

Final Report

Chemical and Biological Characteristics of Emerald Lake and the Streams in its Watershed, and the Responses of the Lake and Streams to Acidic Deposition

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Abstract

The hydrochemistry and aquatic ecology of Emerald Lake (a small, high-altitude lake in the Sierra Nevada, California) and the streams in its watershed have been studied for 5 years (1983-88), with an emphasis on the effects of acidic deposition. Time-series data collected throughout the year are presented for major ions, nutrients, trace metals, chlorophyll, zooplankton, and zoobenthos, and the seasonal and interannual variations in these variables are analyzed. Benthic chambers were used to measure the flux of solutes from sediments and rock surfaces to overlying water. Mass balances were calculated for major solutes in the lake. The hydrochemistry of inflow streams was measured over the course of several spates resulting from storm runoff. A numerical model of phytoplankton production was formulated from productivity measurements and other data. The ecology and population dynamics of the brook trout (Salvelinus fontinalis) were studied in detail, and the distribution of tadpoles of the Pacific treefrog, Hyla regilla, in ponds was surveyed for several years. Experimental acidification of large enclosures in the lake was conducted to determine the responses of the phytoplankton, zooplankton, and zoobenthos. Surveys of nearby lakes showed that Emerald Lake is representative of Sierran lakes with trout.

The overall conclusion of this research is that Emerald Lake is not currently showing serious chemical or biological effects of acidification. Many aquatic animals known to be acid-sensitive are found in the lake and streams, and the trout population does not show signs of acid-induced stress. However, the lake and streams are extraordinarily sensitive to acidification because of their extremely dilute ionic chemistry. Generation of acid neutralizing capacity (ANC) by processes within the lake is insignificant relative to ANC generation by watershed processes. Our experimental work indicates that even slight acidification of the lake will result in changes in the species composition of the zooplankton assemblage. Episodic acidification, particularly during snowmelt, could have direct deleterious effects on sensitive early stages of trout. If acidic deposition were to increase, the lake and streams would be readily affected.

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Summary and Conclusions

Our research on the limnology of Emerald Lake and the streams in its watershed has focussed on 1) describing the seasonal and interannual variability in physical, chemical and biological characteristics, based on 5 years of data (1983-88), 2) detecting chronic and acute effects of acidic deposition, and 3) evaluating the sensitivity of these ecosystems to acidification by possible future increases in acidic deposition. To attain these objectives, we have employed a combination of chemical and biological sampling at regular intervals throughout the year augmented by more intensive sampling at critical times such as during snowmelt and summer rains, studies of the ecology and population dynamics of the aquatic biota, and experimental manipulations designed to elucidate the responses of aquatic organisms to acidification. Conclusions from our research include the following:

Seasonal and interannual variation in hydrochemistry

Seasonal patterns in the chemistry of Emerald Lake are controlled by thermal stratification, by flushing during snowmelt, and by nutrient uptake by phytoplankton during the ice-free season. Much of the interannual variation in the chemistry of Emerald Lake and the streams in its watershed can be explained by variation in the annual quantity of snowfall, which determines the degree of flushing of the lake during snowmelt as well as the duration of the subsequent ice-free season. Additional variation is caused by large summer rain storms, which occur infrequently and are variable in magnitude, and by major avalanches, which are of uncertain frequency and only occurred once during the study. Comparison of mass inputs to mass outputs for major solutes in the lake over two years shows that most of the transport of water and solutes through the lake occurs during the spring snowmelt period, and that the lake has little effect on solute transport on an annual basis.

Processes affecting the ionic composition of the lake

We used a mass-balance model for the lake to quantify fluxes of major solutes during both the summer and under ice cover in the winter. During the ice-free season, silica, base cations, nitrate, and sulfate were lost from the lake water, but flux of ANC was undetectable. No solutes showed detectable fluxes during the winter. These fluxes are compared to measurements of

several potentially important sources and sinks of solutes in the lake. Groundwater seepage is very low and has no detectable effect on lake chemistry. Solute fluxes between overlying water and both fine sediments and submersed rock surfaces were measured with benthic chambers. Most solutes increased in concentration in chambers over fine sediments, but rock surfaces had little effect on solute concentrations. Comparison of the fine-sediment fluxes with those determined from mass balance shows a poor correspondence, however, indicating that sediment-water exchange has little effect on the ionic composition of the lake. Solute fluxes resulting from nutrient uptake by phytoplankton and benthic diatoms were estimated from measurements of primary production (phytoplankton), the observed loss of silica in the lake (diatoms), and the average elemental stoichiometry of algal biomass. These estimates show that solute fluxes resulting from phytoplankton growth are large relative to those resulting from benthic diatom growth. Comparison of solute fluxes determined from mass balances during the summer with those estimated to result from phytoplankton growth shows a good correspondence, indicating that phytoplankton growth alone can explain the solute fluxes observed in the lake. This hypothesis is consistent with the observation that solute fluxes were undetectable in the lake during the winter, when phytoplankton growth is light-limited.

Episodic acidification of the lake and streams

Episodic acidification of Emerald Lake and the streams in its watershed can occur during snowmelt (analyzed by Dozier et al. 1987) and during the occasional intense rain storms in the summer and autumn. Summer rain at Emerald Lake is acidic and high in solutes compared with snow. Two storms in mid-July 1984 were large enough to change the normal summer conditions in the lake, although the lake pH fell only to 5.8 and returned to normal (6.0-6.3) soon after the storms. The long-lasting effects of these storms on the lake were caused largely by the hydrological effects of the rain (flushing, mixing, and transport of particulate material into the lake from the watershed), which were more important than the effects of the chemistry of the rain.

Smaller summer storms of < 1.5-cm depth are common, and runoff from these storms temporarily affects the chemistry of the inflows, but does not cause notable changes in the chemistry of the lake. Runoff from two such storms in September 1987 caused marked but ephemeral changes in stream

chemistry. The chemical changes could not be predicted by assuming conservative mixing of rain and stream waters, indicating that substantial changes in the chemistry of rainwater occurred during runoff. The net effect of these changes was to neutralize acidity and to increase the concentration of ANC in runoff. These changes occurred in runoff from basins dominated by bare rock surfaces as well as in runoff from basins containing greater amounts of soils.

Primary production of phytoplankton

We formulated a numerical model to estimate primary production by phytoplankton over time in Emerald Lake, based on ^{14}C assays of productivity, chlorophyll-*a* concentrations, and measurements of incident solar radiation and water transparency. Total annual production by phytoplankton in Emerald Lake, assuming negligible production under ice, was 5970, 7370, and 6460 mg C m⁻² in 1984, 1985, and 1987, respectively. These rates are on the low end of the range that is generally considered oligotrophic. Examination of the relation between environmental variables and production did not reveal a consistently dominant environmental factor that might control production, although thermal stratification coincided with reduced production in 1984 and 1987. During the ice-free season, light levels were adequate to support production throughout the water column, and excessive light in the surface waters probably resulted in photoinhibition of phytoplankton production.

Ecology of zooplankton and zoobenthos

The zooplankton assemblage in Emerald Lake was dominated by a copepod (Diaptomus signicauda), three cladocerans (Daphnia rosea, Holopedium gibberum, Bosmina longirostris), and five rotifers (Keratella taurocephala, K. quadrangula, Polyarthra vulgaris, Conochilus unicornis, Trichocerca capucina). Nearly all of the zooplankton species were most abundant during the summer. There were, however, predictable sequences in the appearance and dominance of zooplankton species through the summer, with some species dominating shortly after the disappearance of ice cover (e.g. Holopedium gibberum) and others dominating in late summer (e.g. Daphnia rosea). There were substantial interannual variations in the abundances of particular species of zooplankton that, in some cases, appear related to interannual variation in the length of the ice-free season. For example, species which dominate late in the summer (e.g. D. rosea) remained

at relatively low densities throughout 1986, probably because of the persistence of ice into July of that year and the subsequent reduction in the duration of the ice-free season.

In Emerald Lake, the zoobenthos was dominated by midge larvae (Chironomidae), aquatic earthworms (Oligochaeta), water mites, and benthic microcrustaceans. Sponges (Spongilla lacustris) occurred on rock surfaces in shallow waters. In the inflow and outflow streams, the zoobenthos and the drift (organisms carried by stream currents) were dominated by midge larvae and blackfly larvae (Simulium and Prosimulium). We also found larvae of various mayflies (Baetis, Ephemerelellidae) and caddisflies (Rhyacophila) in all streams, and in the outflow, we found stonefly larvae (Nemouridae), water mites, earthworms, and fingernail clams (Pisidium sp.). In the outflow stream, densities of zoobenthos were generally higher on rock substrates, particularly those covered by moss, than on soft substrates such as sand and mud. In the streams, most taxa peaked in abundance in summer or early autumn, although there was much spatial and temporal variation in abundances. Densities and drift of most stream taxa were lower in the summer of 1986 than in the other years, probably reflecting the shorter growing season.

Ecology of fish and amphibians

The Brook Trout (Salvelinus fontinalis) was the only fish species found in Emerald Lake as well as in nearby lakes and streams. Population sizes of juvenile and adult brook trout were relatively constant from year to year. However, population sizes of young-of-the-year trout varied five to ten fold among years. The number of eggs surviving the spawning season was primarily limited by the availability of suitable spawning sites. The large interannual variation in the survival of eggs, embryos, and fry was related to interannual variation in physical disturbances of the habitat (avalanches and resultant floods; drought; freezing of gravel beds harboring eggs).

Growth of trout was rapid during early life stages, but decreased as fish aged, and after 3 years growth rates were negligible. The population was dominated by old (3-6 years, maximum 11 years) individuals of small size (most were < 20-cm long). The condition, gonad to body weight ratios, and fecundity of adult trout, and the growth rates of young-of-the-year trout, were lower in 1986 than in other years, probably because of the unusually short ice-free season. Trout in Emerald Lake ate primarily chironomids, cladocerans, and

terrestrial insects. while trout in the outflow fed on a variety of terrestrial and aquatic insects. Terrestrial insects were more important in the diets of large than small individuals.

The only amphibian occurring in the vicinity of Emerald Lake was the Pacific Treefrog (Hyla regilla), which generally breeds only in ephemeral waterbodies. Tadpoles of this species were found in 12 of 15 ponds surveyed in the summers of 1985, 1986, and 1987. The occurrence and abundance of tadpoles appeared unrelated to pond size, persistence, elevation, or pH (range, 5.3-7.2).

Directions for Future Research

Hydrochemical monitoring program at Emerald Lake

We strongly recommend continuation of the hydrochemical monitoring program at Emerald Lake and the streams in its watershed. Our work so far has shown that interannual variability is high, largely because of the variability of precipitation, and we have little information on how well the 5 years of study represent the typical range of variation. In addition, continued monitoring would show the effects of future changes in acidic deposition. This monitoring could be done at monthly or bimonthly intervals, with more intensive sampling during snowmelt and summer storms (see below).

Biological monitoring program at Emerald Lake

Biological monitoring is equally important as and complementary to the hydrochemical monitoring. However, rather than continue to collect quantitative samples of all of the major ecological groups, efforts could be focussed on a few groups that are known to be sensitive indicators of acidification. Our investigations indicate that the zooplankton assemblage, in particular, should be closely monitored because it shows sensitive responses to acidification, certain species are an important food source for trout, and because quantitative samples can be collected and processed readily. The stream zoobenthos should also be monitored, but qualitative sampling at less frequent intervals may be adequate. Continued monitoring of the trout population is recommended; future studies of trout at Emerald Lake should focus on the abundance and growth of sensitive early stages.

Expansion of trout studies

Variation in the response of trout populations to acidification results principally from 1) regional differences in the hydrology, chemistry, and food base of waters in which they occur, and 2) differences in the strains or species of trout present, which may vary in their tolerances to acidification. The brook trout, which is the only trout present in the Emerald Lake system, is known to be relatively tolerant of increased acidity. The rainbow trout (Salmo gairdneri), on the other hand, is also widely distributed in the High Sierra and is known to be much more sensitive to acid inputs than is the brook trout. There is no information on the acid sensitivity of the native

golden trout (Salmo aguabonita); however, its close relationship with the rainbow trout suggests that this species would also be sensitive to acidification. Furthermore, golden and rainbow trout spawn in the spring, coincident with short-term acidification associated with snowmelt. We propose three additional classes of trout investigations:

- 1) Detailed studies of the population dynamics and ecology of golden and rainbow trout in Sierran lakes and streams. These data would establish a baseline for assessing the current and future condition of these populations.
- 2) A field survey of the distribution and abundance of trout populations in Sierran waterbodies, as well as an extensive review of the literature and records. Concordant surveys of hydrochemistry will allow us to characterize the chemical sensitivity of trout waters to acidification. The survey data will be used to construct a regional assessment, including an economic analysis, of the impact of different acid deposition scenarios on Californian trout fisheries.
- 3) Experimental studies of the effect of acidification on the strains of brook, rainbow, and golden trout present in the High Sierra. This information is needed to complement the survey data, providing direct evidence for the effects of acidification on these species. Field experiments using large enclosures could be combined with laboratory experiments.

Expansion of amphibian studies

Although mountain yellow-legged frogs (Rana muscosa) should have been present in the Emerald Lake basin, we found only Hyla regilla in our amphibian surveys. Other investigators have noted that R. muscosa has disappeared from large areas of the Sierra Nevada. The literature indicates that species of Rana are much more sensitive to acidification than are species of Hyla. Furthermore, the small ponds where tadpoles occur are particularly sensitive to acidification because their water tends to be weakly buffered. Because R. muscosa has disappeared from areas that are affected by acidic deposition but by few other anthropogenic impacts, acidification of their breeding sites may be responsible. We encourage studies on the causes of decline of this species: the best approach would involve field surveys as well as experimental work in the field and in the laboratory. R. muscosa could be one of our most

sensitive early-warning indicators of environmental stress associated with acidification.

Intensive sampling during snowmelt

We need to continue the increased frequency and spatial coverage of hydrochemical and biological sampling during snowmelt, which is the most likely period for episodic acidification to occur. Particular effort is required during the initial phase of snowmelt, when elution of solutes from the snowpack may be enhanced. We sampled intensively during the initial phase of snowmelt in spring 1987, but because of the small snowpack and unusually variable weather at that time, the situation may not have been typical.

Acidification experiments during snowmelt

The effects of pH depressions during snowmelt on zooplankton, stream invertebrates, and early stages of trout merit further investigation. Experimental acidification of lake enclosures and of artificial stream channels during snowmelt would allow us to examine the responses of invertebrates and trout; this work would complement our previous studies of the effects of acidification during the summer.

Intensive sampling during summer rain storms

Runoff from rain storms can also result in episodic acidification of aquatic habitats. Intensive sampling during such storms is logistically difficult, but is not impossible. In 1987, we successfully sampled during and immediately after several summer rains, but these were relatively small storms. Nevertheless, the data show strong changes in inflow stream chemistry. Similar sampling during larger rain storms is required to evaluate the effects of these episodes on the lake and stream habitats. The analytical protocol for these samples should include, in addition to the routinely measured variables, measurements of stable isotopic ratios (oxygen and hydrogen) and of total and organic particulate material.

Telemetric transfer of data from remote instrument sites

The success of our instrumental monitoring at Emerald Lake could be improved considerably if the instrumentation were linked directly to laboratories by telemetry, in addition to on-site data storage on electronic

loggers. This would enable us to monitor the performance of the equipment, as well as to detect episodic events as they occur, so that sampling could be promptly initiated.

Investigation of unexplained patterns in ionic chemistry

Several questions have arisen from analysis of the major ion chemistry of the inflows, and these could probably be answered by additional sampling and experimental measurements. Sulfate shows little variation in concentration throughout the year; elucidation of the mechanism responsible for this regulation is critical to our understanding of the effects of the watershed on runoff chemistry. Sources and sinks of nitrate in the watershed need further study; biological uptake may play a major role in the seasonal retention of nitrate. Chloride appears to be retained in the lake, but the mechanism for this is unknown; we should investigate the possibility that uptake by the aquatic biota is responsible for the loss of chloride from the lake water. The relative importance of accelerated weathering, ion exchange, and sorption in the watershed to the buffering of acidity from precipitation at Emerald Lake is currently not well understood, and merits further research.

Organic compounds may be important to acid-base chemistry in the watershed and in the lake. Ionic charge balances suggest that organic acids are an important component of the total ionic content of precipitation and storm runoff at Emerald Lake. However, this evidence is circumstantial, and our analytical protocol has not included routine measurement of these compounds. Future sampling should include measurement and some characterization of these compounds in precipitation, runoff, and in the lake, particularly during snowmelt and runoff from summer storms. In addition, we should routinely measure dissolved inorganic carbon by gas chromatography for comparison with acid neutralizing capacity (ANC) measured by titrimetry, because organic acids can interfere with the titrimetric estimation of ANC.

Effects of the lake's ice layer on chemical mass balance

During winter sampling, we should sample the ice layer of the lake, which is actually composed mainly of slush with hard ice interlayers, to determine its effect on the lake chemistry. This work would show whether "freeze-out" of solutes from lake water is significant, and if the ice layer should be considered as snow, as lake water, or as a mixture of the two in

the mass-balance model for the lake. Collection of integrated samples of the ice layer at several sites across the lake will be necessary if the data are to be useful for mass-balance purposes.

Chapter I

Introduction

Acidic precipitation has recently been reported in many areas of California (California Air Resources Board 1988). Acidic deposition also occurs in the form of particles, gases, and fogs (John et al. 1984, Jacob et al. 1985 and 1986, Waldman et al. 1985, Bytnerowicz et al. 1987, Bytnerowicz and Olszyk 1988). In the Sierra Nevada, acidic precipitation has been documented during portions of the year in the Tahoe basin and on both the eastern and western slopes (Leonard et al. 1981, Melack et al. 1982, Stohlgren and Parsons 1987, Dozier et al. 1987). The lakes and streams of the Sierra Nevada are among the most weakly buffered in the world (Landers et al. 1987), and are thus potentially susceptible to acidification by atmospheric deposition.

Research objectives

At the start of our research in 1983, it was not known if acidic deposition affected the biota of Sierran waterbodies, or how these systems would respond to increased acid inputs. The aim of our research has been to answer these questions. We chose Emerald Lake, located in Sequoia National Park, as the focus of our studies because it is representative of subalpine and alpine waters in the Sierra Nevada, and is accessible throughout the year. The principal objectives of the research reported here are:

- 1) Analysis of seasonal and interannual patterns in the physical and chemical characteristics of the lake, its inflowing streams, and its outflow. In Chapter II, we analyze seasonal changes in the lake and stream environments over the period August 1986-April 1988. Chapter III contains an analysis of interannual variability in the 1983-88 time series of physical and chemical variables in the lake and streams, as well as an input-output budget for major solutes in the lake, calculated at monthly intervals over two years. This work enables us to understand the baseline conditions in the ecosystem, which is necessary to distinguish the effects of acidic deposition from natural seasonal and interannual variability.
- 2) Processes modifying the ionic composition within the lake (Chapter IV). We combine the input-output solute budget with a mass-balance model for the lake to estimate fluxes of solutes within the lake during the summer and

winter. The observed fluxes are compared with potential sources and sinks of solutes in the lake, including groundwater flow, exchanges of solutes between overlying water and both the sediments and submersed rock surfaces on the lake bottom, and nutrient uptake by algae. Solute fluxes are important because they can modify the ionic composition of the lake water, and their net effect may be to either generate or consume acid neutralizing capacity (ANC).

- 3) Measurement of the short-term effects of storm runoff on the chemistry of Emerald Lake and its inflows (Chapter V). We report data on the chemical changes in the streams during and immediately following summer rains. Without special sampling, these ephemeral changes might not be detected by routine sampling at weekly or longer intervals.
- 4) Experimental investigation of the sensitivity of the lake biota to acidification (Chapter VI). We here report the results of our experiments using enclosures in Emerald Lake, which were designed to examine the responses of zooplankton and zoobenthos to various levels of acidification. These recent experiments provide more detailed information to confirm the results of our earlier experiments (Melack et al. 1987).
- 5) Measurement and modelling of primary production by phytoplankton in Emerald Lake (Chapter VII). This information is fundamental to our understanding of the ecology and biogeochemistry of the lake.
- 6) Investigation of the community ecology of zooplankton and zoobenthos in Emerald Lake and its outflow (Chapter VIII). In addition to their ecological importance, there is considerable interest in the potential of these organisms as indicators of acidification.
- 7) Intensive study of the population dynamics and ecology of the brook trout in Emerald Lake (Chapter IX). We present a particularly detailed analysis for the Brook Trout, the only fish species in Emerald Lake, because of its ecological importance as well as its aesthetic and recreational value. This chapter also includes data on the distribution and population dynamics of the Pacific Treefrog in the vicinity of Emerald Lake.
- 8) Chemical and biological survey of lakes in the basin of the Kaweah River (Marble Fork) (Chapter X). Characterization of the chemical and biological variability among Sierran lakes helps us to establish the generality of our findings from Emerald Lake.

Description of study site

Emerald Lake (36°35'N, 118°40'W) is a small (2.72 ha) cirque lake located at an elevation of 2800 m in the Sierra Nevada (Fig. I-1). The 120-ha watershed of the lake is granitic with many steep slopes (mean slope, 31°; Dozier et al. 1987). Bedrock in the basin is composed mainly of granodiorite, with some mafic inclusions, aplite dikes, and pegmatite veins (Sisson and Moore 1984, Clow 1987). Conversion of plagioclase to kaolinite is the predominant weathering reaction in the Emerald Lake basin (Clow 1987). Poorly developed soils cover about 20% of the watershed, and these are acidic and weakly buffered (Huntington and Akeson 1987, Lund et al. 1987). The primary clay minerals are illite and several types of vermiculite (Weintraub 1986).

Vegetation is sparse (Rundel et al. 1988), including only scattered coniferous trees, although low woody shrubs are often abundant where soils occur. In the lake and streams, the only abundant vascular plants are mosses and quillworts (Isoetes), but the biomass of these plants is low.

Precipitation in the Emerald Lake basin is strongly seasonal, and snowfall accounts for most of the atmospheric deposition of water and ions into the basin (Dozier et al. 1989). The quantity of snowfall is variable among years; for example, almost 300 cm fell in water year 1986 and less than 90 cm fell in water year 1987. Mean daily air temperatures are typically 6 to 13°C in summer and -4 to 4°C in winter.

Emerald Lake is fed by 2 to 8 inflows, depending on the season, and is continuously drained by a single outflow (Fig. I-2). The inflowing streams are shallow (2-3 cm) and narrow (50 cm), and most flow over bedrock at the lake shore. The outflow is deeper (20 cm) and wider (1.5 m), and consists of alternating pools and riffles. Willows (Salix spp.) are abundant along all of the streams, and larger trees (Pinus spp.) are found along the outflow. Filamentous algae and mosses are common on submersed rock surfaces during the summer. Two relatively large pools are located along the outflow about 100 m below the lake.

Emerald Lake and the streams in its watershed are weakly buffered, calcium-bicarbonate waters, which are typical of high-altitude Sierran waterbodies (Melack et al. 1985). Figure I-2 is a bathymetric map of the lake; its mean depth is 5.9 m and its maximum depth is 10.5 m. The lake volume changes by < 10% over the year. Hypsographic (depth-area) and depth-volume

curves for the lake at its typical mid-summer water level are given in Figure I-3. Figure I-4 shows the composition of the lake bottom. Soft sediments composed mainly of silt and clay occur below a depth of 7-8 m. There are accumulations of sand and gravel in the vicinity of the inflowing streams, and below the major joints at the northeastern and western ends of the lake.

The lake is typically ice-covered after November, and the inflowing streams soon become buried under ice and snow. Open areas usually persist in the outflow throughout the winter. Successive snowfalls push the ice on the lake downward, causing lake water to seep up through the snow and form a new hard ice layer at the surface. Wind-blown snow and occasional avalanches increase the accumulation of snow on the lake surface. This process results in a very thick ice layer that is composed mostly of slush, with thinner interlayers of hard ice (Stoddard 1988). Very little light penetrates to the water column under ice cover. In winters with heavy snowfall, the ice can come to occupy the majority of the lake volume, and it may subsequently persist until well into the summer. During the five years of this study, the ice disappeared from the lake between mid-May and late July.

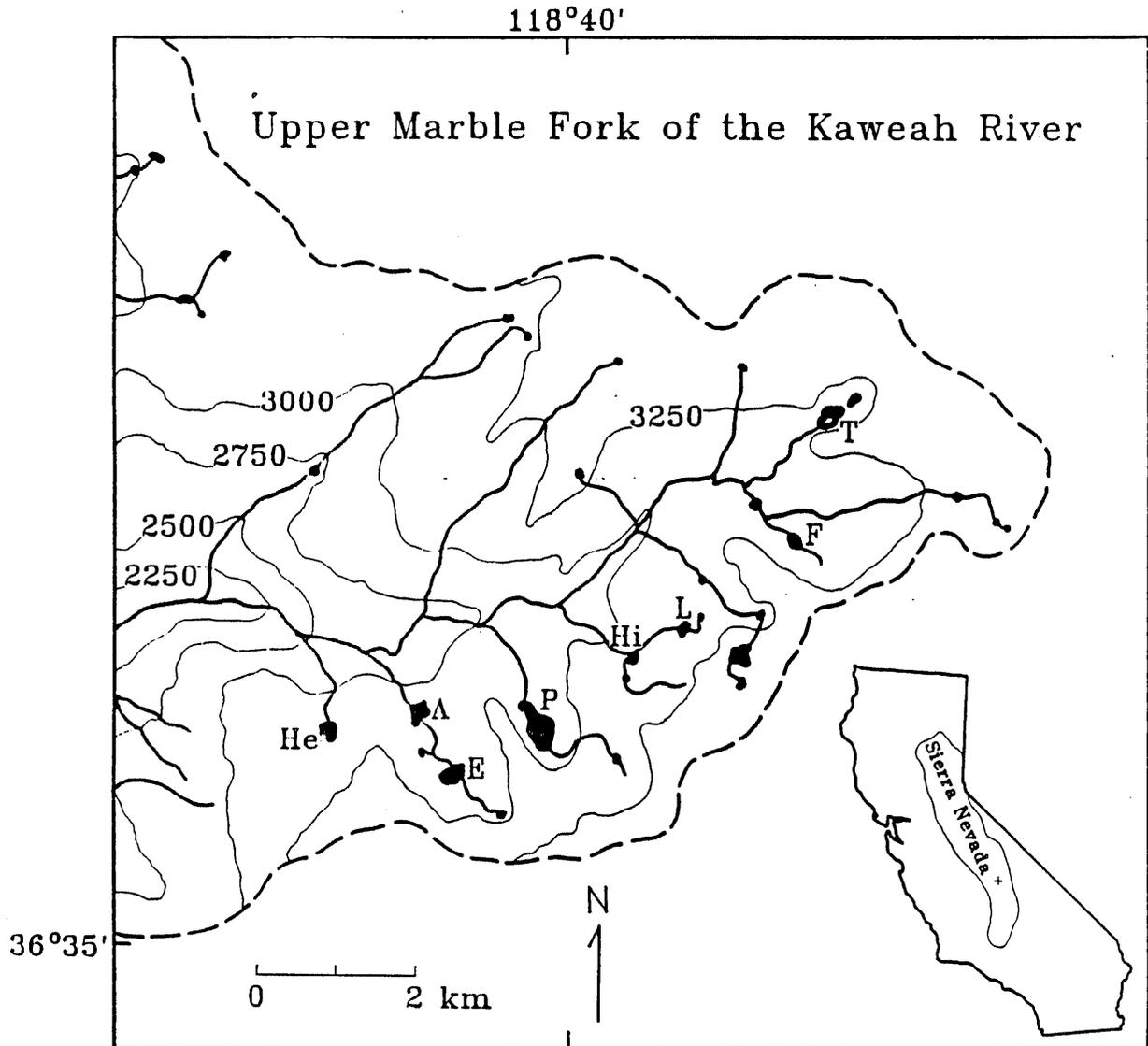


Fig. I-1. Location of Emerald Lake and neighboring lakes in the basin of the Kaweah River (Upper Marble Fork). The basin is on the western slope of the Sierra Nevada in California (inset). Elevation contours are in meters. Lake names are abbreviated as follows: E - Emerald Lake, A - Aster, He - Heather, P - Pear, Hi - Hidden, L - Lyness, F - Frog, and T - Topaz.

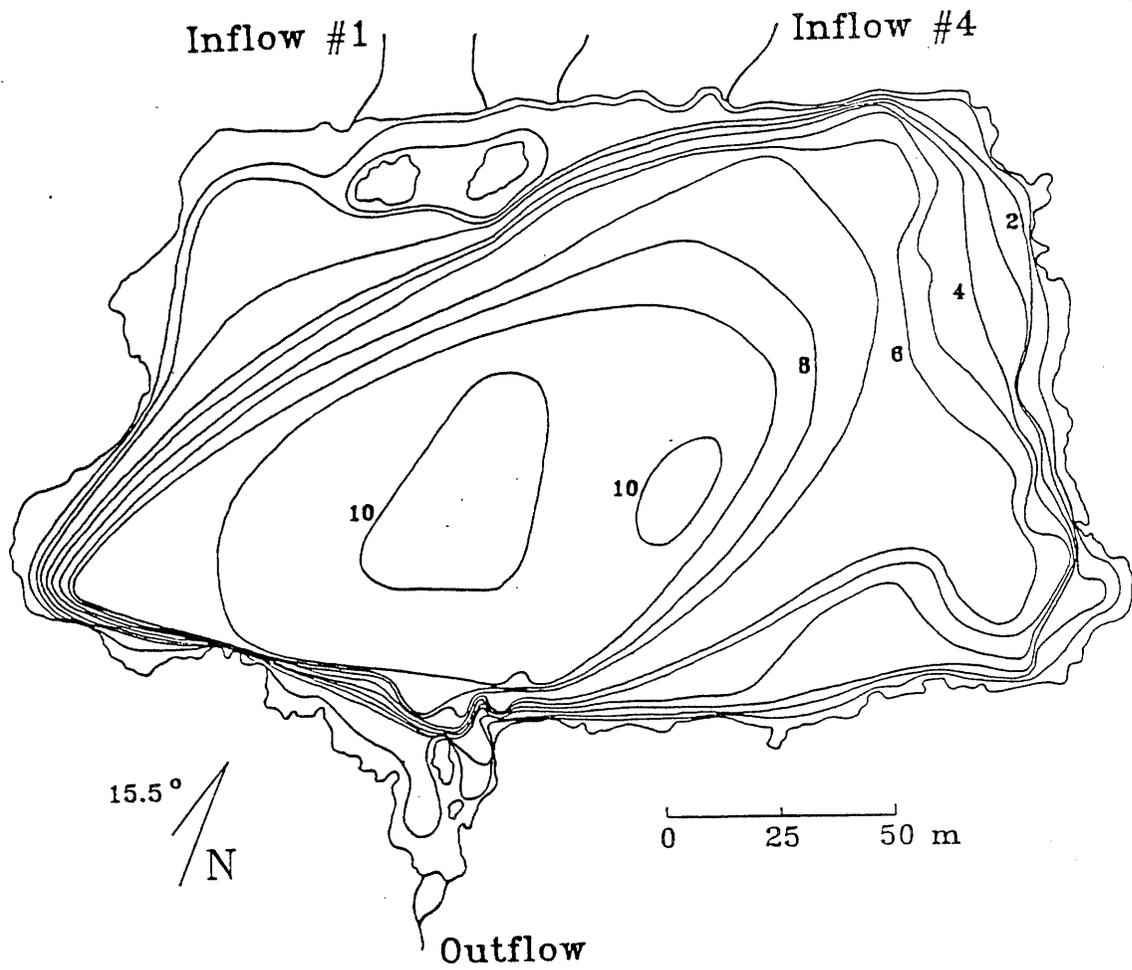


Fig. I-2. Bathymetric map of Emerald Lake. Depth contours are in meters.

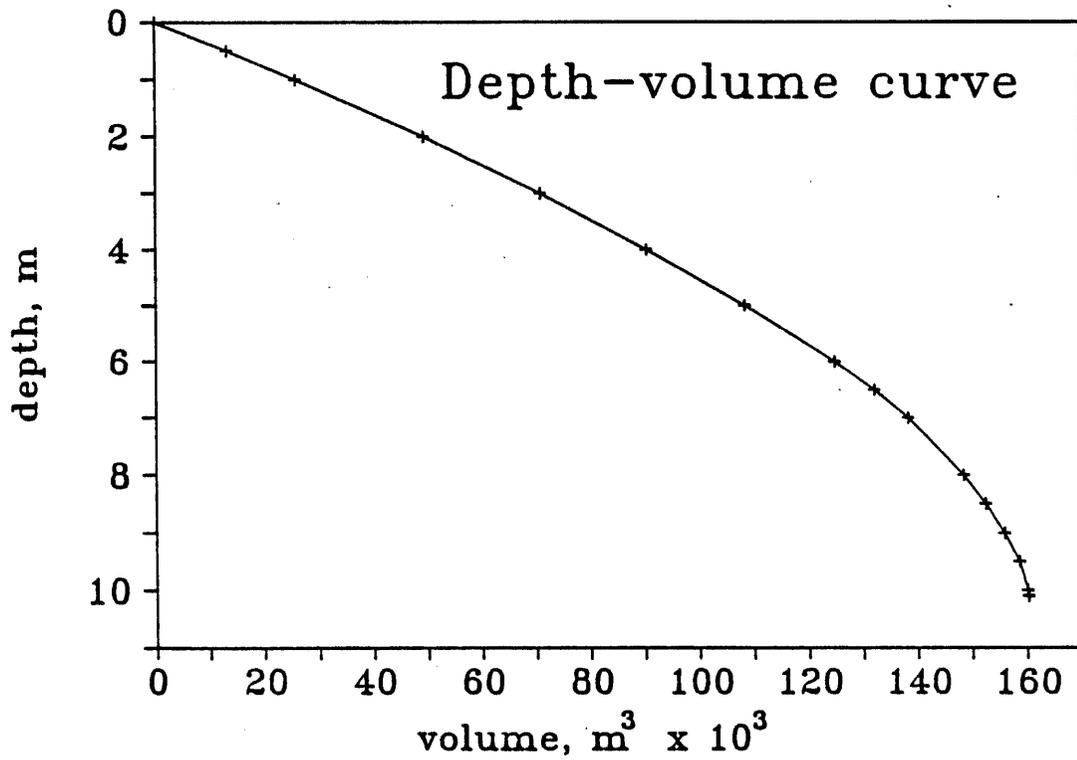
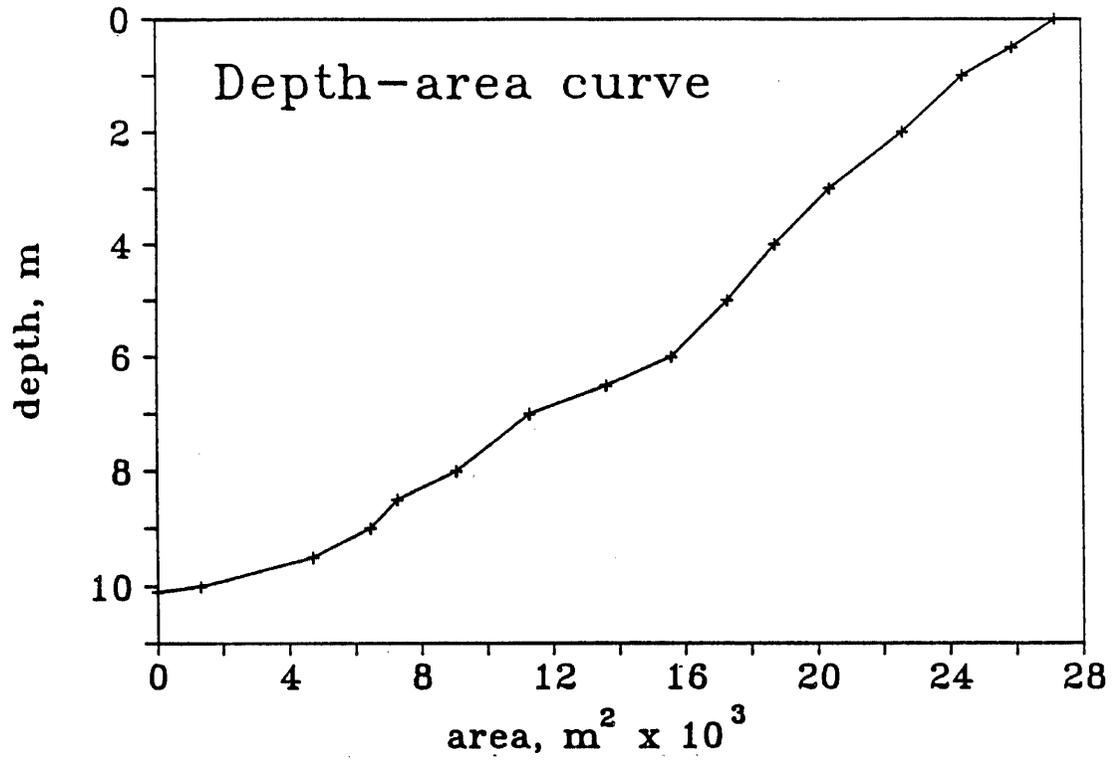


Fig. I-3. Hypsographic (depth-area) and depth-volume curves for Emerald Lake at mid-summer stage.

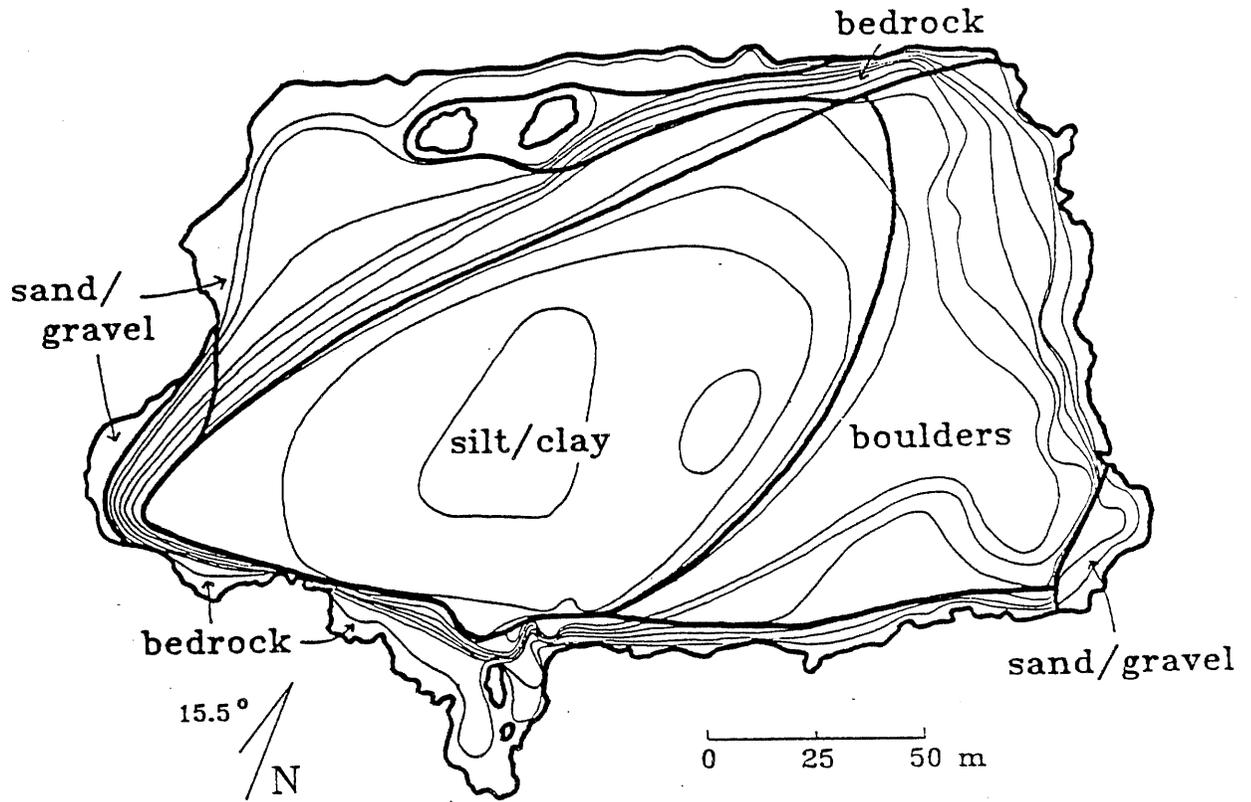


Fig. I-4. Bottom types in Emerald Lake.

Chapter II

Hydrochemistry of Emerald Lake: Seasonal patterns(August 1986-April 1988)

A major focus of our research at Emerald Lake has been the sampling program designed to characterize seasonal patterns in the chemistry of the lake and its inflows and outflow. The time-series data on lake and stream chemistry is also used for the construction of a mass-balance model for the watershed (Chapters III and IV). Samples were collected throughout the year, with more intense work during the ice-free season, when the lake is most productive, and during snowmelt, when much of the annual runoff passes through the streams and lake. The time-series data provide us with information on the major seasonal and episodic events of importance to the aquatic ecosystem. This information is fundamental to our understanding of the biogeochemistry and ecology of the Emerald Lake ecosystem, and of the present and possible future impact of acidic deposition on lakes and streams in the Sierra Nevada.

In this chapter, we examine the seasonal patterns in physical and chemical variables in the lake and streams over the period August 1986-April 1988. Time-series data from before this period were analyzed in detail by Melack et al. (1987). Interannual variation in our 1983-88 time series of physical and chemical variables is analyzed in the following chapter, which also includes annual mass balances for major solutes in the lake.

Methods

The lake was sampled approximately biweekly during the ice-free seasons of 1986 and 1987 and during snowmelt in 1986, and at intervals of 4-6 weeks under ice between November and March. Samples were collected from four depths at the center of the lake. The inflows and outflow were sampled near the lake (Chapter I: Fig. I-2), generally at weekly or biweekly intervals. We have not included data from all of these sites in this report, although all of the sites have been incorporated into our mass-balance calculations (Chapters III and IV). We chose Inflow #1 to represent the inflow streams because it is one of the two main inflows to the lake in terms of total annual discharge, and because it usually flows throughout the year. Variation in discharge and chemistry among the inflows is analyzed by Dozier et al. (1989) and Dracup et

al. (in preparation). For the lake, we present data from near the surface and near the bottom, to emphasize the vertical heterogeneity that develops during thermal stratification. We also present the outflow data.

Lake samples were collected with either a peristaltic pump (under ice) or a plastic Kemmerer sampler; streams were sampled with a small polyethylene bottle or, at the lowest flow, with a plastic syringe. Vertical profiles of temperature (thermistor: $\pm 0.2^\circ\text{C}$) and dissolved oxygen (polarographic electrode: $\pm 0.1 \text{ mg L}^{-1}$) were measured when lake samples were collected. Lake and stream samples were immediately placed in a dark bag and either filtered in a tent at the lake shore, or, in the winter, on the eve of collection at a nearby cabin. All samples were kept cool and in the dark during transport and storage. Laboratory analyses for labile soluble components (pH, ANC, ammonium, and phosphate) were normally completed within several days of collection, and the remaining analyses were performed 3-6 months after collection. Iron and aluminum were analyzed 3-12 months after collection. Our extensive experience with the chemical analysis of water samples from the Emerald Lake watershed has shown repeatedly that, with proper storage conditions, these delays are acceptable and do not result in detectable changes in sample chemistry.

Samples were filtered through glass-fiber paper (Gelman AE; 1- μm pore size), which had been combusted for 2 hours at 500°C to remove organic contamination. At least 300 mL of water was passed through the filter as a pre-rinse to remove soluble salts before filtered water was collected for chemical analysis. Subsamples of unfiltered water were also collected. Samples were stored in polyethylene bottles that had been cleaned with 10% HCl solution and thoroughly rinsed with deionized water. Unfiltered and filtered (Nucleopore 0.1- μm) subsamples for analysis of iron, aluminum, and manganese were acidified with Ultrex HNO_3 in the field. For each lake sample, two filters were frozen for later analysis of chlorophyll-a, and one filter was stored in a desiccator for later analysis of particulate carbon and nitrogen.

In the laboratory, pH of the unfiltered subsample was measured with a combination electrode designed for samples of low ionic strength, and acid neutralizing capacity (ANC) was determined by incremental titration with 0.1 N HCl. Specific conductance of unfiltered water was measured with a conductivity bridge, and readings were standardized to 25°C . A filtered subsample was analyzed for ammonium by the indophenol blue method, for orthophosphate by the

molybdenum blue-ascorbate method, and for silica by the silico-molybdate method (Strickland and Parsons 1972). The filtered subsample was also analyzed for calcium, magnesium, sodium, and potassium by flame atomic absorption, and ion chromatography was used to measure chloride, sulfate, and nitrate. Iron, aluminum, and manganese (data presented in Chapter III) were analyzed by atomic absorption with the graphite furnace technique. Material retained by the glass-fiber filters was analyzed for chlorophyll-*a* by fluorometric measurement after the filter was placed in 90% acetone and macerated with a Teflon pestle (Wetzel and Likens 1979). Particulate carbon and nitrogen were determined on another filter by combustion in an elemental analyzer. Total nitrogen (filtered samples) and total phosphorus (filtered and unfiltered samples) were determined using the combined persulfate digestion method of Valderrama (1981).

We routinely employ a variety of approaches to ensure that our chemical data are of the highest possible quality. Laboratory analyses are calibrated in every run with standard solutions of concentrations similar to those of the samples, and when necessary multiple standard levels are routinely included (atomic absorption and ion chromatography). The accuracy of our analyses is also checked by periodic analysis of certified standards from the U.S. Environmental Protection Agency and the National Bureau of Standards (results given in Sickman and Melack 1989), and we participate in several interlaboratory comparison studies (e.g., Melack 1989). We have occasionally used the method of standard additions to ensure that matrix interferences are not a problem with the Emerald Lake samples. Special care is taken with pH measurements because of the extremely low ionic strength of our samples: after calibration of the meter with standard buffer solutions of pH 7.00 and 4.00, we measure the pH of 10^{-5} and 10^{-4} N solutions of HCl; calibration is repeated if the measured pH values of these solutions differ from the expected values by more than 0.1 unit.

The precision of our measurements is routinely monitored using analytical replicates, and sampling error is occasionally checked by collection of duplicate samples. As an example of our typical precision, chemical data for duplicate samples collected during 1987 are summarized in Table II-1. The coefficients of variation reported in the table are affected by both sampling and analytical error; the precision of our routine analytical replicates is typically similar to or better than that reported in the table. Ammonium, aluminum, iron, pH, and chlorophyll-*a* show relatively high errors. Ammonium and

chlorophyll-*a* were always analyzed in duplicate subsamples, and aluminum and iron were measured by replicate injections. Ammonium shows relatively high error because concentrations in the lake and streams are generally close to our analytical detection limit; our precision for ammonium is better at higher concentrations, such as those found in summer rainfall. In Emerald Lake, ammonium is usually much less abundant than nitrate, and the uncertainty for ammonium has little effect on our nitrogen mass balance for the lake. We have considered the analytical error in these particular variables during our interpretation of the data in this report; values which appear anomalous and occurred on only a single date are possibly inaccurate and should not be interpreted as if they were definitive.

The accuracy of our chemical data is further checked by calculation of ionic charge balance and theoretical conductance from the individual ionic concentrations in each sample (Golterman and Clymo 1969). If measured ionic concentrations are accurate and all of the important ions have been measured, the sum of cations should equal the sum of anions (in equivalents), because aqueous solutions are electrically neutral. In the lake and stream samples collected between August 1986-April 1988 (N = 336), ionic charges balanced within $5 \mu\text{eq L}^{-1}$ in 81% of the samples, and within $10 \mu\text{eq L}^{-1}$ in 93%. The mean difference between the sums of cations and anions was $0 \mu\text{eq L}^{-1}$. Comparison of theoretical with measured conductance also yields information on the accuracy of the individual ionic concentrations, as well as the accuracy of the conductance measurements (Golterman and Clymo 1969). The theoretical conductance was within 20% of the measured values in 87% of our 1986-88 samples (N = 321), and the mean ratio of theoretical to measured conductance was 0.98. These data imply that our analytical protocol includes all of the important ionic species, that errors in our measurements are not detectably biased, and that our analytical error is not large.

We are not presenting all of the available chemistry data in this report. Certain variables such as organic phosphorus and nitrogen were analyzed mainly for incorporation into the mass-balance model. Several variables were not included because they do not change seasonally, such as orthophosphate, which was nearly always close to our detection limit.

Results

Discharge rates for Inflow #1 and the Outflow are shown in Figure II-1. These data are from Dozier et al. (1987 and 1989), and were obtained by converting depth-transducer measurements taken at 15-minute intervals to discharge rates using rating curves, then calculating weekly total discharge from the discharge rates. Seasonal peaks in weekly discharge caused by snowmelt are an order of magnitude greater than the weekly discharge during the rest of the year. The snowmelt period lasted through August in 1986 because of the unusually large snowpack from the previous winter. Smaller peaks at other times resulted mainly from precipitation in the autumn, before the snowpack became persistent. In October 1987, Inflow #1 became dry (all of the other inflows were also dry at this time), and the Outflow nearly stopped flowing. Summer rains in 1986 and 1987 were too small to have any effect on these plots. The timing of the discharge peaks is the same in Inflow #1 and the Outflow, except that the mid-April peak in Inflow #1 does not match the nearest Outflow peak, which was in mid-May. This difference in timing could be related to spatial heterogeneity in snowmelt across the basin (Dozier et al. 1989).

The time series for major solutes in Inflow #1 are presented in Figures II-2 through II-7. The discharge curve from Figure II-1 is included along the top of each figure, and horizontal bars along the top of the discharge panel indicate the periods when the lake was ice-covered.

The pH of Inflow #1 was variable but usually remained between 6.0-6.5 during the summer of 1986, and during the spring and summer of 1987 (Fig. II-2). During the winter of 1987-88, pH dropped to 5.5-5.8. Discharge was low at this time (Fig. II-1) and the stream was under snow. When discharge increased with increasing snowmelt in late March and April 1988, the pH rose to the normal summer range. The concentration of acid neutralizing capacity (ANC) was also variable (Fig. II-2). In contrast to pH, the concentration of ANC during the winter of 1987-88 resembled that of the preceding summer months.

Seasonal patterns in the concentrations of base cations (Figs. II-3 and II-4) are clearly visible in Inflow #1. In general, concentrations are low during peak discharge, begin to increase late in the summer as discharge drops off, and reach maxima during the winter when the stream was snow-covered. Calcium and magnesium reached considerably higher concentrations during the winter of 1986-87 than during the following winter. Sodium and potassium show

a similar pattern, but the concentrations of these ions peak sharply just before discharge increases in the spring of 1987, and sodium concentrations were more variable during the summer of 1987 than were those of the other base cations.

The nitrate concentration was markedly lower during July–September than during the rest of the year (Fig. II-5). The seasonal pattern of nitrate generally resembles that of the base cations. However, compared with the pattern in base cation concentrations, the summer decrease in nitrate concentration is more abrupt, is displaced to about a month later, and is followed by a more abrupt increase. The concentration of sulfate was usually in the range of 5–8 $\mu\text{eq L}^{-1}$, and showed little seasonal change (Fig. II-5). The greatest variation in sulfate concentration occurred during snowmelt (Dozier et al. 1989), and during September and October 1987, when storm runoff affected the stream (Chapter V).

Seasonal changes in the concentration of chloride in Inflow #1 (Fig. II-6) resemble the pattern for base cations (Figs. II-3 and II-4). A pronounced peak in chloride concentration coincided with peaks in sodium and potassium early in the snowmelt period (31 March 1987), before discharge increased greatly (Fig. II-1). The specific conductance of Inflow #1 (Fig. II-6) reflects the seasonal patterns discussed above for base cations, nitrate, and chloride. In addition, the higher ionic strength of the stream water during the winter of 1986–87 compared to that of the following winter, which has been apparent from the concentrations of individual ions, is confirmed by specific conductance.

The concentration of silica in Inflow #1 (Fig. II-7) follows a seasonal pattern that is very similar to the pattern of base cations and conductance. However, silica reached similar concentrations during the two winters, in contrast to the greater ionic strength of the stream during the winter of 1986–87. Ammonium concentrations remain low during most of the year in Inflow #1 (Fig. II-7), with the exception of 8 June 1987, when storm runoff affected the stream.

Figure II-8 is a time series of temperature and dissolved oxygen near the surface and near the bottom of the lake, with the ice depth plotted along the top. Time series of important chemical variables near the surface and near the bottom of the lake are presented in Figures II-9 through II-15. Samples for chemical analysis were taken at a depth of 1.0 m or, when the ice cover was close to 1-m thick, at 1.5 m. Bottom samples were always from

9-9.5 m. The data for temperature and dissolved oxygen data match the sampling depths.

Seasonal changes in the thermal structure of Emerald Lake must be considered before chemical patterns can be interpreted. The lake was dimictic, mixing completely in the spring and fall. During inverse stratification under ice, the concentration of dissolved oxygen dropped steadily in the hypolimnion but anoxia did not occur. The water column mixed completely for a short period coincident with the disappearance of the ice in May 1987.

Summer stratification developed quickly and lasted until late August. During this period, temperatures rose steadily throughout the water column. Concentrations of dissolved oxygen decreased as water temperatures increased, particularly in the hypolimnion. The lake mixed completely at the end of August, and weak thermal gradients occurred as the water temperature dropped steadily until ice formed and inverse stratification developed in December. The entire water column probably mixed periodically during September and October. The fall mixing period lasted much longer than the spring mixing. Concentrations of dissolved oxygen were not strongly affected by seasonal variation in phytoplankton photosynthesis (Chapter VII).

Surface and bottom waters were similar in pH during mixing, then tended to diverge during stratification (Fig. II-9). There is a seasonal pattern of increased lake pH during the ice-free season, followed by decreased pH under ice. The pH was considerably lower near the surface under ice during the winter of 1987-88 than during the preceding winter.

The seasonal pattern in the concentration of ANC in the surface water of the lake (Fig. II-9) resembled that of ANC in Inflow #1 (Fig. II-2). In the lake, the concentration of ANC in the bottom water resembled that in the surface water during mixing and summer stratification, but increased during inverse stratification under ice.

The seasonal patterns in the concentrations of base cations in the lake (Figs. II-10 and II-11) were generally similar to each other. There was less similarity between the patterns of base cations in the surface water of the lake and in Inflow #1 (Figs. II-3 and II-4) than there was for pH and ANC; base cation concentrations in the lake during the winter of 1986-87 remained lower than those in the inflow. The peaks in base cation concentrations in Inflow #1 during snowmelt (1987), when discharge was much higher, do appear in the surface water of the lake. The two winters showed contrasting patterns in

base cation concentrations in the bottom water; concentrations in the hypolimnion were similar to or lower than those in the epilimnion under ice in the first winter (1986-87), but were higher in the second winter. There was a net increase in base cation concentrations in the lake over the sampling period.

The concentration of nitrate showed a pronounced seasonal pattern in the lake (Fig. II-12) that resembles the pattern of nitrate in Inflow #1 (Fig. II-5). Surface water increased in nitrate concentration as the inflow discharge increased during snowmelt (1987), reflecting the greater flushing of the epilimnion. Complete mixing of the water column increased the concentration of nitrate in the bottom water during May. As inflow discharge dropped, the concentration of nitrate decreased throughout the water column. The nitrate concentration in Inflow #1 also decreased dramatically at this time. During summer stratification, nitrate was lower in concentration in the hypolimnion than in the epilimnion.

Sulfate changed little in concentration in the lake between seasons (Fig. II-12), showing a pattern much like that of sulfate in Inflow #1 (Fig. II-5), except for a large peak in the concentration of sulfate in the surface water during snowmelt. Sulfate concentrations show a net increase over the sampling period that resembles the increase in base cations noted above.

The seasonal pattern in the concentration of chloride in the surface water of the lake (Fig. II-13) is similar to that of chloride in Inflow #1. The sharp peak in chloride concentration in Inflow #1 during snowmelt on 31 March 1987 was not detected in the surface water of the lake, however. Comparison of the chloride concentrations in the surface and bottom waters during periods of thermal stratification does not reveal a consistent pattern.

Specific conductance in the lake (Fig. II-13) shows that the ionic strength of the lake water varied little with depth during the ice-free season, but was higher in the hypolimnion during winter stratification. The ionic peaks in the surface water during snowmelt in 1987 caused a temporary reversal in this pattern. The net increase in the concentrations of certain ions in the lake over the sampling period is also evident from the rise in specific conductance.

The seasonal change in silica concentration in the surface water of the lake (Fig. II-14) corresponded only approximately to the pattern of silica in Inflow #1 (Fig. II-7). The concentration of silica in the surface water

increased during winter stratification, but did not match that of Inflow #1 (50-60 μM), even at peak inflow discharge during snowmelt. Silica varied seasonally over a greater range of concentrations in the bottom water of the lake, increasing under ice and decreasing during the ice-free season to below the minimum concentrations of Inflow #1. Complete mixing of the water column after summer stratification rapidly increased the silica concentration in the bottom water.

Concentrations of ammonium were low in the lake throughout the ice-free season (Fig. II-14). Under ice, however, ammonium concentrations increased considerably relative to the low concentration in Inflow #1 during this time (Fig. II-7), particularly in the bottom water. Concentrations fell abruptly throughout the water column upon loss of the ice layer and complete mixing of the water column in the spring of 1987.

Concentrations of particulate carbon and chlorophyll-*a* in Emerald Lake are shown in Figure II-15. During the ice-free season of 1987, concentrations of particulate carbon and chlorophyll were variable, and this variation was much greater than our analytical error (Table II-1). Spatial and temporal variation in the abundance of phytoplankton and detrital particulates at the sampling site could have caused this variation. Particulate carbon and chlorophyll-*a* were higher in concentration at 9.5 m than at 1.0 m during the ice-free season. Chlorophyll was undetectable under ice in 1988.

The outflow chemistry is of interest principally because comparison of inflow and outflow chemistry shows the role of the lake in controlling or moderating the chemistry of water flowing through the lake. We use the outflow chemistry in our mass-balance calculations in Chapters III and IV, and we investigate the processes that modify the solute chemistry within the lake in Chapter IV. In this section, we present the time series for major solute concentrations in the Emerald Lake Outflow (Figures II-16 through II-21).

The seasonal patterns in concentrations of major solutes in the Emerald Lake Outflow follow those in the surface water of the lake throughout most of the year. During snowmelt in 1987, however, when through-flow was high and the lake was under ice, there were several differences between the solute concentrations in the outflow and the lake surface water. The pH of the outflow tended to be slightly lower during snowmelt, and there is poor agreement in the peaks in sulfate and chloride concentrations at the two sites

(31 March 1987). Ionic concentrations can be variable among the inflow streams during snowmelt (Dozier et al. 1989).

Discussion

Seasonal patterns in the chemistry of the lake are strongly affected by the annual cycle of autumn mixing, winter stratification under ice, spring mixing, and summer stratification. Superimposed on this pattern are the flushing in spring that results from snowmelt, and the increased biological activity during the ice-free season. All of these factors are controlled by the climate, and particularly by the annual accumulation of snow in the watershed.

Stratification of the water column in the lake affects its chemistry in several ways. During stratification in both the summer and winter, the inflowing water usually flows through the epilimnion, which most closely matches its temperature (and therefore its density). The flushing effect of this water is enhanced during stratification because of the smaller volume of water in the epilimnion. The hypolimnion is effectively isolated from the inflowing water, and this, together with the high ratio of sediment surface area to hypolimnetic volume, theoretically increases the potential influence of sediment-water exchange on the chemistry of the hypolimnion (Chapter IV; Amundson et al. 1988).

The accumulation of solutes released from the sediments could explain the increases in hypolimnetic concentrations of ANC, base cations, silica, and ammonium during winter stratification (Figs. II-9, -10, -11, and -14). However, Welch and Bergmann (1985), in a study of small arctic lakes under ice cover, found that heat released from the sediments drives a circulation pattern in which water beneath the ice layer, which is enriched in solutes by cryoconcentration, moves laterally and then downslope to the lake bottom. This mechanism resulted in hypolimnetic increases in solute concentrations over the course of the winter without a change in the total mass of solutes in the lake. A similar process might account for the hypolimnetic accumulation of solutes in Emerald Lake under ice cover. The effect of sediment-water exchanges on the solute budget of the lake is evaluated in Chapter IV.

The hypolimnetic accumulation of solutes observed during winter stratification was observed during summer stratification for ANC and base cations, but not for silica and ammonium. Silica and ammonium accumulation in

the hypolimnion may not occur during the summer because these solutes are assimilated by benthic algae and phytoplankton (Chapter IV). Diatoms are common on the sediment surface (Melack et al. 1987), and phytoplankton biomass (as indicated by chlorophyll-*a*; Fig. II-15, Chapter VII) is often greater in the hypolimnion than in the epilimnion during the summer. The concentration of silica in the hypolimnion decreased during summer stratification to $< 20 \mu\text{M}$ (Fig. II-14). Nitrate depletion is also evident in the hypolimnion during summer stratification (Fig. II-12; Chapter IV). Algal uptake of nutrients from the hypolimnion is significant only during the ice-free season; algal productivity is very low under ice because of light limitation (Chapters IV and VII; Welch et al. 1987).

The influence of inflowing water on the chemistry of the lake is greatest when discharge peaks during snowmelt. At first, the epilimnion is flushed by inflowing water because discharge increases while the lake is still ice-covered. When the ice melts and the lake mixes completely, continued high discharge of the inflows affects the chemistry of the entire lake. At this point, the lake is filled with meltwater from the snow of the preceding winter. The net increase in ionic strength over the sampling period resulted because flushing of the lake during snowmelt in 1986 created lower ionic concentrations than did flushing during snowmelt in 1987. This difference is explained by the larger quantity of snow deposited in the watershed during the winter of 1985-86, which resulted in greater runoff during snowmelt (Dozier et al. 1989). The seasonal pattern of increasing ionic strength after flushing is similar in the two years despite the difference in the initial concentrations.

Even during periods of low discharge, the inflows affect the chemistry of the lake, particularly during thermal stratification. Concentrations of certain solutes in Inflow #1 reflect the seasonal variation in the proportion of stream discharge that has come into close contact with soils and mineral weathering products. During the late summer and under the snowpack, when there is little snowmelt and the stream is comprised mainly of baseflow, concentrations of base cations and silica are higher than at other times (Figs. II-3, -4, and -7). Concentrations of nitrate, on the other hand, appear to be kept low by biological demand during the growing season, but increase greatly during snowmelt (Fig. II-5). The source of the nitrate is uncertain and is a topic of continuing research (Dozier et al. 1989). Biotic uptake of nitrate may explain the abrupt changes in nitrate concentrations in Inflow #1 that correspond with

the beginning and the end of the terrestrial growing season (July-September). Sulfate concentrations in Inflow #1 show remarkably little seasonal variation (Fig. II-5); there is evidently a control mechanism (such as adsorption in soils) that is presently unidentified.

The controlling factors discussed above can be consolidated into a generalized chronology of the seasonal events in the lake. Ice formation in the lake around early December is accompanied by the development of inverse stratification, and accumulation of snow on the ice soon makes light levels in the lake inadequate to support autotrophic algae. Inflow discharge into the lake is low throughout the winter, before snowmelt begins in March or April. However, the inflows mix only with the epilimnion under ice, and their increasing solute concentrations result in a detectable increase in the concentrations of the epilimnion. Meanwhile, solutes accumulate in the hypolimnion by a mechanism which is not presently understood.

When the snow begins to melt, inflow discharge increases greatly. The epilimnion is flushed under ice by inflowing water, and once the ice disappears, the lake mixes completely. The entire lake is flushed for a brief period that corresponds with the peak discharge of the inflows. At this point, the lake is filled with meltwater from the snow of the preceding winter.

Summer stratification develops rapidly after spring mixing, and persists until late August or September. The rate of flushing of the epilimnion drops off during this period, although the concentrations of solutes in the inflowing water increase. The epilimnion is occasionally subject to the effects of flushing by runoff from summer storms (Chapter V), but the storms during this sampling period were not large enough to cause detectable changes in lake chemistry. Solute concentrations accumulate in the hypolimnion during summer stratification, except for silica and ammonium, which are reduced in concentration by algal uptake. The lake mixes completely in September, and continues to mix periodically until ice forms. At this point, the lake chemistry still resembles that of the meltwater from the preceding spring, but inflowing stream water and uptake of nutrients by algae over the course of the summer have affected solute concentrations (Chapter IV).

Conclusions

Seasonal changes in the physical and chemical environment of Emerald Lake are controlled largely by mixing and stratification of the water column,

flushing of the lake in the spring by snowmelt runoff, and algal growth during the ice-free season. The lake tends to moderate the chemistry of inflowing water before it flows out of the lake, but this moderating effect is lessened during stratification, when only the epilimnion mixes with water flowing through the lake, and during peak discharge, when the entire lake volume is flushed by inflowing water.

Table II-1. Mean concentrations and coefficients of variation (CV; standard deviation as a percentage of the mean) for field duplicates collected during 1987. Data for solutes are calculated from 11 pairs, including lake, stream, and groundwater samples. Chlorophyll and particulate C and N were calculated from 5 pairs of lake samples.

analyte	mean concentration	mean CV, %
H ⁺	0.9 $\mu\text{eq L}^{-1}$	9.8
ANC	37.0 $\mu\text{eq L}^{-1}$	4.1
Ca ²⁺	28.8 $\mu\text{eq L}^{-1}$	0.9
Mg ²⁺	5.1 $\mu\text{eq L}^{-1}$	1.4
Na ⁺	14.3 $\mu\text{eq L}^{-1}$	1.6
K ⁺	4.0 $\mu\text{eq L}^{-1}$	1.4
Cl ⁻	5.3 $\mu\text{eq L}^{-1}$	1.9
NO ₃ ⁻	3.5 $\mu\text{eq L}^{-1}$	1.4
SO ₄ ²⁻	8.1 $\mu\text{eq L}^{-1}$	0.5
NH ₄ ⁺	0.2 $\mu\text{eq L}^{-1}$	15.0
conductance	6.2 $\mu\text{S cm}^{-1}$	1.0
Si	37.5 μM	0.6
Fe (total)	0.4 μM	9.0
Al (total)	1.0 μM	16.2
chlorophyll-a	0.7 $\mu\text{g L}^{-1}$	9.9
partic. C	17.3 μM	4.4
partic. N	2.3 μM	3.3

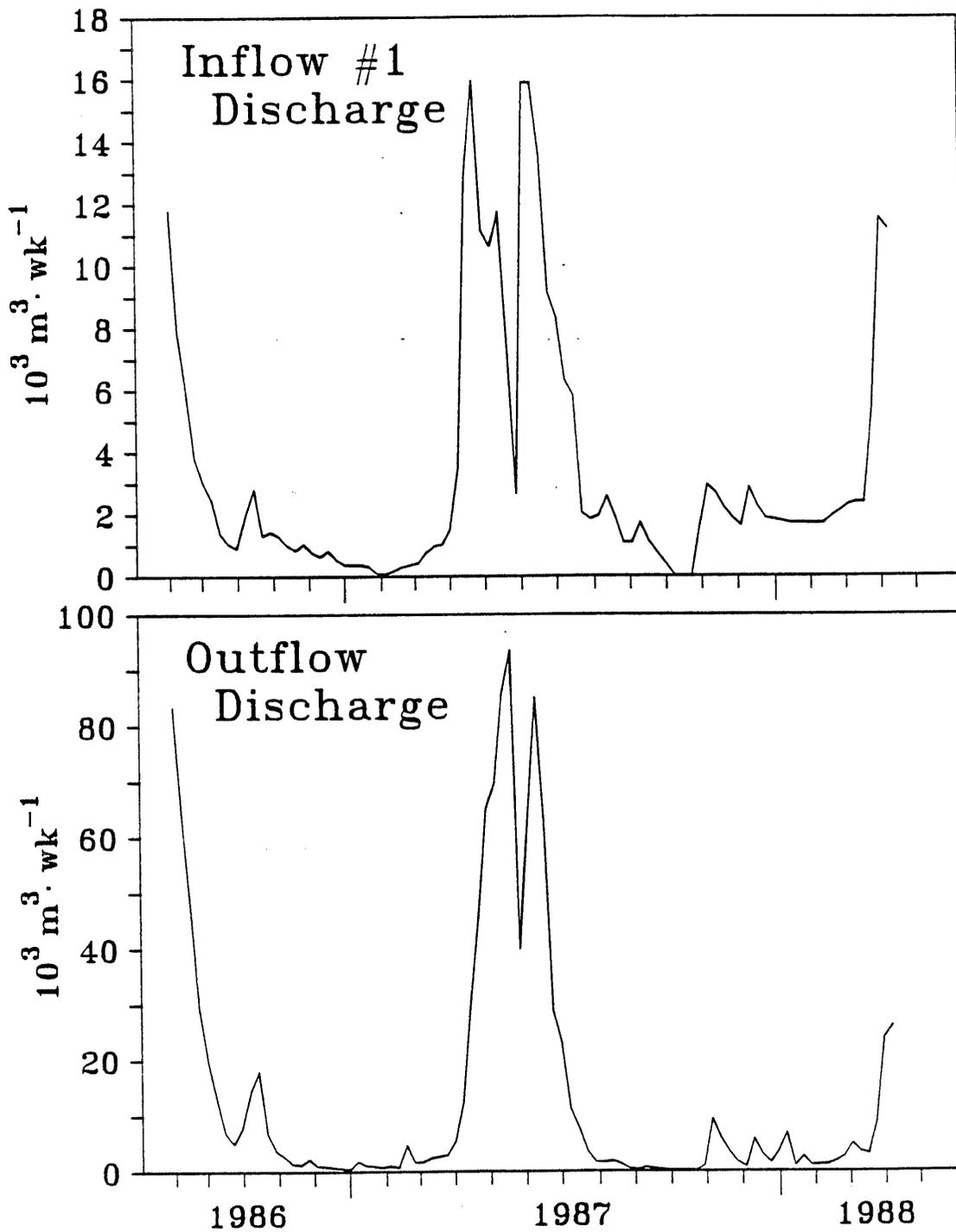


Fig. II-1. Discharges of Inflow #1 and the outflow, August 1986-April 1988.

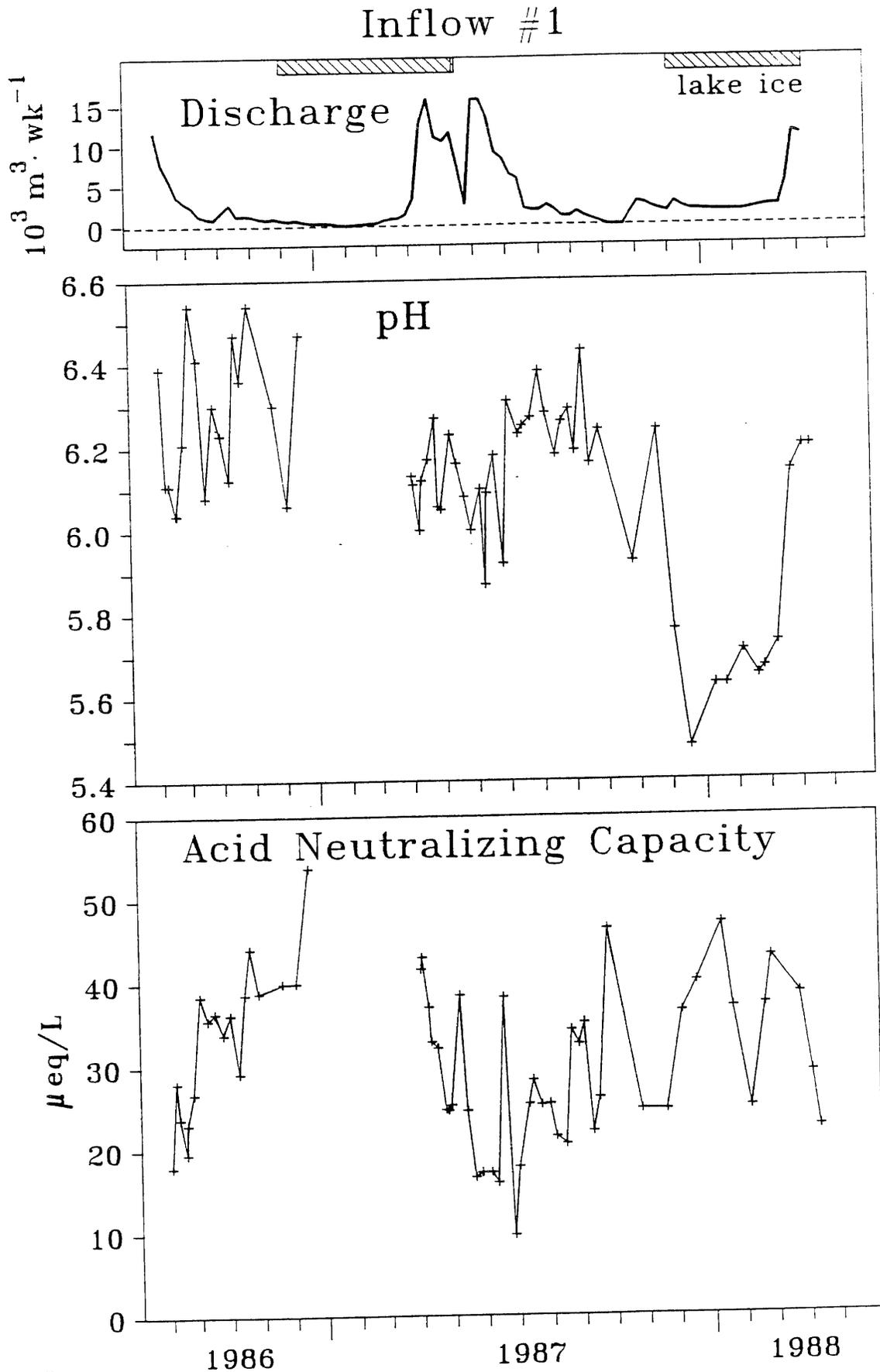


Fig. II-2. Inflow #1, 1986-88: pH and ANC.

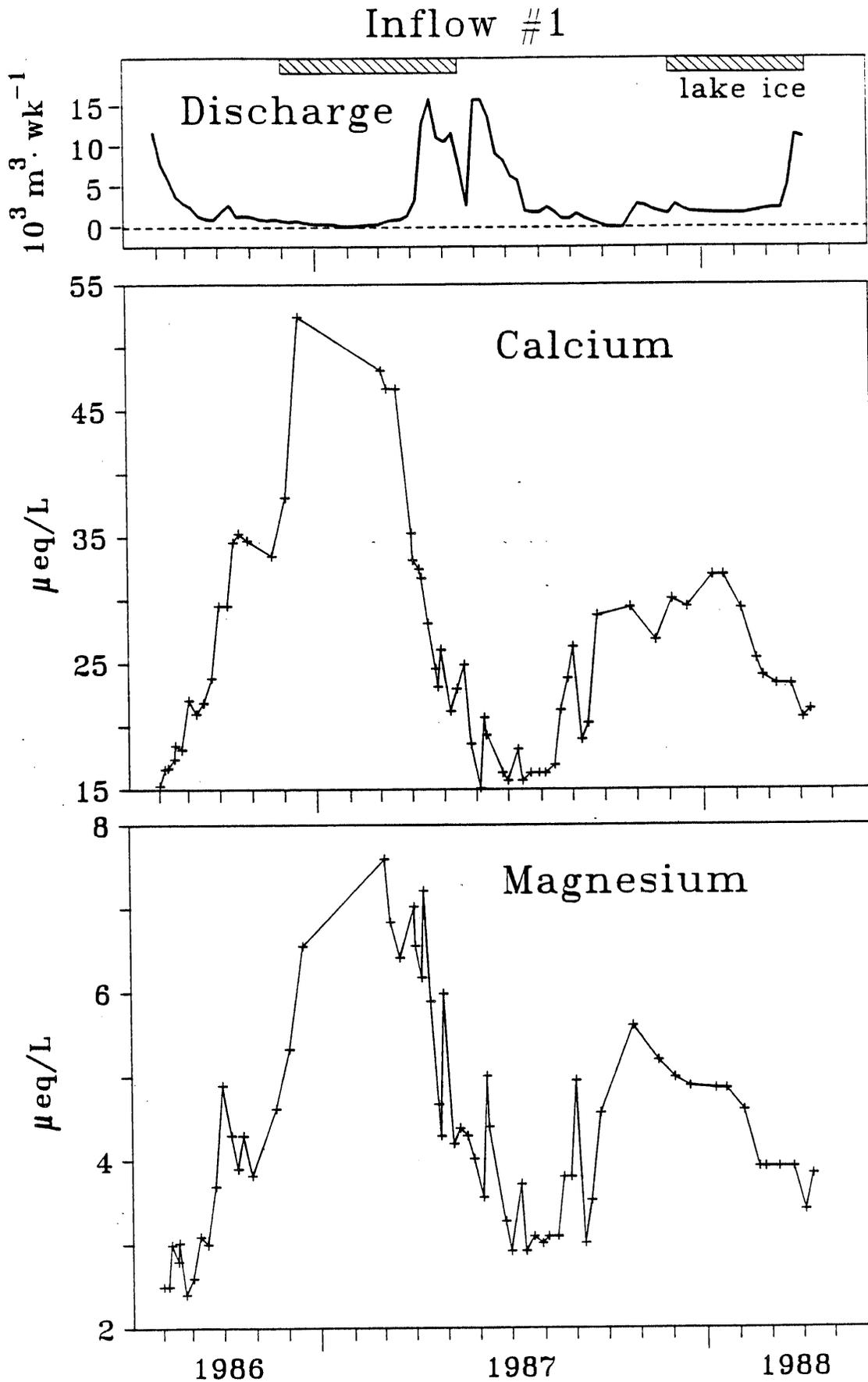


Fig. II-3. Inflow #1, 1986-88: calcium and magnesium.

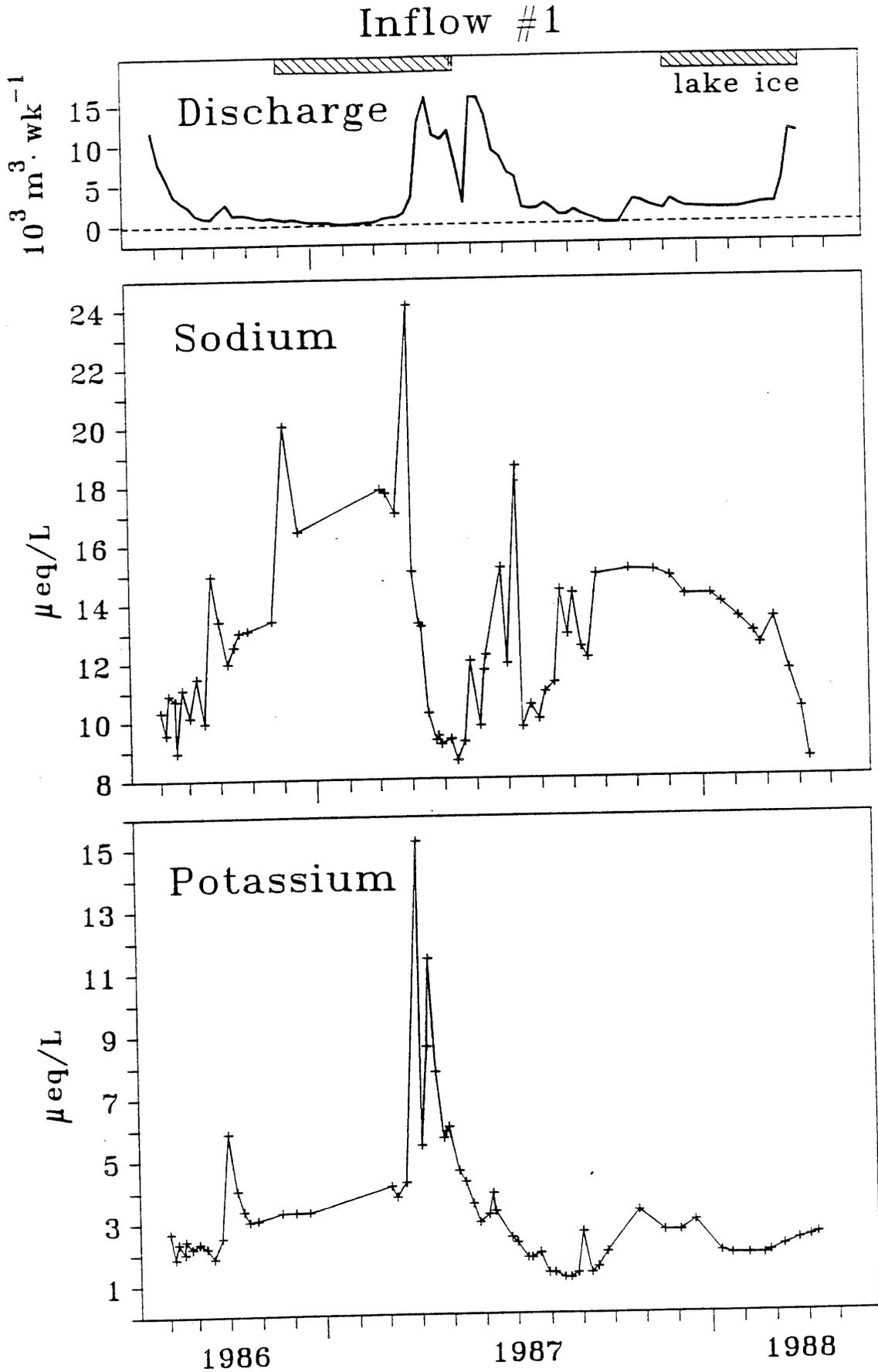


Fig. II-4. Inflow #1, 1986-88: sodium and potassium.

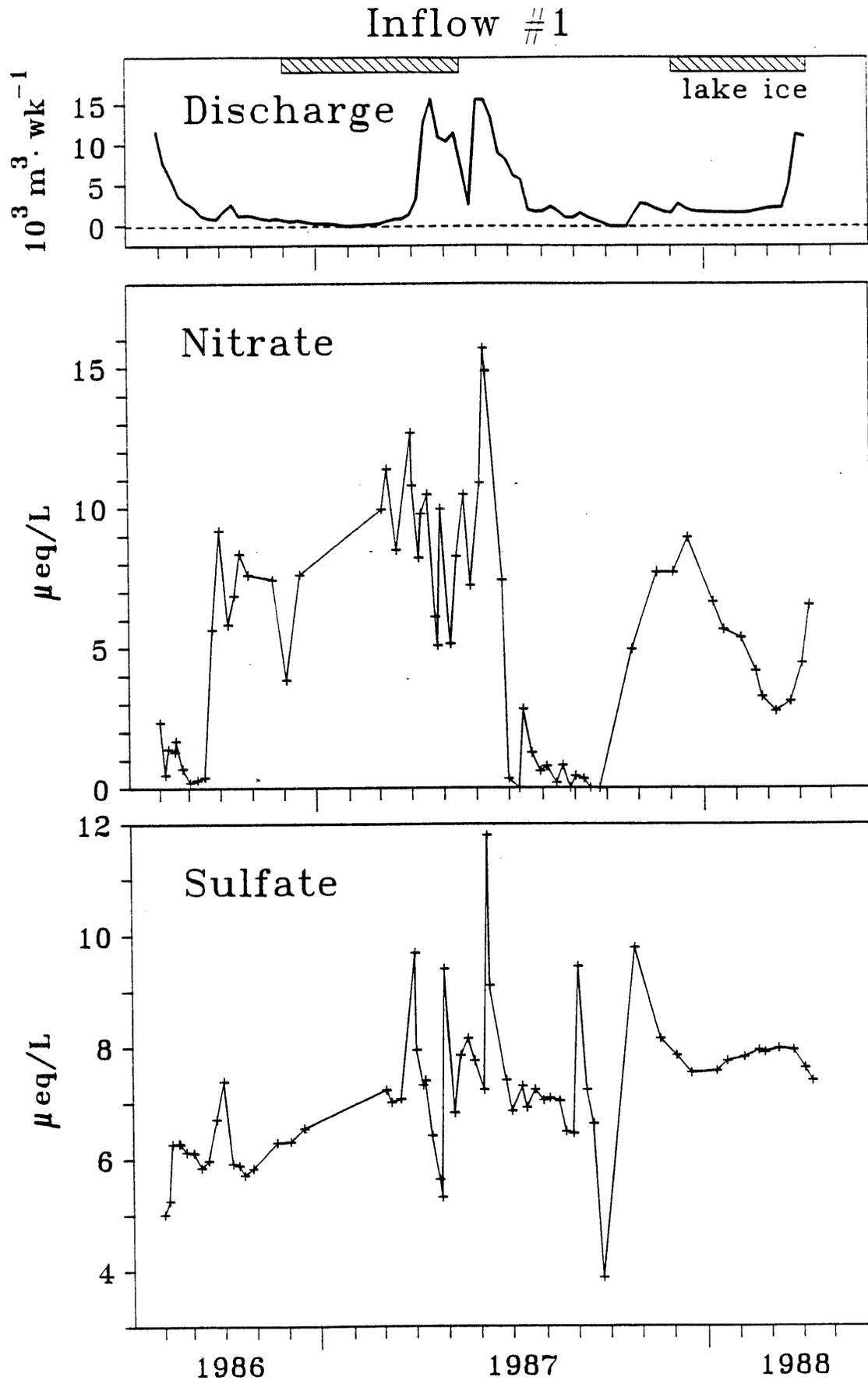


Fig. II-5. Inflow #1, 1986-88: nitrate and sulfate.

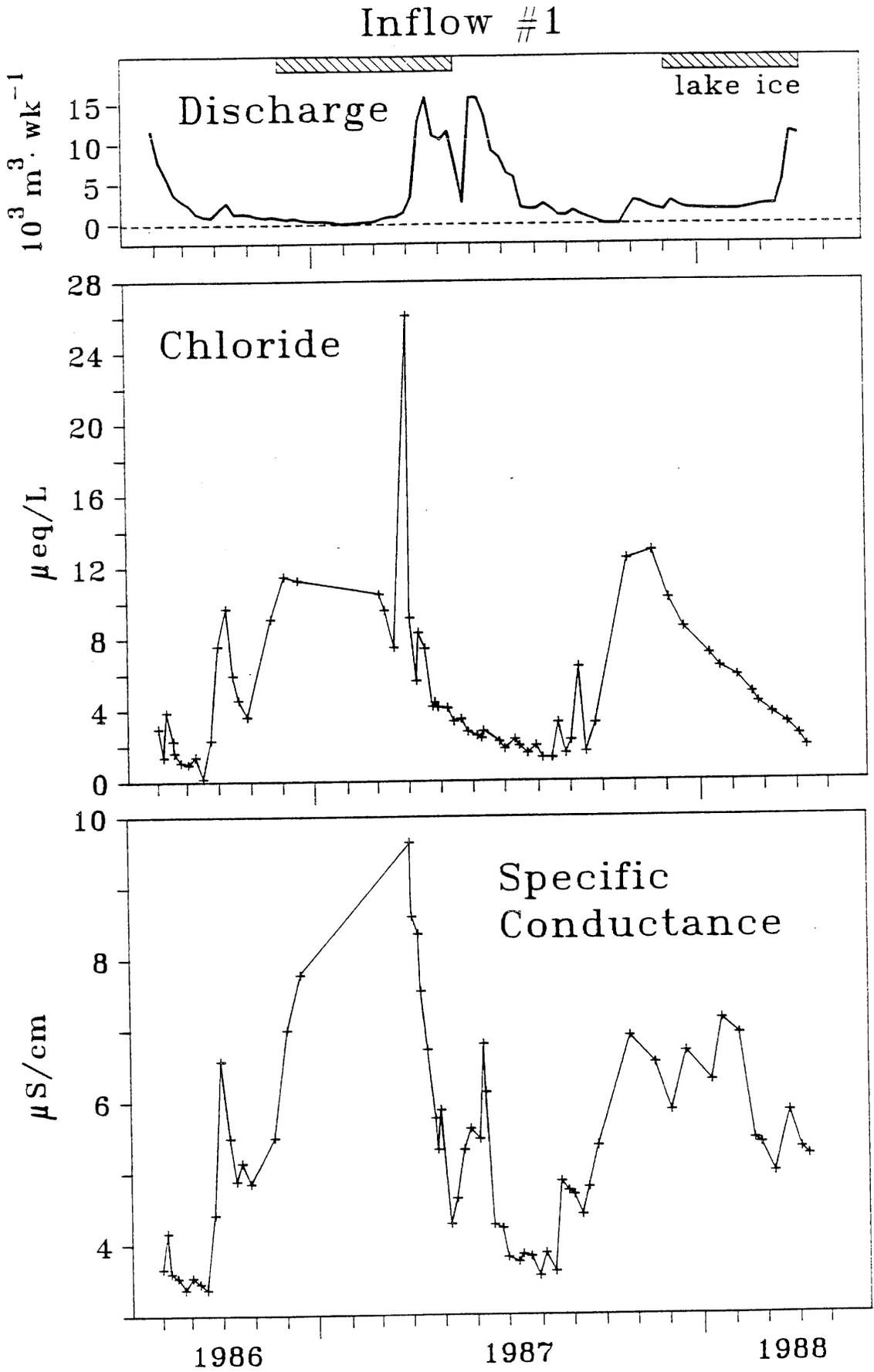


Fig. II-6. Inflow #1, 1986-88: chloride and conductance.

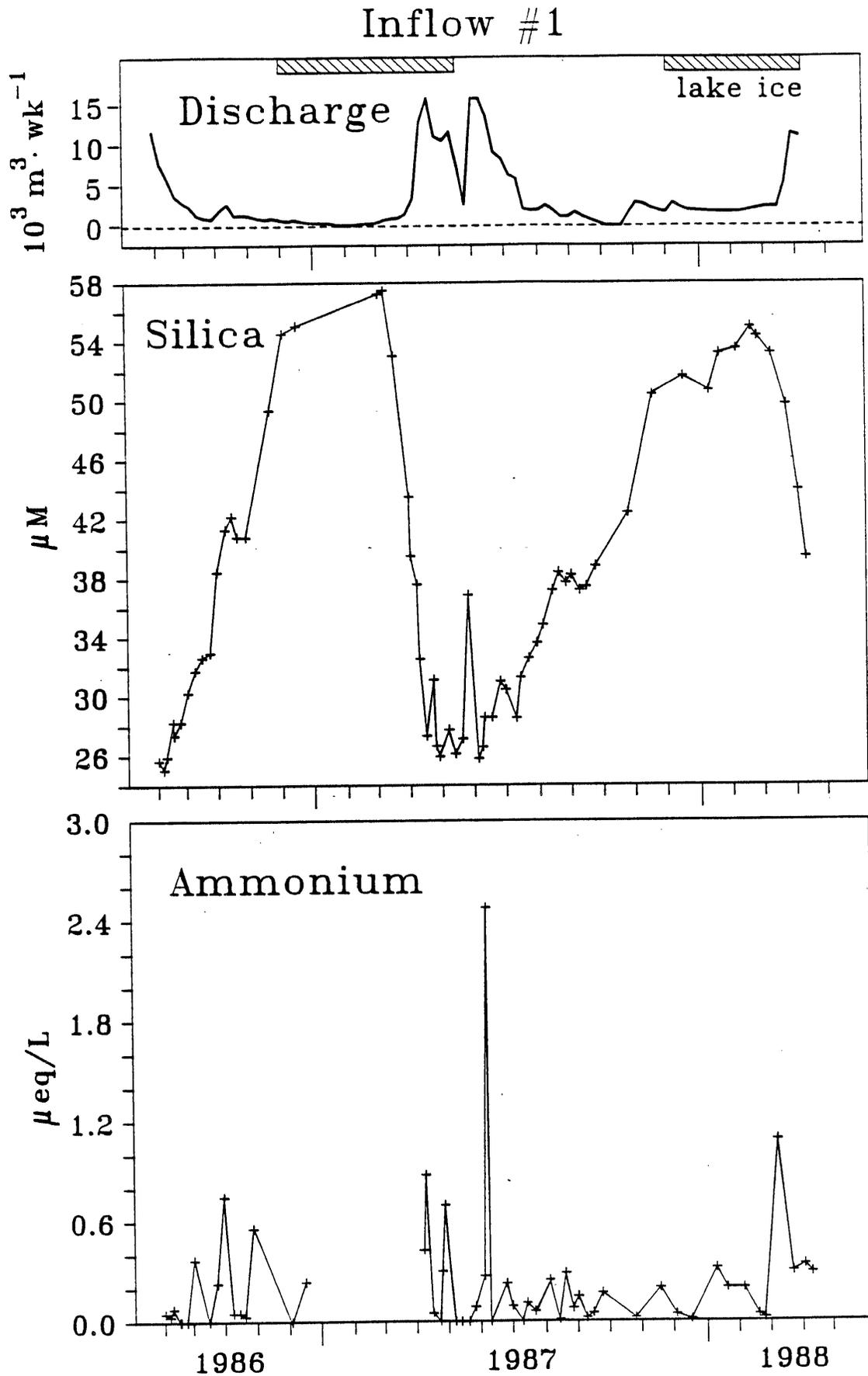


Fig. II-7. Inflow #1, 1986-88: silica and ammonium.

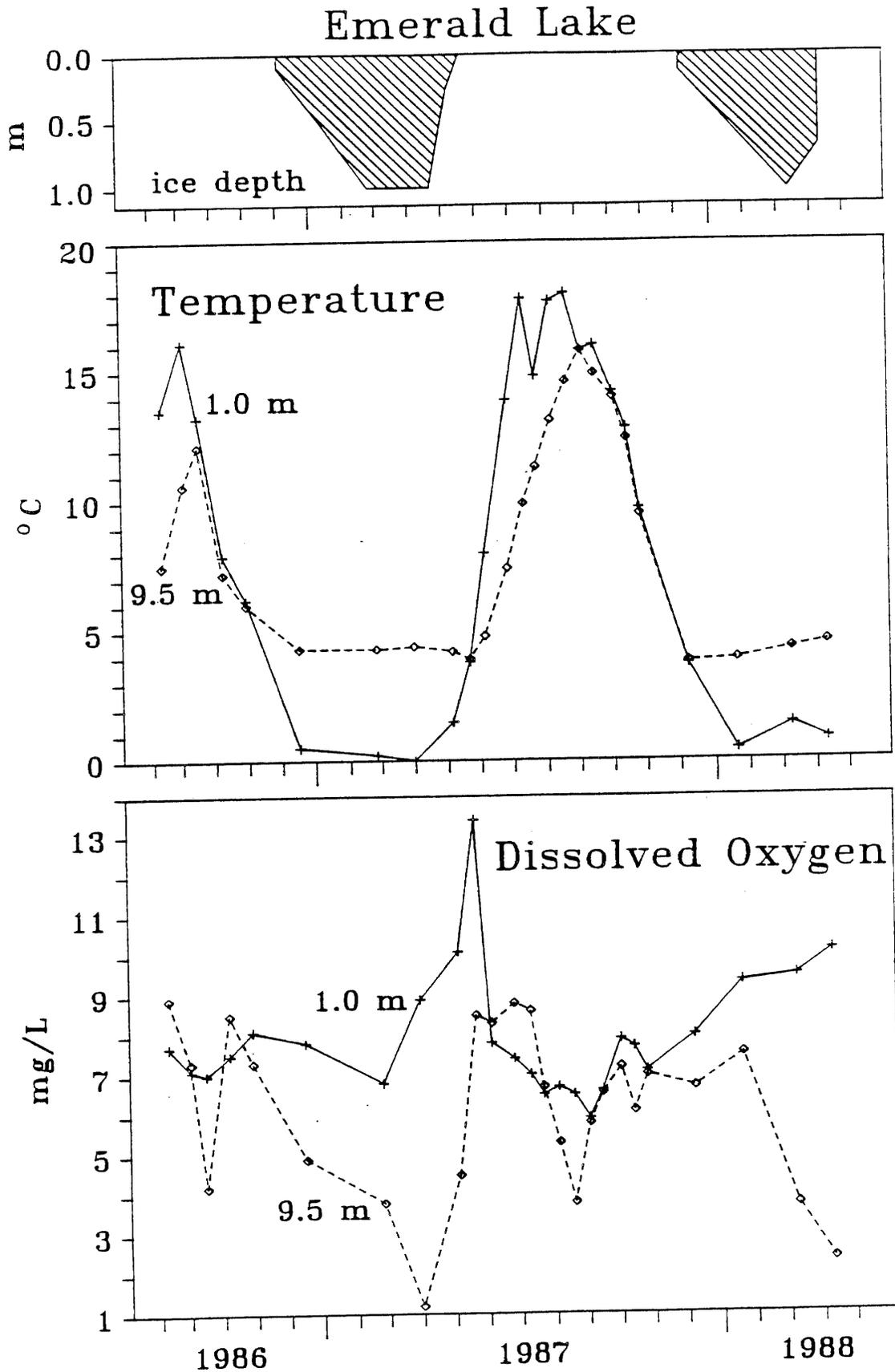


Fig. II-8. Emerald Lake, 1986-88: temperature and dissolved oxygen.

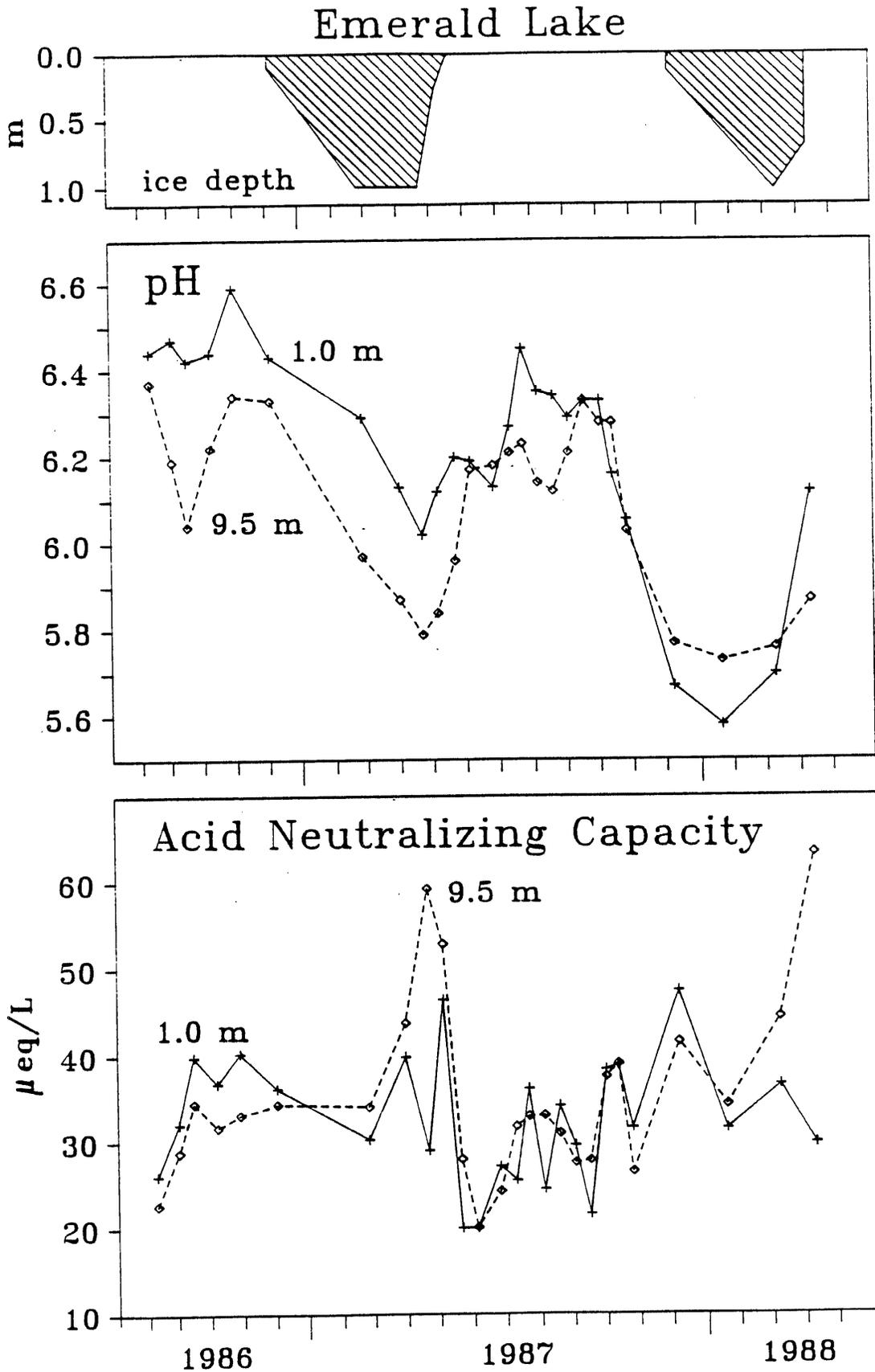


Fig. II-9. Emerald Lake, 1986-88: pH and ANC.

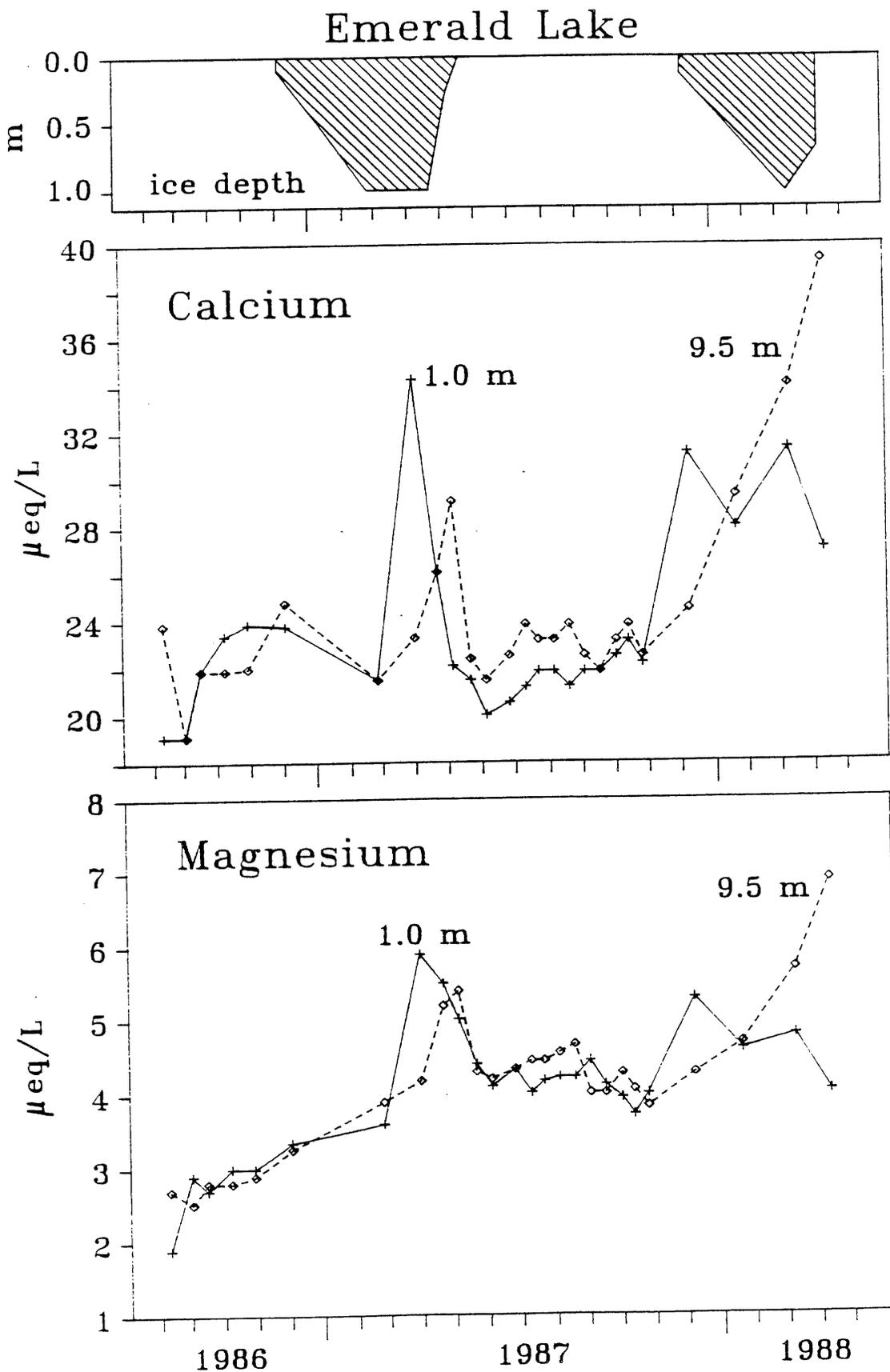


Fig. II-10. Emerald Lake, 1986-88: calcium and magnesium.

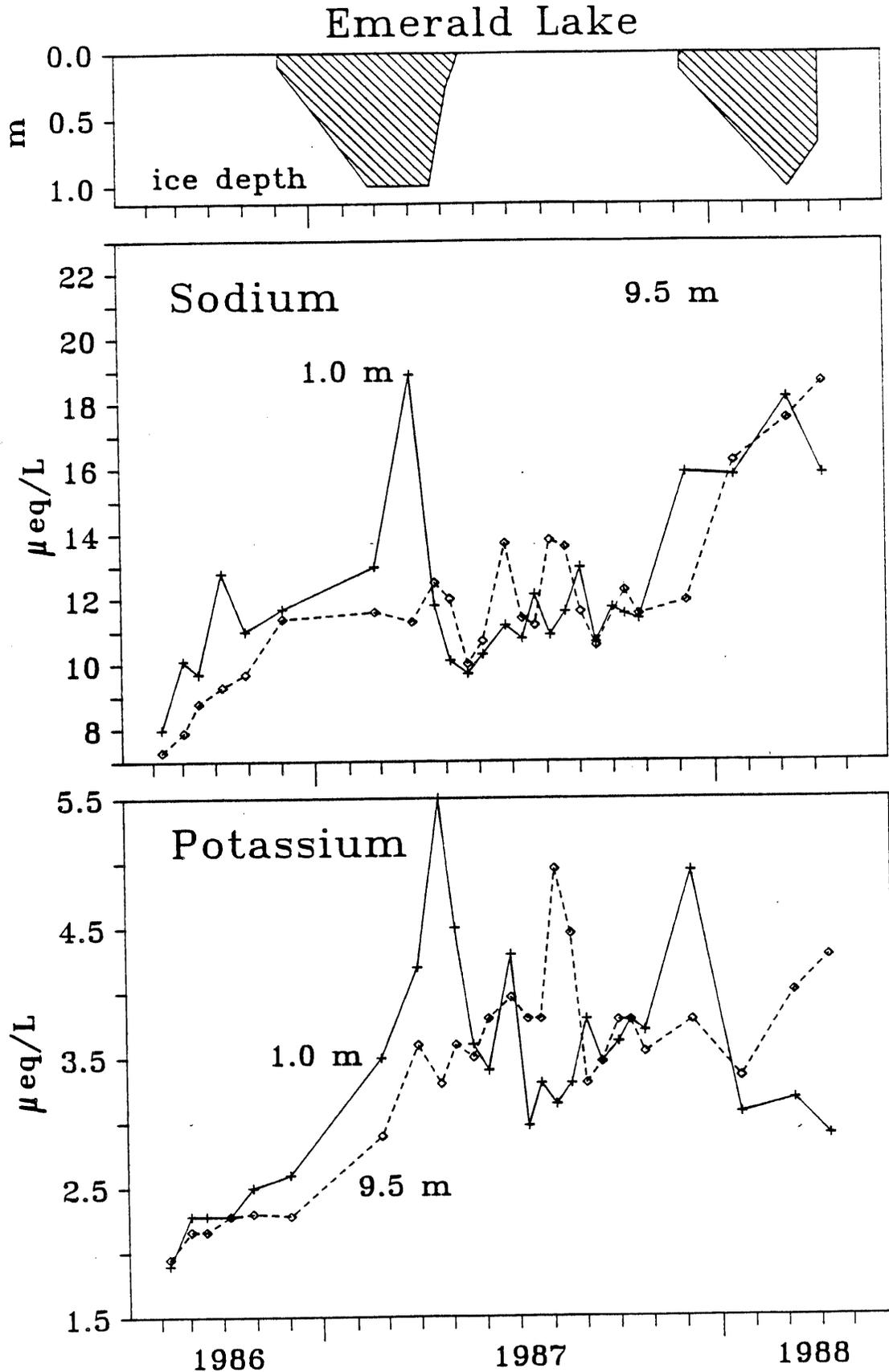


Fig. II-11. Emerald Lake, 1986-88: sodium and potassium.

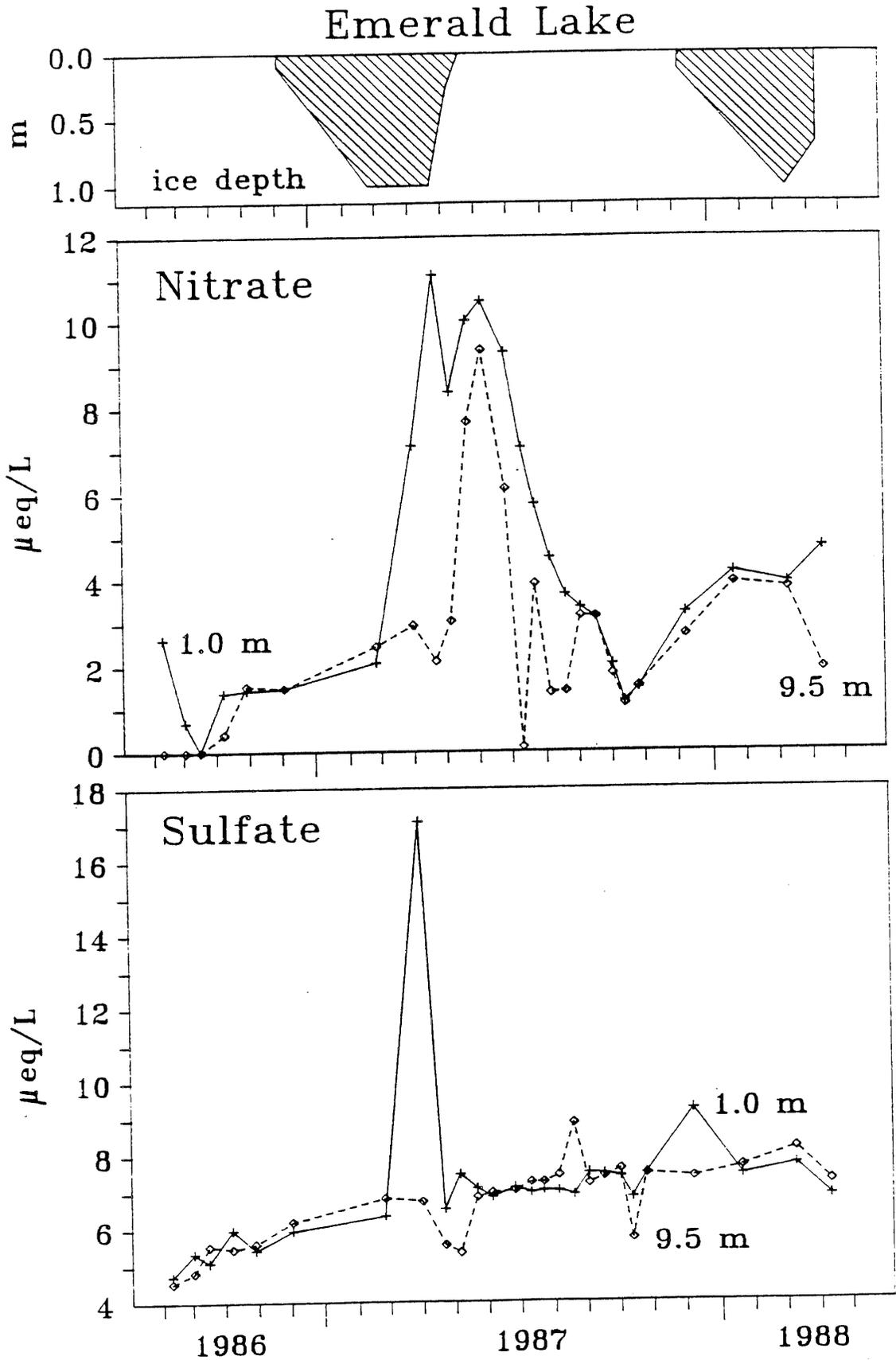


Fig. II-12. Emerald Lake, 1986-88: nitrate and sulfate.

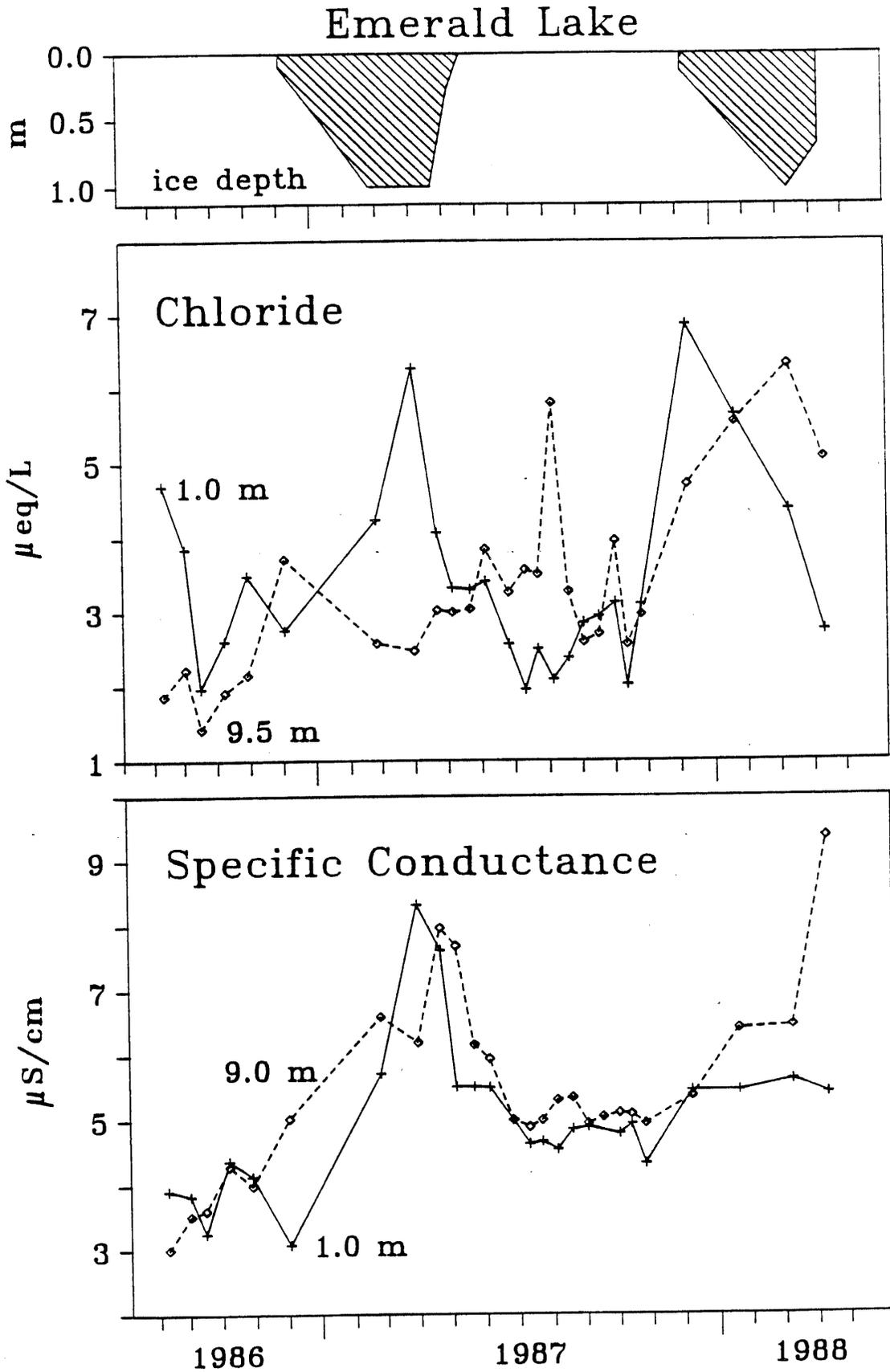


Fig. II-13. Emerald Lake, 1986-88: chloride and conductance.

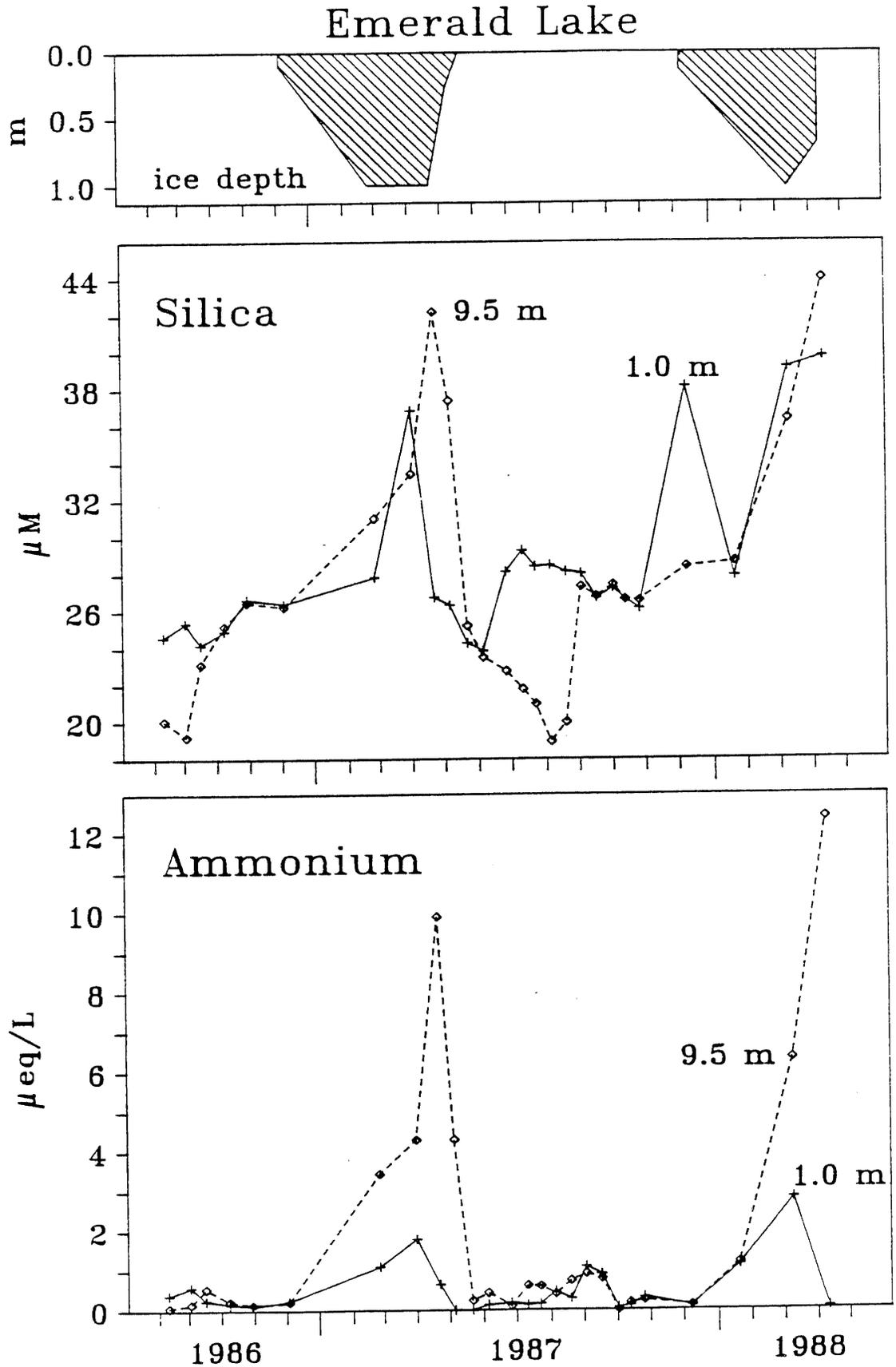


Fig. II-14. Emerald Lake, 1986-88: silica and ammonium.

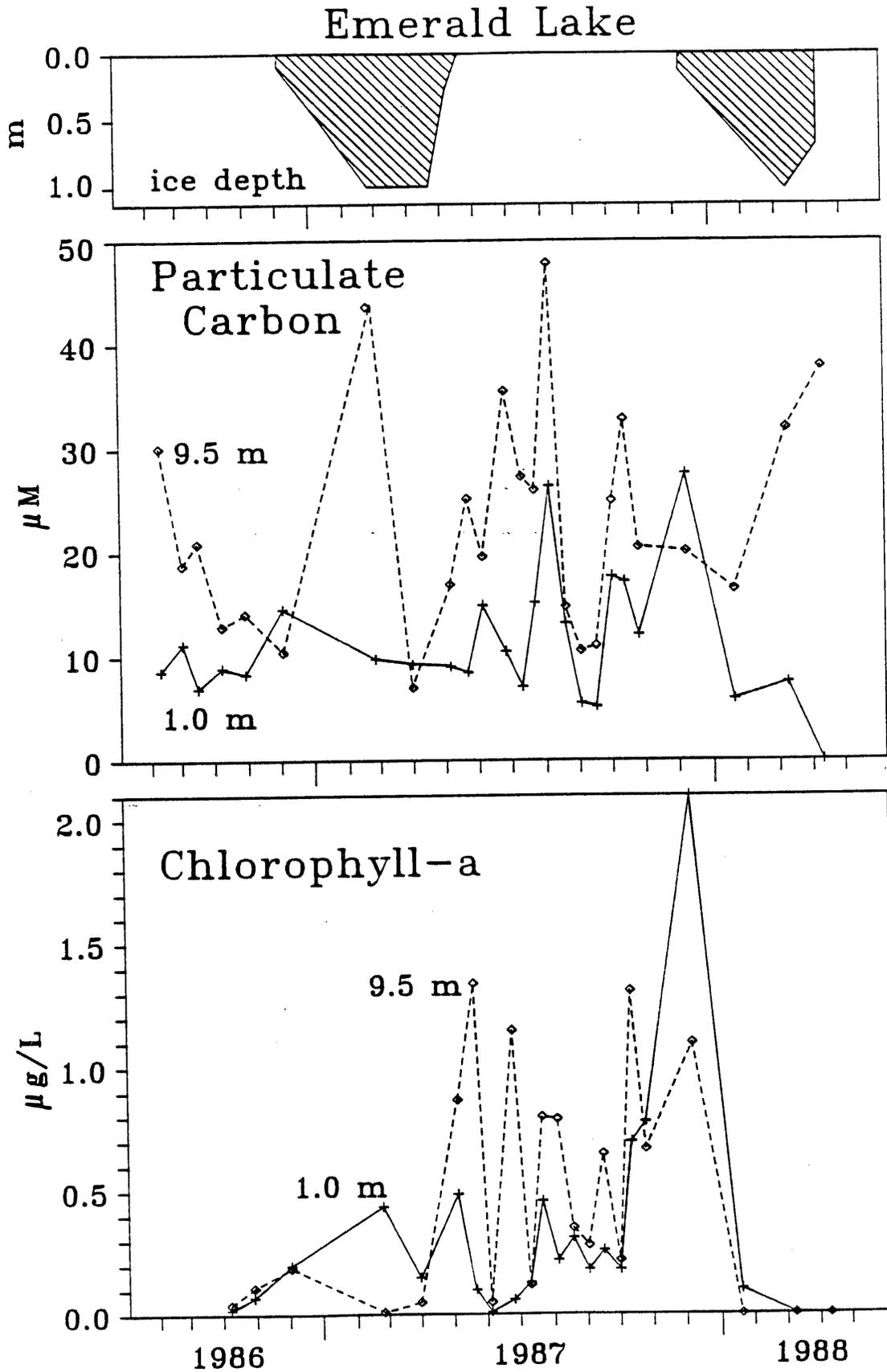


Fig. II-15. Emerald Lake, 1986-88: particulate carbon and chlorophyll-a.

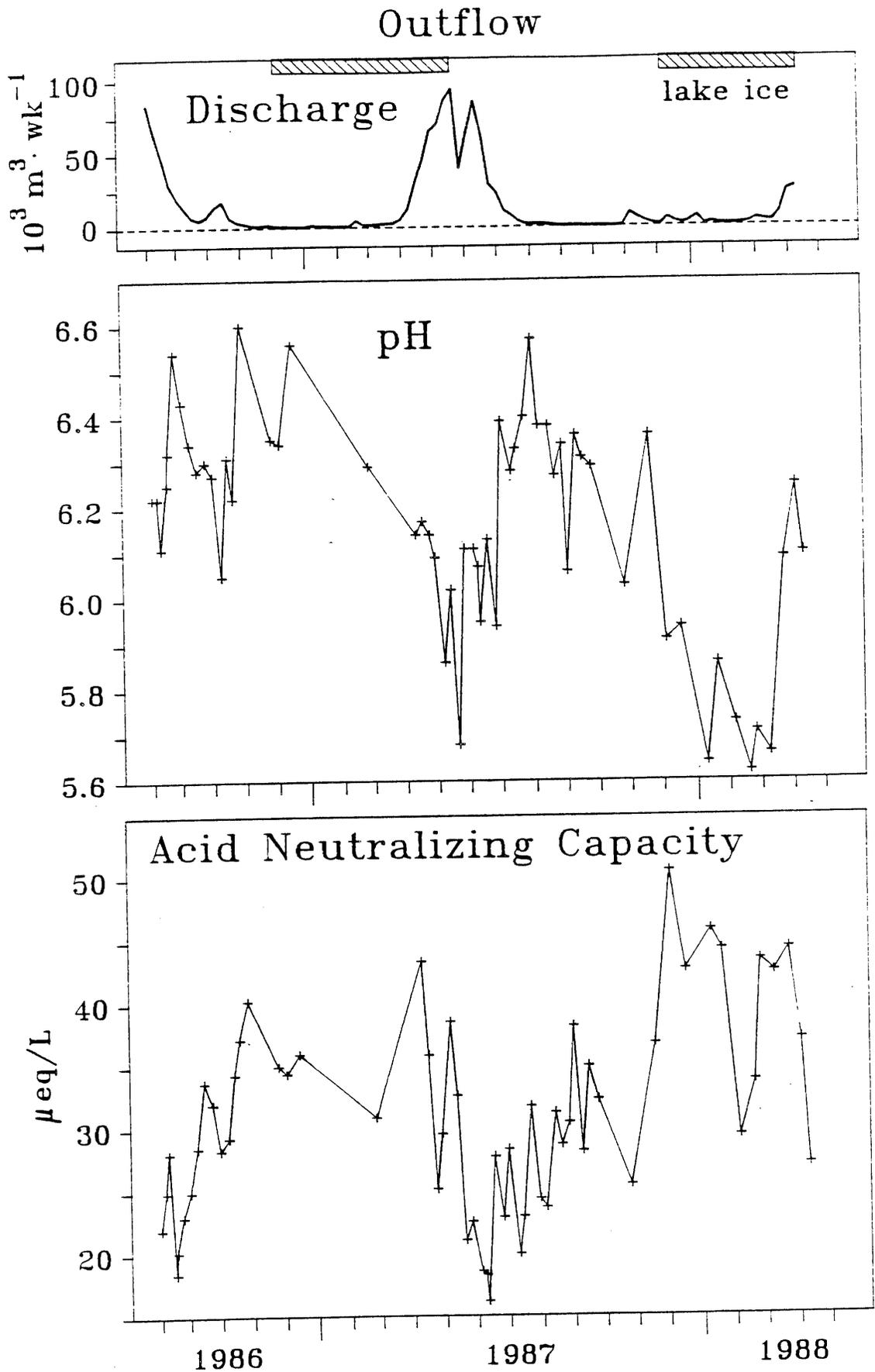


Fig. II-16. Outflow, 1986-88: pH and ANC.

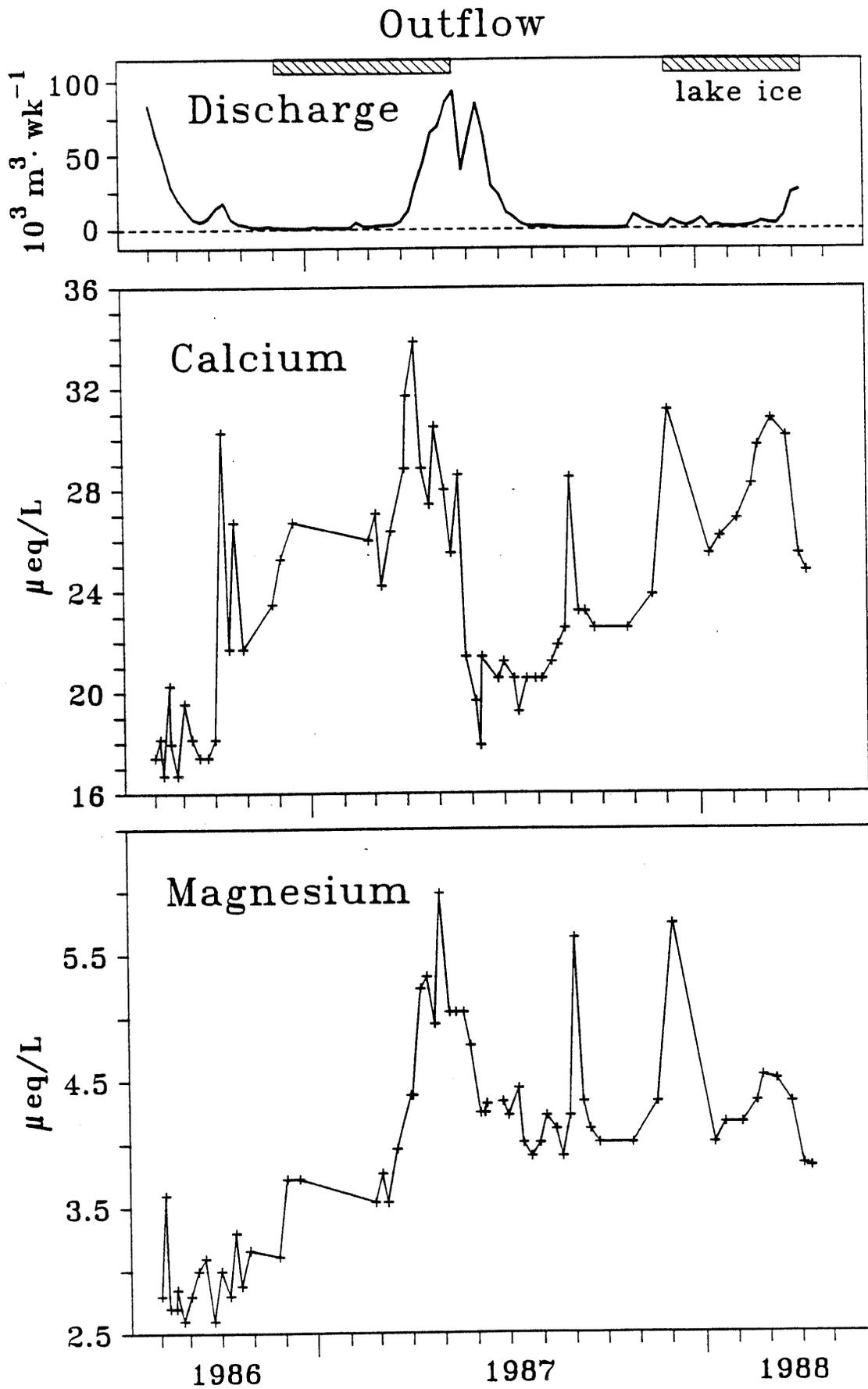


Fig. II-17. Outflow, 1986-88: calcium and magnesium.

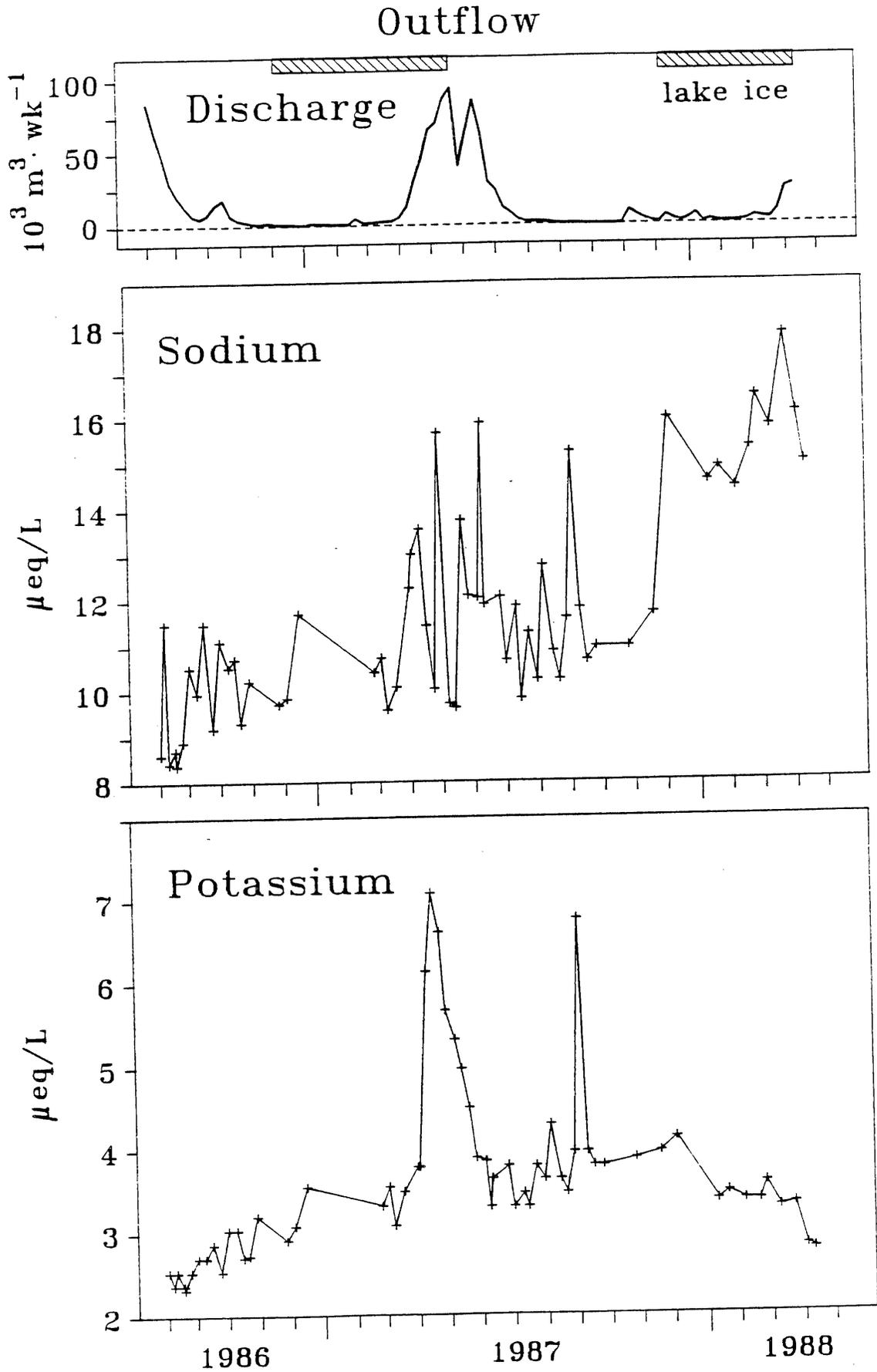


Fig. II-18. Outflow, 1986-88: sodium and potassium.

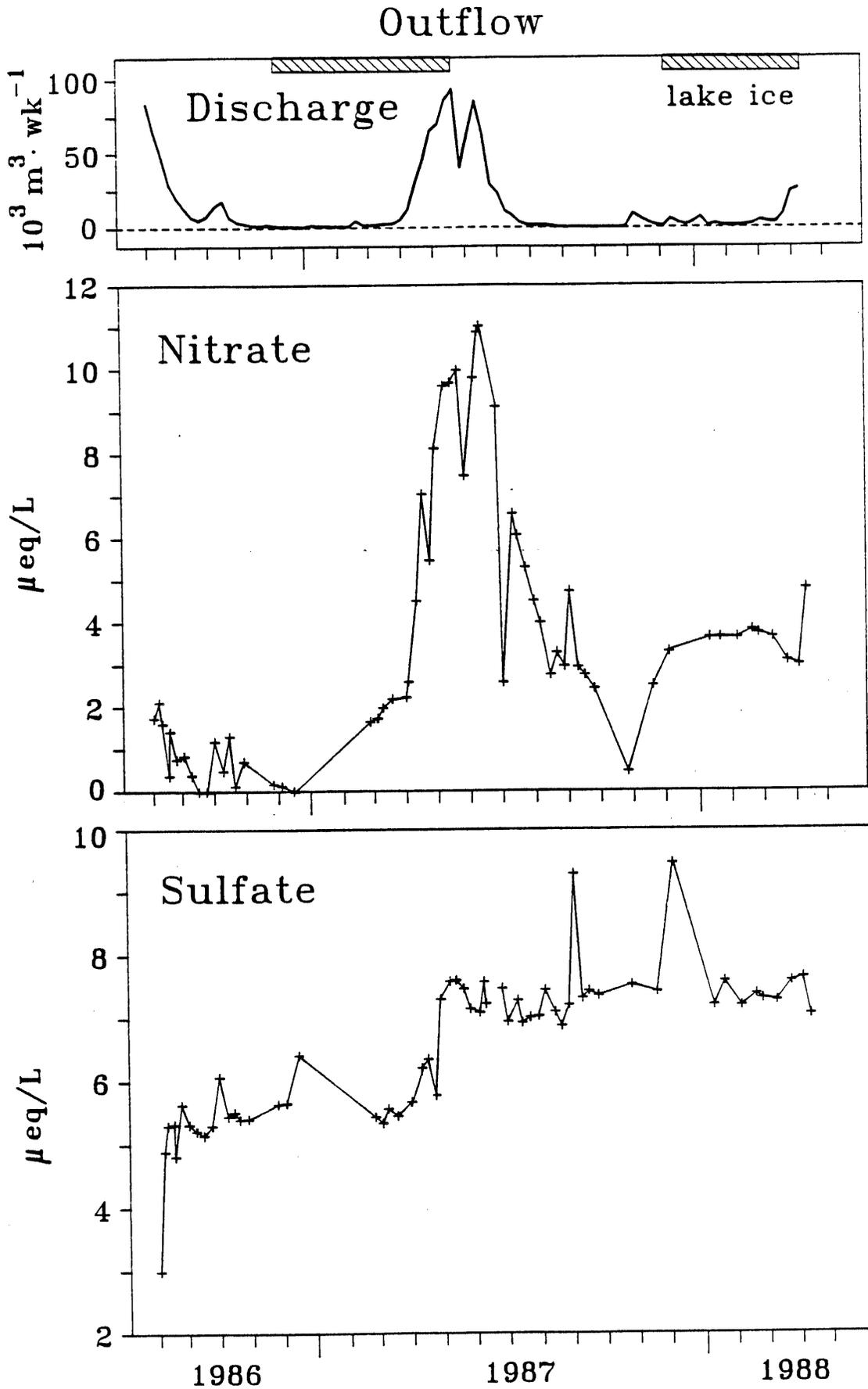


Fig. II-19. Outflow, 1986-88: nitrate and sulfate.

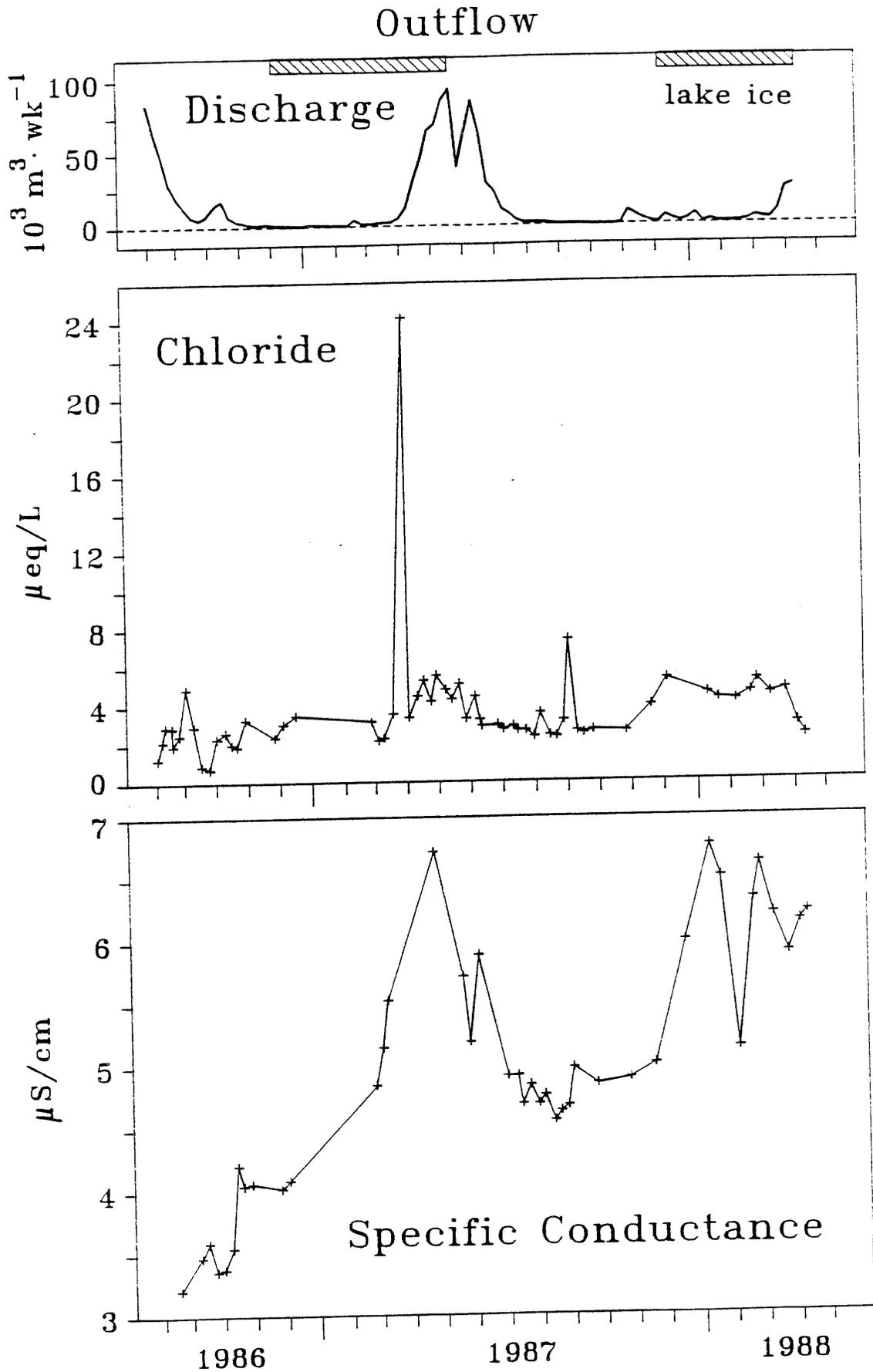


Fig. II-20. Outflow, 1986-88: chloride and conductance.

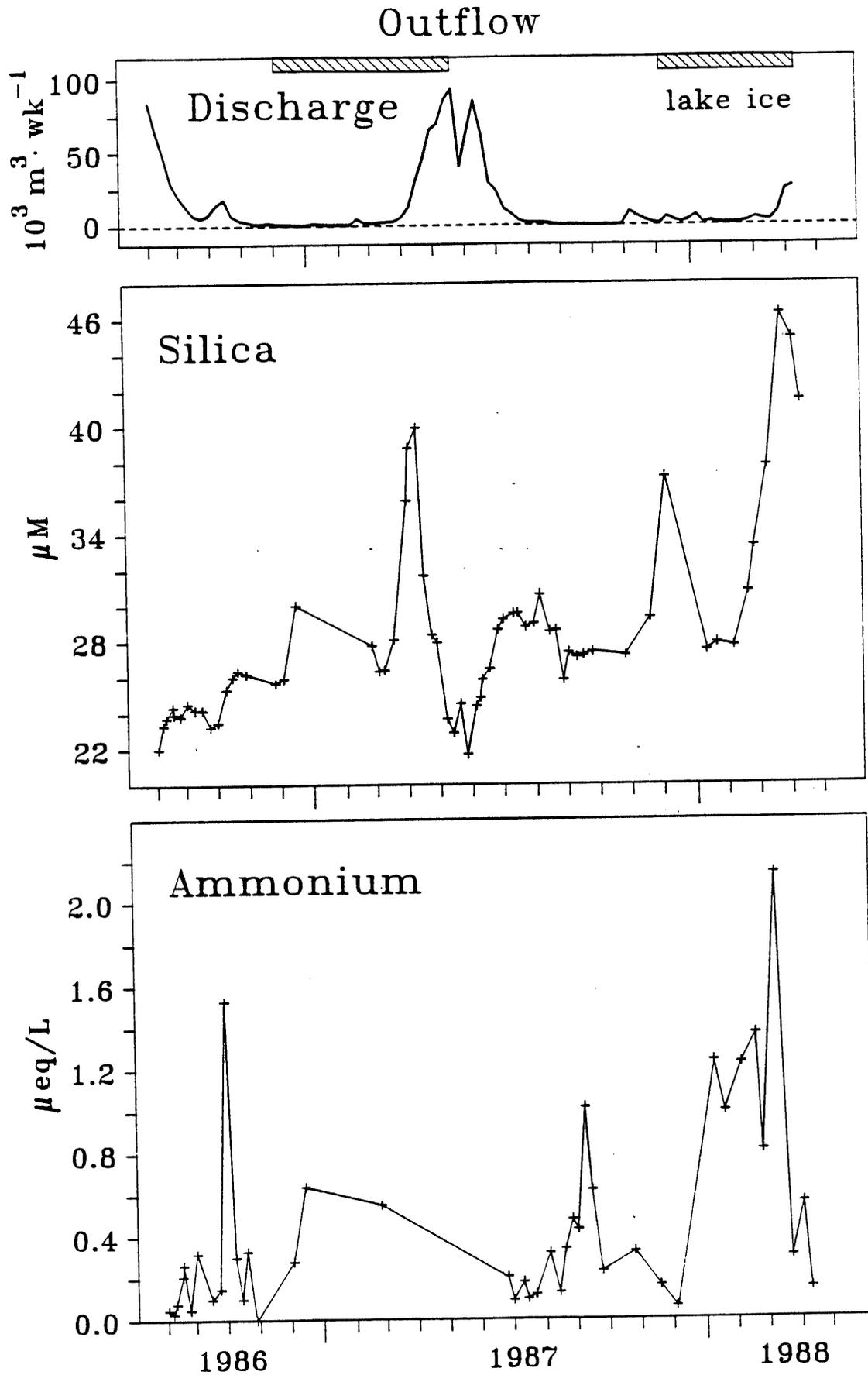


Fig. II-21. Outflow, 1986-88: silica and ammonium.

Chapter III

Hydrochemistry of Emerald Lake: Interannual variability and annual mass balances

We have sampled surface waters in the Emerald Lake watershed continuously for five years (June 1983–April 1988). The general seasonal patterns in lake and stream chemistry that are discussed in the previous chapter can be observed in most years, but substantial variation in the timing and magnitude of these patterns is evident, some of which can be attributed to climatic variation. Infrequent episodic events such as avalanches and large storms also explain some of the variability in the chemistry of the lake. The purpose of this chapter is to examine interannual variability in the physical and chemical characteristics of the lake and its inflows and outflow. In addition, we analyze the mass balance for major solutes in the lake over two years with contrasting hydrologic conditions: 1986, a year of particularly high snowfall, and 1987, when snowfall was relatively low. The mass-balance analysis in this chapter provides information on the effect of the lake on transport of major solutes, on an annual basis. We present in Chapter IV a more detailed analysis of the specific processes in the lake that affect the mass balance for major solutes.

*Methods**Hydrochemical sampling and analyses*

Sampling and analytical methods were basically the same throughout the 5-year sampling period. Methods of sampling, laboratory analysis, and quality assurance are discussed in detail in the previous chapter as well as in Melack et al. (1987). Our sampling intervals varied over the 5-year period. The lake and streams were sampled more frequently during snowmelt (typically April–June) in 1986, 1987, and 1988 than in the earlier years. The inflows and outflow were sampled at variable intervals during the winters except for the winter of 1987–88, when they were sampled regularly every two weeks. An exceptionally long interval of > 5 months between sampling dates in 1985–86 appears on the graphs as a gap in the line between points.

On most dates, the surface water was sampled at 1 m and the bottom water was sampled at 9–10 m. However, when the ice depth was > 1 m, we either sampled at 0.5 m below the bottom of the ice (1987–88) or used the 4-m

sample to represent surface water (previous years). The ice depth reached 6 m late in the winter of 1985-86; at this time, the surface-water sample was taken from 7 m below the top of the ice, and the bottom-water sample was from 9.5 m.

Calculation of mass balances

Mass balances for major solutes were calculated for the water years 1986 (1 October 1985-30 September 1986) and 1987 (1 October 1986-30 September 1987). As a prerequisite to our chemical mass balance, we calculated a water budget for the lake at daily intervals from the measurements reported by Dozier et al. (1987 and 1989). The water budget included the following terms:

$$\Sigma I + P + A - O - E \pm \delta S = \epsilon$$

where

ΣI = sum of inflow stream discharges;

P = precipitation on the lake surface;

A = transport of snow onto the lake surface by an avalanche in February 1986, estimated from the increase in ice depth (this term was used only once);

O = outflow stream discharge;

E = evaporation from the lake surface (ice-free season) or sublimation from the lake surface (ice-covered);

δS = change in lake storage, calculated from stage measurements; and

ϵ = residual.

Several adjustments in the water budget were required to avoid artefacts in our chemical mass balances that would result from the imbalances in the water budget. We eliminated the residual term by adding $|\epsilon|$ to the discharge of Inflow #2 (negative residuals) or to the discharge of the outflow (positive residuals). The water budget also required adjustment for large snowfalls (> 1-cm snow water equivalent). Large residuals were associated with these snowfalls because snow depth measurements were generally taken several days after a snowfall. The increasing weight of the snow on the ice cover of the lake caused the outflow discharge to increase notably during the storm. We used the peaks in daily outflow discharge to apportion the snowfall among the day(s) of a particular storm, thereby synchronizing the precipitation input with the increased outflow discharge and eliminating the large residuals that

resulted from the delay in sampling. The water budget was balanced after these adjustments.

Transport of mass into and out of the lake was calculated using the adjusted water budget and our data on concentrations of solutes in the inflow and outflow streams, as well as data on precipitation chemistry from Dozier et al. (1987 and 1989). Each stream sampling date was taken as the midpoint of a time interval during which transport was calculated from the solute concentrations (as equivalents) for that date and the daily discharges. Chemical data were not available on all dates from the minor inflows (Inflow #4 and several ephemeral streams along the eastern shore); in these cases, we used the chemistry of Inflow #2 to represent the chemistry of the minor inflows.

Results

Hydrochemical time series

Concentrations of major solutes in Inflow #1 over the period from June 1983-April 1988 are graphed in Figures III-1 through III-6. Discharge estimates are not available for the entire period, but the discharge for 1986-88 is shown in Chapter II (Fig. II-1). The magnitude of the peak discharge during snowmelt was variable because the total snowfall varied among years. The horizontal bars along the top of the upper panels indicate the period of ice cover on the lake, which also corresponds approximately to the presence of a heavy snowpack in the watershed.

The pH of Inflow #1 usually ranged from 5.9-6.5 during the summer months (Fig. III-1), tending to increase between peak discharge in the spring and low discharge in the late summer and fall. The pH of Inflow #1 was unusually low early in the summer of 1983, following a severe winter with heavy snowpack. The decreased pH in Inflow #1 during the winter of 1987-88 may not be unique because that was the only winter with regular and frequent stream sampling. The concentration of ANC in Inflow #1 (Fig. III-1) consistently shows an annual pattern of decrease during peak discharge at snowmelt, followed by gradual increase through the year until snowmelt of the following year. This decrease occurs in the latter part of the peak discharge period. The major difference between years is the magnitude of the decrease in ANC concentration during snowmelt; the concentration dropped furthest (to below 10 ueq L^{-1}) in 1983 and 1984.

Seasonal patterns in the concentrations of the base cations (Figs. III-2 and III-3), nitrate (Fig. III-4), sulfate (Fig. III-4), chloride (Fig. III-5), and silica (Fig. III-6) in Inflow #1 over the 5-year sampling period resemble the patterns for the 1986-88 sampling period discussed in Chapter II, and specific conductance (Fig. III-5) reflects these patterns. The major difference between years is in the magnitude of the winter peak in ionic concentrations. The sharp peaks in sodium, potassium, and chloride concentrations in Inflow #1 during snowmelt in March 1987 may not be unusual, because sampling of the streams in preceding years did not cover the initial phase of snowmelt. Ammonium varied considerably in concentration but was usually below $0.5 \mu\text{eq L}^{-1}$ in Inflow #1 (Fig. III-6); much of this variation could be analytical error because the concentrations are close to our detection limit (Chapter II).

Figures III-7 and III-8 are time-series for iron, aluminum, and manganese in Inflow #1. Although there is considerable variation in patterns, concentrations of iron and manganese appear to increase as the stream discharge decreases in late summer, peaking around September. Aluminum does not show a consistent pattern between years. All three metals show larger variation in the particulate fraction than in the soluble fraction, probably due to the variability in transport of suspended particulates. Analytical error is unlikely to be largely responsible for the variation observed here (Chapter II: Table II-1).

Temperature and dissolved oxygen in the surface and bottom waters of the lake over the 5-year sampling period are graphed in Figure III-9. The temperature data reveal a consistent annual cycle of several months of complete mixing in the fall, inverse stratification during winter under ice, a short period of complete mixing when the ice melted, followed by a period of summer stratification. Some interannual variation in this pattern is apparent from Figure III-9. The persistence of ice cover through early July in 1983 apparently prevented the development of summer stratification, and water temperatures remained relatively low throughout the summer. During the summer of 1984, summer stratification was interrupted by mixing in July, but mixing was followed by a rapid return to stratified conditions. The concentration of dissolved oxygen decreased in the bottom water during both summer and winter stratification periods (Fig. III-9), although anoxia or near-anoxia occurred only occasionally.

Transparency of the lake is indicated by the Secchi disk depths in Figure III-10. During the ice-free season, the entire water column of the lake was usually euphotic (Chapter VII). The water was exceptionally turbid after the storms in July 1984 (Chapters V and VII). Secchi depths were not measured under ice cover.

Interannual variation in pH and the concentration of ANC in the surface water of the lake (Fig. III-11) follows that of pH and ANC in Inflow #1 (Fig. III-1). ANC increased in concentration in the hypolimnion during stratification. As in Inflow #1, pH decreased in the epilimnion during winter stratification, although the magnitude of this decrease varied. The concentration of ANC in both the surface and bottom waters dropped after a large storm in July 1984; ANC became undetectable in the surface water.

The seasonal patterns in other major solutes in the lake (Figs. III-12 through III-16) were generally similar among years, although differences in the magnitudes of the seasonal changes are apparent. Ionic concentrations decreased each spring as the lake was flushed with meltwater; these decreases were most marked in 1983 and 1986. Seasonal patterns in these solutes are analyzed in detail in Chapter II.

Iron, aluminum, and manganese in the lake are shown in Figures III-17, -18, and -19, respectively. In the surface water, the concentration of total iron was highest during mixing events. At 9.5 m, the concentration of total iron peaked during thermal stratification. Particulate iron evidently accumulated in the hypolimnion of the lake over the course of thermal stratification, particularly during the winter, and mixed into the epilimnion when the water column mixed in the spring and fall. The magnitude of increase in iron concentration in the surface water appears related to the severity of the preceding stratification period. The highest peaks in the concentration of total iron in surface water occurred at fall mixing after the summer of 1984, which was a period of exceptionally strong stratification, and upon spring mixing after the exceptionally heavy ice cover of winter 1986.

Aluminum did not show a consistent pattern among years (Fig. III-18). The unusual peaks in aluminum concentrations in late 1986 did not coincide with peaks in aluminum in Inflow #1. Manganese showed little variation at 1.0 m, but increased sharply in concentration at 9.5 m during winter thermal stratification (Fig. III-19). As with iron, the increase was much greater during winter stratification than during summer stratification. In contrast to iron,

the increase in manganese was largely due to the soluble fraction. After mixing of the water column in the spring, the concentration of manganese dropped precipitously in the hypolimnion but, curiously, no concomitant increase occurred in the surface water. The concentration of manganese in the surface water was higher in 1984 than in later years. No data are available for manganese in deeper lake waters during 1984.

Concentrations of particulate carbon and chlorophyll-*a* were variable among years in the lake (Fig. III-20). During the ice-free seasons, chlorophyll-*a* and particulate carbon concentrations were often greater in the bottom water. Phytoplankton biomass, as indicated by chlorophyll-*a*, was very low under ice in the winter of 1987-88, but was not particularly low under ice during the previous winters. Chlorophyll-*a* concentrations in the surface water peaked on two dates (December 1984 and 1987) shortly after ice formation. This particular period was not sampled in the other years, however. During winter stratification in all years except 1984-85, high concentrations of particulate carbon occurred at 9.5 m, but these were not accompanied by increases in chlorophyll-*a*.

The concentrations of major solutes and trace metals in the Emerald Lake outflow are graphed in Figures III-21 through III-28. Seasonal patterns of these variables in the outflow were generally similar to those in the surface water of the lake.

Mass balance for major solutes

The results of the mass-balance calculations for selected solutes are presented in Figures III-29 and III-30. The data have been summed to monthly intervals, and inputs (positive), outputs (negative), and the residual are graphed for each water year. The seasonal patterns of mass inputs and outputs show the expected dominance of transport during the spring snowmelt period. There are only a few periods in which the residuals are large enough to suggest that processes within the lake modified solute concentrations. The positive residuals (inputs exceed outputs) for nitrate and silica during the late spring and summer of 1987 suggest retention of these solutes in the lake, presumably by biotic uptake. The switch from negative to positive residuals for H^+ during snowmelt and summer in both water years is unexplained, but suggests that the lake switches from a small source to a small sink for protons. The processes within the lake that affect the ionic composition of the water are investigated

in more detail in Chapter IV, which contains additional interpretation of the chemical mass balance for the lake.

The ratios of the annual inputs to annual outputs of mass show the net effect of the lake on solute transport (Table III-1). We consider the uncertainty in these ratios to be approximately $\pm 25\%$. Using this criterion, we cannot distinguish any effects of the lake on solute transport during water year 1986, and only nitrate and perhaps silica show effects (retention by the lake) during water year 1987.

Discussion

Much of the interannual variability in the chemistry of Emerald Lake and the streams in its watershed can be explained by natural variability in the annual quantity of snowfall. The depth of precipitation falling as snow was measured for the last four winters of the study by Dozier et al. (1989); the snow water equivalents were 1046, 2380, 780, and 860 mm for the water years 1985-88, respectively. Our field observations indicate that snowfall was relatively heavy in the winter of 1982-83, and that snowfall in the winter of 1983-84 was similar to that of water years 1987 and 1988. Additional variability in the chemistry of the lake and streams is caused by summer rain storms, which occur infrequently and are variable in magnitude, and by major avalanches, which are of uncertain frequency but only occurred once during the study. Figure III-31 summarizes the variation in these factors that we have observed over the 5-year sampling period.

The snowpack tends to accumulate in the watershed until the spring snowmelt period, which typically begins in April (Dozier et al. 1987). The snowmelt period varies in duration, however, depending on the total snow quantity and on the weather. Snow in the watershed and ice on the lake surface persisted into July in 1983 and 1986, thereby shortening the subsequent ice-free seasons considerably (Fig. III-31). Annual production of algae, invertebrates, and fishes in the lake can vary substantially between years because of the variable length of the ice-free season (Chapters VII, VIII, and IX). Strub et al. (1985) reached similar conclusions regarding causes of the interannual variation observed in Castle Lake in Northern California.

Heavy deposition of snow also results in increased flushing of the lake with meltwater during snowmelt. The decrease in ionic concentrations was greater during snowmelt in 1983 and 1986 than in the other years (Fig. III-15)

because the entire lake was flushed with the relatively dilute water carried into the lake by the inflows (Chapter II).

Snowfall was much lighter in the winters of 1986-87 and 1987-88 than in 1982-83 and 1985-86. Nearly all of the snow in the watershed melted early in the summer of 1987. Consequently, the discharges of Inflow #1 and the outflow were unusually low throughout the summer, and flow practically ceased in September (Fig. II-1).

A large avalanche carried snow onto the surface of the lake in mid-February 1986 (Fig. III-31). The snow pushed the ice downward, displacing a substantial proportion of the lake volume out of the lake through the outflow channel, and increased the thickness of the layer of ice and snow over the lake to 6 m at the center of the lake. This layer subsequently persisted into July. The outflow channel was scoured by debris when the lake water was forced out, resulting in heavy mortality of larval trout (Cooper et al. 1988a).

Summer rain at Emerald Lake is acidic and high in solutes compared with snow (Melack et al. 1982: Chapter V). Even small summer storms can affect the chemistry of the inflows (Chapter V), but the effects are ephemeral. Two storms in mid-July 1984 were large enough to change the normal summer conditions in the lake (Fig. III-31). The first storm (17 July) brought 4.5 cm of rain, and 1.1 cm fell in the second storm (21 July). The pH of the rain in the first storm was 4.3; the second one was not sampled. We sampled the lake on 22 July. The storms had disrupted summer stratification, causing complete mixing of the water column, but the lake restratified rapidly (Fig. III-9). The pH and the concentration of ANC decreased throughout the water column, and ANC became undetectable in the surface water (Fig. III-11). The storm runoff caused the lake to become much more turbid than usual (Fig. III-11). The consequent reduction in light transmission through the water column may have suppressed algal growth in the hypolimnion, thereby enhancing the depletion of dissolved oxygen in the hypolimnion in following weeks (Fig. III-9). The unusually large peak in phytoplankton biomass during the autumn mixing (Fig. III-20) may have been stimulated by the availability of nutrients that had accumulated in the hypolimnion. Most of the effects of these storms that we have noted can be explained by the hydrological effects of the rain (flushing, mixing, and transport of particulate material into the lake from the watershed), rather than by the chemistry of the rain.

The chemical mass balance for major solutes during water years 1986 and 1987 shows that, on an annual basis, the lake has little influence on the transport of solutes. This is not surprising, given the large annual snowfall and subsequent runoff, and the large watershed area relative to the size of the lake (Kelly et al. 1987, Kelly 1988, Schaffer and Church 1989). The observation that lake effects were detectable for two solutes (nitrate and silica) during the ice-free season of 1987, but were undetectable during 1986, is consistent with the aforementioned differences in the timing and magnitude of snowmelt runoff between the two years. The shorter ice-free season and higher flushing rates in 1986 probably resulted in reduced effects of biotic uptake on solute concentrations, compared with 1987.

Conclusions

Examination of the 5-year time series of the chemistry of Emerald Lake and the streams in its watershed reveals recurrent seasonal patterns that are largely determined by climatic factors. Interannual variation in the timing and magnitude of seasonal changes is driven largely by variation in the annual quantity of snowfall. Heavy snowfall results in increased flushing of the lake during snowmelt and delays the start of the ice-free season. Reduction in the duration of the ice-free season is potentially important because the production of algae, invertebrates, and fishes in the lake could be reduced. After winters with light snowfall, the streams decrease to very low discharge over the course of the summer and fall, or dry completely.

A heavy avalanche in 1986 and intense summer rains in 1984 also changed the seasonal patterns in chemistry of the lake and streams. Summer rains in other years were not large enough to significantly affect the lake, although the streams were affected. The effects of the rain appeared to be primarily hydrological rather than chemical.

The annual mass balances for major solutes in Emerald Lake show that the lake has little influence on solute transport. The ionic composition of the lake water is determined by the chemistry of precipitation, and by watershed processes that modify the chemistry of runoff before it reaches the lake.

Emerald Lake and the streams in its watershed are susceptible to acidification because of their extremely low ionic strength. However, because snow, which is less acidic than rain, is the predominant form of precipitation,

these water bodies are not currently showing serious acute or chronic chemical effects of acidic deposition. The natural variation in climate, particularly in the quantity of snowfall, results in considerable interannual variation in the physical and chemical characteristics of these aquatic environments.

Table III-1. Ratios of mass inputs to mass outputs for selected solutes in Emerald Lake, over two water years (1 October-30 September). See text for explanation of mass-balance calculations.

solute	inputs:outputs	
	water yr 1986	water yr 1987
H ⁺	1.00	1.01
ANC	0.96	1.02
Ca ²⁺	0.89	1.14
Cl ⁻	0.90	1.09
NO ₃ ⁻	0.90	1.47
SO ₄ ²⁻	1.02	1.16
Si	0.96	1.28

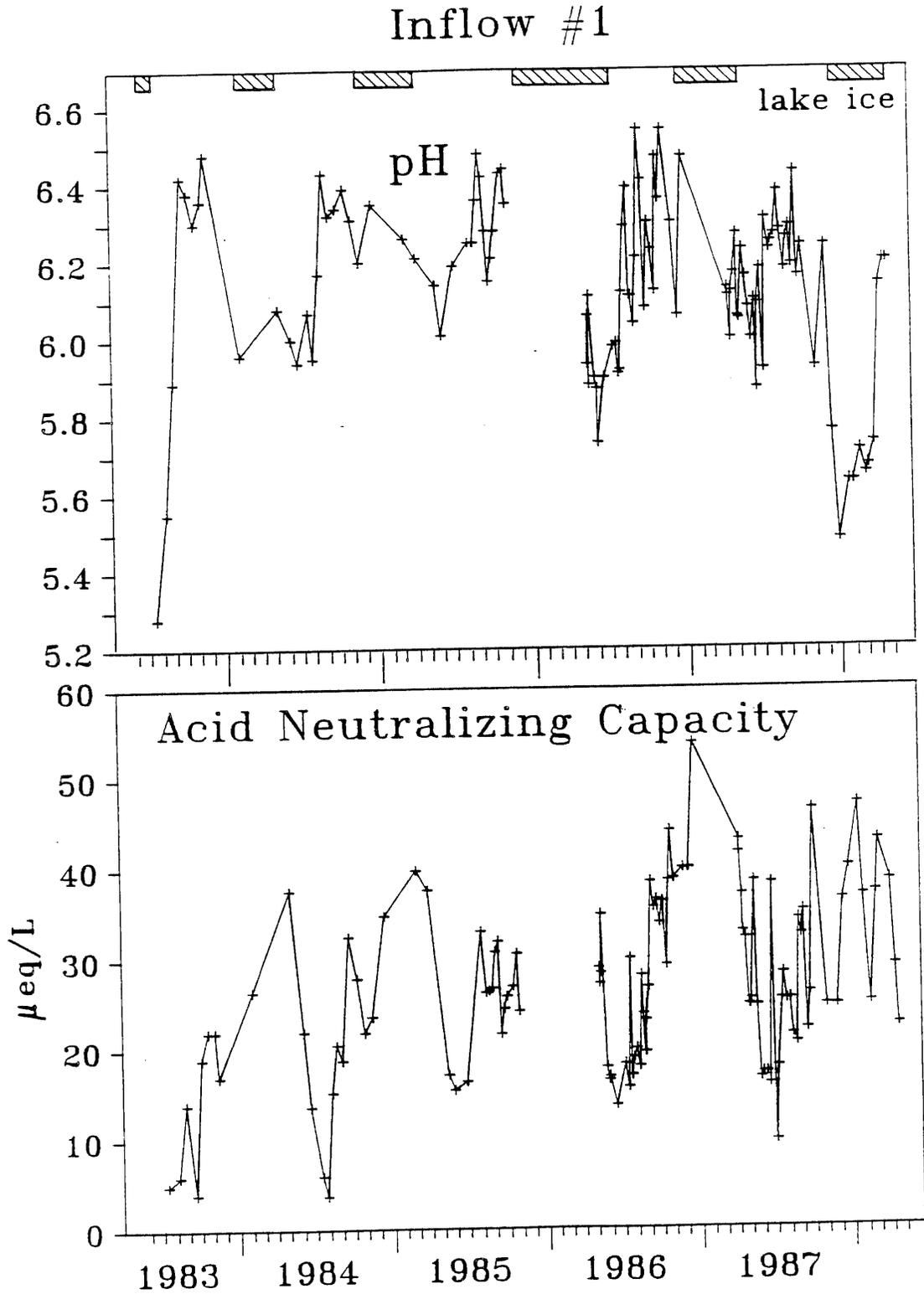


Fig. III-1. Inflow #1, 1983-88: pH and ANC.

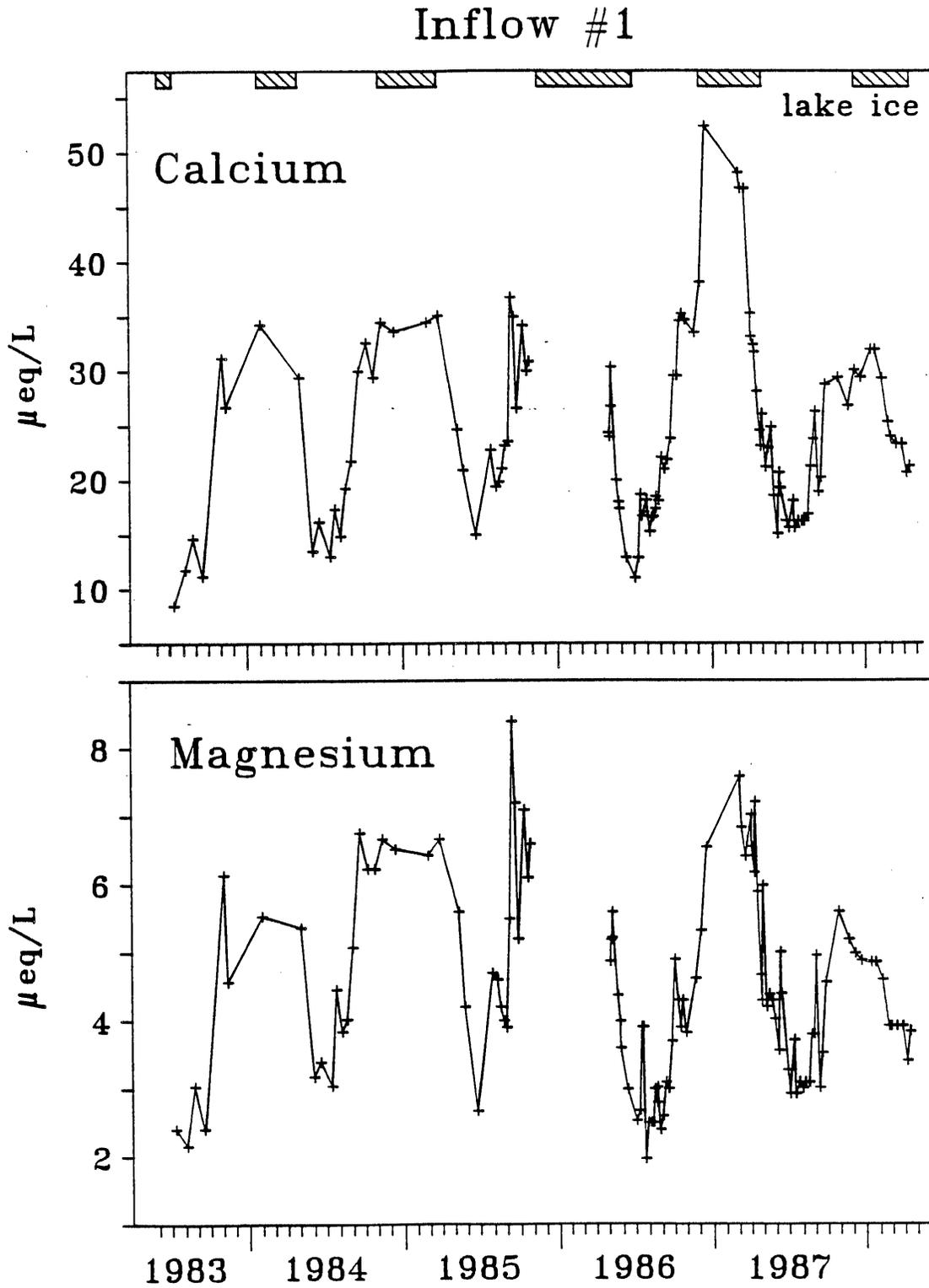


Fig. III-2. Inflow #1, 1983-88: calcium and magnesium.

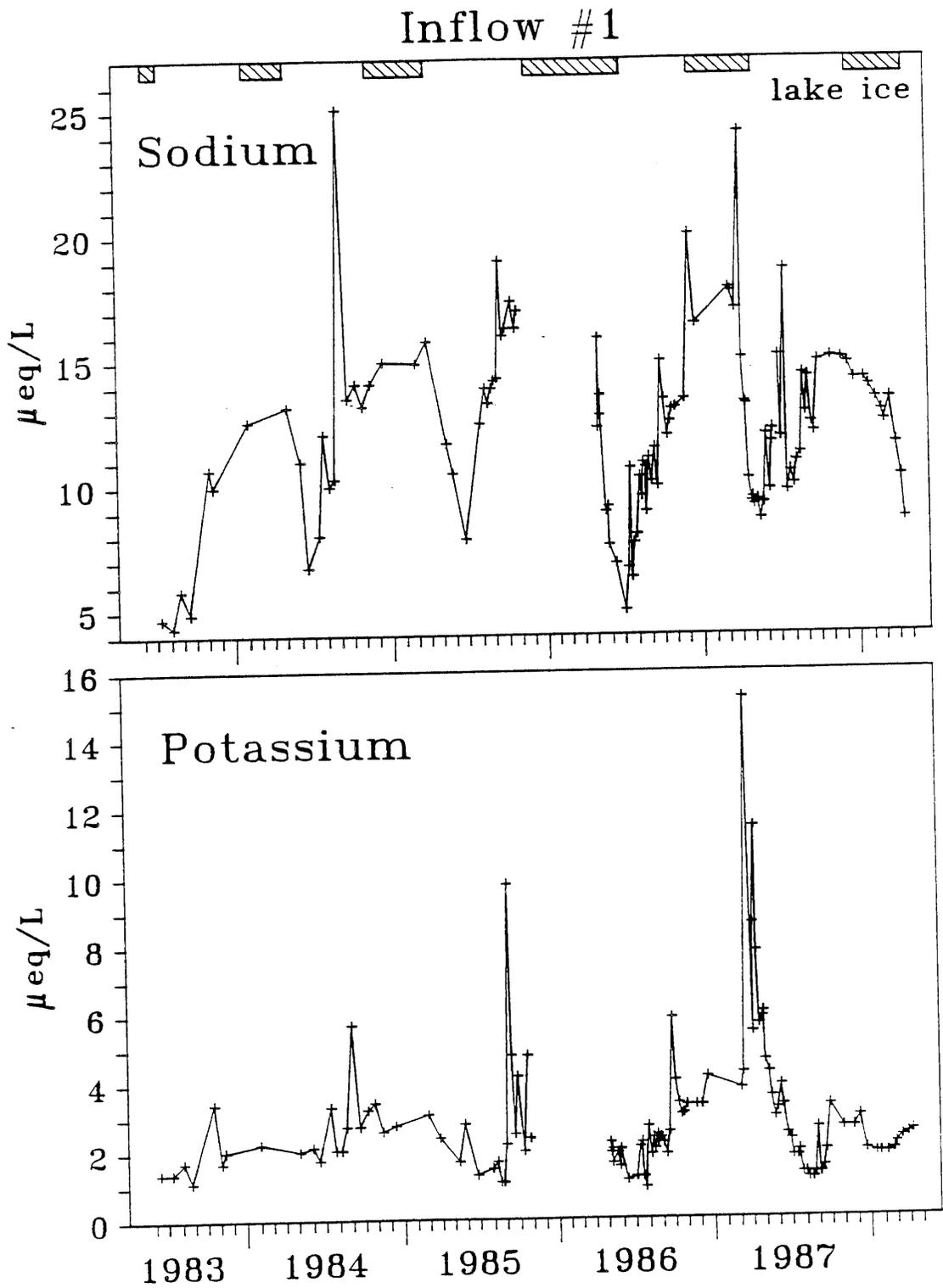


Fig. III-3. Inflow #1, 1983-88: sodium and potassium.

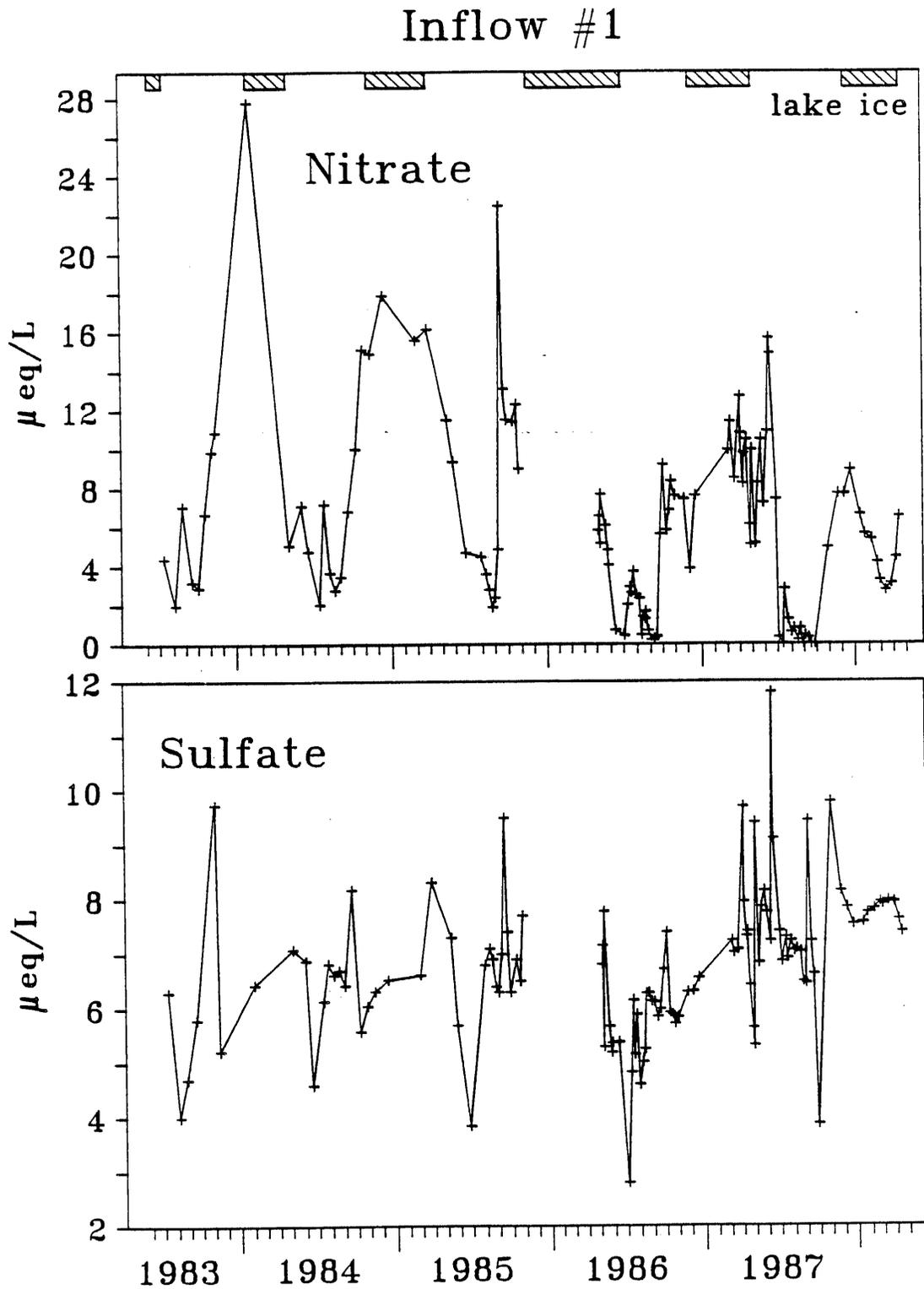


Fig. III-4. Inflow #1, 1983-88: nitrate and sulfate.

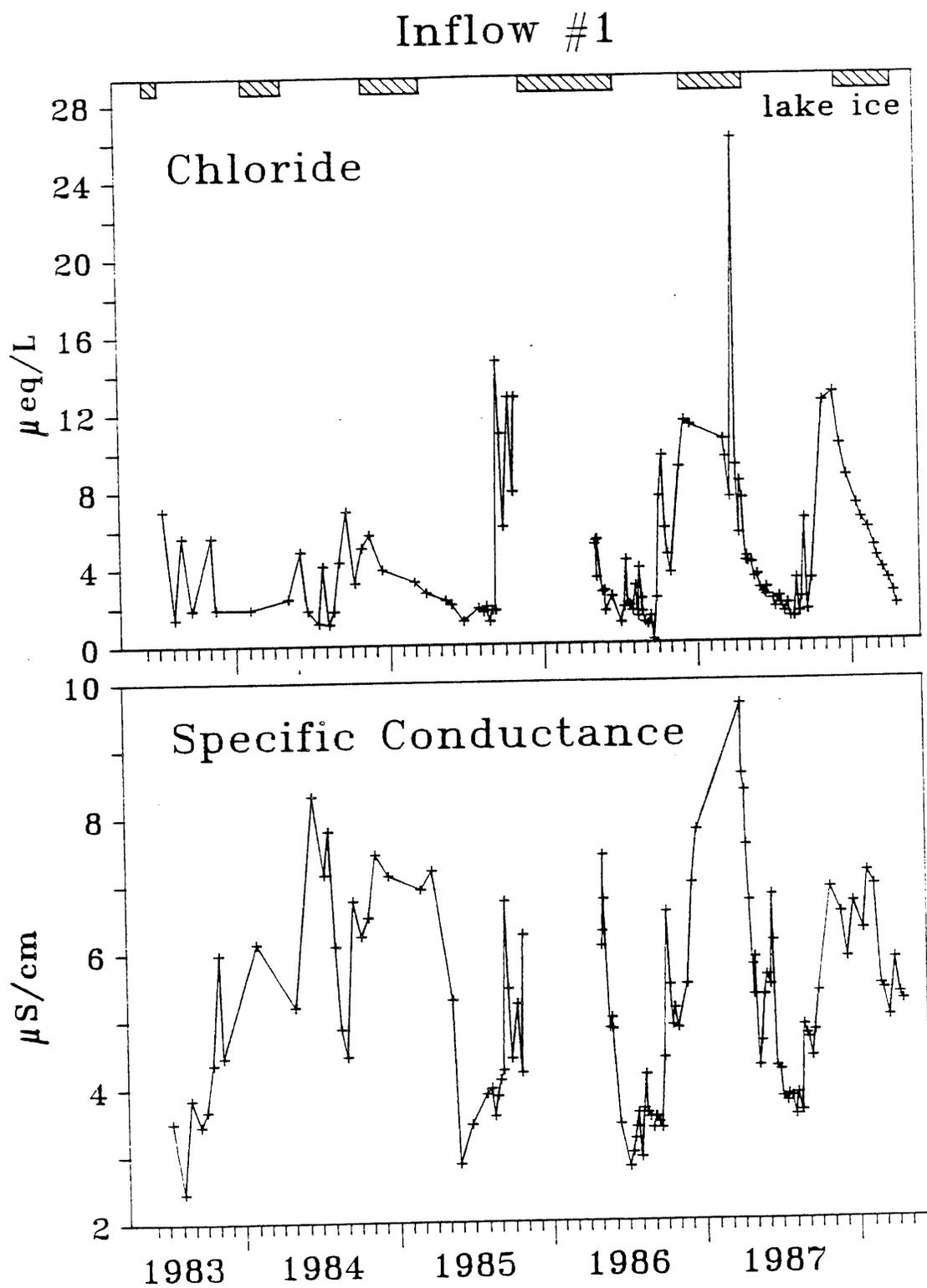


Fig. III-5. Inflow #1, 1983-88: chloride and conductance.

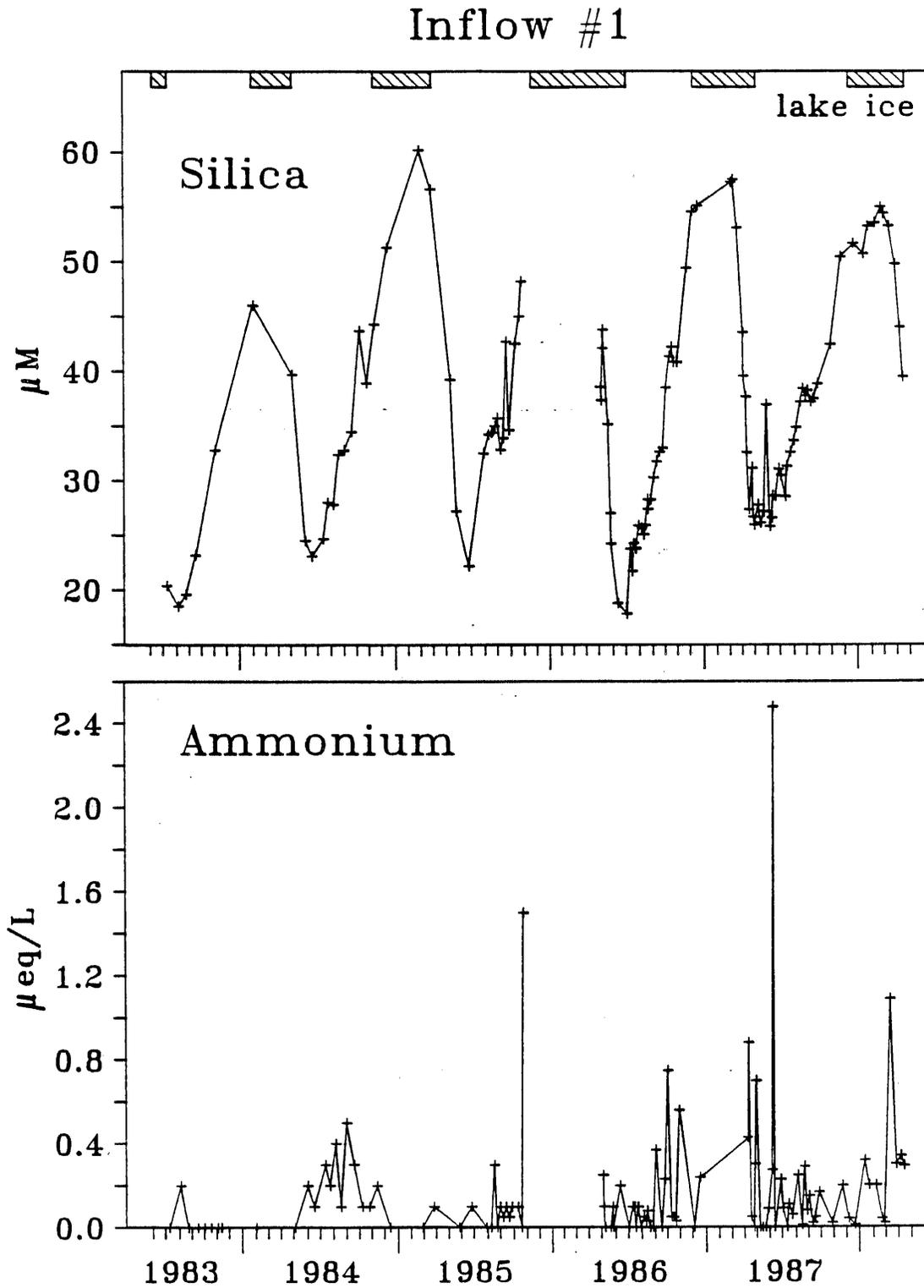


Fig. III-6. Inflow #1, 1983-88: silica and ammonium.

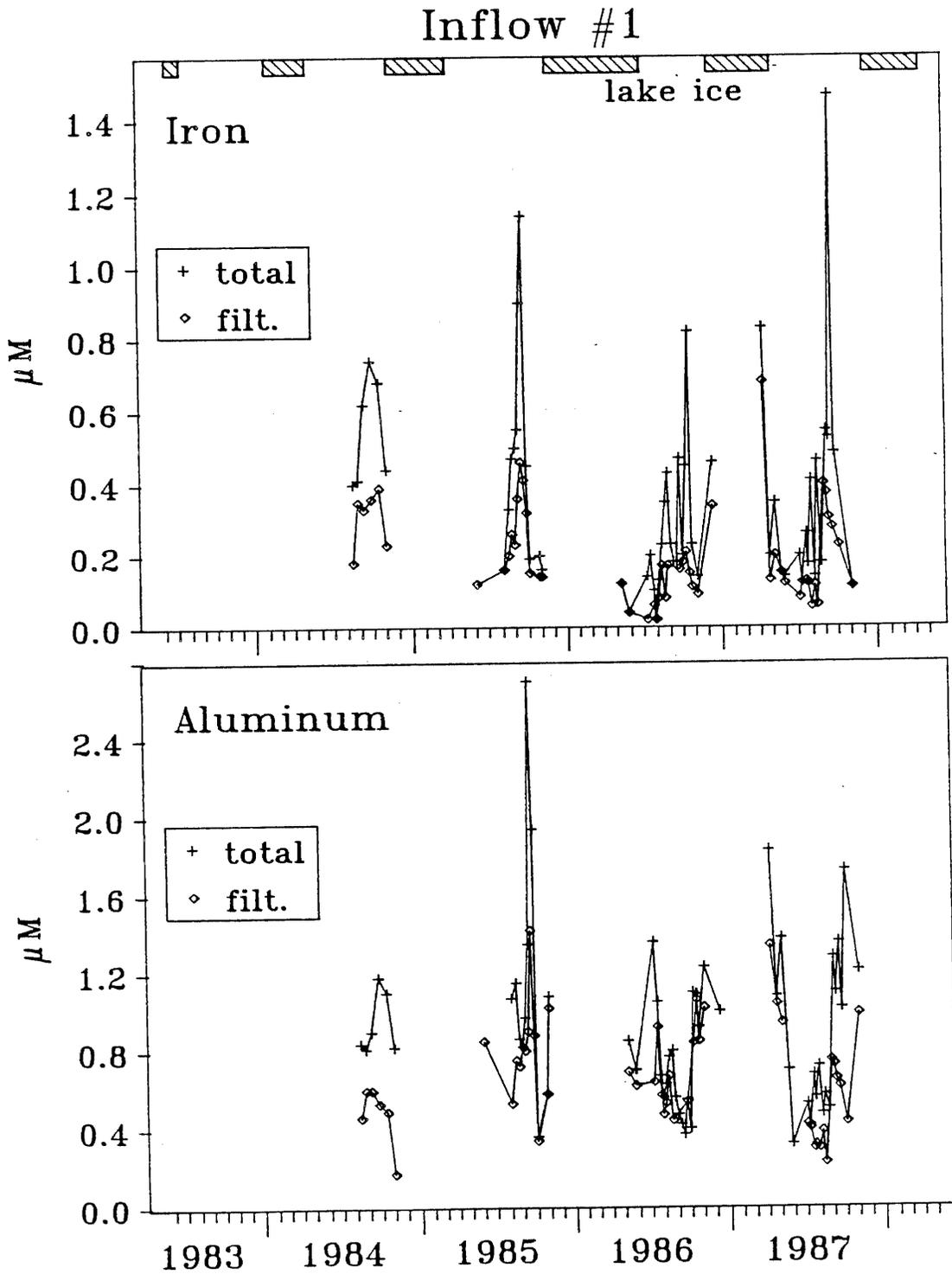


Fig. III-7. Inflow #1, 1983-88: iron and aluminum.

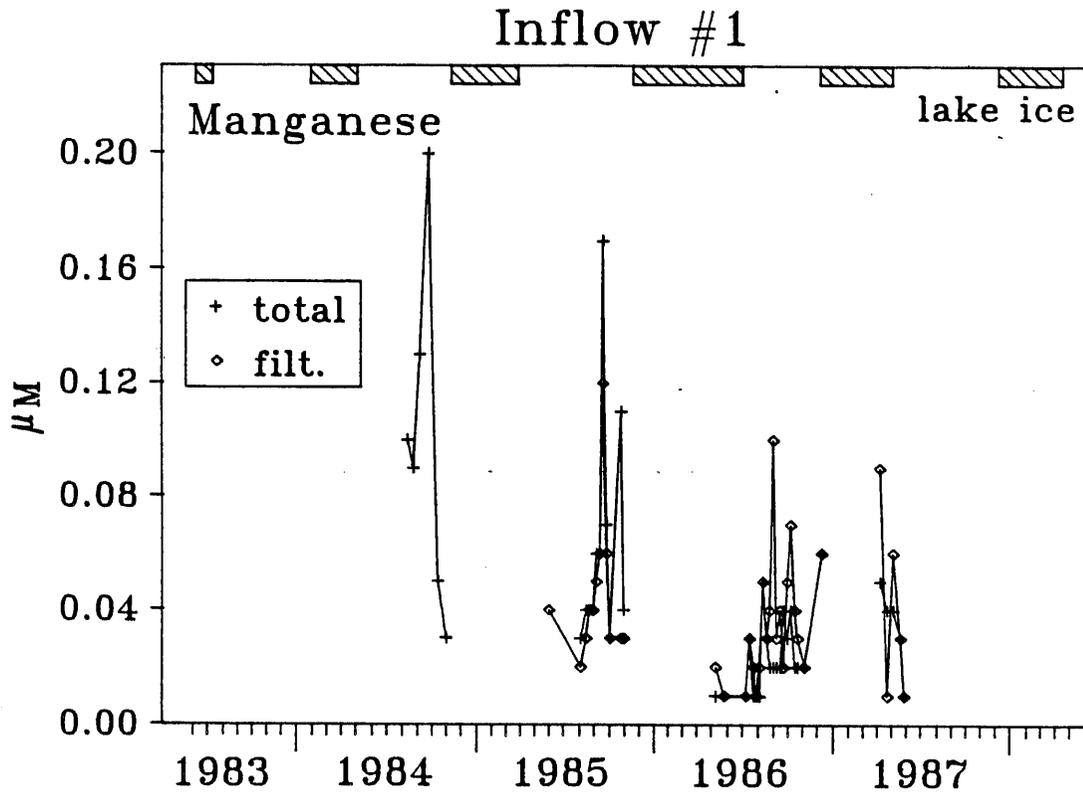


Fig. III-8. Inflow #1, 1983-88: manganese.

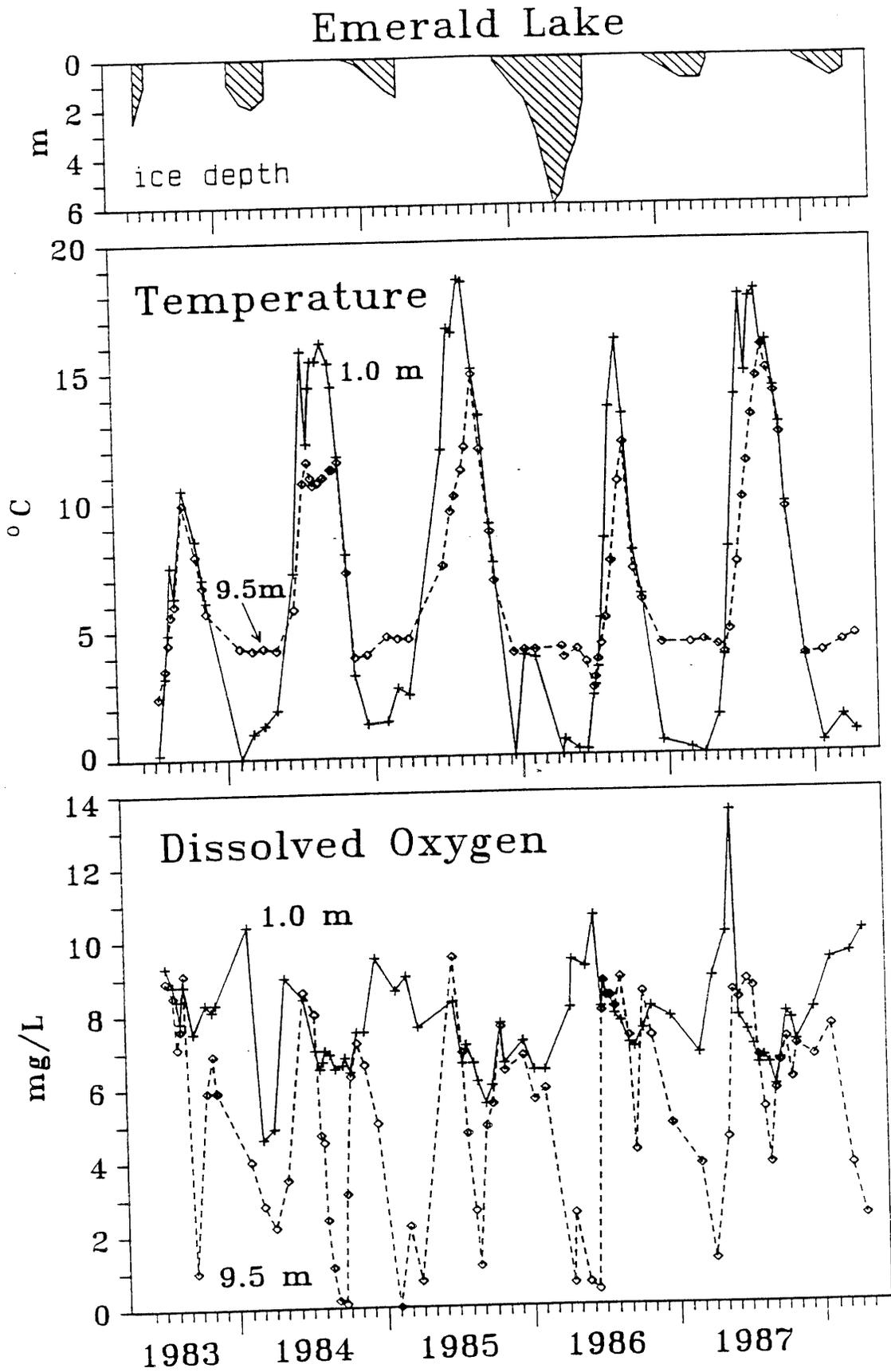


Fig. III-9. Emerald Lake, 1983-88: temperature and dissolved oxygen.

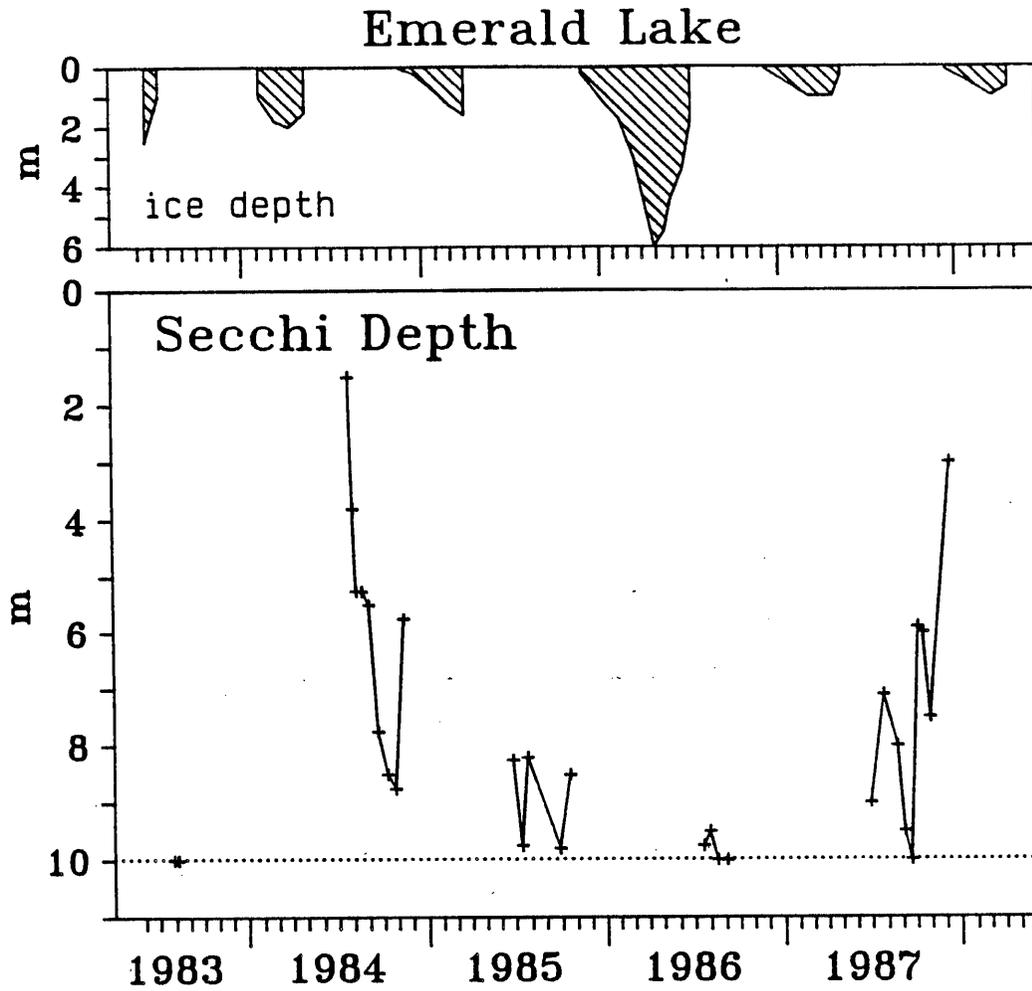


Fig. III-10. Emerald Lake, 1983-88: transparency, measured as Secchi depth.

Emerald Lake

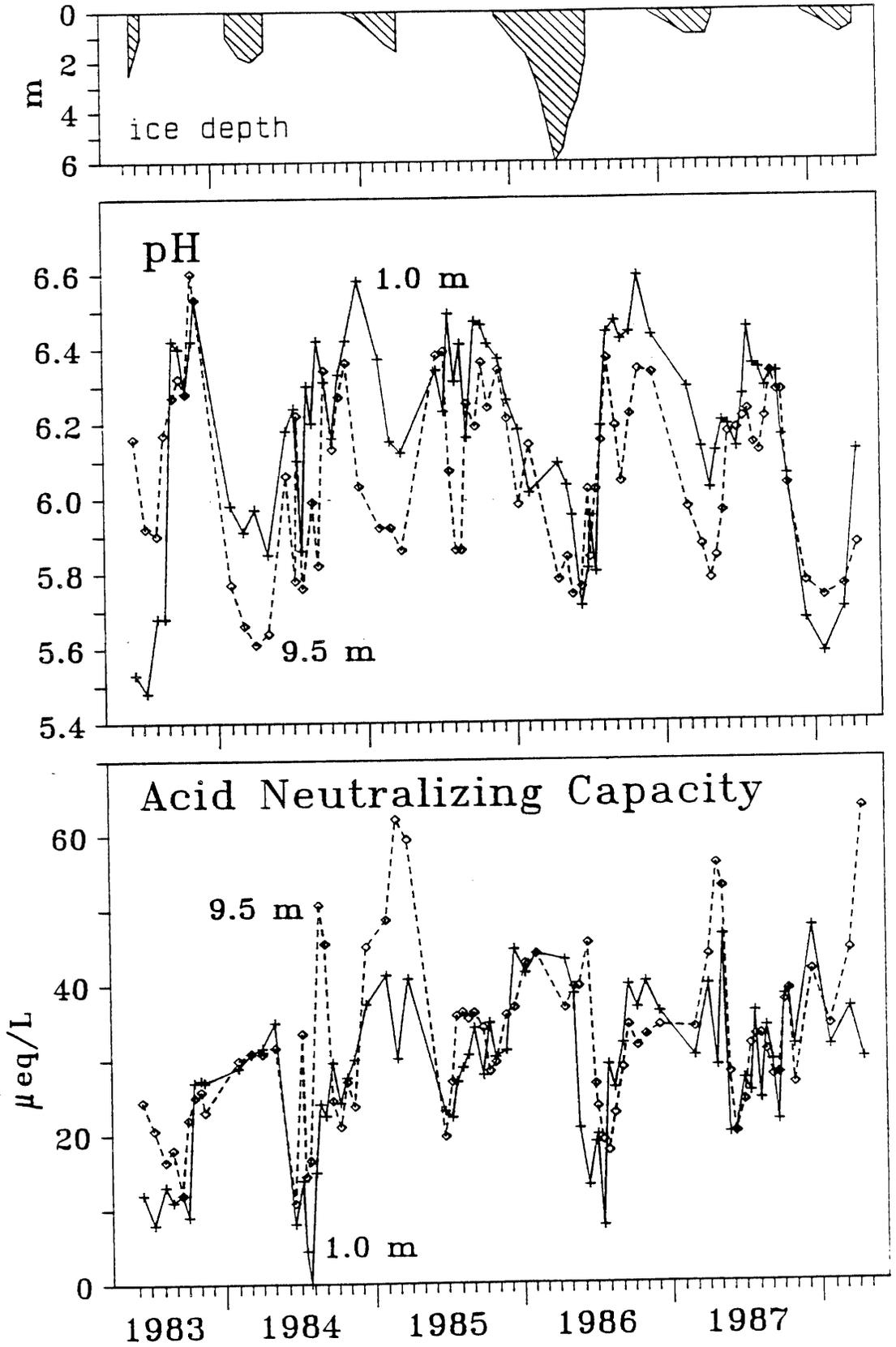


Fig. III-11. Emerald Lake, 1983-88: pH and ANC.

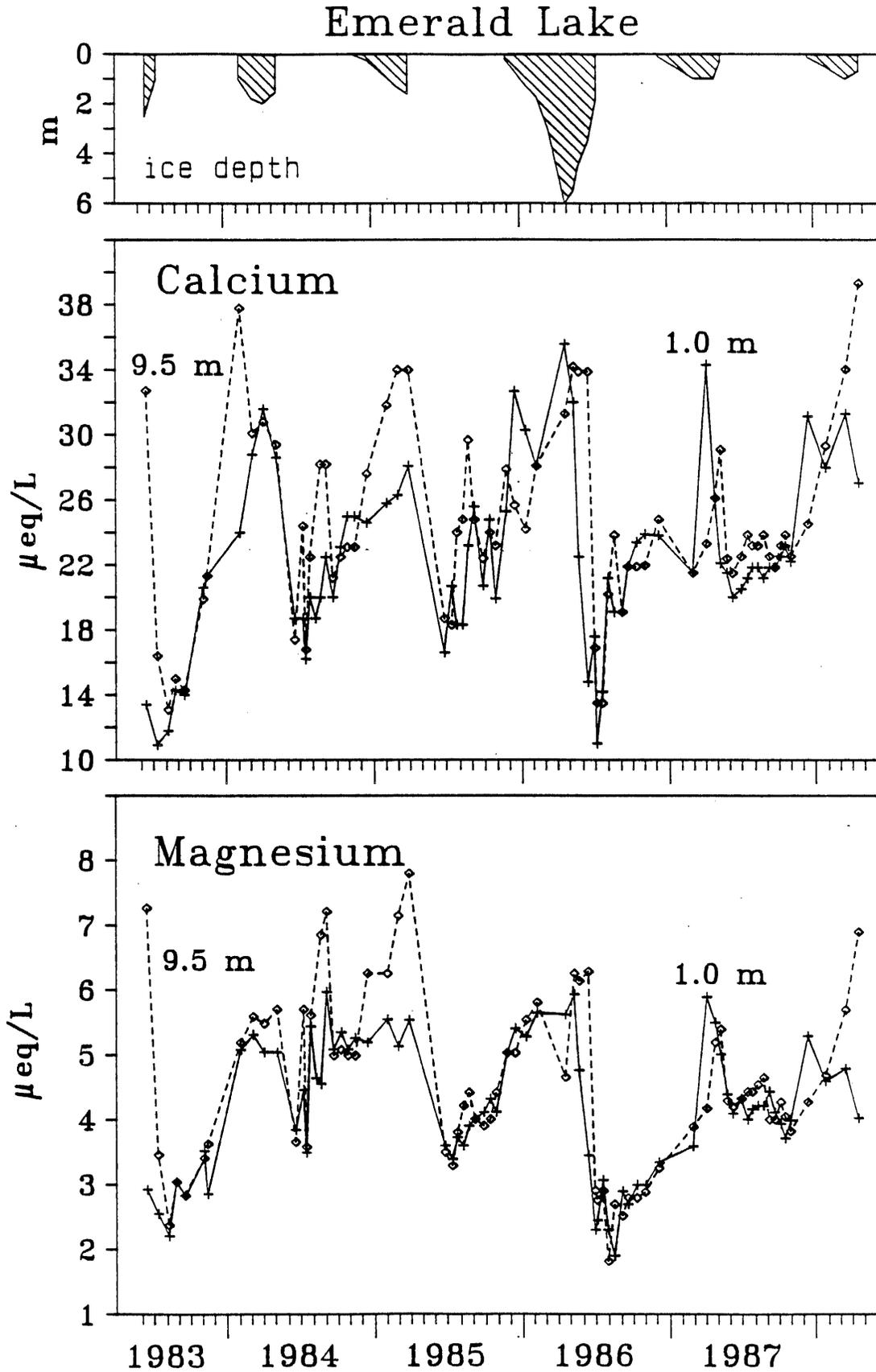


Fig. III-12. Emerald Lake, 1983-88: calcium and magnesium.

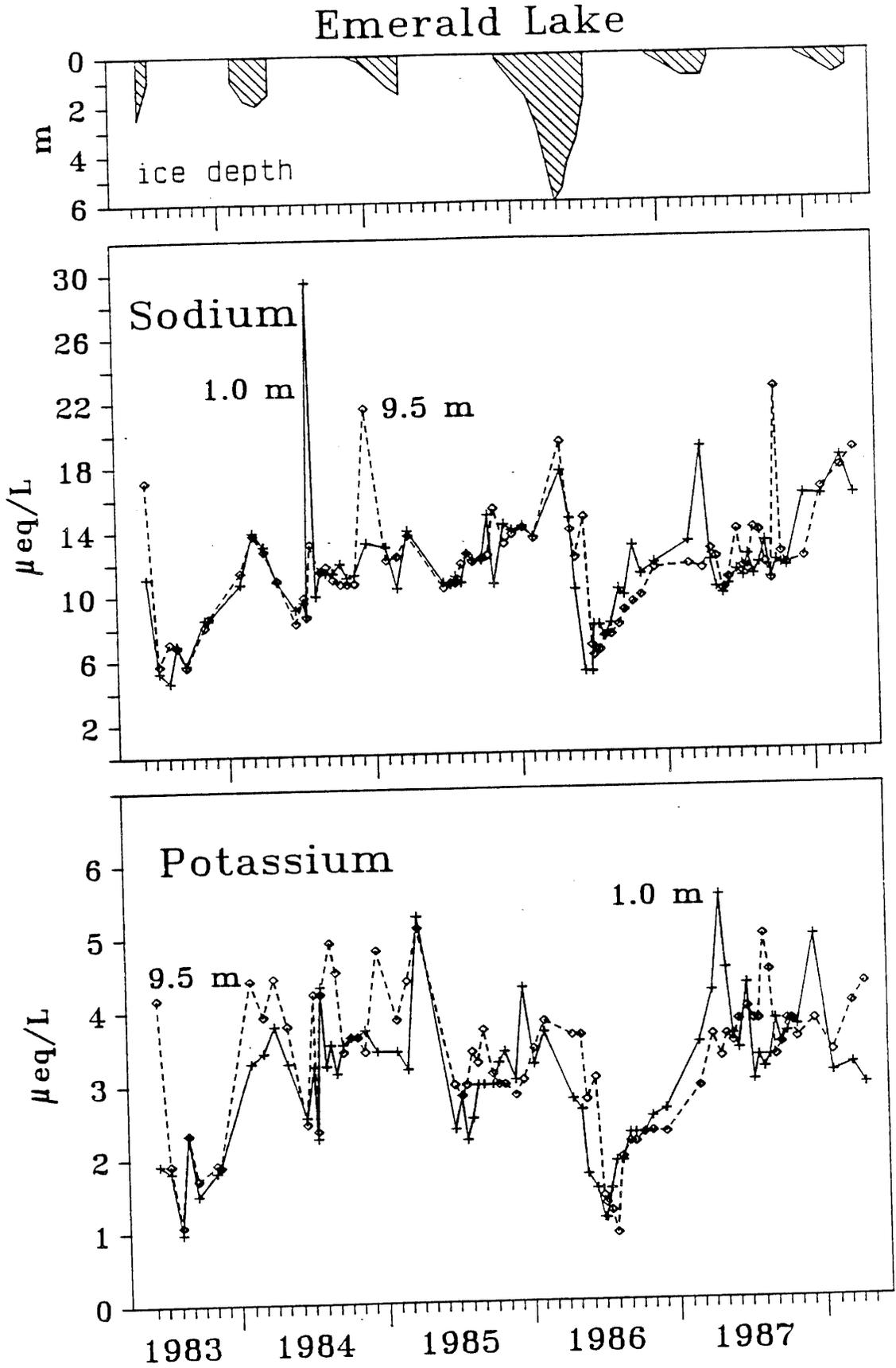


Fig. III-13. Emerald Lake, 1983-88: sodium and potassium.

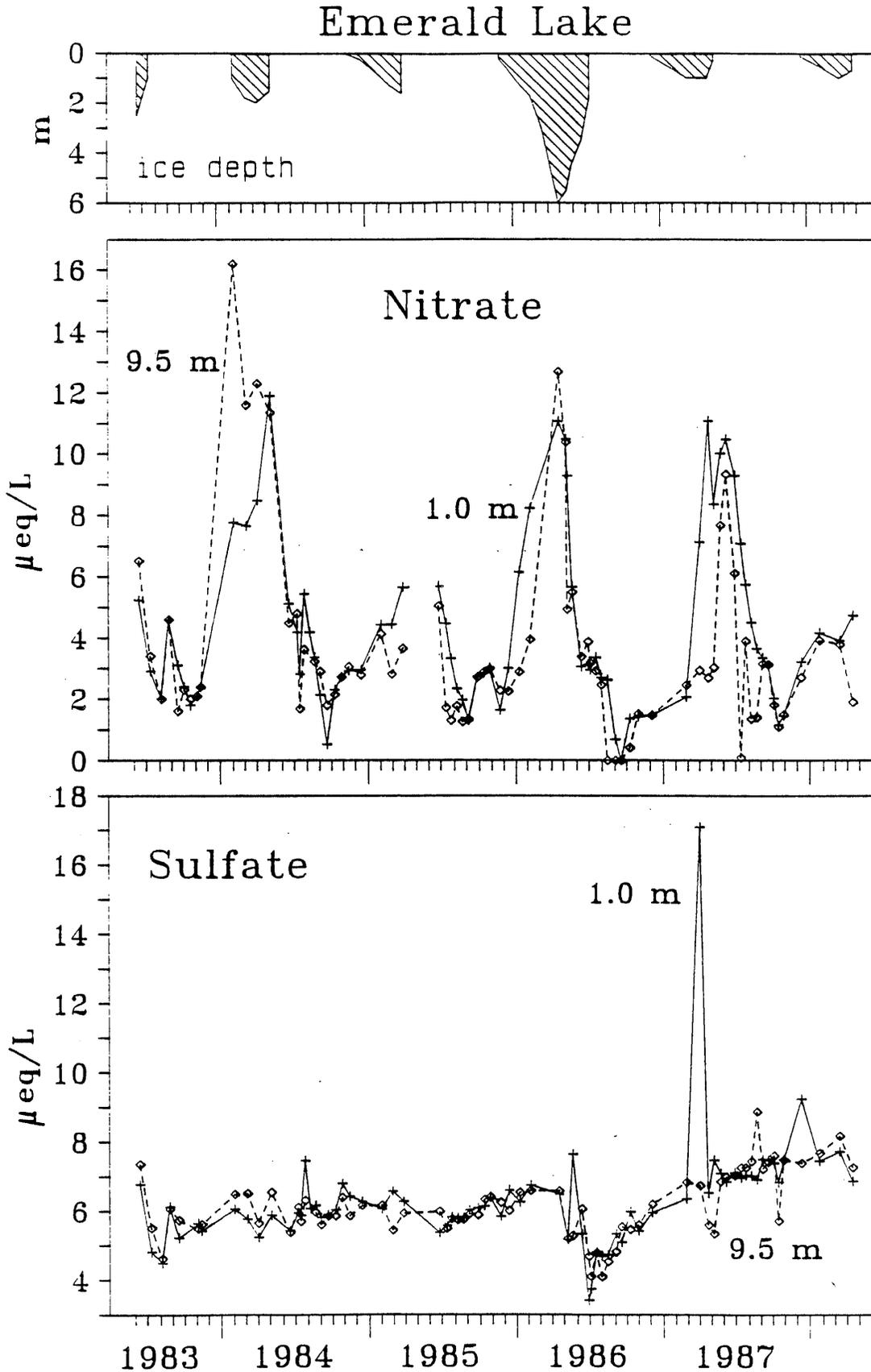


Fig. III-14. Emerald Lake, 1983-88: nitrate and sulfate.

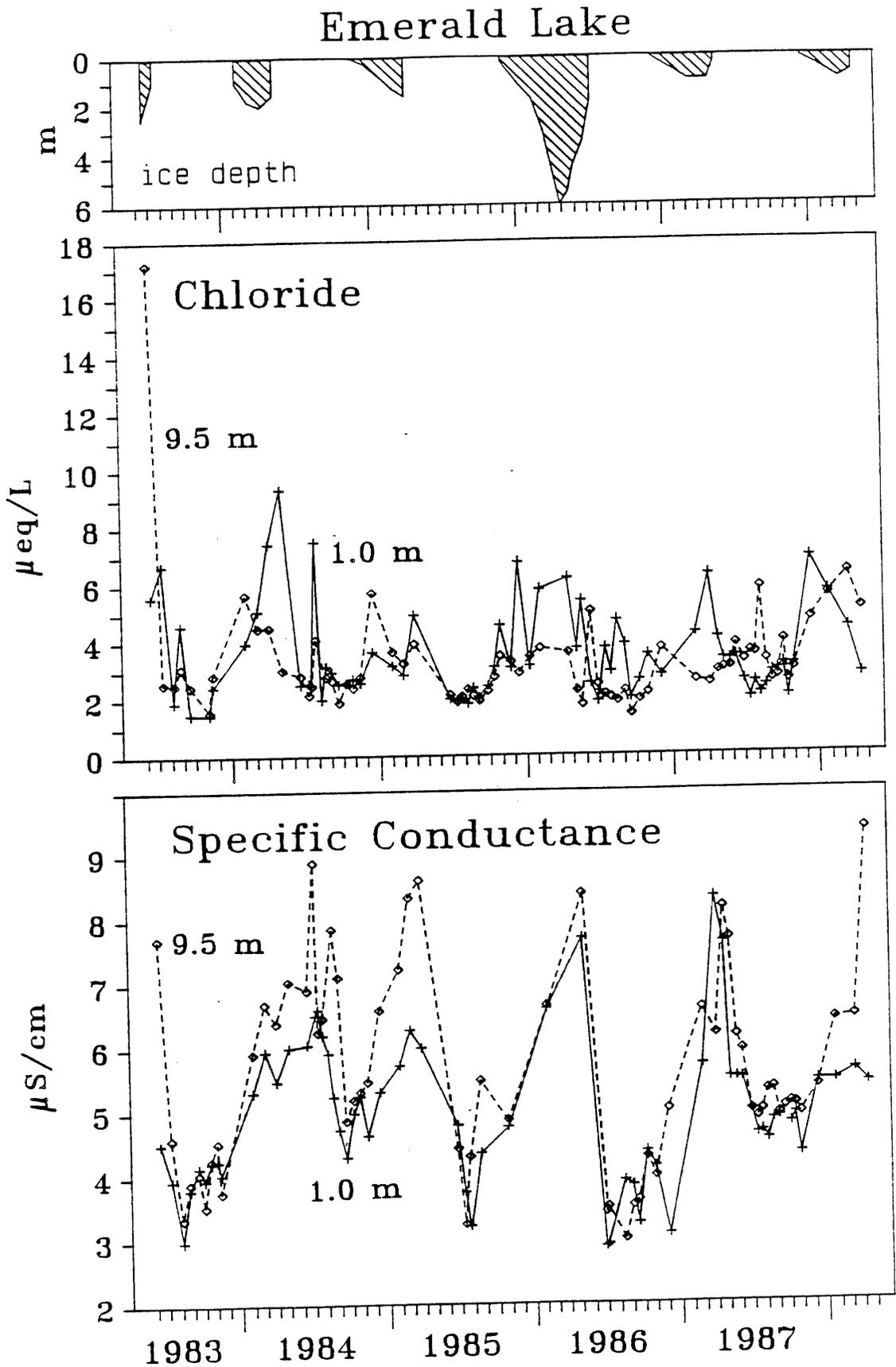


Fig. III-15. Emerald Lake, 1983-88: chloride and conductance.

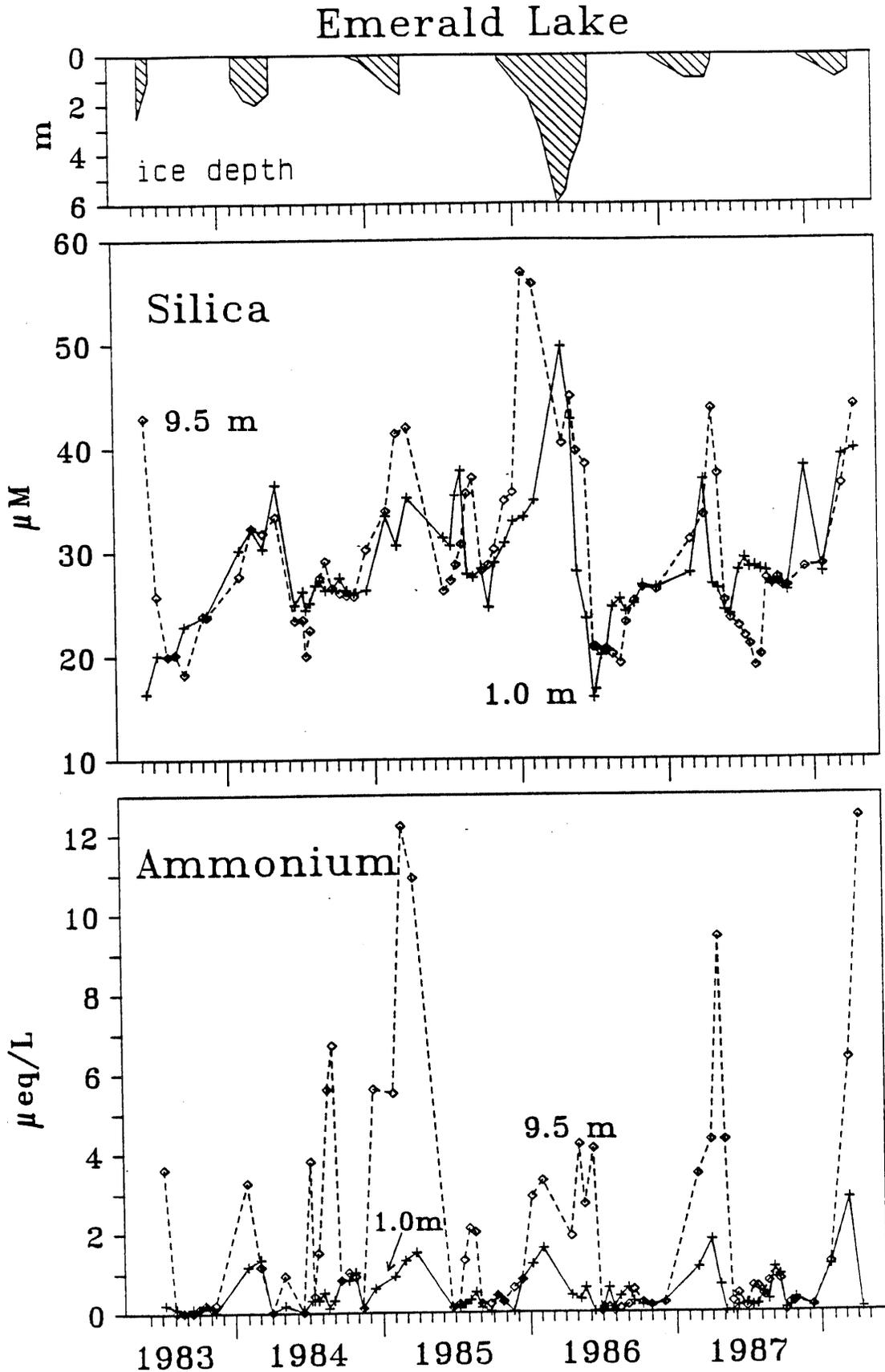


Fig. III-16. Emerald Lake, 1983-88: silica and ammonium.

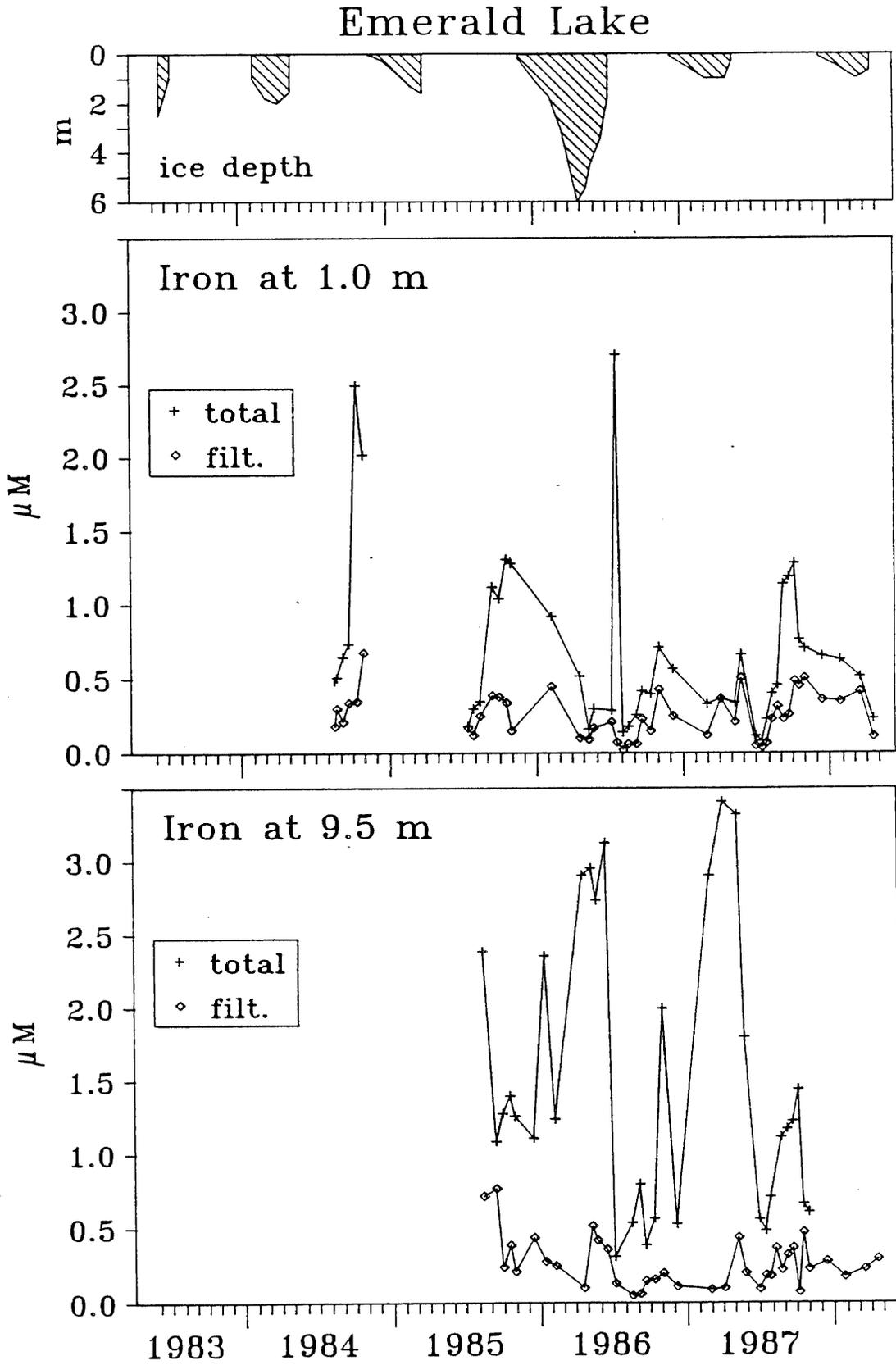


Fig. III-17. Emerald Lake, 1983-88: iron.

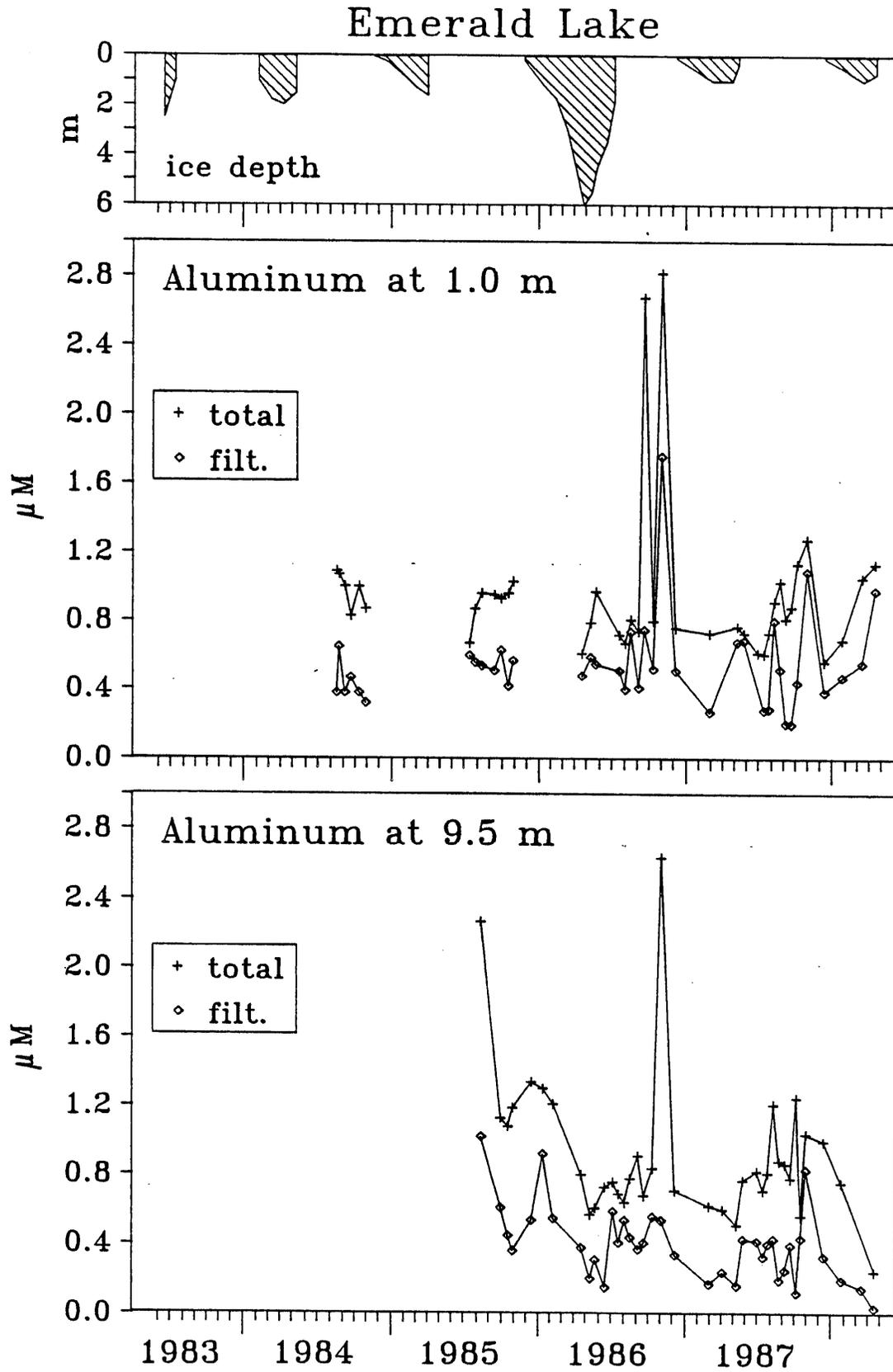


Fig. III-18. Emerald Lake, 1983-88: aluminum.

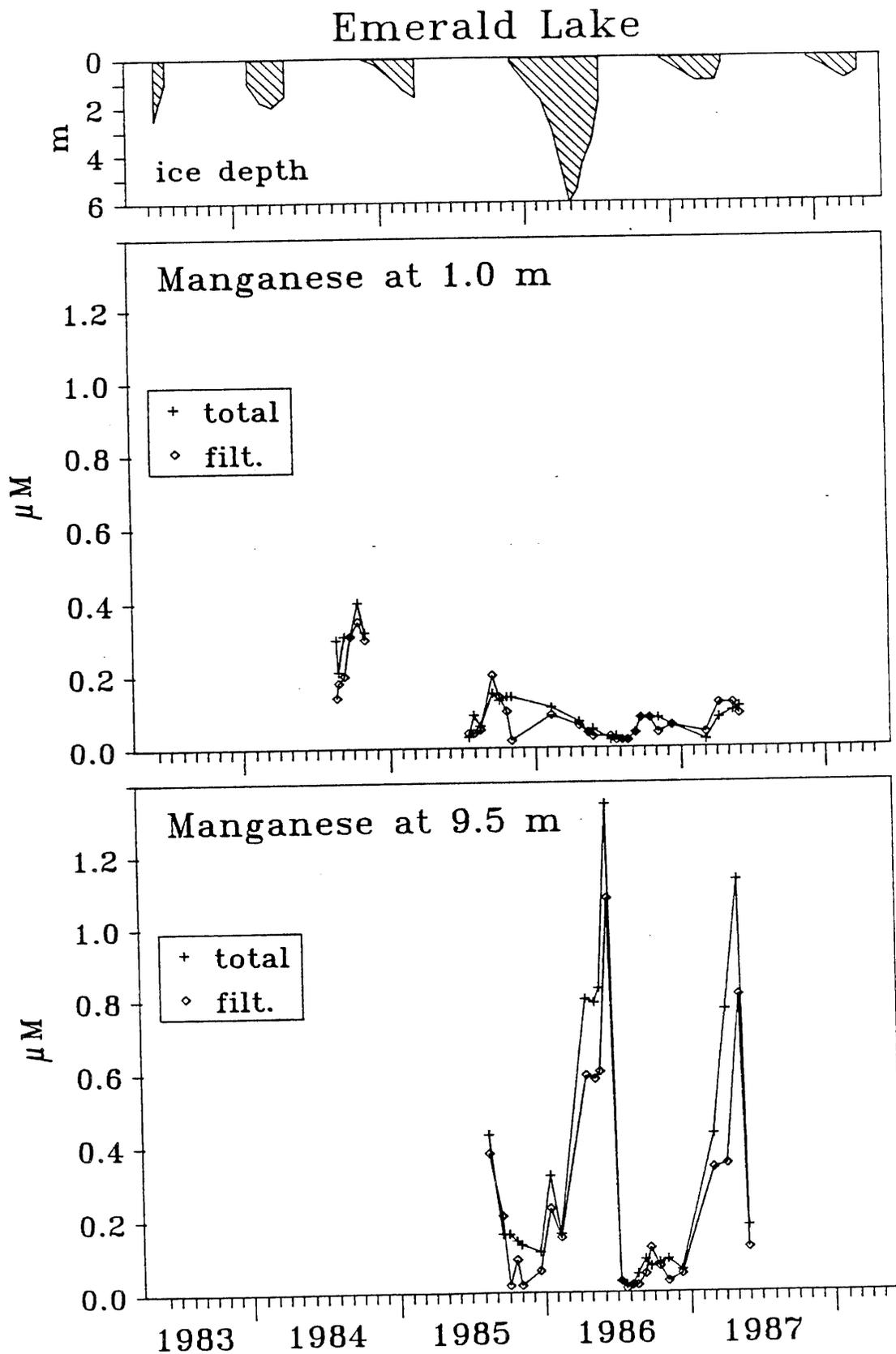


Fig. III-19. Emerald Lake, 1983-88: manganese.

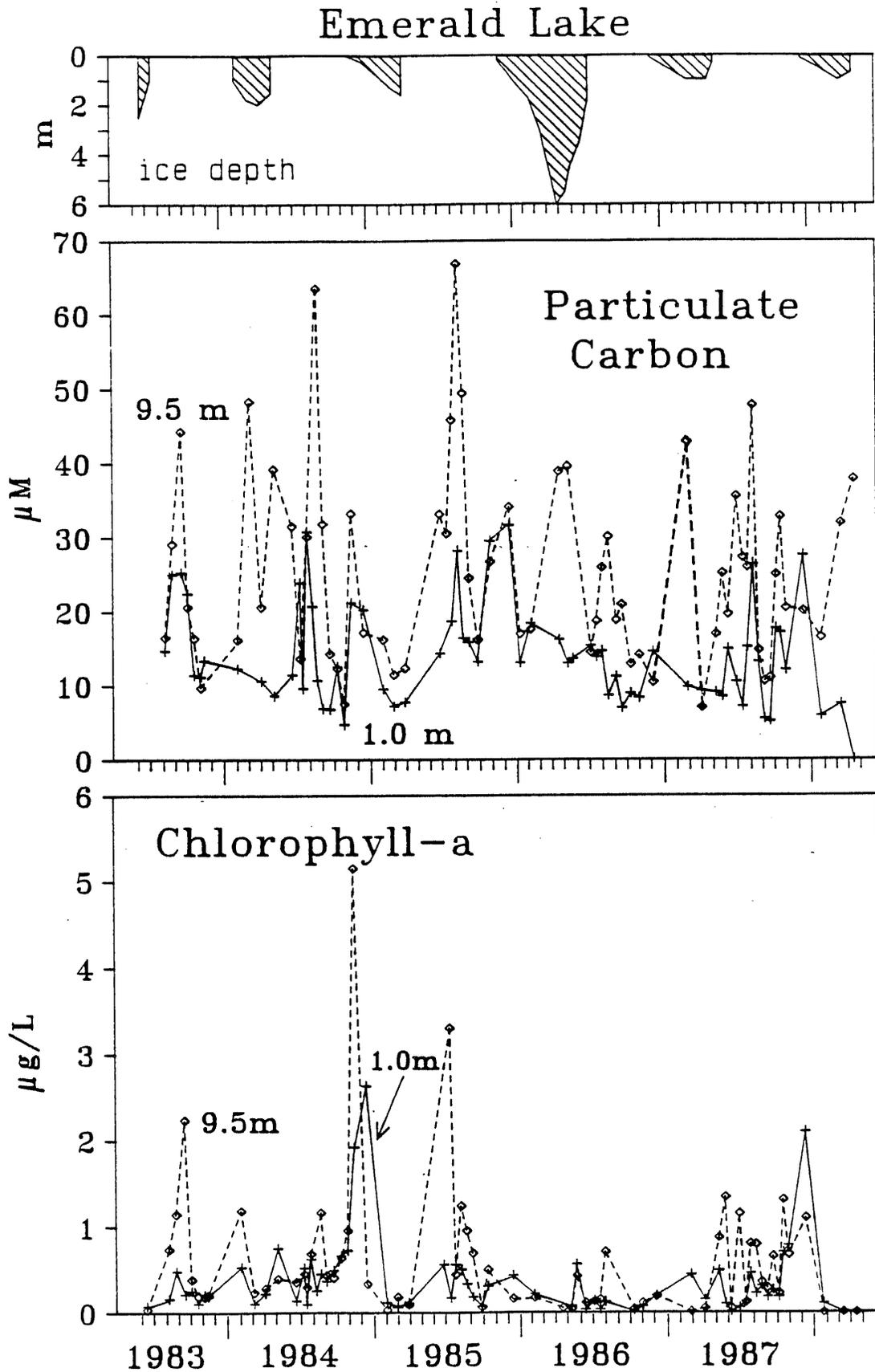


Fig. III-20. Emerald Lake, 1983-88: particulate carbon and chlorophyll-a

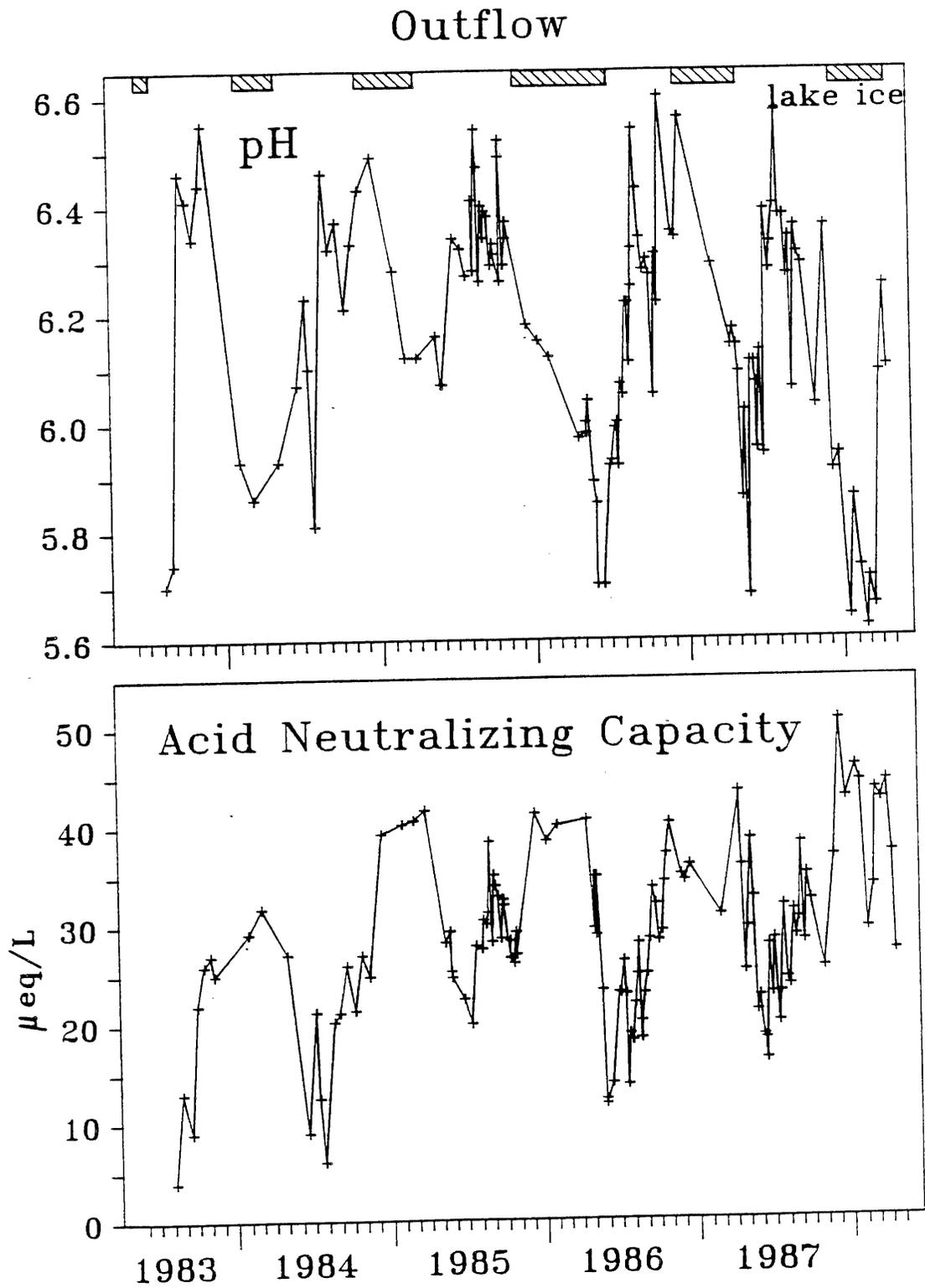


Fig. III-21. Outflow: pH and ANC.

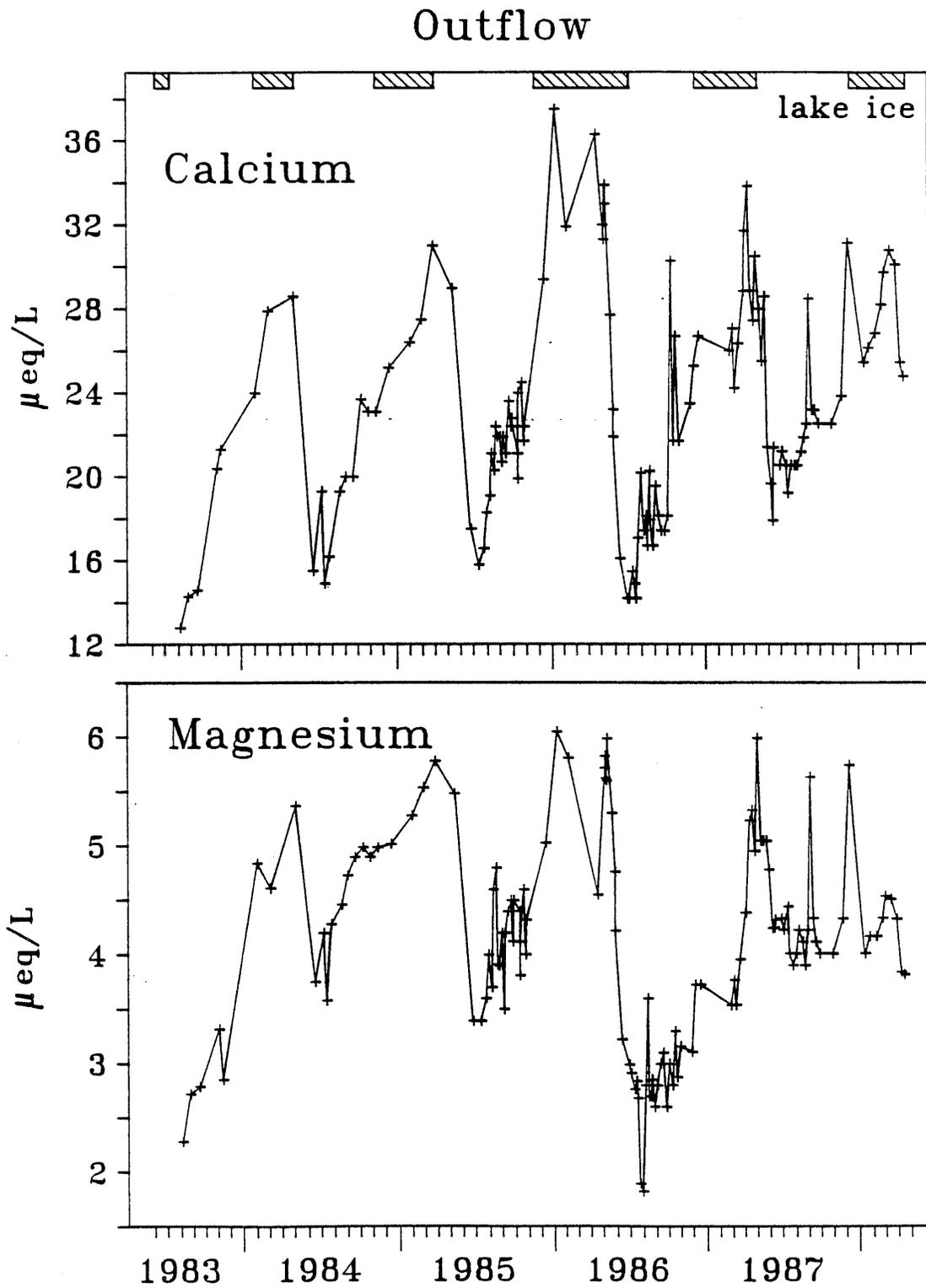


Fig. III-22. Outflow: calcium and magnesium.

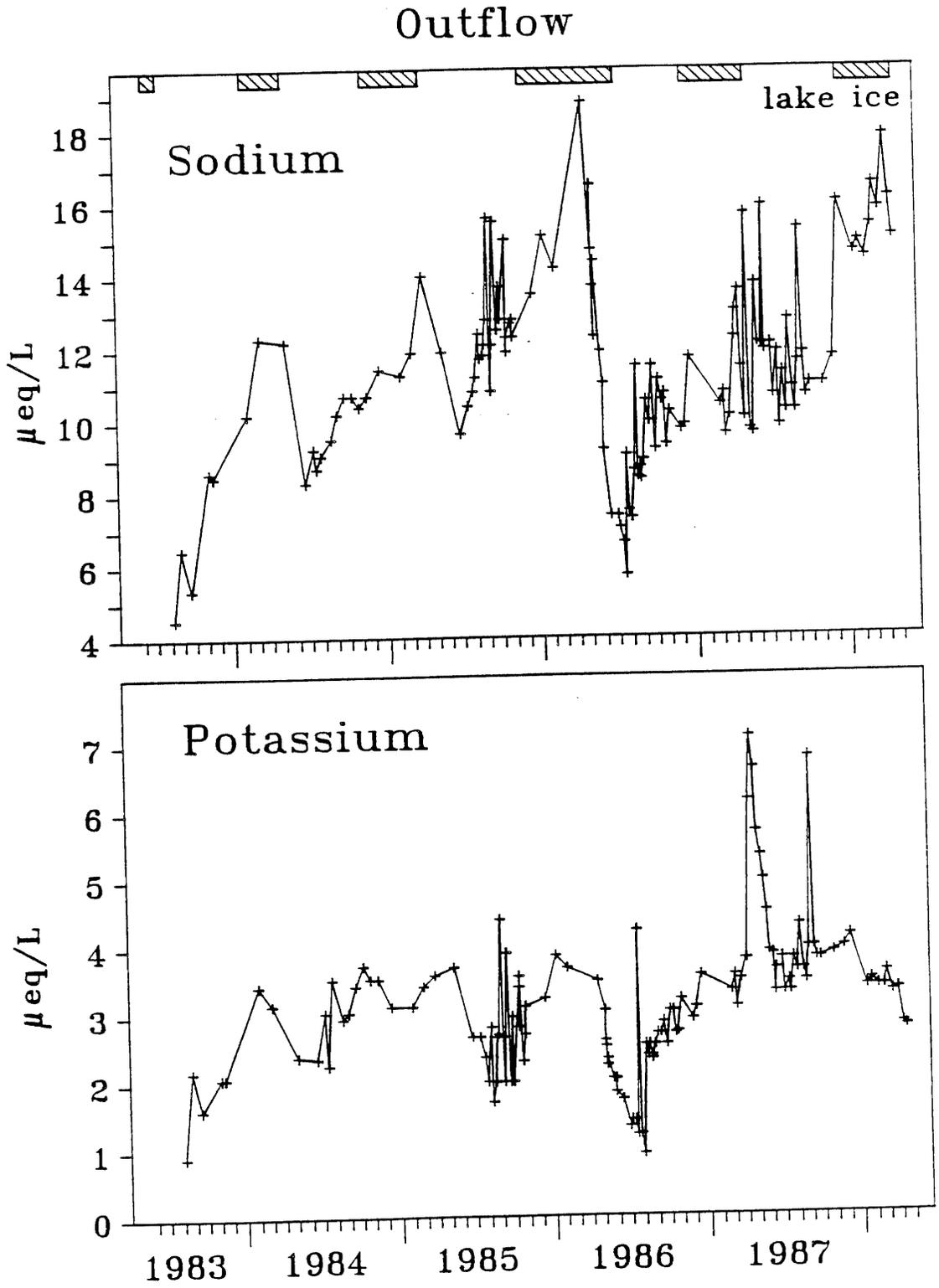


Fig. III-23. Outflow: sodium and potassium.

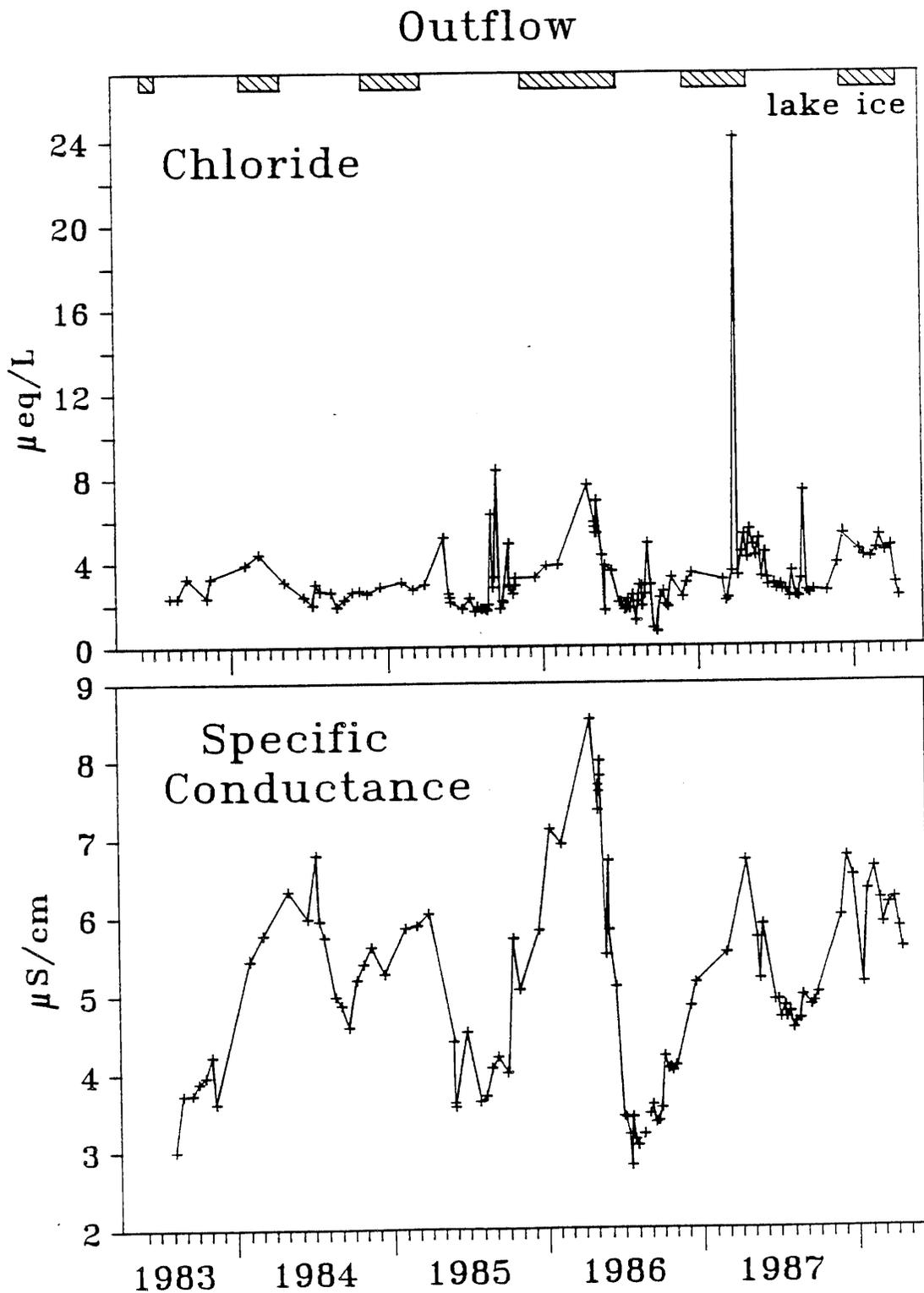


Fig. III-25. Outflow: chloride and conductance.

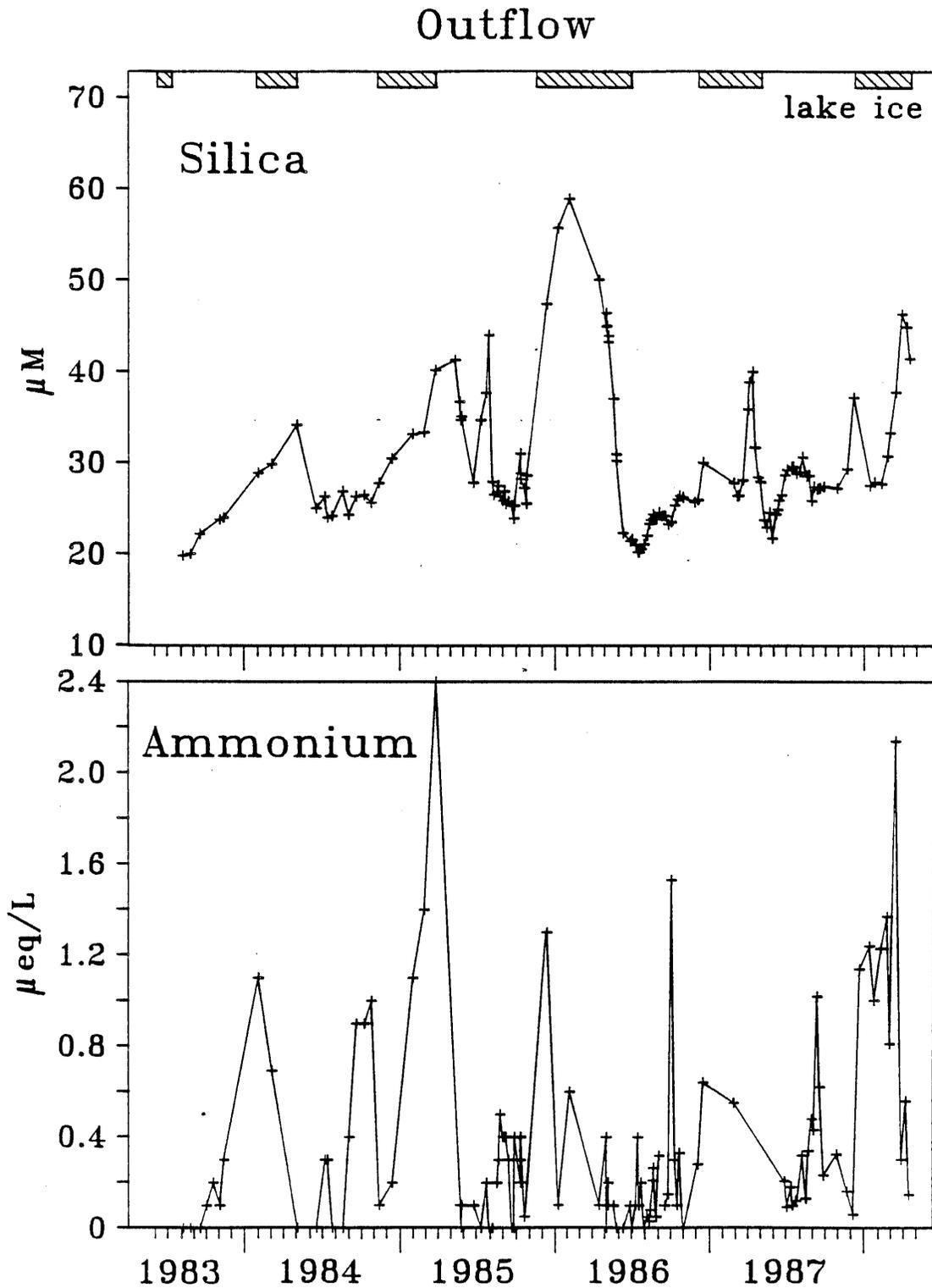


Fig. III-26. Outflow: silica and ammonium.

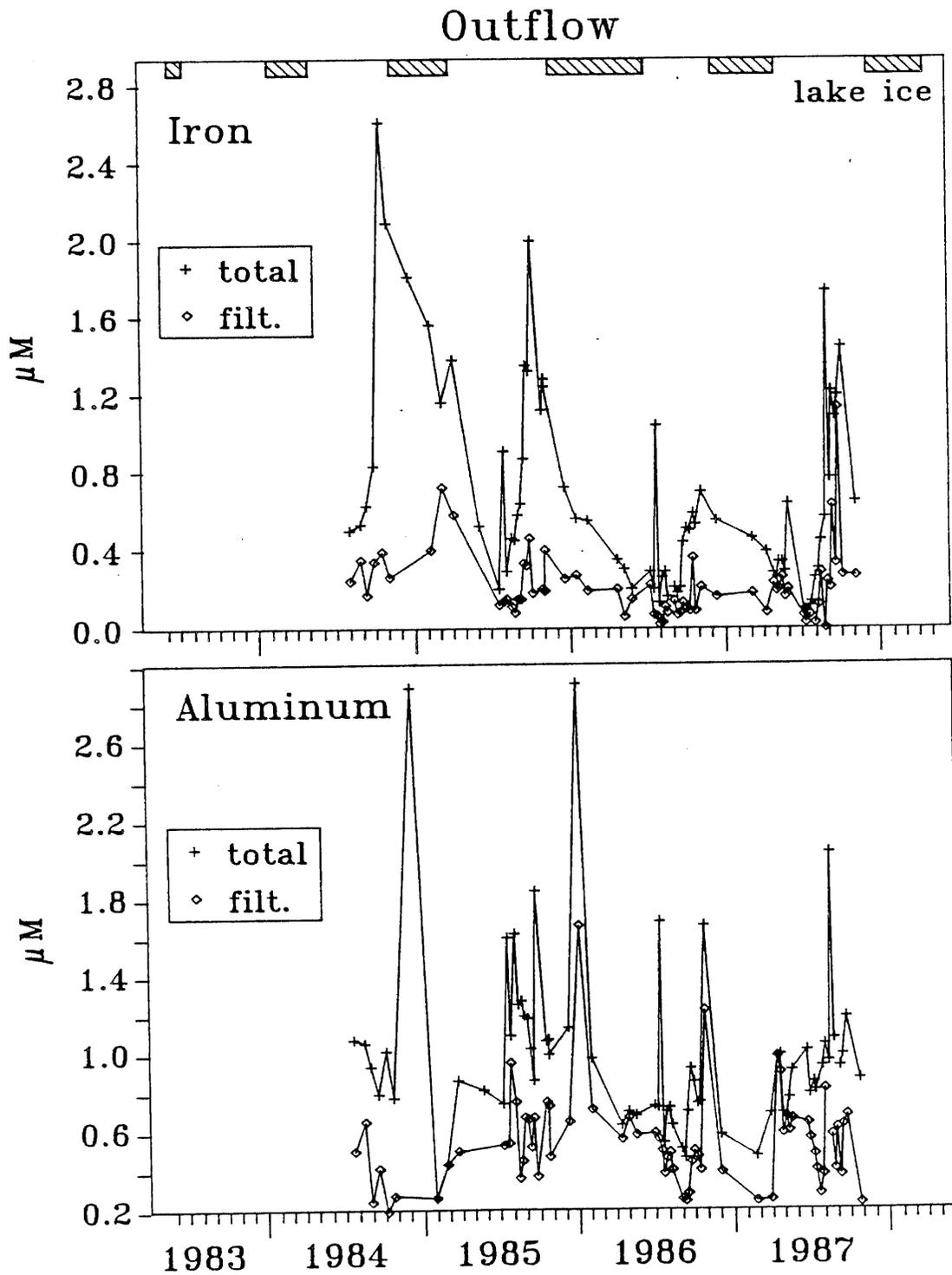


Fig. III-27. Outflow: iron and aluminum.

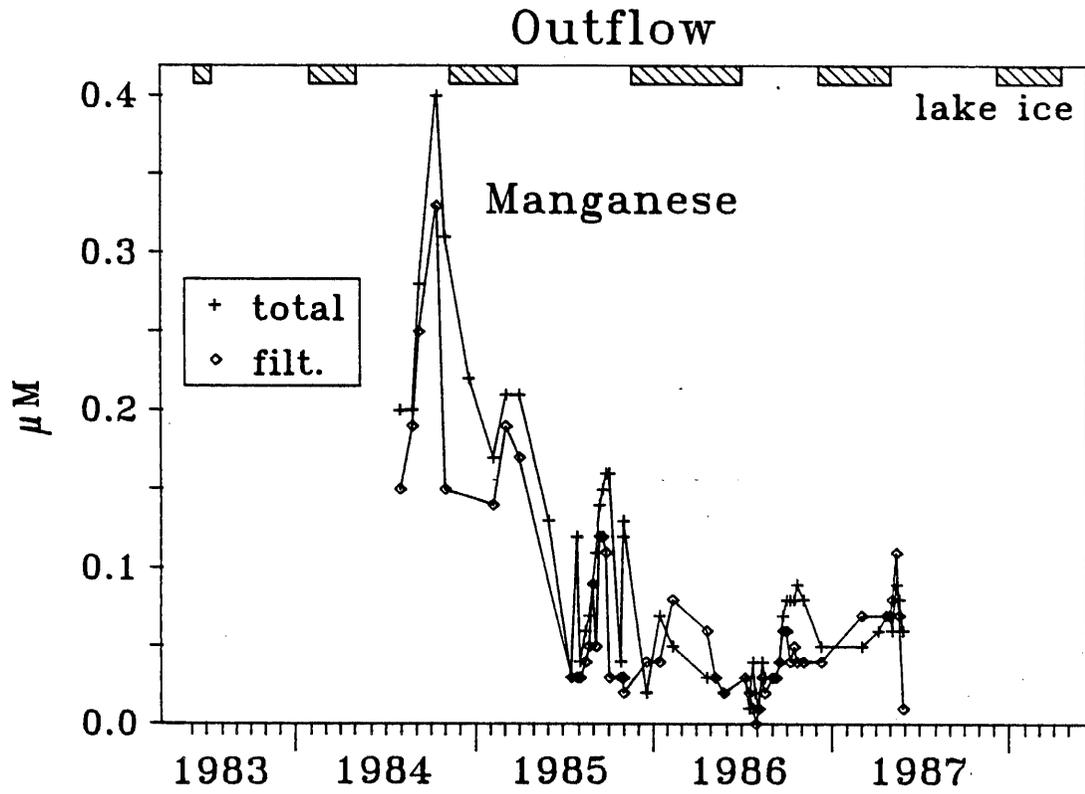


Fig. III-28. Outflow: manganese.

Water-year 1985

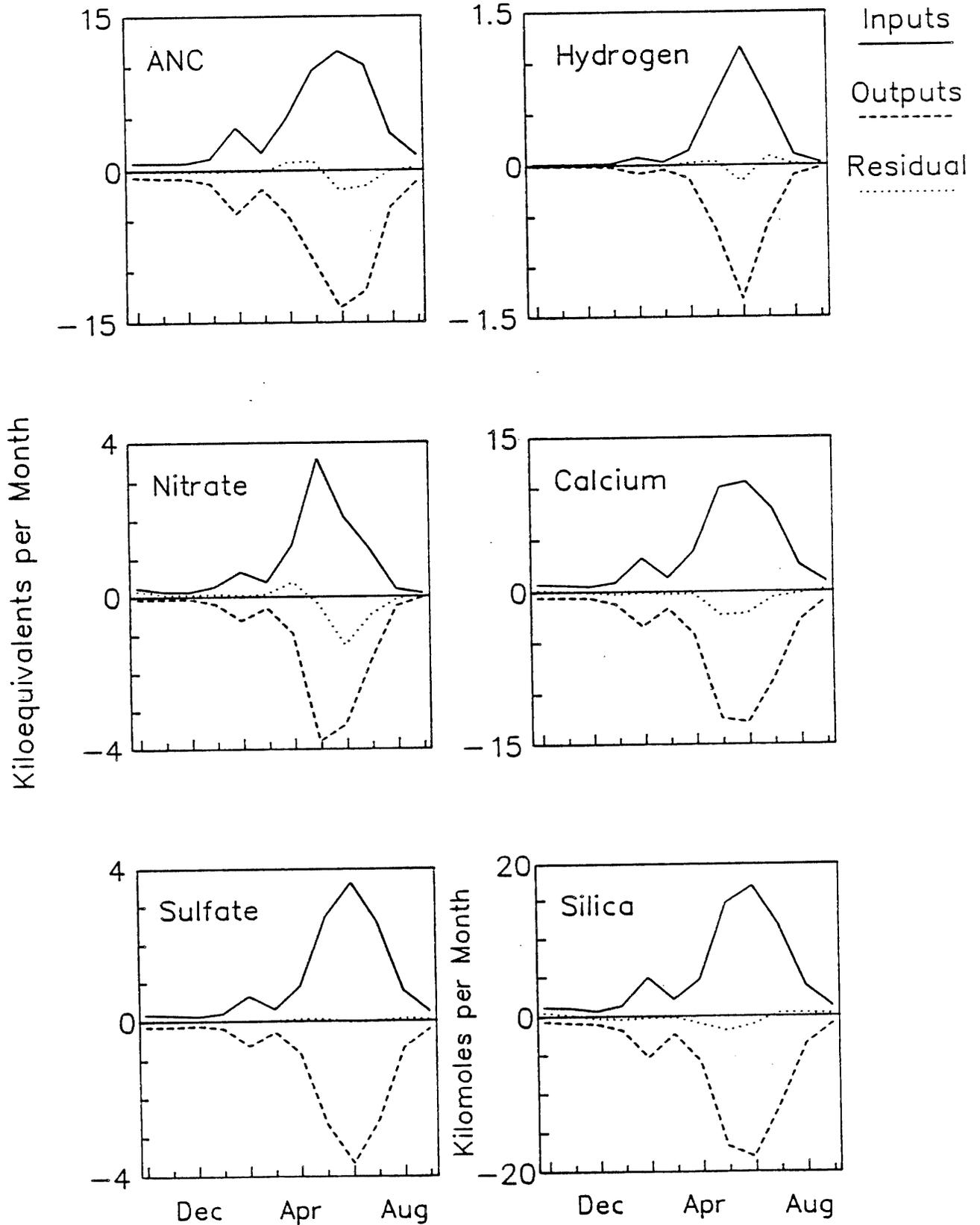


Fig. III-29. Monthly variation in mass inputs (positive), outputs (negative), and the residuals for selected solutes in Emerald Lake, water year 1986.

Water-year 1987

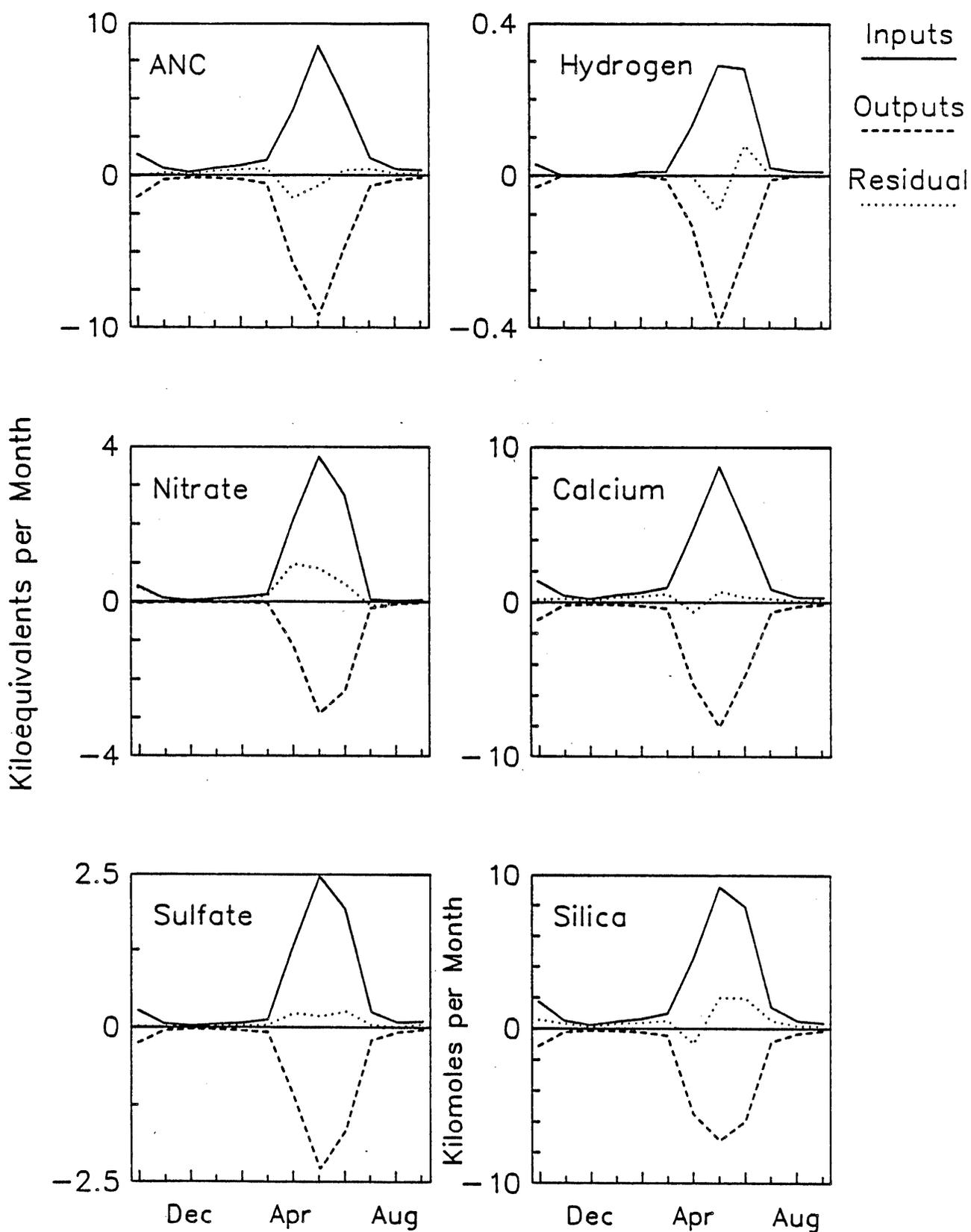


Fig. III-30. Monthly variation in mass inputs (positive), outputs (negative), and the residuals for selected solutes in Emerald Lake, water year 1987.

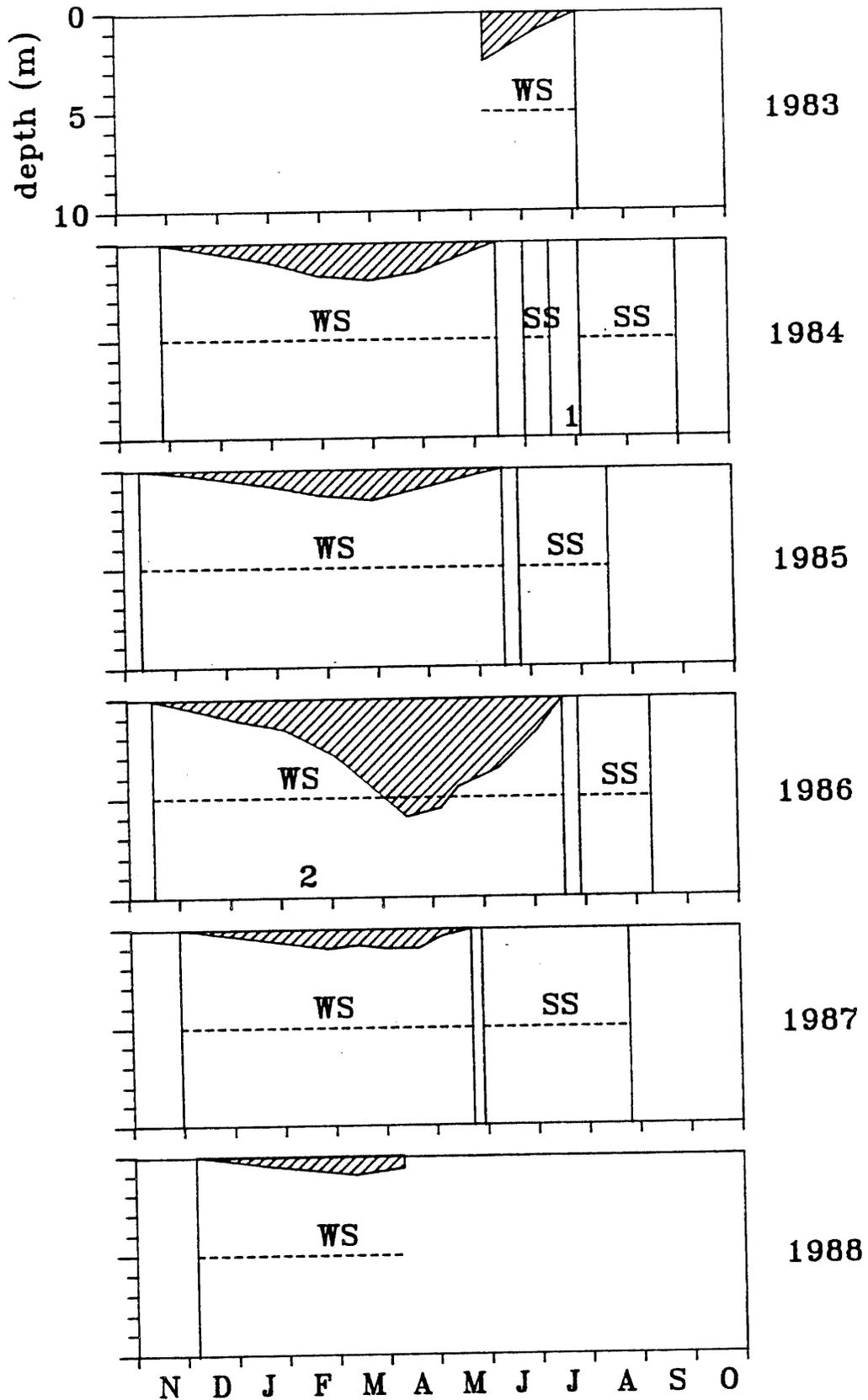


Fig. III-31. Interannual variation in the timing of major seasonal and episodic events that influenced the chemistry of the lake. Cross-hatching shows the depth of the ice; vertical lines show the beginning and end of mixing events; dashed lines indicate the presence of thermal stratification; WS = winter stratification; SS = summer stratification; 1 = timing of the summer 1984 rain storms; 2 = timing of the 1986 avalanche.

Chapter IV

Processes affecting the ionic composition of Emerald Lake

Investigations of the acidification of lakes and their watersheds by atmospheric deposition have revealed several key processes by which acidic inputs are neutralized; these processes include chemical weathering, ion exchange and redox reactions mediated by microorganisms (Schnoor and Stumm 1985, Brezonik et al. 1987). Sensitivity of lakes to acidification is largely determined by the capacity of these processes to neutralize acidity in both the lake and in its watershed (Kelly et al. 1982, Schindler et al. 1986). In this chapter, we use a mass-balance approach to quantify fluxes of major solutes that occur within the lake, and we compare these fluxes to measurements of several potentially important sources and sinks of solutes in the lake, including groundwater flow, fluxes between the sediments and overlying water, fluxes between submersed rock surfaces and overlying water, and nutrient uptake by algae.

Mass balance for major solutes

The mass balance for major solutes in the lake over two years is presented in Chapter III, which contains details on methods of calculation of mass inputs and outputs and presents the results at monthly intervals. The results show that most of the annual transport of solutes through the lake occurs during the spring snowmelt period, when stream discharges are high. Fluxes of solutes resulting from processes within the lake can best be quantified by analysis of the mass balance of the lake during periods of low inflow.

Figure IV-1 shows the discharge of the Emerald Lake outflow over the annual cycle during which we have the most complete data available for calculations of inputs and outputs of solutes. Within this annual cycle, we chose two periods of relatively low flushing rates for an examination of the mass balance of the lake: summer 1987 (25 June-25 October; 123 days) and winter 1987-88 (7 December-22 March; 107 days)(Fig. IV-1). During the summer period, the lake remained thermally stratified until the end of August, when the entire water column mixed during several unusually cool days (Fig. II-8). Although weak thermal gradients occurred throughout September and October, the decreasing temperature near the bottom indicates that the water column mixed

occasionally during this period. Inverse thermal stratification occurred beneath the ice throughout the winter modelling period (Fig. II-8). The entire water column was oxic throughout both modelling periods (Fig. II-8).

Methods

For the first day in each modelling period, we calculated the total mass of each solute in the lake, using the solute concentrations measured at four depths (Chapter II), the lake volume (calculated from the measured stage height and the depth-volume curve in Figure I-3), and the thermal profiles measured at depth intervals of 0.5-1 m (to divide the water column into four strata). Inputs and outputs of mass through the streams were calculated at daily intervals over the course of the modelling period using discharge and chemical data, as explained in Chapter III. Only Inflows #1, #2, and #4 had significant discharges during the two modelling periods. In addition, we calculated inputs of mass through precipitation on the lake surface during the summer period from data on the amount and chemistry of precipitation (Dozier et al. 1989). For each lake sampling date, the following mass-balance equation was used to predict the total mass of each solute in the lake, M_{pred} :

$$M_{pred} = M_{init} + M_{inflows} + M_{precip} - M_{outflow}$$

where M_{init} is the total mass of the solute in the lake on the previous sampling date, $M_{inflows}$ is the sum of the daily transport of mass into the lake by the inflows since the previous lake sampling date, M_{precip} is the loading of mass by wet deposition on the lake surface since the previous lake sampling date, and $M_{outflow}$ is the sum of the daily transport of mass out of the lake by the outflow since the previous lake sampling date.

This model predicts the total mass of a solute expected in the lake if there are no sources or sinks of the solute within the lake. The total mass actually observed in the lake was calculated for each lake sampling date in the same way that we calculated the initial mass. Comparison of the model predictions with the observed mass in the lake shows losses and gains of solutes within the lake.

During the winter modelling period, inputs of mass through precipitation on the lake were not accounted for because the lake was ice-covered. The volume of ice was subtracted from the total lake volume, which was assumed to be constant at $160,000 \text{ m}^3$ (lake stage could not be determined when the water

surface was frozen). The ice volume was calculated on each sampling date from an area-weighted mean of the ice depth, based on measurements at 3-7 sites across the lake. The ice layer increased to a mean depth of 1.17 m by 9 March, and thereafter decreased to 0.84 m (16 April). The ice layer occupied 20% of the total lake volume on 9 March. Most of the ice layer in Emerald Lake was composed of snow mixed with unfrozen lake water (Chapter I); solute transport by flow of lake water up into the overlying ice layer would therefore result in a decrease in the total mass of solutes that we observed in the lake, and the model predictions would be higher than the observed mass. We have not attempted to account for this process in our model because the volume of lake water stored in the ice layer is unknown. Our model also does not account for the slight melt of the ice layer between 9 and 22 March (ice depth decreased from 1.17 to 1.04 m), which would have returned some of the lake solutes to the water column and possibly also added some solutes and water from snow. For these reasons and because sampling of the lake was less frequent (4 dates) during the winter modelling period, the uncertainty of the mass-balance model is likely to be higher during the winter period than during the summer period.

Simple linear regression was used to compare model predictions with the mass observed in the lake. The regression model is appropriate because it integrates all of the sampling dates, thereby reducing the effect of possible errors in our estimates of mass in the lake at the beginning and end of the modelling period. In addition, we use the regression model to compare slopes rather than absolute differences, because the absolute differences are dependent on the initial mass in the lake at the start of the modelling period. The regression model may not be appropriate, however, if the rates of processes in the lake that cause gains and losses of solutes are not approximately constant throughout the modelling period.

To apply the linear regression model, we first subtracted the model predictions from the observed mass on each sampling date to obtain the deviation of the observed mass from that predicted by the model. A line was fit to these deviations over time using simple linear regression, and the slope of the regression line was tested for significance by analysis of variance. Slopes that were statistically significant at $P \leq 0.05$ were considered to represent mean flux rates over the modelling period.

Results and Discussion

Figures IV-2 and IV-3 are examples of the results of the mass-balance modelling for two solutes, ANC and nitrate, during the summer modelling period. For ANC, the slope of the regression of the deviations on time was not significant ($P = 0.26$), indicating that we cannot detect losses or gains of ANC in the lake using our mass-balance approach. In contrast, nitrate shows a highly significant ($P < 0.001$) negative slope, which indicates that nitrate was steadily lost from the lake throughout the summer.

Tables IV-1 and IV-2 give the results of the linear regression analyses for all solutes during the summer and winter periods. Base cations, nitrate, sulfate, and silica showed losses in the lake during the summer. None of the solutes showed detectable fluxes during the winter. Although flux of ANC could not be detected using the mass-balance approach, we can estimate ANC flux during the summer from the significant fluxes of other major ions, assuming that ionic charge balance is maintained. Losses of base cations consume an equivalent amount of ANC, while losses of nitrate and sulfate generate equivalent amounts of ANC (Schnoor and Stumm 1985). The net ANC flux is thus estimated to be 2.64 eq d^{-1} for the summer period. This flux estimate is within the range of uncertainty in our mass-balance model for ANC (Fig. IV-2).

To facilitate comparisons with other flux rates, the statistically significant slopes in Table IV-1, which are whole-lake flux rates in eq d^{-1} , can be expressed on an areal basis ($\text{eq m}^{-2} \text{ d}^{-1}$) by dividing by the lake area of $27,200 \text{ m}^2$. Flux rates in the literature are usually reported in $\text{meq m}^{-2} \text{ y}^{-1}$; these units are obtained by multiplying the slopes by 13.42 (Table IV-3). This conversion of summer flux rates to annual rates should be done only for comparison with other estimates, however, because the mass-balance modelling has shown that flux rates differ between the summer and winter in Emerald Lake.

Groundwater Seepage

Seepage of groundwater into or out of Emerald Lake is potentially important to the water budget and chemical mass balance of the lake. Even small amounts of inflowing groundwater, which may be insignificant to the water budget, could be important for chemical loading if solute concentrations in the groundwater are much higher than in surface inflows. The chemical composition

of groundwater is of particular interest with regard to lake acidification because groundwater can be a substantial source of ANC to lakes in the Sierra Nevada (Stoddard 1987).

Our approach to the investigation of groundwater at Emerald Lake was twofold: 1) we checked the most likely sites in the lake for measurable seepage; and 2) we sampled groundwater emergences (seeps) along the lake shore for chemical analysis. We did not attempt to quantify the inflow or outflow of groundwater at Emerald Lake. Spatial variation in seepage is very large even in lakes with relatively uniform basin morphometry and sediments (McBride and Pfannkuch 1975, Winter 1981). The mosaic of bedrock, talus, gravel, and mud that comprises the bottom of Emerald Lake would make this task extremely difficult. However, we were able to determine the likely importance of groundwater as a source of solutes to the lake.

Methods

To check for the presence of seepage in the lake, we used mini-piezometers and seepage meters. Our piezometers were similar to the design of Lee and Cherry (1978), and were equipped with manometers for greater sensitivity. The mini-piezometer is a 1-m section of PVC pipe (1.3-cm I.D.) with a perforated tip wrapped in 24- μ m Nylon mesh. The perforated end of the pipe was inserted manually into the sediments to a depth of 0.3-0.5 m. Flexible polyethylene tubing (0.3-cm I.D.) extended from the top of the pipe to the water surface. After stabilization, the water level in the tube was compared with the lake level using the manometer. The piezometers provide a measurement of the hydraulic head, or the potential for groundwater flow (Reeve 1965). The presence of a head does not necessarily imply that groundwater flow is occurring because impermeable layers may exist, but the absence of a head does indicate that groundwater flow will not occur.

We constructed seepage meters which, although based on the concept of Lee and Cherry (1978), were made from 20-L polycarbonate water bottles rather than from 55-gal metal drums. The base of the bottle was cut off, and the mouth of the bottle was fitted with a stopper. The stopper included a port with a valve. The meter was pushed 5 cm into the sediments by SCUBA divers, and allowed a few hours to stabilize. A polyethylene bag half-filled with a known volume of water was attached to the mouth, the port valve was opened, and the water volume of the bag was monitored. In deep water, polyethylene

tubing extended from the port to near the surface, so the bags could be monitored without SCUBA. Groundwater seepage would change the water volume inside the bag. Seepage meters are used to quantify seepage flow rates, as well as to obtain samples of inflowing groundwater for chemical analysis (Lee 1977, cf. Winter 1981, Reckhow and Chapra 1983, Shaw and Prepas 1988).

Figure IV-4 depicts the sites of piezometer and seepage meter measurements. All measurements were made in early July 1987. These sites include the two major areas of fine-textured sediments in shallow water as well as the deep sediments in the center at 9.5-m depth.

Seepage may occur through discrete springs or fissures in the rock, particularly in lakes with heterogeneous bottoms. Where groundwater is flowing into the lake, such sites should be detectable from temperature measurements taken along the bottom. In October 1987, we used a thermistor to check for temperature differences near the bottom at several sites that were considered likely to have groundwater inflows (Fig. IV-4). These sites included the two principal trout spawning areas, which were in active use at the time; brook trout are known to spawn preferentially over springs (Webster and Eriksdotter 1976).

Groundwater was sampled for chemical analysis at seeps along the lake shore. During the relatively dry summer of 1987, the only flowing seep was located at the western end of the lake (the "West Seep": Fig. IV-4). The water emerged here on a 30° slope 1-5 m above the lake surface and trickled through the gravel and sand to the lake. The flow rate was constant throughout the summer, then decreased with the onset of freezing temperatures in late October. We sampled this seep 11 times between 9 July and 25 October 1987. In addition, we occasionally sampled another seep ("Pond Seep") from the same soil area, which flowed into Pond #1 of the outflow, below the lake (the inlet marked in Fig. IX-2). This seep emerged above the elevation of the lake.

We also collected samples from shoreline seeps during snowmelt in April 1988. One seep was found along the eastern end of the lake, 10 m north of the East Joint inflow, where groundwater was diverted to the surface by a large bedrock outcropping (the "East Seep": Fig. IV-4). This site was dry the summer before. At the West Seep site that we sampled the previous summer, we excavated several meters of snow to uncover the soil surface. At both sites, we collected water flowing over the soil surface just above the shoreline. Water flowing beneath the soil surface was also sampled at the two sites. PVC

pipes (5-cm dia) were cut in half longitudinally, acid-washed and leached overnight in stream water, then driven at a slight upward angle into the steep banks to collect underground water percolating downward between 0.1-0.35 m into the soil. After allowing several days for stabilization, we sampled water dripping from the pipes.

Results and Discussion

Measurements with piezometers and seepage meters showed no detectable seepage in the lake sediments. Temperature measurements at the two main trout spawning sites also indicated that seepage into the lake was not occurring. Temperature measurements did show groundwater inflow in the very shallow water (<0.2 m) adjacent to the West Seep, where flowing groundwater was visible in the gravel at the shoreline. The flow rate at this site could not be quantified, but appeared negligible compared with the surface inflows.

Chemical analysis of groundwater collected at shoreline seeps indicates that the solute content of groundwater is roughly twice that of the lake water during the summer. Table IV-4 compares the mean chemical composition of groundwater at the West Seep with that of the lake for June-October 1987. Ionic proportions in the two waters were similar, as shown by the ionic bar diagrams in Figure IV-5. An indication of the spatial variability of groundwater is provided by data in Table IV-4, which compares the chemistry of the West Seep with that of the Pond Seep; the chemical composition of groundwater at these two sites was very similar. The groundwater of the West Seep increased slightly in ionic strength over the course of the sampling period.

Table IV-5 and Figure IV-5 compare the chemistry of groundwater collected at two seeps in April 1988 with the lake water chemistry. The surface and underground water samples at each site were treated as replicates because most variables were similar in concentration. The West Seep was slightly more dilute in April than the previous summer, particularly with respect to sulfate, nitrate, and silica. The solute content of the East Seep was considerably higher than that of the West Seep. Both seeps were higher in ionic content than the lake water. This difference is accounted for largely by ANC and calcium, however, and concentrations in the seeps were actually lower for sulfate (both seeps), chloride (West Seep), and nitrate (East Seep).

The evidence presented above indicates that groundwater is unlikely to be significant to the water budget of the lake. The approximate balance of the lake's water budget without the inclusion of groundwater provides additional evidence for the insignificance of seepage at Emerald Lake (R. Kattlemann, personal communication). In theory, however, if groundwater outflow were roughly equal to groundwater inflow the water budget would still balance; in addition, errors in the determination of other components of the water budget usually make the residual term a poor estimator of groundwater (Winter 1981).

Field observations support the hypothesis that seepage is unlikely to be important to the water budget of the lake. The lake basin is a granitic cirque, and bedrock is visible along most of the shoreline. Less than 25% of the shoreline is composed of soil, gravel, or talus that could potentially be routes of groundwater flow into the lake (Fig. IV-4), and the steep slope of most of these areas makes groundwater emergence before the lake likely. The West and East Seeps are located beneath the two longest potential flow paths for groundwater entering the lake, and snow commonly persists into the summer at the top of the chute at the West Seep. These two sites are therefore likely to be the most important groundwater sources to the lake, yet the only detectable seepage into the lake at these sites was in the very shallow water at West Seep. We have not observed any potential routes for groundwater outflow from the lake (except possibly some rock fissures), nor have we found seeps below the lake level in the area downslope from the lake.

The importance of groundwater inflow to the chemical mass balance of the lake depends not only on the volume of inflow, which at Emerald Lake appears to be very small, but also on the solute concentrations in the groundwater relative to those of other inflows. The ionic content of groundwater is higher than that of the lake and surface inflows, but only by a factor of 2. The volume of groundwater inflow would have to be a substantial proportion of the total inflow for chemical transport by groundwater to be important.

Flux between sediments and overlying water

In many lakes, sediments are an important source of solutes to the lake water (Mortimer 1941, Lerman 1979, Hesslein 1980, Herczeg 1987, Cook et al. 1987). Flux of ANC from the sediments to overlying water is considered to be important in buffering inputs of acidity from atmospheric deposition or runoff, particularly in lakes with long water residence times (Oliver and Kelso 1983, Schindler et al. 1986, Anderson and Schiff 1987). Production of ANC in lake sediments has been attributed primarily to mineral weathering (Oliver and Kelso 1983), redox reactions (Schindler et al. 1980, Kilham 1982, Kelly et al. 1982, Cook et al. 1986, and Rudd et al. 1986), and decomposition of sedimented organic matter (Amundson et al. 1988).

Approaches used by researchers to quantify sediment-water fluxes have included 1) experimental measurement of fluxes of major solutes using chambers ("benthic chambers") placed over the sediment surface (Fisher et al. 1982, Dyrssen et al. 1984, Brezonik et al. 1987, Berelson et al. 1988), 2) measurement of the chemical gradients in interstitial waters, from which theoretical flux rates can be calculated (Cook et al. 1987, Brezonik et al. 1987, Berelson et al. 1988, Amundson et al. 1988), and 3) calculation of a mass balance for solutes in the entire lake, or in the hypolimnion of the lake during periods of thermal stratification (Schindler et al. 1986, Brezonik et al. 1987, Eshleman and Hemond 1988). We here report benthic-chamber measurements of the fluxes of solutes between the lake bottom (both fine sediments and submersed rock surfaces) and the overlying water of Emerald Lake. At the end of this chapter, we compare the sediment-water flux measurements to the fluxes determined from the mass balance for the entire lake.

Methods: Benthic chamber design

Fluxes of solutes across the sediment-water interface in Emerald Lake were measured directly using benthic chambers placed over the lake bottom. The plexiglas chambers were 50 cm in diameter and 18-cm high, and were fitted with ports for sampling tubes, a polarographic oxygen electrode, and a small 12-V bilge pump which gently circulated water in the chamber (Fisher et al. 1982, Melack et al. 1987). By running the pump with the tubing disconnected just prior to the onset of each experiment, the chamber was flushed with lake water before samples were collected, thereby reducing the effect of disturbance during installation. The pump constantly circulated water at a rate of

240 mL s⁻¹ (30% of its maximum voltage) during the experiments. Flexible polyethylene tubing (0.8-mm dia) extended from the chamber to the water surface to permit collection of water samples for chemical analysis. A short tube on the top of the chamber allowed replacement of water withdrawn. This withdrawal amounted to approximately 8-19% of the total chamber volume for each experiment; because this dilution effect was not accounted for in our flux calculations, the fluxes are slight underestimates. The vertical wall of the chamber was graduated for determination of the volume of water that was enclosed for each experiment.

Using the alabaster plate technique of Santschi et al. (1983), we measured the shear velocity inside the benthic chamber at a pump speed of 240 mL s⁻¹ as well as at the sediment surface in the lake during late summer 1985 and 1987 (Melack et al. 1987, Hardenbergh, *unpublished data*). The hydrodynamics within the benthic chamber were roughly similar to those measured in situ at the lake bottom; the thickness of the benthic boundary layer inside the chamber (ca. 600 μm) was approximately half that at the lake bottom (ca. 1100 μm) during late summer. The importance of shear velocity to the control of sediment-water flux rates of solutes is not well understood, but several investigators have suggested that it is generally not a rate-limiting factor (Berelson et al. 1988).

Methods: Flux measurements over fine sediments

The benthic chamber was deployed over fine sediments at depths of 8.5-10 m in the center of the lake for three experiments during summer 1987. The chamber was carefully installed by SCUBA divers to minimize disturbance of water near the bottom. The oxygen meter, pump controller, 12-V power supply, and sampling tube were placed in a small raft securely moored above the chamber. The chamber was placed at the bottom and left with all ports open for one day prior to the experiment to allow any disturbed sediment to settle.

The initial water samples were taken from the chamber after closing the ports, starting the pump, and allowing dissolved oxygen and temperature to stabilize (which was usually within 15-30 minutes). At the time of initial sample collection, a water sample was also taken outside the benthic chamber and close to the sediment surface by divers using a plastic syringe. The chemistry of this sample was compared with that of the initial sample from

within the chamber to ensure that sediment disturbance during placement of the chamber did not strongly alter the chemistry of water inside the chamber.

The experiments were run until concentrations of dissolved oxygen inside the chamber dropped below 0.5 mg L^{-1} . The chambers were sampled 5-6 times during each experiment; intervals between sampling varied from 40-60 min. Chemical measurements included pH, ANC, major cations (calcium, magnesium, sodium, potassium), major anions (nitrate, sulfate, chloride), silica, and ammonium. Methods for filtration and chemical analysis of water samples are given in Chapter II.

Methods: Flux measurements over rock surfaces

Measurement of chemical fluxes between submersed rock surfaces and overlying water by enclosing the surfaces in chambers is difficult because they are irregular and spatially heterogeneous. Small chambers that seal against a 50-cm^2 area of rock have been used by Loeb (1981) for measurements of periphytic primary productivity in Lake Tahoe. In our case, numerous measurements with such a small chamber would be required to adequately represent the large spatial variability of the surfaces. In addition, the effects of edge disturbance during installation are higher with a small chamber.

Our measurements were made by placing the benthic chamber designed for use in soft sediments over a pile of rocks on a flat platform. In comparison with chambers over flat rock surfaces, this design increased the ratio of rock surface area to chamber water volume, thereby facilitating our detection of fluxes, and integrated more of the small-scale spatial variation. *Plexiglas* sheets, supported underneath with plywood, were placed in the lake at two sites by divers on 8 July 1987, 6-7 weeks prior to the experiments. The two sites were about 1-m apart in a boulder field at 6.5-m depth at the west-central part of the lake. Seven rocks from the immediate vicinity were collected and placed on each platform, taking care to minimize disturbance of surficial material.

After 6-7 weeks, benthic chambers were used to measure fluxes on each platform. The seal of the chamber on the platform was improved by cutting a section of Tygon tubing longitudinally and fitting it to the bottom edge of the chamber. Divers gently placed the chamber over the rocks on the platform, adding weights on top of the chamber to ensure a good seal. Initial flushing

of the chamber was considered unnecessary because disturbance during its installation appeared minimal. The methods for maintenance of water circulation, measurement of temperature and dissolved oxygen, and collection of water samples were identical to those described above for the fine sediment measurements. Sampling commenced immediately, and continued at variable intervals for approximately 24 hours to encompass the diel cycle of algal photosynthesis. An initial sample was also collected at the same depth outside the chambers to check for disturbance of water inside the chambers during installation. After the experiments, the rocks were recovered for measurement of surface area (by foil wrap) and volume (by water displacement).

The two rock platforms were designated as the northern and southern platforms. The dates of the experiments were 26-27 August 1987 for the northern platform and 2-3 September 1987 for the southern platform. The northern and southern platforms had similar total rock volumes (7.65 and 7.55 L, respectively) and rock surface areas (5000 and 5300 cm², respectively). The *Plexiglas* floors beneath the chambers (area, 1960 cm²) were also covered with algae and sediment by the time the experiments were conducted.

Calculations and statistical analyses

Simple linear regression of concentration on time was used to test for significant changes in the concentrations of solutes over the course of each experiment. The slope of the regression line was tested for significance by analysis of variance. Slopes that were statistically significant at $P \leq 0.05$ were considered to represent mean flux rates ($\mu\text{eq L}^{-1} \text{h}^{-1}$) over the course of the experiment. For the calculation of mean flux rates for all experiments, cases in which the regression slopes were not significant were treated as flux rates of zero.

The mean flux rates for all experiments were converted from volumetric ($\mu\text{eq L}^{-1} \text{h}^{-1}$) to areal values ($\text{meq m}^{-2} \text{y}^{-1}$) using the chamber volume (measured in each experiment; see above) and the area covered by the chamber (0.20 m²). To compare chamber flux measurements with the whole-lake fluxes that we determined by mass balance, chamber fluxes were converted to whole-lake fluxes (meq y^{-1}) using the areal estimates of coverage of the lake bottom by fine sediments (16,300 m²) and by rock surfaces (10,900 m²) (see Chapter I). To facilitate comparison with fluxes reported in other studies, which are usually

determined by mass-balance methods, whole-lake fluxes were converted to units of $\text{meq m}^{-2} \text{ y}^{-1}$ by dividing by the total lake area of 27,200 m^2 .

Results and Discussion

The results of linear regression analyses of solute fluxes in the benthic chambers are given in Table IV-6 (fine sediments) and in Table IV-7 (rock surfaces). All of the major solutes except sodium and chloride showed detectable flux rates in the fine-sediment experiments. Most of the fine-sediment ANC flux resulted from increases in concentrations of ammonium, calcium and potassium and decreases in concentrations of sulfate and nitrate. Silica showed a positive flux comparable to that of ANC in the fine-sediment experiments. These fine-sediment fluxes are based on only three experiments, but they agree approximately in direction and magnitude with fluxes determined from 11 additional experiments from previous years that were reported by Melack et al. (1987). In contrast to the fine sediments, the rock surfaces showed detectable fluxes only for ammonium and silica (positive) and nitrate (negative).

To compare the fine-sediment fluxes with the rock-surface fluxes, we converted the volumetric fluxes to areal fluxes (see *Methods*) because of the different chamber volumes in the two types of experiments. Table IV-8 gives the results of this conversion for the mean fluxes from fine sediments and rock surfaces. Comparison of the areal flux rates in Table IV-8 shows that the rock surfaces are much less important to whole-lake fluxes than are the fine sediments. Rock surfaces appear to be insignificant for whole-lake solute fluxes, except in the case of nitrate.

Our estimate of the rate of ANC flux from the fine sediments to the overlying water is $551 \text{ meq m}^{-2} \text{ y}^{-1}$ (on a whole-lake basis)(Table IV-8). However, ammonium contributes a substantial proportion of the ANC flux, but is unlikely to persist in the oxic water column of Emerald Lake because of oxidation and algal uptake. The flux rate of "persistent ANC" (Kelly et al. 1982, Cook et al. 1987) may therefore be considered as total ANC minus ammonium. The whole-lake flux rate of persistent ANC from the fine sediments is therefore estimated at $271 \text{ meq m}^{-2} \text{ y}^{-1}$.

Estimation of biotic effects on solute chemistry

In the synthesis of aquatic plant biomass, ionic solutes are taken up from the medium and converted to neutral components of the organism. Biotic uptake of each equivalent of nitrate, sulfate and chloride results in an equivalent increase in ANC, and uptake of each equivalent of ammonium and base cations results in an equivalent decrease in ANC (Schnoor and Stumm 1985). The net effect of uptake of ionic solutes during growth of algae and aquatic vascular plants can be acidifying or alkalizing, depending on the molecular forms of the nutrients utilized. The source of nitrogen for aquatic plant growth is particularly important because uptake of ammonium and nitrate have opposite effects on ANC (Lin et al. 1987), and because nitrogen is required in relatively large quantities by plants.

In most fresh waters, the ionic strength is much higher than in Emerald Lake, and even in waters in which aquatic plant production is very high, the uptake of solutes by plants is generally quantitatively insignificant to the major ion chemistry of the water (Wetzel 1983). Lakes of very low ionic strength, such as those in the Sierra Nevada, are most likely to show effects of biotic uptake on major ion chemistry. Such lakes are also the most sensitive to acidification. Biotic uptake must therefore be considered in studies of acid-sensitive lakes as a potential process affecting the ionic composition of the lake water.

Decomposition of biomass ultimately results in the return of solutes to the medium, causing biomass synthesis to be only a temporary sink for solutes. However, if decomposition is spatially or temporally decoupled from synthesis, then these processes will result in localized modifications of the ionic composition of the medium (Schnoor and Stumm 1985). In Emerald Lake, such decoupling may occur by transport of plankton out of the lake through the outflow, or by sedimentation of planktonic biomass out of the water column (Baker et al. 1989) followed by decomposition in the sediments.

The principal groups of aquatic autotrophs in Emerald Lake are the phytoplankton, benthic algae, and benthic mosses and quillworts (Isoetes). We have estimated the primary production of the phytoplankton in Emerald Lake in Chapter VII; the total production for the period 10 July-25 October 1987 was 6.5 g C m^{-2} . We do not know the biomass of mosses and quillworts in Emerald Lake, although personal observations suggest that it could exceed the total phytoplankton production. The mosses and quillworts are rooted in soft

substrates, and it is unknown whether they obtain nutrients primarily from the sediments or from the overlying water. The production of benthic algae in Emerald Lake, which are composed largely of diatoms (Melack et al. 1987), is also unknown.

In Table IV-9, we use our data on the carbon production of phytoplankton during the summer of 1987 and data compiled by Vallentyne (1974) on the elemental composition of algae to estimate the uptake of solutes for the synthesis of phytoplankton biomass in Emerald Lake. The estimated uptake of solutes serves as a maximum estimate of the potential effects of phytoplankton growth on the ionic composition of the lake water; decomposition of the phytoplankton biomass will counteract these effects unless it is completely decoupled from production. We have assumed that essentially all of the inorganic nitrogen taken up by phytoplankton is in the form of nitrate rather than ammonium; this is reasonable given the high concentration of nitrate relative to ammonium in Emerald Lake (Chapter II).

To further examine the hypothesis that phytoplankton uptake accounts for the observed loss of nitrate during the summer period, we have estimated the cumulative daily uptake of nitrogen by the phytoplankton, using our data on daily carbon production from Chapter VII and a C:N mass ratio for algal biomass of 9.3 (from the data of Vallentyne 1974). The cumulative uptake of nitrate is graphed together with the nitrate loss observed from mass balance in Figure IV-6. We consider the close absolute agreement between the two curves to be a fortuitous result of our choice of the C:N ratio, which directly affects our nitrate uptake estimate. C:N mass ratios in algal biomass are generally close to 6 (Reynolds 1984), although freshly sedimented material from sedimentation traps placed in Emerald Lake during summer 1987 (see below) had a C:N mass ratio of 7.0-9.4. Our use of 9.3 is thus somewhat arbitrary. However, the two curves are very similar in shape, which is not dependent on the C:N ratio, suggesting that phytoplankton growth is the cause of the nitrate loss. The divergence of the curves during September and October corresponds with the fall mixing period of the lake (Chapter II). Mixing of the water column could have increased the rate of decomposition of algal biomass at the sediment surface, and possibly resulted in slower sedimentation rates of algal biomass; both of these effects would reduce the decoupling between algal production and decomposition.

We can also estimate the effects of benthic diatom growth on the ionic composition of the lake water by assuming that the silica loss detected by mass balance during the summer modelling period was caused entirely by incorporation of soluble silica into diatom cells. From the mean loss rate of $7.72 \text{ mol Si d}^{-1}$ during the 123-d summer period (Table IV-1), the total loss of silica is estimated at 950 mol, or 26.7 kg Si. If we assume that the mass ratio of Si:C in diatom biomass is approximately 2 (Reynolds 1984), this silica uptake corresponds to 13.3 kg C production in the lake. On an areal basis, this diatom production estimate equals 0.5 g C m^{-2} , or $4.07 \text{ mg C m}^{-2} \text{ d}^{-1}$ over the 123-day modelling period. We have used this production estimate and the data on elemental composition of algal biomass to estimate the uptake of solutes by diatoms (Table IV-10). The potential effect of solute uptake by diatoms on the ionic composition of the lake water is approximately an order of magnitude less than the effect of solute uptake by phytoplankton (Table IV-9).

Comparison of potential sources and sinks of ions to observed fluxes

In this chapter, we have determined solute flux rates in Emerald Lake using a mass-balance approach, and we have examined several potentially important processes that might explain these fluxes. Groundwater does not appear to be important to the solute budget of the lake. With the possible exception of nitrate, fluxes of solutes between submersed rock surfaces and overlying water also appear to be quantitatively unimportant to the solute budget. Fluxes of solutes between fine sediments and overlying water could affect the solute budget. Nutrient uptake by phytoplankton could also be important to the solute budget. In this section, we will analyze the relative roles that these two processes might play in modifying the ionic composition of the lake water.

The solute flux rates determined by mass balance during the summer period are graphed in Figure IV-7, together with the flux rates determined from the fine-sediment benthic-chamber experiments. We chose $\text{meq m}^{-2} \text{ y}^{-1}$ as the common flux units for intercomparison of flux rates because this is conventional in the literature; the use of these units should not imply that these rates occur all year in Emerald Lake. The solute flux rates between fine sediments and overlying water (benthic-chamber fluxes) show little resemblance to the fluxes observed in the lake during the summer period. The

benthic-chamber fluxes are much higher for all solutes except nitrate, and the direction of flux is different for SBC (the sum of base cations), ammonium, and silica.

Figure IV-8 compares the summer mass-balance fluxes with the flux rates estimated to result from nutrient uptake by phytoplankton and benthic diatoms. The directions and magnitudes of solute fluxes in the two panels are similar, suggesting that the ionic fluxes observed in the lake can be explained almost entirely by phytoplankton growth, while a modest amount of diatom growth can explain the observed loss of silica in the lake but has little effect on the ionic fluxes.

The fluxes of individual base cations observed during the summer modelling period are compared to the fluxes estimated to result from phytoplankton growth in Figure IV-9. The ionic proportions of the summer mass-balance fluxes are different from those in phytoplankton biomass; the loss of sodium in the lake exceeds that of potassium on an equivalent basis, while phytoplankton biomass is expected to contain more potassium than sodium. This difference suggests that the phytoplankton in Emerald Lake may accumulate sodium in place of potassium. In experiments with algal cultures, Lund (1965) found that sodium could be substituted for potassium as a nutrient for algae. In Emerald Lake, substitution of sodium for potassium in algal cells may be energetically favorable to the organisms because concentrations of potassium are very low, while concentrations of sodium are relatively high (Chapter II). The published assays of the elemental composition of algae are for species from waters of higher ionic strength, in which all of the base cations are abundant. We are unaware of any data on the elemental composition of algae in lakes of extremely low ionic strength such as Emerald Lake. We therefore conclude that the difference in base cation fluxes in Figure IV-9 does not refute the hypothesis that algal growth explains the solute fluxes observed in Emerald Lake.

Of the potential sources and sinks of solutes in Emerald Lake that we have examined here, phytoplankton growth appears to have the greatest effect on the ionic composition of the lake water. The directions and magnitudes of solute fluxes observed in the lake during summer 1987 resemble those predicted to result from phytoplankton growth, based on our primary production measurements and on the elemental composition of algal biomass. The absence of detectable fluxes of solutes in the lake during the winter modelling period,

when the light levels in the water column were too low to support autotrophic algae (Chapter VII), also provides support for the hypothesis that algal growth explains the solute fluxes.

Decomposition of phytoplankton biomass must be spatially or temporally decoupled from its production for phytoplankton growth to explain the observed fluxes of solutes. Possible mechanisms for such decoupling include advective transport out of the lake and sedimentation from the water column. A maximum estimate of the advective loss of biomass during the summer period was calculated from data on concentrations of particulate carbon in the surface water of the lake (Fig. II-15) and from the daily measurements of outflow discharge in Dozier et al. (1989). Sedimentation losses were calculated from the carbon content of material collected in sedimentation traps, which we sampled at intervals of 12-23 days between 21 July-25 October 1987. The traps consisted of triplicate cylinders (7.5-cm diameter, 25-cm deep) mounted at a depth of 8.5 m in the central part of the lake. Particulate material from the traps was collected on glass-fiber filters and analyzed for particulate carbon by the methods given in Chapter II. For the period of 21 July-25 October, the total carbon production by phytoplankton was 161 kg C (entire lake)(Chapter VII). During the same period, 2 kg of particulate carbon was transported through the outflow, and 116 kg of particulate carbon sedimented from the water column. These data show that sedimentation was a much more important pathway of biomass loss from the water column during the summer than was outflow from the lake.

Comparison of ANC flux rates in Emerald Lake with those reported for other lakes

We compare the estimates of ANC flux in Emerald Lake that we have determined by mass balance and by benthic-chamber measurements over the fine sediments with ANC flux rates reported for other lakes in Table IV-11. Our benthic-chamber flux estimate appears high compared with values that have been reported in the literature for other lakes, and is also considerably higher than that predicted for Emerald Lake on the basis of sediment interstitial-water chemistry ($18 \text{ meq m}^{-2} \text{ y}^{-1}$ based on base cations only: Amundson et al. 1988). We are unaware of other studies of dilute waters in which benthic chambers have been used to measure sediment-water fluxes of ANC. Based on the data in Table IV-10, our mass-balance estimate of ANC flux agrees

approximately with rates for other lakes, while our benthic-chamber estimate appears to overestimate ANC flux. This observation is consistent with our interpretation of the data in this chapter: direct measurements of sediment-water fluxes of solutes in Emerald Lake do not reflect the actual fluxes of solutes in the lake, as observed using mass balance. Phytoplankton growth appears to be the most important process affecting the ionic composition of the lake water, and this process is important only during the ice-free season.

Table IV-1. Results of linear regression analyses of the deviation of solute mass in the lake from the predictions of the input-output model, for the summer 1987 modelling period. The slope of the regression line represents the change in equivalents per day (mol d^{-1} for Si). Slopes are considered statistically significant as estimates of mean flux rates if the probability level (prob.) is ≤ 0.05 (as emphasized in bold type). S.E. = standard error; SBC = sum of base cations.

	r^2	slope	S.E.	$F_{(1,8)}$	prob.
Summer 1987:					
ANC	0.15	6.11	5.07	1.45	0.26
SBC	0.47	-6.74	2.53	7.07	0.029
Ca ²⁺	0.40	-2.24	0.97	5.30	0.050
Mg ²⁺	0.84	-1.15	0.18	42.7	0.000
Na ⁺	0.60	-3.32	0.96	12.1	0.008
K ⁺	0.57	0.50	0.15	10.8	0.011
NH ₄ ⁻	0.03	-0.22	0.43	0.27	0.61
NO ₃ ⁻	0.96	-8.77	0.66	175	0.000
SO ₄ ²⁻	0.61	-0.93	0.26	12.4	0.008
Cl ⁻	0.14	0.30	0.27	1.27	0.29
Si	0.93	-7.72	0.72	115	0.000

Table IV-2. Results of linear regression analyses of the deviation of solute mass in the lake from the predictions of the input-output model, for the winter 1987-88 modelling period. The slope of the regression line represents the change in equivalents per day (mol d^{-1} for Si). Slopes are considered statistically significant as estimates of mean flux rates if the probability level (prob.) is ≤ 0.05 (none of the slopes in this table are significant). S.E. = standard error; SBC = sum of base cations.

	r^2	slope	S.E.	F _(1,2)	prob.
Winter 1987-88:					
ANC	0.58	-10.49	6.33	2.74	0.24
SBC	0.07	1.52	3.87	0.15	0.73
Ca ²⁺	0.04	0.90	3.16	0.08	0.80
Mg ²⁺	0.06	0.32	0.93	0.12	0.76
Na ⁺	0.12	1.27	2.49	0.26	0.66
K ⁺	0.40	-0.99	0.86	1.36	0.36
NH ₄ ⁺	0.57	3.13	1.91	2.68	0.24
NO ₃ ⁻	0.01	-0.08	0.77	0.01	0.93
SO ₄ ²⁻	0.27	-0.77	0.90	0.74	0.48
Cl ⁻	0.69	-1.38	0.65	4.46	0.17
Si*	0.83	-14.11	6.38	4.90	0.27

* the regression for silica is based on 3 instead of 4 dates because silica data were not available for 22 March.

Table IV-3. Conversion of the units of solute flux rates determined by mass balance from the regression slopes in eq d^{-1} to areal flux rates in $\text{meq m}^{-2} \text{y}^{-1}$. Silica is expressed on a molar basis. n.s. = slope was not statistically significant. See text for explanation.

	regression slope (eq d^{-1})	areal flux rate ($\text{meq m}^{-2} \text{y}^{-1}$)
Summer 1987:		
ANC	n.s.	--
Ca^{2+}	-2.24	-30
Mg^{2+}	-1.15	-15
Na^{-}	-3.32	-45
K^{+}	0.50	7
NH_4^{+}	n.s.	--
NO_3^{-}	-8.77	-118
SO_4^{2-}	-0.93	-12
Cl^{-}	n.s.	--
Si	-7.72	-103

Table IV-4. Comparison of the chemistry of groundwater at seeps along the lake with the chemistry of the lake water during summer 1987. Groundwater data are means (not volume-weighted) for 9 sampling dates (West Seep) or 4 sampling dates (Pond Seep). Lake data are volume-weighted means (entire lake) for 25 June-25 October 1987.

	Emerald Lake	West Seep	Pond Seep
Summer 1987:			
pH	6.3	6.5	6.3
ANC	31	59	61
Ca ²⁺	22	41	42
Mg ²⁺	4.1	6.2	6.3
Na ⁺	12	28	25
K ⁺	3.5	4.7	3.6
Cl ⁻	2.7	3.0	3.1
NO ₃ ⁻	4.0	6.5	6.0
SO ₄ ²⁻	7.2	6.9	7.9
Si	27.3	74	79
Σ cations	41.8	80	78
Σ anions	45.2	76	78

Table IV-5. Comparison of the chemistry of groundwater at seeps along the lake with the chemistry of the lake water during April 1988. Groundwater data are means (not volume-weighted) of surface and underground samples for 2 sampling dates (West Seep) or 3 sampling dates (East Seep). Lake data are volume-weighted means (entire lake) for 10 April 1988.

	Emerald Lake	West Seep	East Seep
April 1988:			
pH	6.0	6.2	6.5
ANC	36	54	97
Ca ²⁺	32	44	83
Mg ²⁺	5.1	5.1	4.6
Na ⁺	16	21	22
K ⁺	3.4	5.0	3.9
Cl ⁻	4.1	2.7	4.8
NO ₃ ⁻	4.7	9.2	0.0
SO ₄ ²⁻	7.6	4.4	6.0
Si	35	51	63
Σ cations	60	76	114
Σ anions	53	70	108

Table IV-6. Results of linear regression analyses of the changes in solute concentrations in the benthic chambers placed over fine sediments. The slope of the regression line represents the change in $\mu\text{eq L}^{-1} \text{h}^{-1}$ ($\mu\text{mol L}^{-1} \text{h}^{-1}$ for Si). Slopes are considered statistically significant as estimates of mean flux rates if the probability level (prob.) is ≤ 0.05 (as emphasized in bold type). Means are calculated with insignificant slopes treated as zero. S.E. = standard error; SBC = sum of base cations.

	r^2	slope	S.E.	$F_{(1,5)}$	prob.
Fine sediments:					
ANC: exp. 1	0.94	2.09	0.25	67.8	0.001
exp. 2	0.89	3.15	0.56	32.0	0.005
exp. 3	0.34	0.64	0.40	2.52	0.17
mean slope		1.75			
Ca ²⁺ : exp. 1	0.32	0.49	0.36	1.85	0.24
exp. 2	0.71	1.71	0.54	9.97	0.034
exp. 3	0.07	-0.109	0.185	0.35	0.58
mean slope		0.57			
Mg ²⁺ : exp. 1	0.05	-0.11	0.25	0.22	0.66
exp. 2	0.90	0.27	0.046	34.5	0.004
exp. 3	0.88	-0.029	0.005	36.8	0.002
mean slope		-0.080			
Na ⁺ : exp. 1	0.47	0.51	0.54	0.90	0.52
exp. 2	0.50	0.23	0.12	4.06	0.11
exp. 3	0.13	0.17	0.20	0.76	0.42
mean slope		0			
K ⁺ : exp. 1	0.98	0.009	0.040	0.040	0.85
exp. 2	0.83	0.054	0.012	19.7	0.011
exp. 3	0.65	0.059	0.019	9.39	0.028
mean slope		0.038			
NH ₄ ⁺ : exp. 1	0.93	0.489	0.066	54.3	0.002
exp. 2	0.96	1.76	0.18	93.1	0.001
exp. 3	0.97	0.313	0.024	168	0.000
mean slope		0.85			

(table continues on following page)

Table IV-6. Continued.

	r^2	slope	S.E.	F (1,5)	prob.	
Fine sediments:						
NO ₃ ⁻ :	exp. 1	0.98	-0.072	0.005	222	0.000
	exp. 2	0.92	-0.087	0.013	45.7	0.003
	exp. 3	0.02	-0.0007	0.025	0.0008	0.98
	mean slope		-0.053			
SO ₄ ²⁻ :	exp. 1	0.87	-0.242	0.047	26.1	0.007
	exp. 2	1.00	-0.380	0.012	1076	0.000
	exp. 3	0.97	-0.115	0.010	140	0.000
	mean slope		-0.25			
Cl ⁻ :	exp. 1	0.02	0.053	0.19	0.074	0.80
	exp. 2	0.48	0.030	0.016	3.68	0.13
	exp. 3	0.28	-0.032	0.023	1.95	0.22
	mean slope		0			
Si:	exp. 1	0.02	-0.337	1.32	0.065	0.81
	exp. 2	0.99	4.26	0.17	604	0.000
	exp. 3	0.98	1.14	0.080	201	0.000
	mean slope		1.8			

Table IV-7. Results of linear regression analyses of the changes in solute concentrations in the benthic chambers placed over rock surfaces. See Table 6 for explanation. Regressions were not performed for Mg^{2+} , Na^+ , K^+ , and Cl^- because these ions showed no changes in concentration over time. Exp. 1 = northern platform; exp. 2 = southern platform.

	r^2	slope	S.E.	F _(1,5)	prob.
Rock surfaces:					
ANC: exp. 1	0.03	-0.053	0.096	0.31	0.59
exp. 2	0.003	0.010	0.099	0.011	0.92
mean slope		0			
Ca ²⁺ : exp. 1	0.13	-0.054	0.046	1.38	0.27
exp. 2	0.01	-0.018	0.078	0.055	0.83
mean slope		0			
NH ₄ ⁺ : exp. 1	0.73	0.013	0.003	23.8	0.009
exp. 2	0.23	0.006	0.005	1.17	0.34
mean slope		0.007			
NO ₃ ⁻ : exp. 1	0.90	-0.039	0.004	80.7	0.000
exp. 2	0.60	-0.011	0.005	5.97	0.071
mean slope		-0.019			
SO ₄ ²⁻ : exp. 1	0.22	-3.02	0.002	2.58	0.14
exp. 2	0.004	-0.003	0.003	0.015	0.91
mean slope		0			
Si: exp. 1	0.14	0.028	0.023	1.52	0.25
exp. 2	0.74	0.043	0.013	11.2	0.029
mean slope		0.021			

Table IV-8. Conversion of sediment-water flux rates from volumetric ($\mu\text{eq L}^{-1} \text{h}^{-1}$ in the benthic chamber) to areal rates ($\text{meq m}^{-2} \text{y}^{-1}$; whole-lake basis). See text for explanation.

	benthic-chamber flux ($\mu\text{eq L}^{-1} \text{h}^{-1}$)		whole-lake flux ($\text{meq m}^{-2} \text{y}^{-1}$)	
	sediments	rock	sediments	rock
ANC	1.75	0	551	--
Ca ²⁺	0.57	0	179	--
Mg ²⁺	0.080	0	25	--
Na ⁺	0	0	--	--
K ⁺	0.038	0	14	--
NH ₄ ⁺	0.85	0.007	280	1.2
NO ₃ ⁻	-0.053	-0.019	-17	-3.4
SO ₄ ²⁻	-0.25	0	-82	--
Cl ⁻	0	0	--	--
Si	1.8	0.021	607	3.7

Table IV-9. Estimation of nutrient uptake by phytoplankton in Emerald Lake during the summer modelling period (25 June- 25 October 1987), based on the integral primary production estimates in Chapter VII (Table VII-1) and on the elemental composition of algae (data compiled by Vallentyne 1974). SBC = sum of base cations.

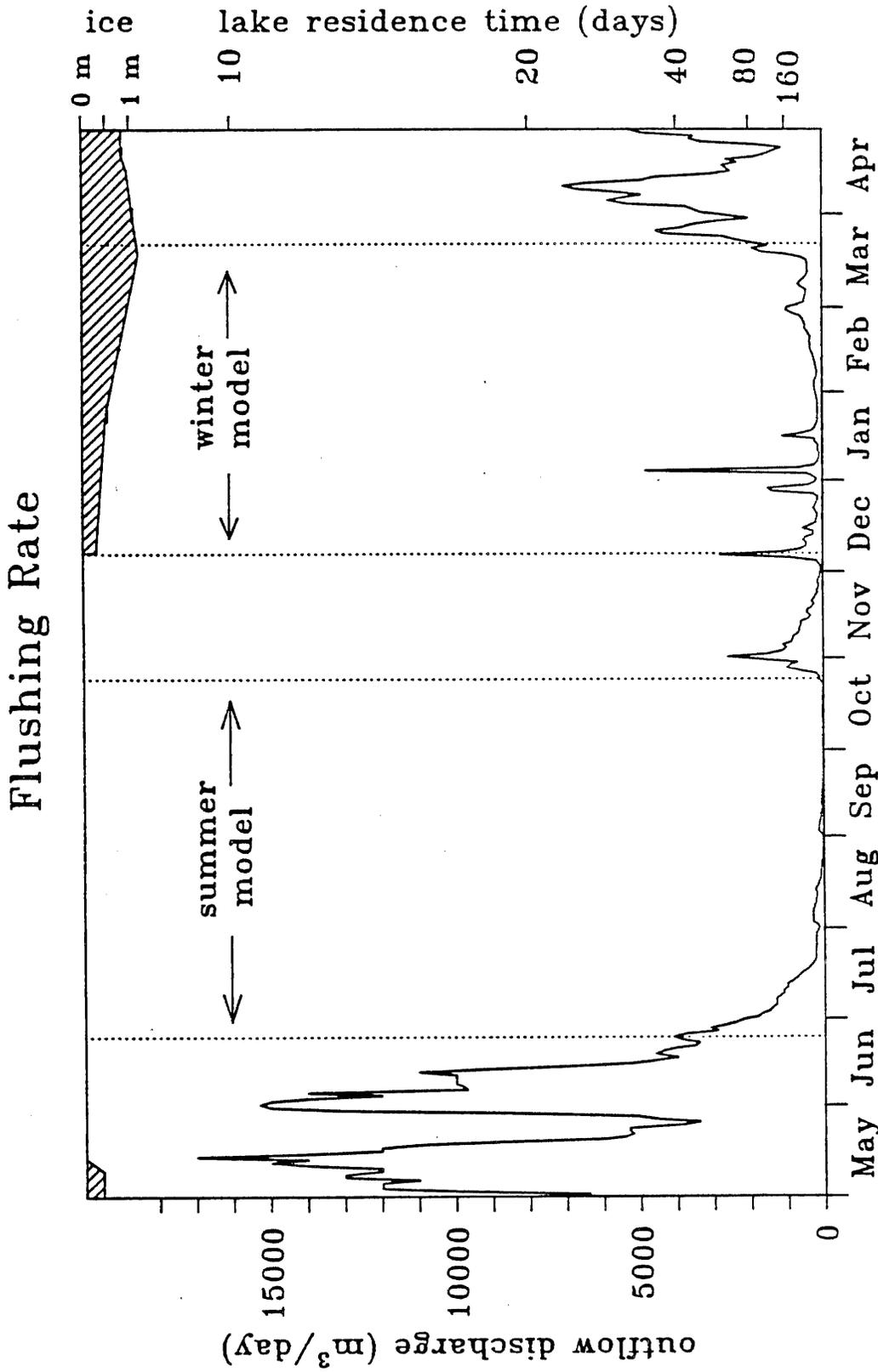
element	% wet wt. in algal biomass	mean daily uptake (mg m ⁻² d ⁻¹)	mean daily uptake (meq m ⁻² d ⁻¹)
Carbon	6.5	60	--
Nitrogen	0.7	6.5	0.46 (as NO ₃ ⁻)
Calcium	0.4	3.7	0.19
Magnesium	0.07	0.65	0.05
Sodium	0.04	0.37	0.02
Potassium	0.3	2.8	0.07
SBC	0.81	7.5	0.33
Sulfur	0.06	0.55	0.011 (SO ₄ ²⁻)
Chlorine	0.06	0.55	0.016

Table IV-10. Estimation of nutrient uptake by benthic diatoms in Emerald Lake during the summer modelling period (25 June-25 October 1987), based on the silica loss observed using mass balance for the lake. Carbon uptake was estimated from silica loss by assuming a Si:C mass ratio of 2; uptake of other elements was estimated from the elemental composition of algae (data compiled by Vallentyne 1974). SBC = sum of base cations.

element	% wet wt. in algal biomass	mean daily uptake ($\text{mg m}^{-2} \text{d}^{-1}$)	mean daily uptake ($\text{meq m}^{-2} \text{d}^{-1}$)
Silicon	--	8.0	--
Carbon	6.5	4.0	--
Nitrogen	0.7	0.43	0.03 (as NO_3^-)
Calcium	0.4	0.25	0.01
Magnesium	0.07	0.04	0.004
Sodium	0.04	0.025	0.001
Potassium	0.3	0.18	0.005
SBC	0.81	0.50	0.02
Sulfur	0.06	0.04	0.002 (SO_4^{2-})
Chlorine	0.06	0.04	0.001

Table IV-11. Comparison of flux rates of ANC estimated in this study with rates reported in the literature. Three independent methods have been used to estimate flux rates of ANC: mass balance for the entire lake, calculation of theoretical flux rates based on chemical gradients measured in sediment pore (interstitial) waters, and direct measurement of sediment-water fluxes using benthic chambers. ELA = Experimental Lakes Area (Ontario, Canada).

Study Site	Method	ANC Flux ($\text{meq m}^{-2} \text{ y}^{-1}$)	Reference
Emerald Lake	mass bal.	≈47	this study
	chamber	271 (whole lake; persistent ANC)	this study
	pore water	≈18 (fine sediments)	Amundson et al. 1988
ELA Lake 239 (unacidified)	mass bal.	74	Schindler et al. 1986
	pore water	220	Cook et al. 1986
ELA Lake 223 (acidified)	mass bal.	402	Schindler et al. 1986
	pore water	35	Schiff and Anderson 1986
Vandercook L. Wisconsin	mass bal.	75	Lin et al. 1987
Bickford Res. Mass.	mass bal.	78	Eshleman and Hemond 1988
Langtjern Norway	mass bal.	118	Wright 1983
Dart's Lake New York	mass bal.	48	Schafran and Driscoll 1987
Little Rock L. Wisconsin	pore water	50	Cook et al. 1987
4 Wisc. lakes	pore water	-30 to 200	Schiff and Anderson 1986



1987-88

Fig. IV-1. The time periods of the summer and winter mass-balance models in relation to the flushing of the lake by inflowing stream water. The modelling periods were selected to cover periods of low flushing (long residence time). Residence time was calculated by dividing the lake volume (m^3) by the outflow discharge ($m^3 d^{-1}$) for each day. Outflow discharge data are from Dozier (*l.* 1989).

Acid Neutralizing Capacity

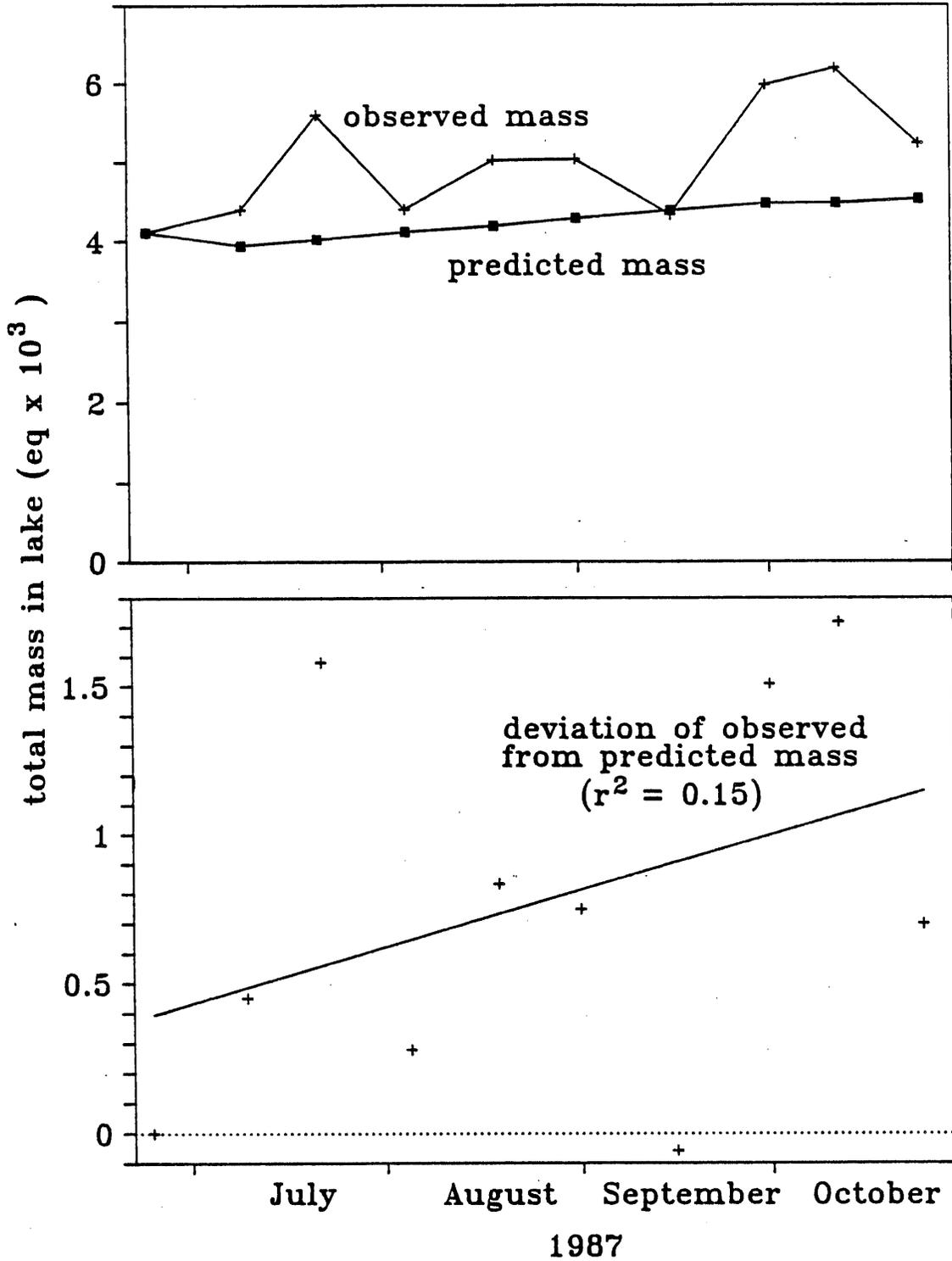


Fig. IV-2. Comparison of the observed mass of ANC in the lake with that predicted by the mass-balance model, for the summer modelling period. See text for explanation.

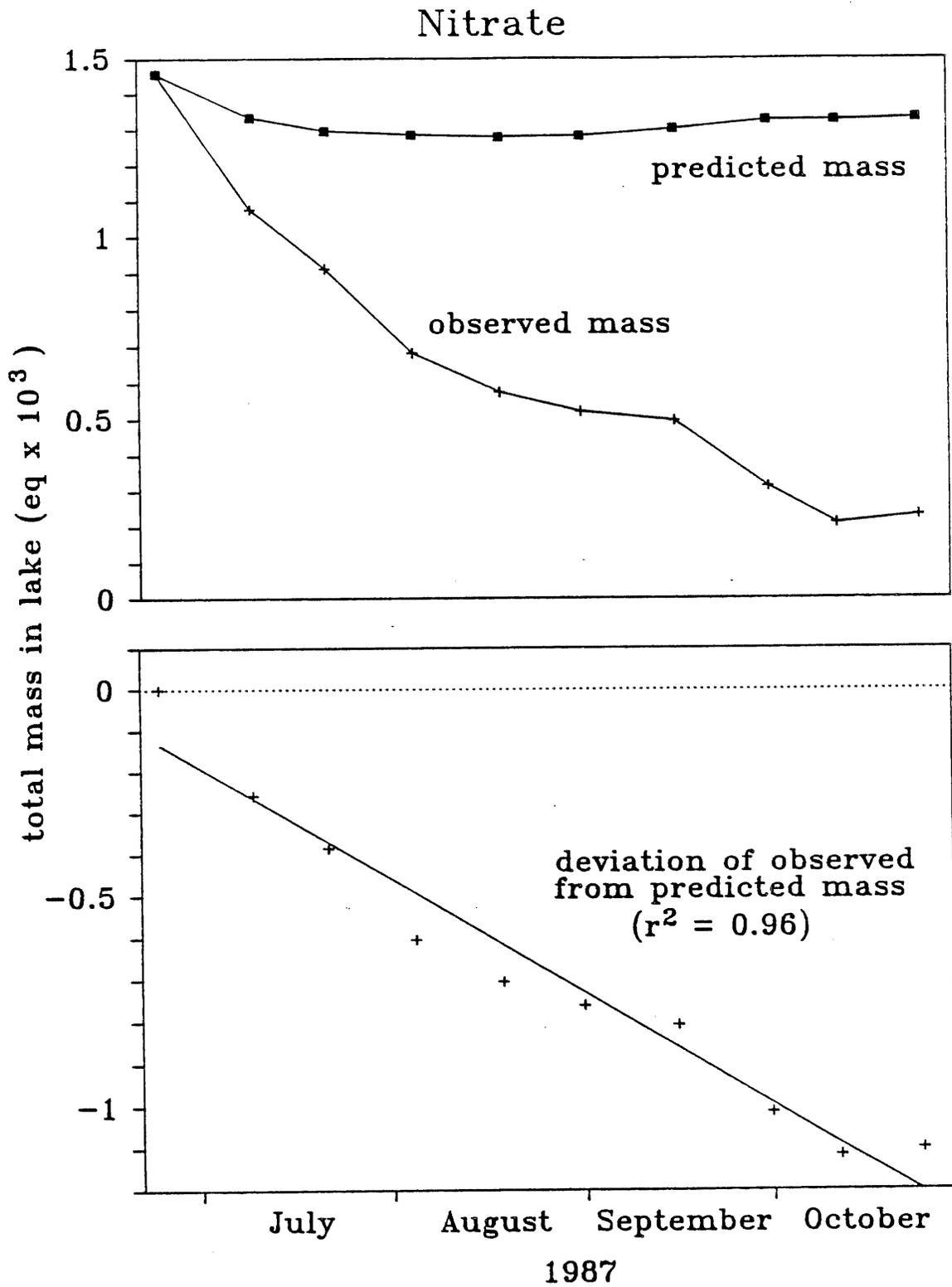


Fig. IV-3. Comparison of the observed mass of nitrate in the lake with that predicted by the mass-balance model, for the summer modelling period. See text for explanation.

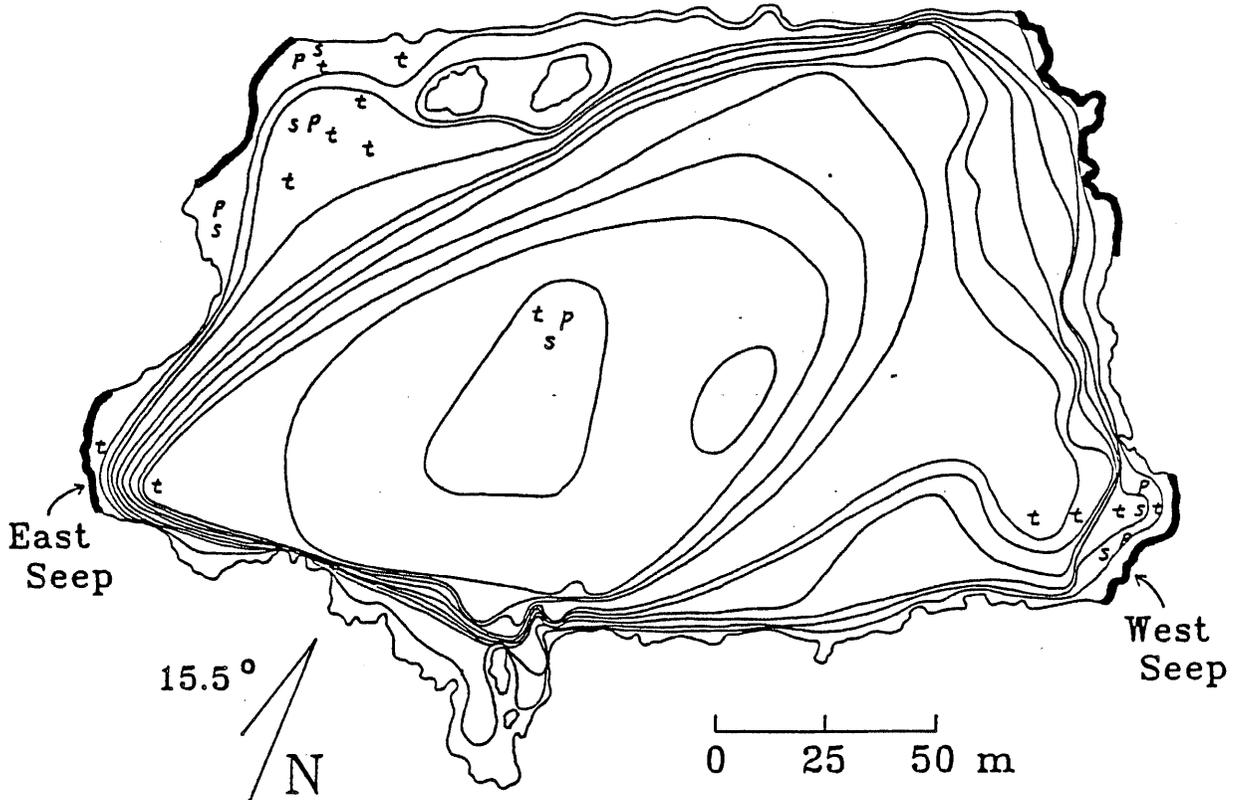


Fig. IV-4. Location of groundwater sampling sites in the lake. Bold lines along shore indicate areas of soils and colluvium through which groundwater could potentially flow. In addition to sampling the seeps marked here, we also made seepage meter measurements in July 1987 at sites marked "s", piezometer measurements in July 1987 at sites marked "p", and bottom temperature measurements in October 1987 at sites marked "t".

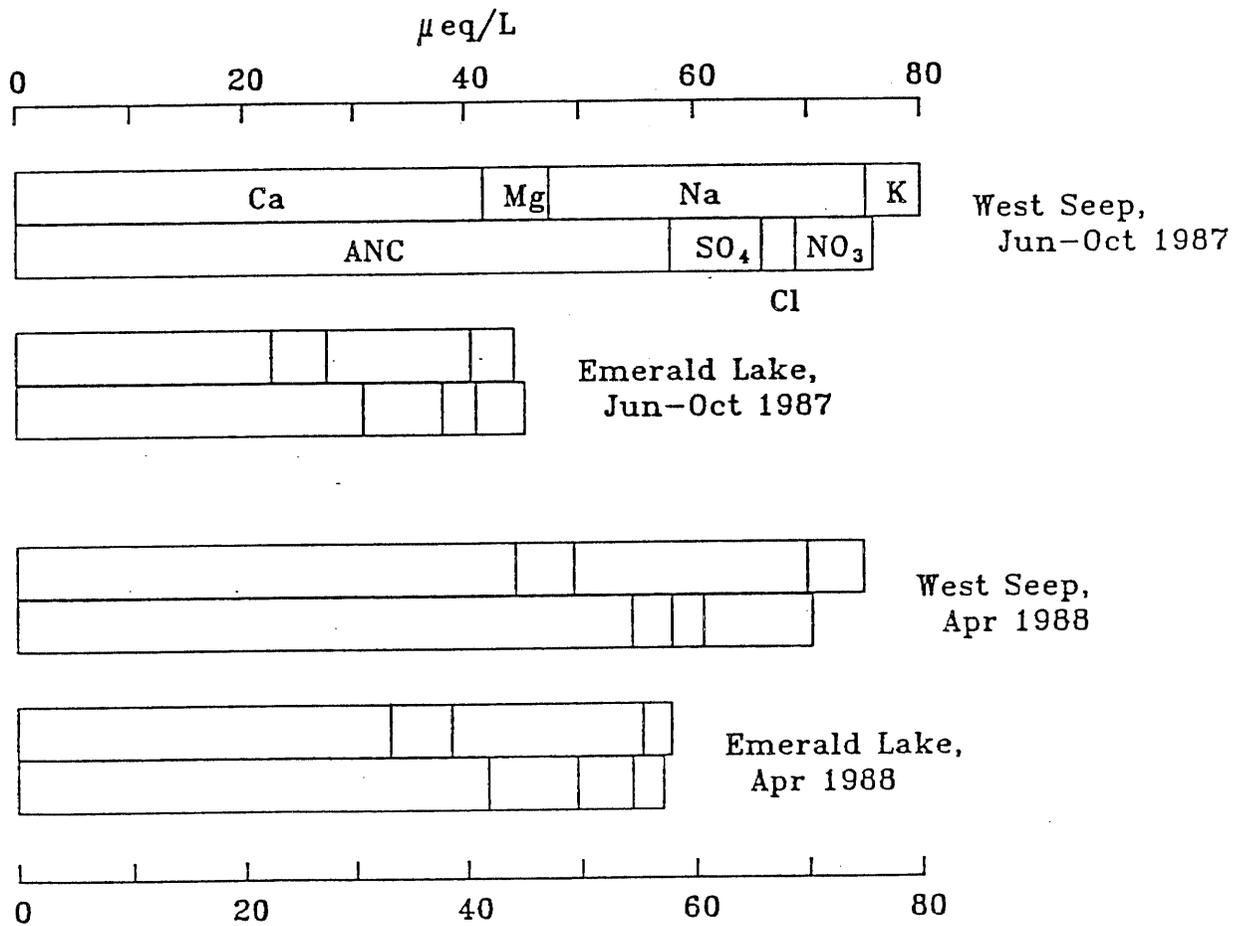


Fig. IV-5. Ionic bar diagrams comparing the chemistry of groundwater (West Seep) with that of the lake during June-October 1987 and April 1988.

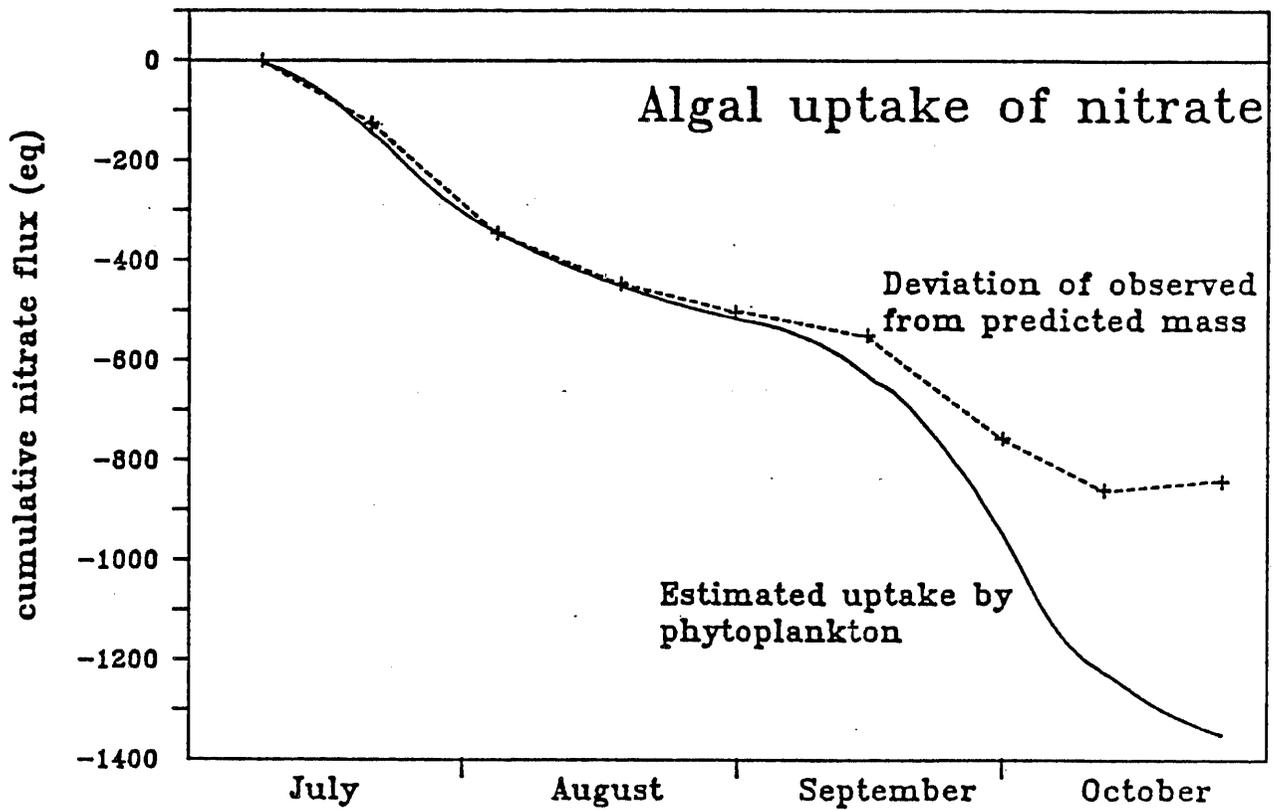


Fig. IV-6. Comparison of the cumulative daily uptake of nitrate by phytoplankton (estimated from carbon production) with the nitrate loss observed in the lake using mass balance. Units are flux of nitrate (eq) in the entire lake.

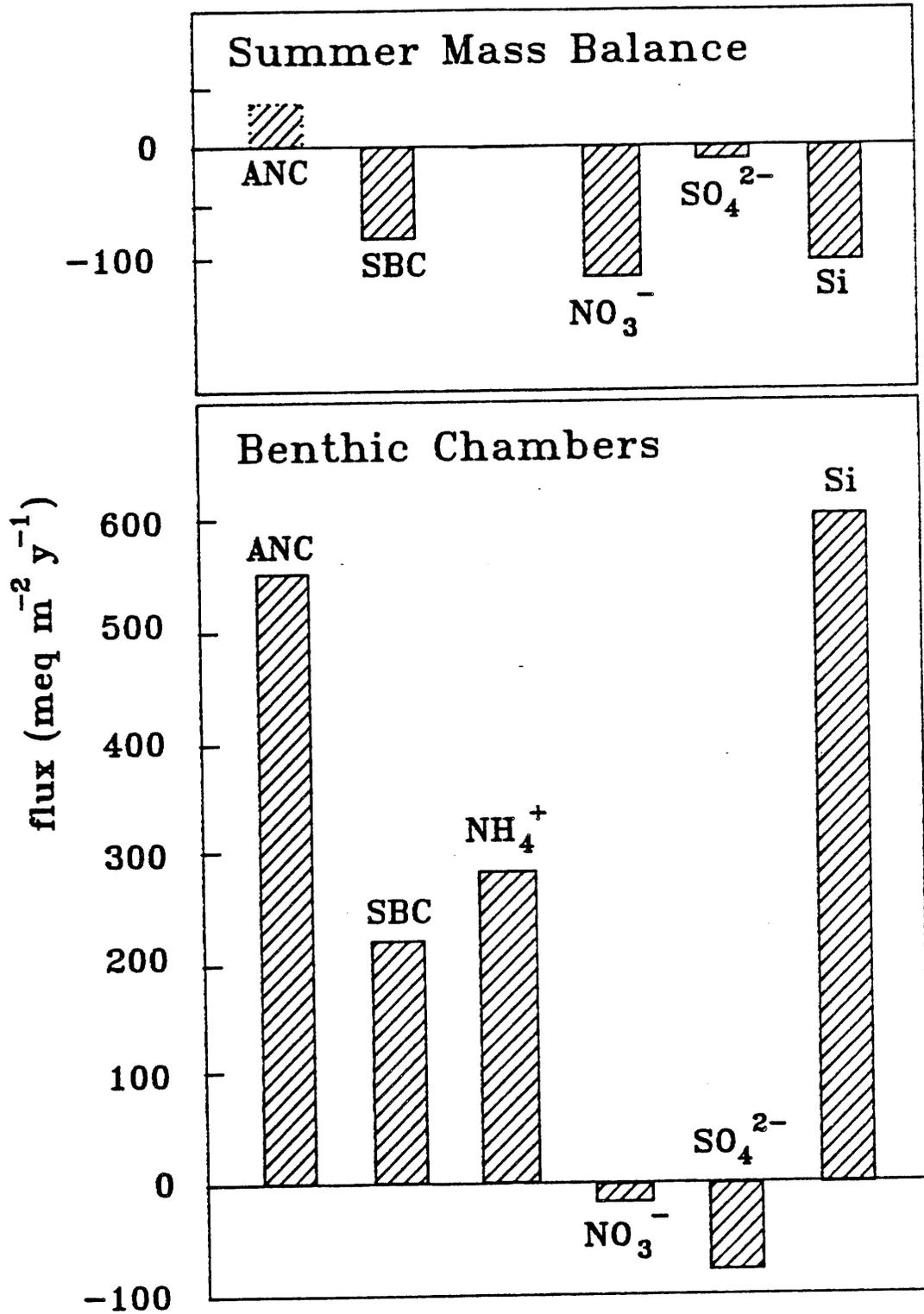


Fig. IV-7. Comparison of the solute fluxes determined by mass balance during the summer period with the fluxes measured over fine sediments using benthic chambers. The mass-balance flux of ANC was determined from the other solute fluxes by ionic charge balance.

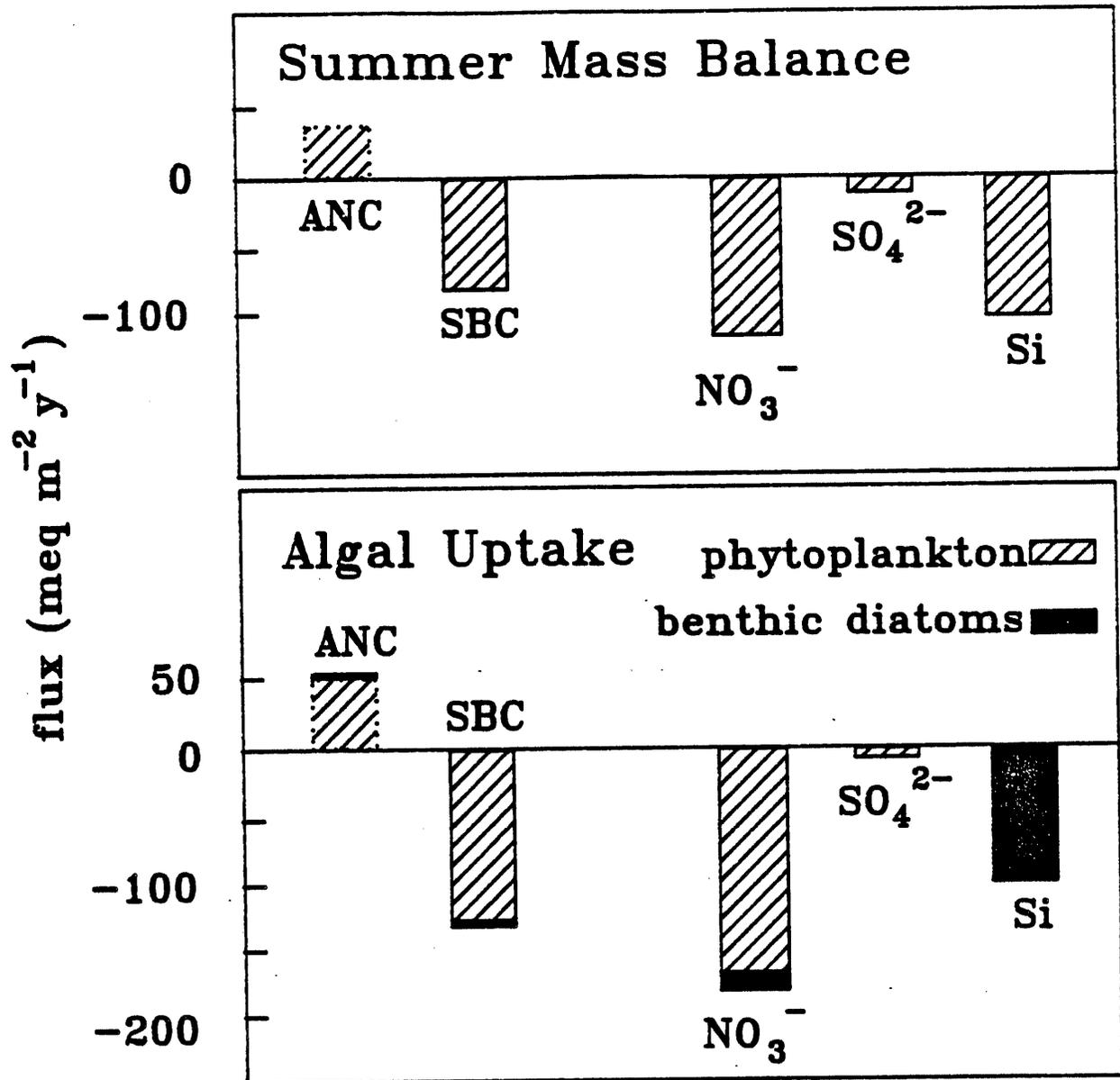


Fig. IV-8. Comparison of the solute fluxes determined by mass balance during the summer period with the fluxes estimated to result from nutrient uptake by phytoplankton and benthic diatoms. The fluxes of ANC were determined from the other solute fluxes by ionic charge balance.

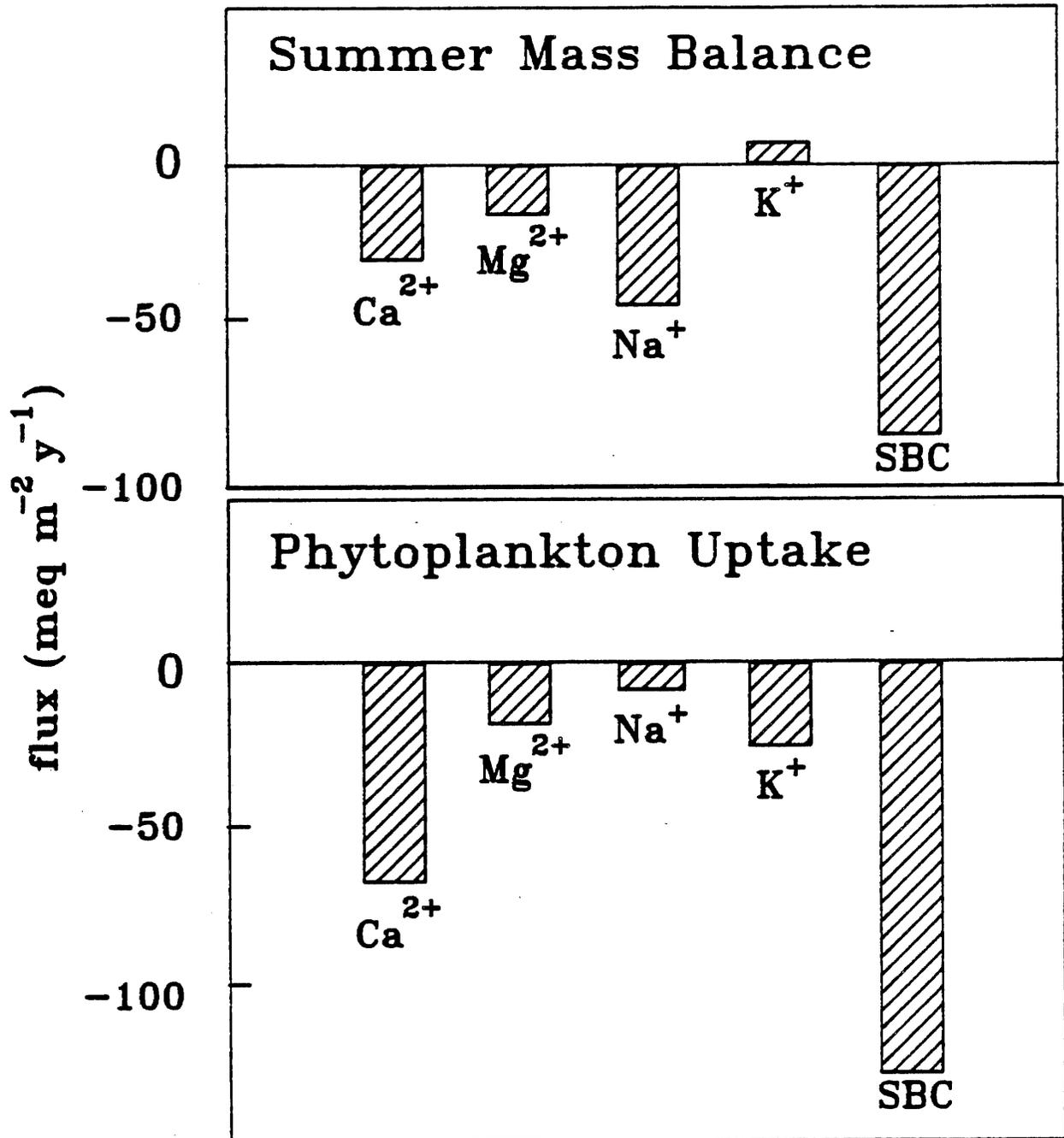


Fig. IV-9. Comparison of the individual base cation fluxes determined by mass balance during the summer period with the fluxes estimated to result from nutrient uptake by phytoplankton.