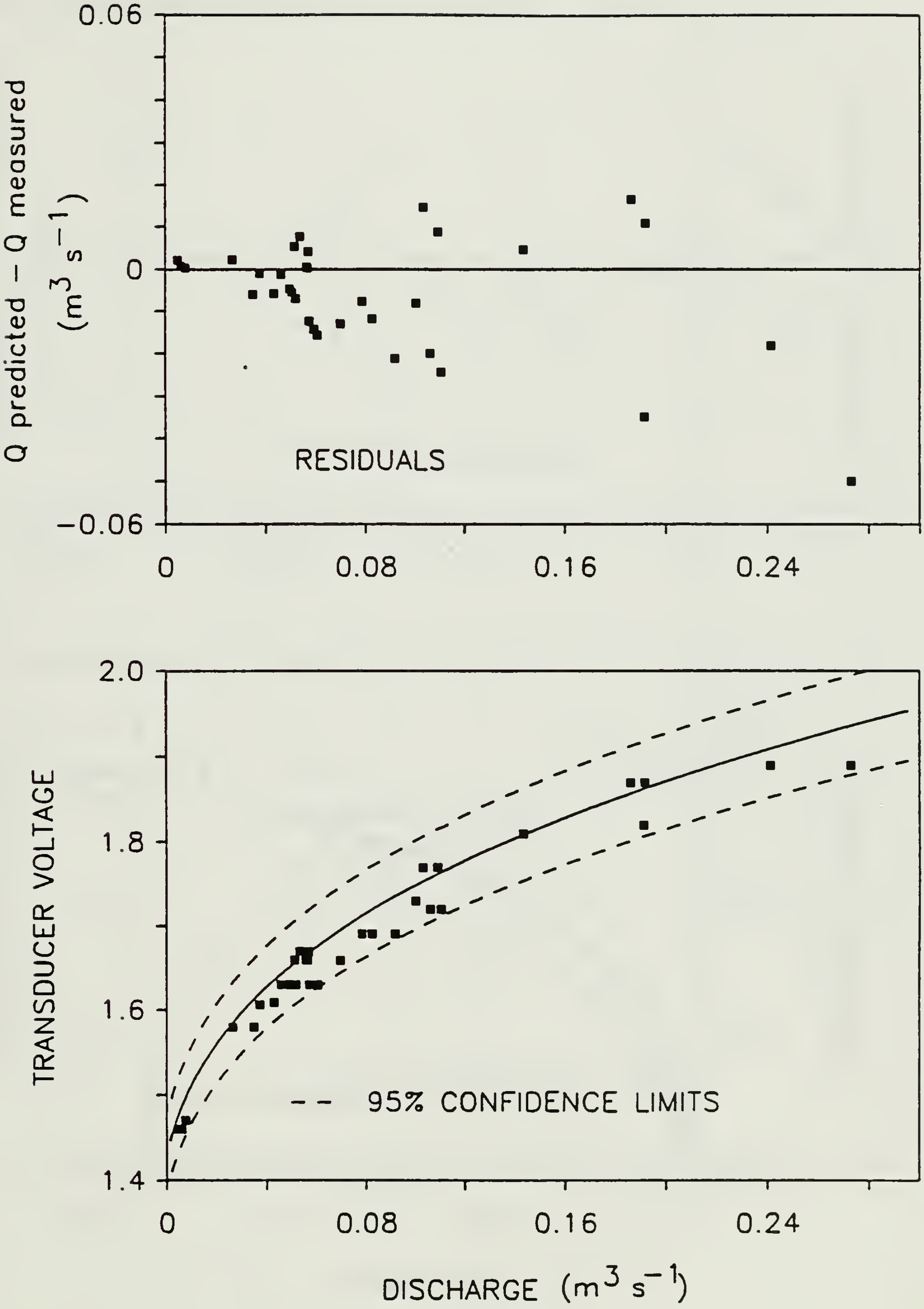


Figure 37. Topaz Outflow rating curve and curve residuals. Dashed lines are 95% confidence limits.

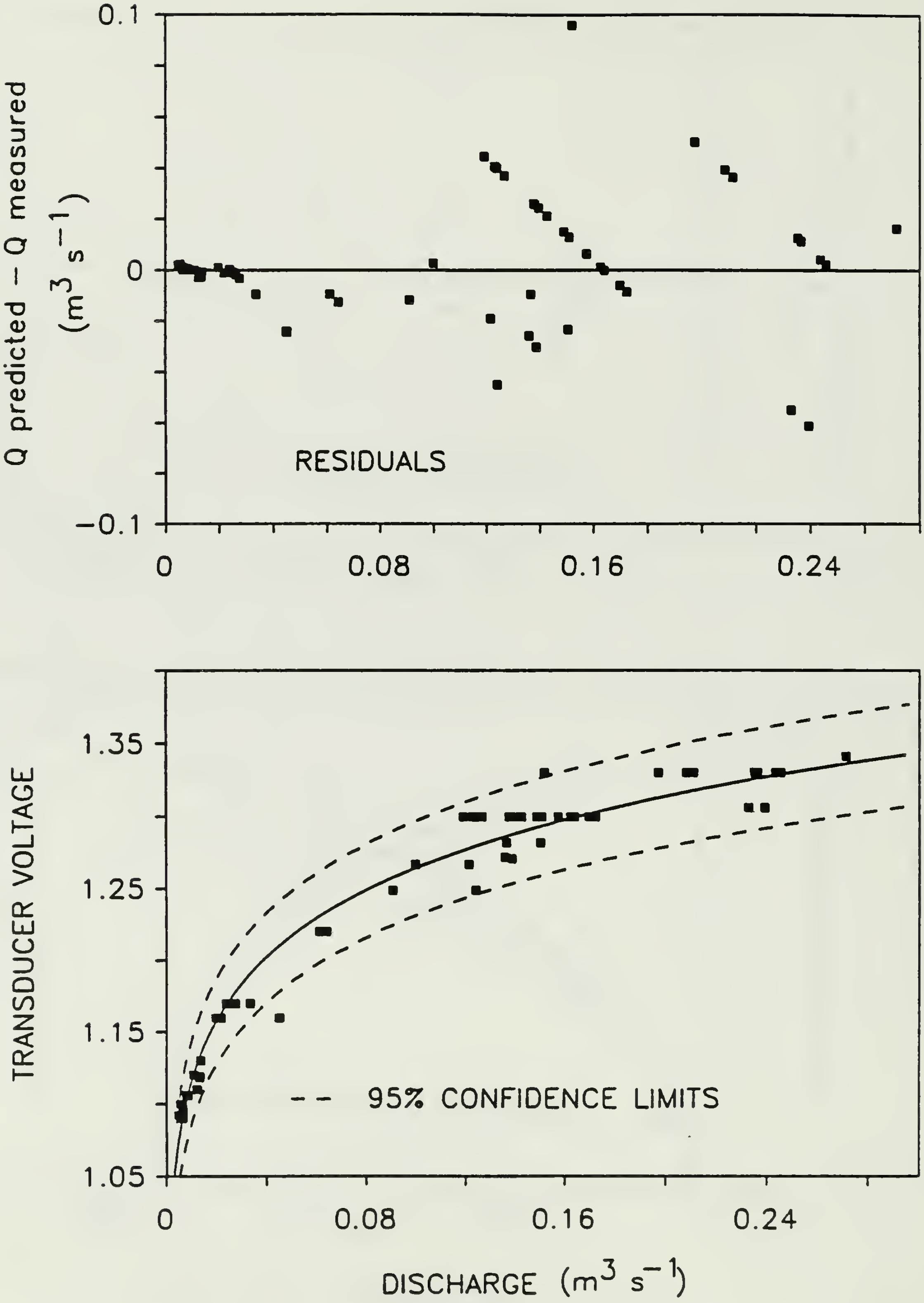


Figure 38. Ruby Outflow rating curve and curve residuals. Dashed lines are 95% confidence limits.

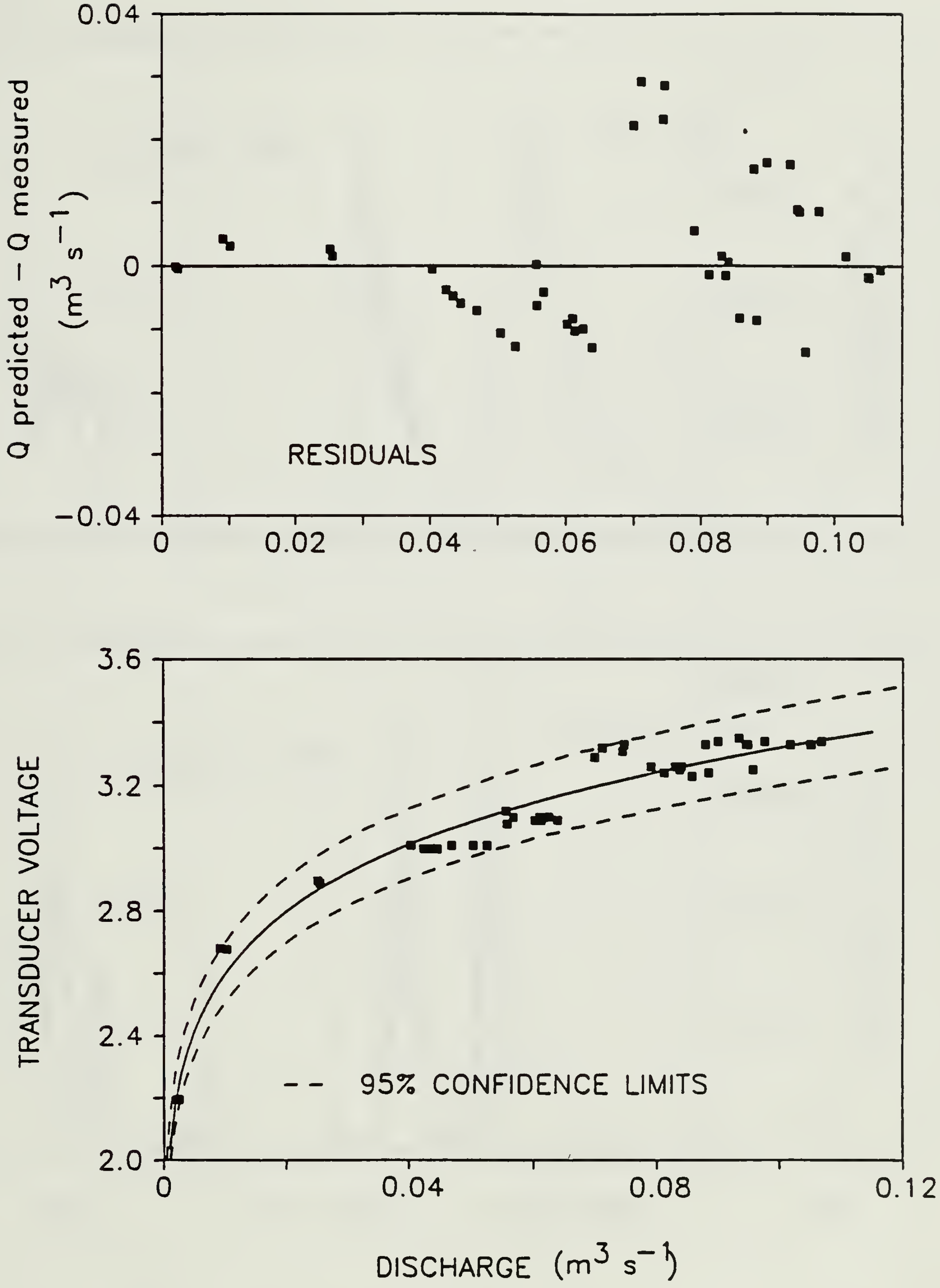


Figure 39. Crystal Outflow rating curve and curve residuals. Dashed lines are 95% confidence limits.

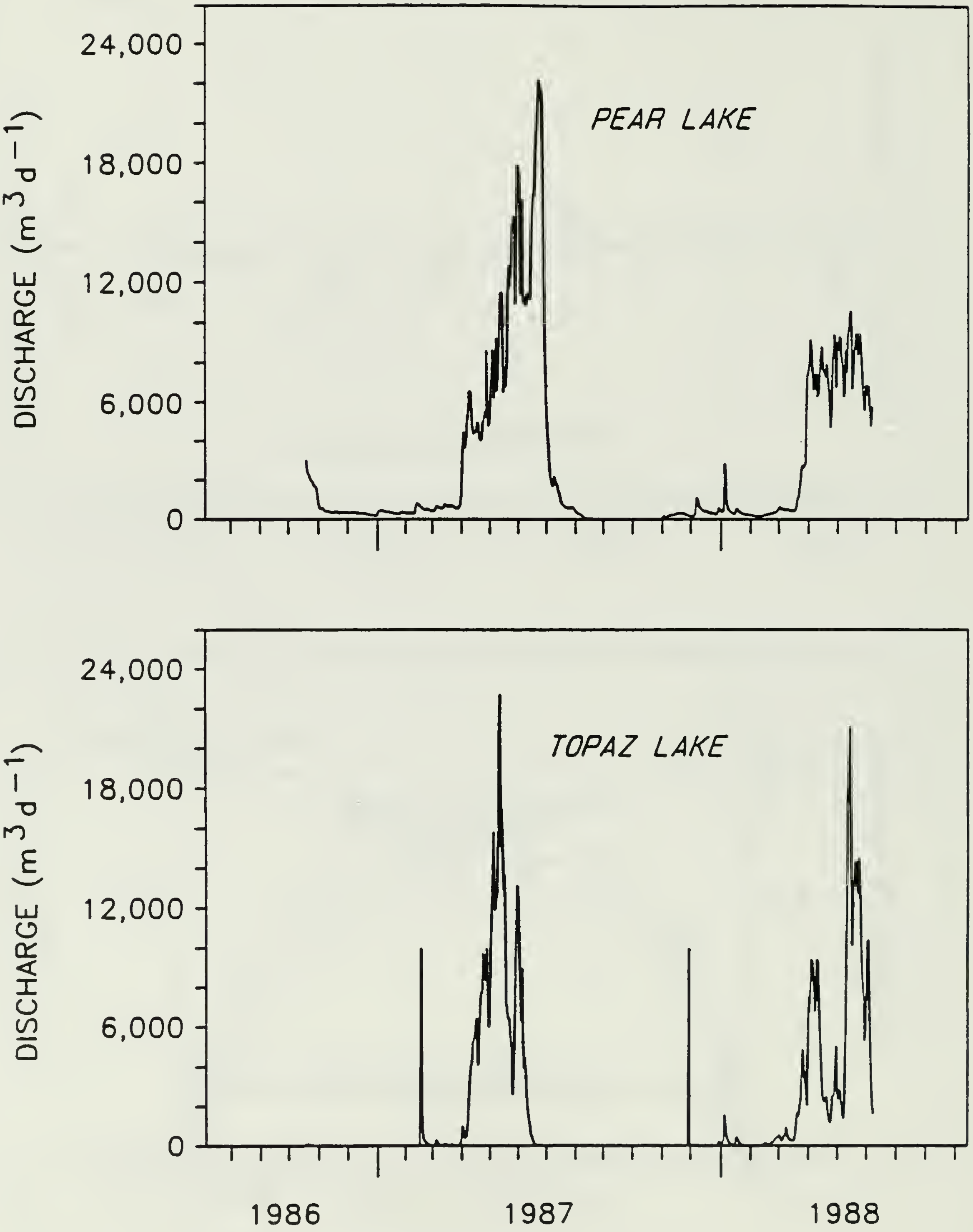


Figure 40. Outflow discharge for Pear and Topaz Lakes for the period October 1986 through June 1988.

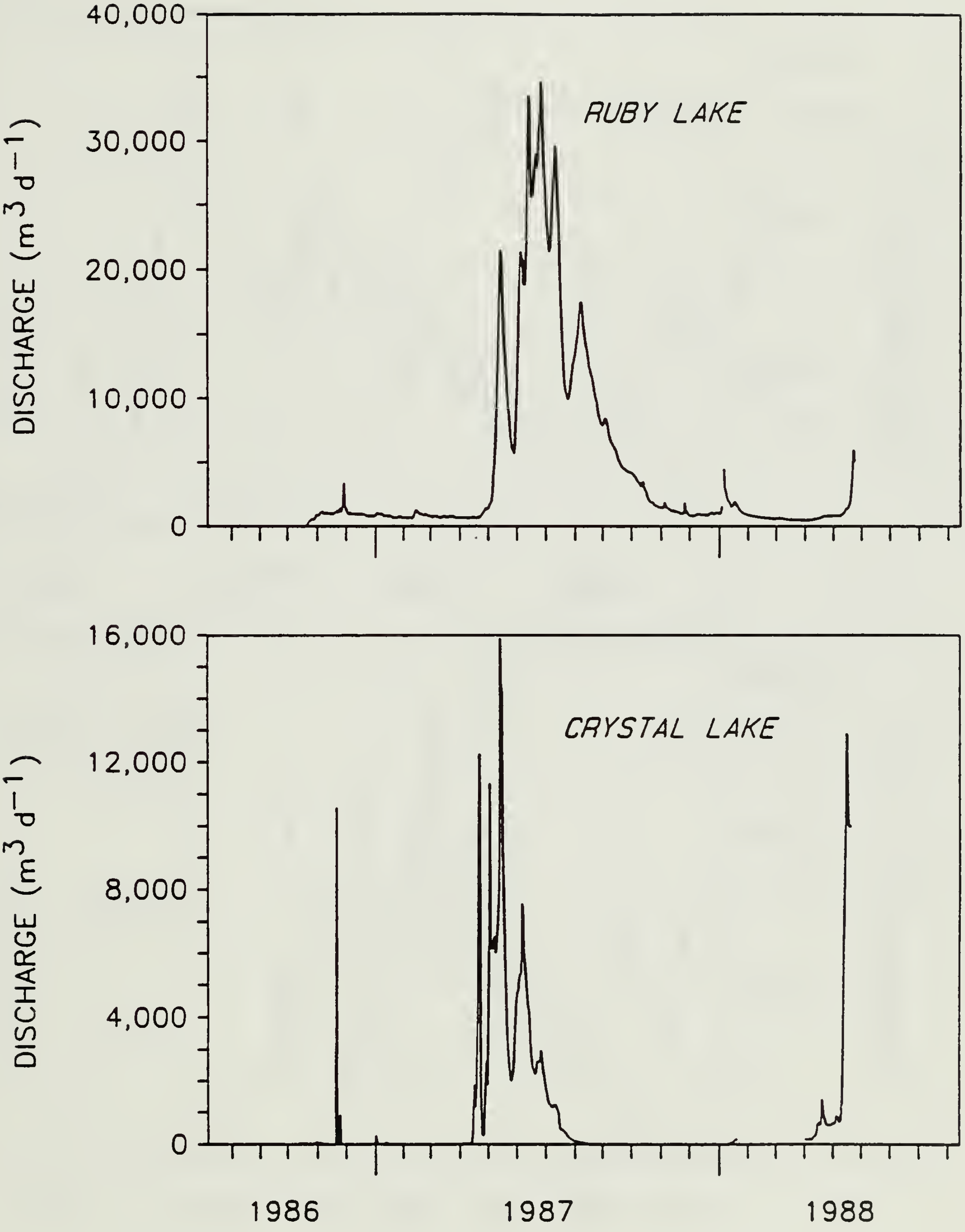


Figure 41. Outflow discharge for Ruby and Crystal Lakes for the period October 1986 through June 1988.

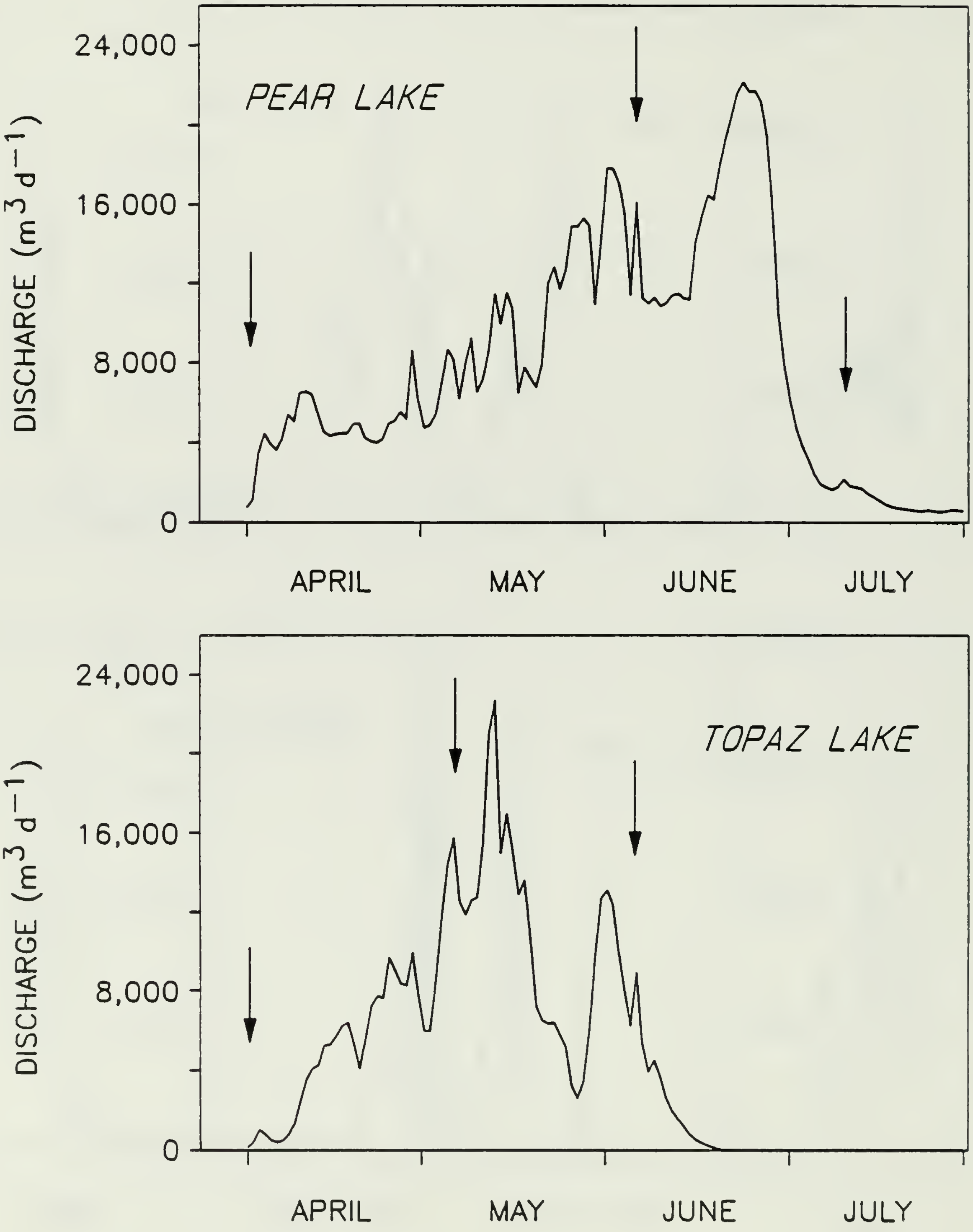


Figure 42. Outflow discharge for Pear and Topaz Lakes during the snowmelt period of 1987. Arrows indicate dates when water samples were collected.

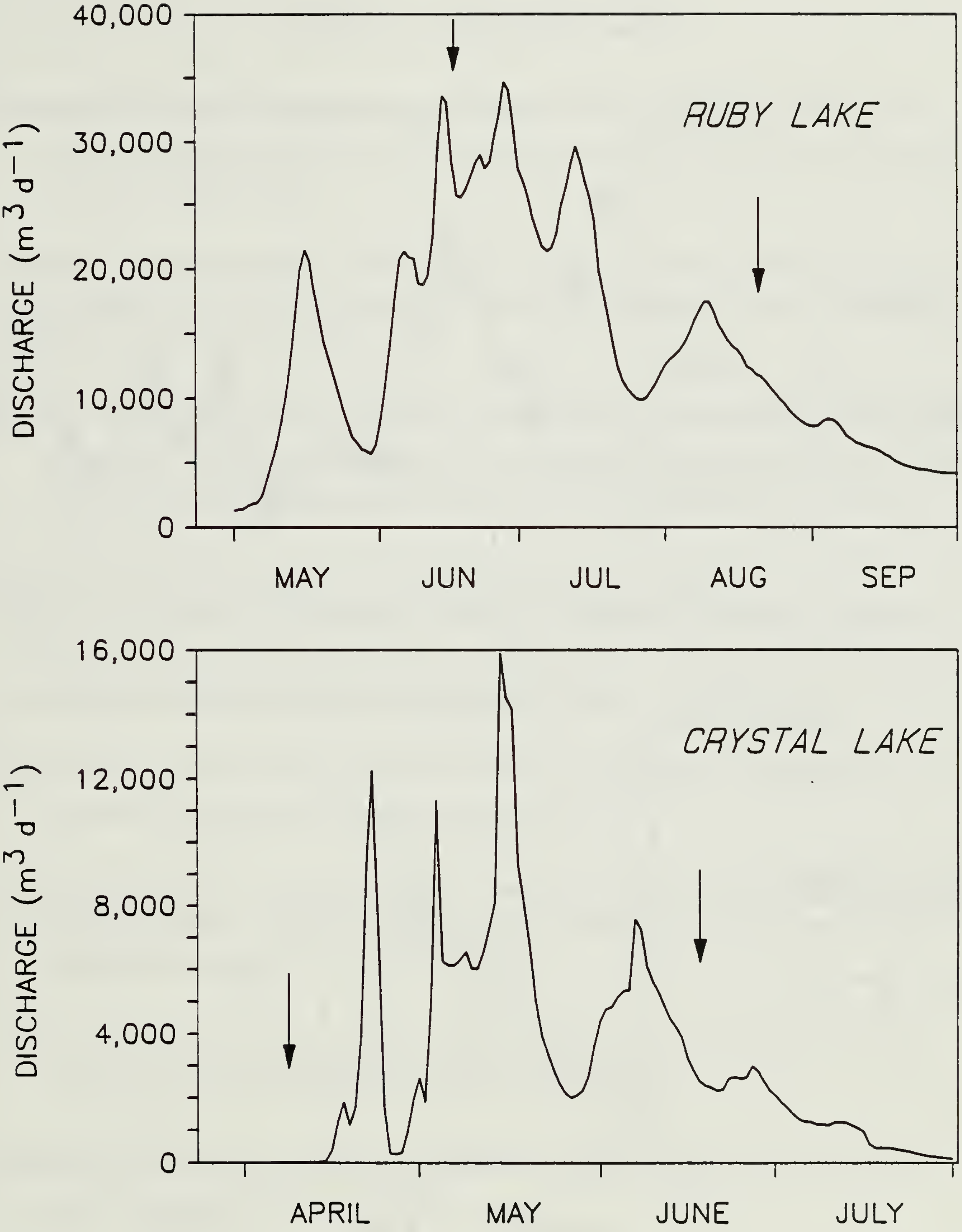


Figure 43. Outflow discharge for Ruby and Crystal Lakes during the snowmelt period of 1987. Arrows indicate dates when water samples were collected.

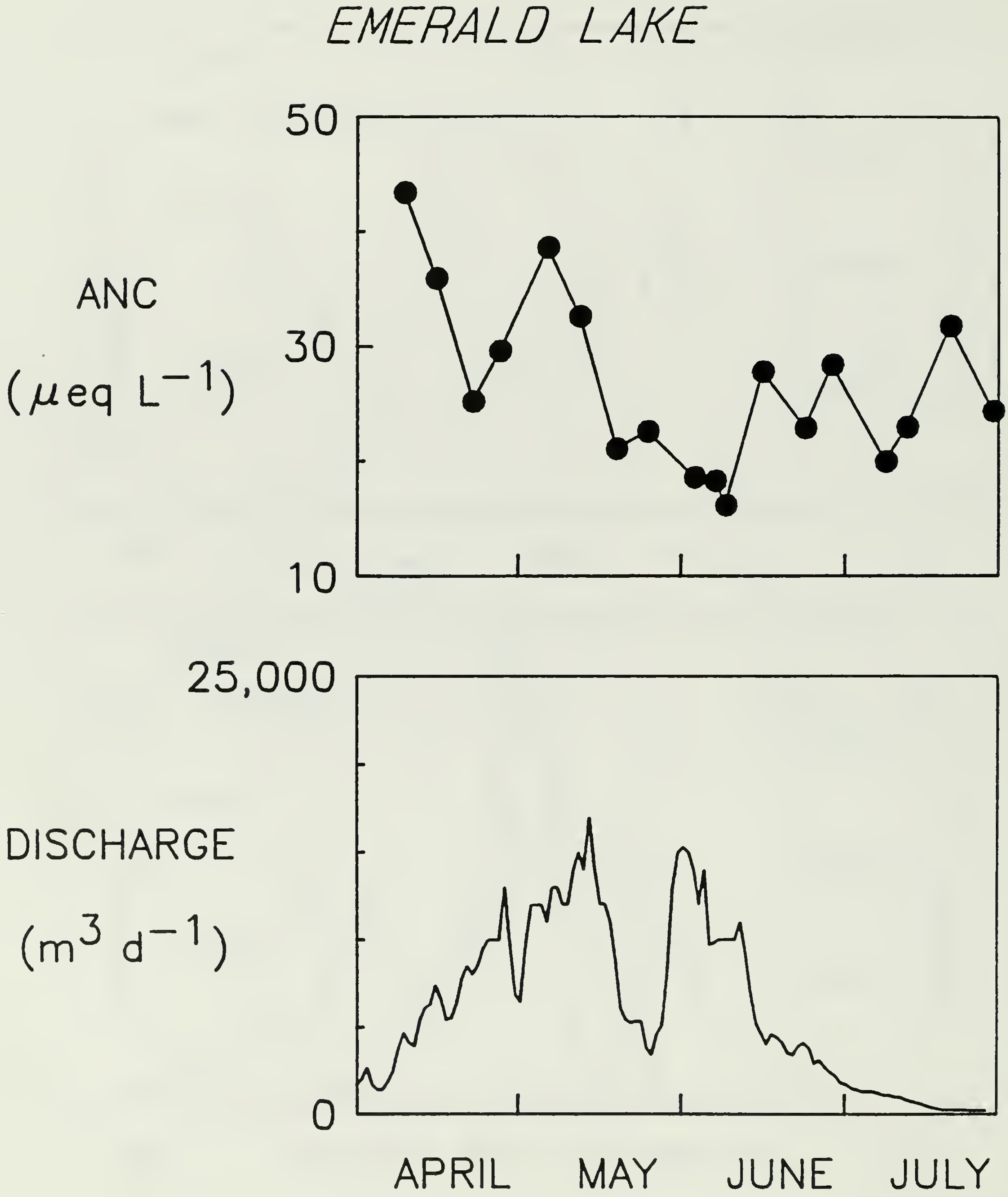


Figure 44. Outflow discharge and ANC for Emerald Lake during the snowmelt period of 1987.

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