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The Role of Sediments in Controlling the Chemistry of Subalpine Lakes in the Sierra Nevada, California

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

THE ROLE OF SEDIMENTS IN CONTROLLING THE CHEMISTRY OF SUBALPINE LAKES IN THE SIERRA NEVADA, CALIFORNIA

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ABSTRACT

The importance of sediments in buffering lake water from acidic deposition was assessed by using a diffusion based approach to calculate the flux of alkalinity, and other chemical constituents, from sediments to lake water in three subalpine Sierran lakes. The approach requires the measurement or estimation of temperature, concentration gradients, deposition velocities, diffusion coefficients, porosity, and tortuosity within the sediments and their pore waters.

Concentration gradients were measured by sampling sediment pore waters with *in situ* samplers. The other parameters needed for the alkalinity flux calculations were either determined from sediment analyses or from values obtained in the literature.

Calculations of fluxes from the deep sediments show that they are dominated by products of organic matter decomposition and mineral weathering. Calculations based on measured gradients indicate that diffusive transport in freshwater sediments is significantly affected by activity coefficient gradients, coulomb forces, and complex formation. These calculated fluxes represent a low estimate, because materials produced at or near the sediment-water interface are not included.

Annual average base cation fluxes from deep sediments (the major source of permanent alkalinity contributions to the lake waters) are roughly 8, 5, and 12 neq $cm^{-2}day^{-1}$ for Eastern Brook Lake, Emerald Lake, and Mosquito Lake. Fluxes of base cations from the deep sediments represent a permanent contribution of

alkalinity to the water column. Calculated for the entire sediment area, these fluxes are 600, 200, and 400 eq yr^{-1}. Normalizing to lake volume, they are 4, 1, and 10 ueq $l^{-1}yr^{-1}$. We estimate that the "confidence interval" for these numbers ranges from one half to double the stated value. Assuming the hydrologic residence times are roughly equal, the sediments in Mosquito Lake, the shallowest lake, have the most influence on lakewater chemistry, and the sediments of Emerald Lake, the deepest lake, have the least influence.

We estimate that the sediments are contributing less than 10 % of the lake's total alkalinity. During periods when water is rapidly moving through the lakes, the sediments have little influence on water chemistry. However, during periods of the year when inflows are minimal, sediments exert a greater control on the lake's water.

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Disclaimer

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

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SUMMARY AND CONCLUSIONS

1. Introduction

Lake sediments, like other watershed components, have a role in determining the suceptibility of subalpine Sierran lakes to acid deposition. While their importance as a source of alkalinity for oligotrophic lakes has been suspected, little is known of their quantitative importance in Sierran lakes. This report focuses on the results of a study designed to calculate the rate of chemical exchange between the sediments and the lake water. These exchanges typically result from chemical and physical changes that occur in the sediments subsequent to deposition. Such changes and the processes causing them are referred to as diagenesis.

2. Method for Determining Sediment Fluxes

The method chosen to determine the fluxes of alkalinity from the sediments to the overlying lakewater relies primarily on the calculation of fluxes from measured concentration gradients in the pore waters. The basic principle is Fick's First Law of Diffusion:

$$q = -D\ dC/dx$$

where q is flux, dC/dx is the concentration gradient, and D is the diffusion coefficient. Concentration gradients are found by measuring the pore water concentrations at various depths in the sediments. The diffusion coefficients are taken from the literature with adjustments made for conditions encountered in the lakes studied.

3. Characteristics of Lakes Chosen for Study

The three lakes chosen for study were Emerald, Eastern Brook, and Mosquito, which lie in the subalpine zone of the western slope, eastern slope, and summit of the central Sierra Nevada, respectively. While these three watersheds have slight differences in bedrock lithology and topographies, they all are typical of the Sierra in that they are dominated by granitic rock and have lake water alkalinities below 150 ueq/l during summer months.

4. Characteristics of Sediments

The sediments at the bottom of these lakes have resulted from sedimentation during the Holocene epoch. Coring in Eastern Brook and Mosquito lakes penetrated to fine sands and silts derived from glacial outwash. Rates of sedimentation, based on Pb-210 dating and *in situ* sediment traps, resulted in estimates of current sedimentation ranging from 5 to 55 mg of mineral solids per cm^2 per year.

Sediments were examined intensively in their upper portions (25 cm) and less intensively throughout a greater depth sequence (up to 4 m). The upper 25 cm of the sediments represents, at most, several hundred years of sedimentation and, by measuring chemical and mineralogical parameters of these sediments, allowed us to identify weathering and decomposition processes which may be occurring at relatively rapid rates.

4.1. Organic Matter and Iron Chemistry of Sediments

Based on changes in sediment chemistry with depth, it appears that two processes may be occurring at rapid rates. First, the organic matter content of the sediments in all three lakes decreases with increasing depth, indicating relatively rapid losses through microbial decomposition. The initial content of organic matter varies with the lake, ranging from 12 to 25%. In general, there is a 5 % reduction in the organic matter content between the surface and depths of 25 cm. Iron hydroxide is the second property whose variation with depth appears to result from diagenetic change. In all sediment cores, the concentration decreases with increasing depth as a result of the dissolution of this component under anaerobic conditions. While the rapid decrease in organic matter and iron hydroxides with depth may be interpreted to be from diagenetic losses, an alternate hypothesis may be that they simply represent changes in deposition rates over the period of several hundred years.

4.2 Silicate Minerals in Sediments

Weathering of silicate clay minerals did not occur rapidly enough in the upper portions of the sediments to be detectable by X-ray diffraction techniques, although weathering of silicate minerals and diatoms is presumed to be occurring based on the winter and the spring run-off period, as well as in the summer during major runoff events, gave higher sedimentation rates and were close to estimated rates based on radio-isotope dating.

5. Porewater Chemistry of the Sediments

The chemical composition of the sediment pore waters is a very sensitive indicator of the chemical reactions occurring in the sediments. Pore waters were measured using *in situ* sampling probes, or "peepers". These probes allowed us to determine the porewater chemistry in discrete depth intervals, thus giving us a perspective of the direction of diffusion-driven fluxes as well as the mechanisms controlling the chemistry of the pore waters. Finally, the measurement of pore waters in different seasons allowed us a view of seasonal dynamics of lakewater chemistry and its effect on the chemical exchange between the lake waters and the sediments.

5.1. Dissolved Gases in Pore Waters

High concentrations of CH_4 in the pore waters indicate that the bulk of organic matter decomposition occurs under anaerobic conditions. In addition to CH_4, even higher concentrations of CO_2 were present and a large transfer of C from the sediments to the lakes is obviously occurring each year.

5.2. Ammonium in Pore Waters

In conjunction with the release of C, the anaerobic decomposition releases large quantities of N as NH_4^+, which is eventually transported to the low-N lake waters which lie above.

5.3. Dissolved Iron and Manganese in Pore Waters

As a result of anaerobic conditions, iron and manganese are present in the solution phase in high concentrations, presumably in a reduced form. The metal concentrations, in conjunction with decreasing iron hydroxide concentrations with increasing sediment depth, indicate that the dissolution of iron-bearing solids is an important diagenetic process.

5.4. Base Cations in Pore Waters

The presence of base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) in conjunction with SiO_2, indicates a possible combination of cation release from organic matter decomposition and silicate mineral weathering. However, a portion of the SiO_2 is probably a result of the weathering of diatom frustules, a biogenic opal mineral which does not contain appreciable quantities of base cations. Therefore, the correlation of cations with SiO_2 is not convincing proof of mineral weathering; rather, much of the base cation concentration may be the result of organic matter decomposition.

5.5. Alkalinity in Pore Waters

The major anion associated with the elevated concentrations of Fe^{2+}, Mn^{2+}, NH_4^+, and base cations is HCO_3^-. Since HCO_3^- is the major species composing lakewater alkalinity, the diffusion of this anion along with the associated cations represents an appreciable buffering source for the overlying lakes. However, much of the potential alkalinity is lost as Fe^{2+}, Mn^{2+}, and NH_4^+

diffuse into the lake and are oxidized or assimilated by biological processes. Thus, the most permanent source of alkalinity is the HCO_3 associated with the base cations, which are not susceptable to redox reactions once they have diffused into the oxygenated waters of the lake.

5.6. Seasonal Changes in Concentrations of Pore Water

The concentration profiles of the "summer", or open water, peepers indicate relatively rapid transport in the bottom water. The "winter", or under ice, peepers are characterized by relatively slow transport of bottom water. The reason for the transport difference is the presence of wind-generated seiches in the open-water lakes and their absence in the under-ice lakes. This difference holds even in a summer stratified condition, because, while transport across the thermocline may be very slow, vertical mixing below the thermocline is still relatively high. In the under-ice peepers, the slowness of transport in the overlying water enables us to see what is invisible in the summer peepers: the high rate of organic-matter mineralization at the sediment-water interface. This slow transport causes reaction products to accumulate at the site of the reaction, producing the peaks visible at the sediment-water interface in the winter peepers. The slowness of the transport also means that oxygen becomes depleted faster than it can be replenished by diffusion. Hence reduced products, such as NH_4^+, Fe^{2+},and CH_4 accumulate. After the depletion of oxygen, NO_3^+ and Mn^{2+}; Fe^{2+} becomes the preferred electron acceptor (Berner, 1980 p. 82). The presence of a reservoir of oxidized iron and labile organic matter at the sediment-water interface sustains a relatively rapid rate of mineralization even after oxygen depletion.

The development of a concentration peak at the sediment-water interface causes the diffusion of alkalinity and base cations into the sediments as well as into the water column. A similiar, but weaker effect occurs during summer stratification, due to the accumulation of mineralization products below the thermocline. The concentrations of base cations in the porewater near the sediment-water interface thus become higher than during periods when the lake is well mixed. After overturn, the bottom water, which has an accumulation of nutrients and alkalinity, mixes quickly into the lake, while the sediments release their buildup of nutrients and alkalinity more slowly, probably contributing alkalinity at an accelerated rate for a few weeks after overturn. Peepers that were sampled in mid-September and early October had base cation fluxes more than double those of the July and August peepers (see Tables in Chapter 4). So, while fluxes of base cations decrease during stratification, after overturn the gradients across the sediment-water interface become abnormally high, which results in enhanced fluxes into the water column until the gradients stabilize. Since these effects probably do not change mineralization rates in the bulk of the sediments, which are permanently anoxic, the flux swings at the sediment-water interface can be viewed as oscillations in an otherwise constant flux from the deep sediments.

6. Importance of Sediments in the Acid Neutralizing Capacities of

the Lakes

Calculations of fluxes from the deep sediments show that they are dominated by products of organic matter decomposition, except for iron and possibly silica. Calculations based on measured gradients indicate that molecular diffusion in freshwater sediments is significantly affected by activity coefficient gradients, coulomb forces, and complex formation. Our calculated fluxes represent a low estimate because materials produced at or near the sediment-water interface are not included.

6.1 Flux Estimates

Annual average base cation fluxes from deep sediments are roughly 8, 5, and 12 neq cm^{-2} day^{-1} for Eastern Brook Lake, Emerald Lake, and Mosquito Lake. Fluxes of base cations from the deep sediments represent a permanent contribution of alkalinity to the water column. Calculated for the entire sediment area, these fluxes are 600, 200, and 400 eq yr^{-1}. Normalizing to lake volume, they are 4, 1, and 10 ueq L^{-1} yr^{-1}. We estimate that the "confidence interval for these numbers range from one half to double the stated values. Assuming the hydrologic residence times are roughly equal, the sediments in Mosquito Lake, the shallowest lake, have the most influence on lakewater chemistry and the sediments of Emerald, the deepest lake, have the least influence.

6.2 Relationship of Sediment-Produced Alkalinity to Other Sources in the Watershed

We estimate that the sediments are contributing less than 10% of the lake's total alkalinity. During periods when water is rapidly moving through the lakes, sediments have little influence on water chemistry. However, during periods of the year when inflows are minimal, sediments exert a greater control on the lake's water chemistry.

RECOMMENDATIONS FOR FURTHER RESEARCH

There are several areas where more research is needed to answer additional questions developed during this work. Also, it is important to place this study into the broader context of the other ecological components of the watershed. Following are some specific recommendations which will address these topics:

(1) A detailed chemical analysis of organic matter in the lake and in sediments by depth. This would provide a way of determining exactly which species were coming from organic matter decomposition and which from mineral dissolution. In addition to complete elemental analyses, photosynthetic pigment analysis and stable C isotopes would also be useful in fully understanding the organic matter cycle in these lakes.

(2) Sensitive measurements of water inflow or outflow through the sediments. Exceedingly low rates of advection have a profound effect on both porewater profiles and fluxes and remain an ambiguous point in diagenetic modeling.

(3) Measurements of denitrification. A possible approach would be the use of ^{15}N and intact cores. Denitrification is probably already a major source of in-lake alkalinity generation and could be an important response to additional acid loading, especially

in California, where the nitrate:sulfate ratio is relatively high in acidic deposition.

(4) Measurements of sulfate reduction, also perhaps using intact cores and isotopic procedures. This process, along with denitrification, is important in assessing the future response of Sierran lakes to acidic deposition.

(5) Better hypolimnion and whole-lake measurements in the lake. Our work supplemented by some additional study (recommendations 1-4) would provide an adequate understanding of the mechanisms of sediment-related alkalinity generation. What is lacking are good measurements of in-lake (mostly sediment-related) alkalinity generation, and the only way to get good measurements seems to be through hypolimnion and whole-lake mass balance studies. Hypolimnion mass balances are practical, because the transport across the thermocline is slow enough that lake inflows and outflows can be ignored. The most important missing element is good bottom water measurements, and these could be obtained with dialysis samplers (similar to our interstitial water samplers) placed in a vertical array covering the bottom meter of the lake. Whole lake mass balances are also needed, but, in addition to bottom water measurements, inflow, outflow, and evaporation measurements are also required. These are much more difficult to obtain. They could be done, however, under the right conditions, for example, in the late summer, when snowmelt has greatly decreased and the inflow streams are relatively well defined. It would be especially valuable to have whole-lake and hypolimnion

mass balances done at the same time, since these would separate hypolimnetic and epilimnetic in-lake processes. This separation would be useful to model episodic acidification of the epilimnion.

(6) Three-dimensional mapping of the sediment body, using a non-intrusive sound reflection technique. The depth of the sediments have an important effect on the flux of most decomposition products produced in the deep sediments. Such a mapping would also answer the homogeneity question without having to collect an excessive number of cores.

(7) An exploration of the tortuosity-porosity relationship. Perhaps a two-pronged approach: tritium diffusion into intact cores and formation-factor measurements. Tortuosity is both very important and, currently, very uncertain.

(8) A thorough set of solid-phase sulfur analyses with depth, distinguishing organic and inorganic. The quantity and type of sulfur in the sediments with depth would provide an indication of current rates of sulfate reduction, which would suggest how the lake might respond to future sulfate loading.

RECOMMENDATIONS FOR INCORPORATING SEDIMENTS INTO A MECHANISTIC WATERSHED MODEL

The ARB should integrate this work into the work done by other researchers and develop an integrated watershed model which will adequately assess the ability of subalpine watersheds to buffer current and increased loads of acidic deposition. The ARB needs to consider all sources of alkalinity in Sierran watersheds, including lake sediments, and how the rates at which they supply alkalinity may change under different scenarios of sulfuric and nitric acid and NH_4^+ deposition in order to assess the potential for chronic and episodic acidification of Sierran lakes.

1. For assessing the potential for chronic acidification, a sediment or in-lake component should be included in a mechanistic watershed model. On an annual average basis this component could consist of a constant rate of base-cation flux across the sediment-water interface and a rate of NO_3^- and SO_4^{2-} reduction proportional to average water column concentration of these species. Estimates of these rates are available now, based on Melack et al. (1987), our work, and other literature, but better estimates should be obtained through research recommendation # 5 above.

2. To assess the potential for whole-lake episodic acidification, a sediment or in-lake component should also be included in a mechanistic watershed model. This is a more difficult task than assessing the potential for chronic acidification, since it requires a much finer temporal resolution. To obtain this kind of temporal resolution, lake transport must be modeled, since most

in-lake alkalinity generation depends on the rate of transport of oxygen, NO_3^-, and SO_4^{2-} to the sediment-water interface, and transport of base cations from the sediment-water interface into the water column.

3. To assess the potential for episodic acidification of the epilimnion alone, a sediment or in-lake component should similarly be included. However, this is a simpler task than modeling whole lake episodic acidification, since the epilimnion can be assumed to be well mixed. In this case, the in-lake component can be handled similarly to the chronic case, using a constant rate of base-cation flux across the sediment-water interface of the epilimnetic sediments and a rate of NO_3^- and SO_4^{2-} reduction proportional to average water column concentration of these species.

POLICY-RELATED RECOMMENDATIONS

1. When the Air Resources Board considers standards to protect sensitive lakes and watersheds from damage caused by acidic deposition, they will need to know all the sources of alkalinity generation within the lake and the watershed. One such source is the lake sediments. If this "alkalinity budget" is known, then it will be possible to predict the level of acidic inputs, wet and dry, that will be protective of surface water quality.

2. To predict the timing and severity of acidic episodes, watershed and lake models will need to include a module that simulates sediment contributions to lakewater alkalinity. Once we understand how acidic deposition changes surface-water quality, we can then use these models to set deposition levels of acidic materials that will prevent acidification damage to water quality and biota. Knowing this acceptable level of acidity in annual or seasonal deposition will allow the Air Resources Board to promulgate regulations to control the emissions of precursors. These regulations, if stringent enough, will keep levels of acid deposition low enough to protect aquatic biota and water quality in high-elevation lakes and streams.

CHAPTER 1

INTRODUCTION

1.1. Overview

The quantities of acidic deposition which may harm lakes in the western United States, and the time scales over which this harm may occur are important policy questions. Because the sediments of lakes are important sources of acid neutralizing substances, understanding the dynamics of sediment-produced alkalinity is a key to understanding the process of lake acidification. This report incorporates field work, laboratory studies, and mathematical modeling in order to achieve a general understanding of how much alkalinity the sediments of alpine lakes can produce, under what conditions, and over what time scales.

1.2 Possible Methods for Determining the Influence of Sediments on Lake Water Chemistry

There are four basic ways of determining what sediments are adding or removing from the overlying lake water:

1. Direct measurements using benthic chambers. A benthic chamber is a bell-jar-like apparatus fitted with sampling and stirring ports, placed directly on a small area of the sediments, enclosing a known volume of the overlying water. By sampling the water in the enclosed chamber over a time interval, the data needed to

calculate the flux is obtained.

2. Indirect measurements using lake mass balances. Time-series measurements of the lake and of the stream and atmospheric inflows to and outflows from the lake provide the data to calculate the sediments fluxes by difference.

3. Calculation from measured gradients. Concentrations of chemical species are analyzed in porewater samples. Fluxes are calculated from these data using diffusion theory.

4. Mechanistic reaction and transport modeling. Chemical reactions and transport processes are inferred from porewater and solid phase profiles and incorporated into a numerical model.

A summary of the advantages and disadvantages of each method is presented in Table 1.

Our estimates of sediment fluxes of alkalinity to the lake water rely on the method of calculating fluxes from measured concentration gradients. Since our best information indicates there is no impressed water flow through the sediments, and the velocity resulting from sedimentation is negligible, transport is assumed to be entirely diffusive. The basic principle used is Fick's First Law of Diffusion, which states that the flux is the product of the concentration gradient and a constant, the diffusion coefficient. Concentration gradients are found by measuring the concentration of chemical constituents at a series of sediment porewater depths. The gradient can then be calculated between any two of them; it is simply the difference in the concentration between the two depths divided by the distance between them. There are some further complications, but the basic principle is as described.

Method	Advantages	Disadvantages
Benthic chambers	Direct flux measurement; examination of specific sediment areas.	Sediment disturbance; alteration of transport and chemistry in overlying water.
Whole lake mass balance	Direct flux measurement; undisturbed bottom environment.	High uncertainties in lake inflow and outflow measurements; inability to distinguish sediment types.
Calculations based on measured porewater profiles	Undisturbed bottom environment; profiles allow inference of diagenetic processes and testing of transport and reaction modeling.	Difficulty of measuring small gradients; difficulty of measuring molecular and eddy diffusion coefficients.
Mechanistic model of reaction and transport in the sediments	Exploration of mechanistic hypotheses.	Other methods required for measurement of required parameters and verification; uncertainty in required parameters.

Table 1. Summary of advantages and disadvantages of methods for determining sediment-water fluxes.

Melack et al. (1987) did some direct flux measurements on Emerald Lake using benthic chambers, whole-lake mass balances, and limnocorrals (devices like large benthic chambers). These data provided a useful comparison with and complement to gradient-calculated fluxes.

To do a flux calculation from a concentration gradient, we need to know temperature, concentration, concentration gradient, velocity, diffusion coefficient, porosity, and tortuosity. The measurement of porosity and deposition velocities is detailed in Chapter 2. Tortuosity is estimated from porosity. Temperature and concentration data are described in Chapter 3. Concentration gradients are calculated from concentrations. Molecular diffusion coefficients and their temperature dependence are calculated using data from the literature. Finally the details and results of the flux calculations are described in Chapter 4.

1.3. Objectives

The overall objective of this research is to assess the role that sediments play in mediating, retarding, or ameliorating lake acidification. To acheive this goal, thr rate of chemical exchange between the lake and the sediments must be known. Several related questions are:

1) does the rate of exchange between the lakes and sediments vary seasonally?

2) does this exchange vary under different scenarios of acidification?

3) what are the major chemical reactions occuring in the sediments?

4) what is the nature of the sediments?

To determine the types and rates of chemical exchange, a mathematical modeling approach was adopted. However, the use of the model requires an adequate set of empirical data characterizing the chemistry and mineralogy of the sediments and their pore water.

This report is arranged in a series of chapters designed to present much of the data collected over the course of this study. Chapter 2 describes the general charactertics of the sediments. Chapter 3 focuses on the chemistry of the interstitial water of the sediments and on the general chemical reactions which are controlling the pore and lakewater chemistry. Chapter 4 is concerned with the modeling of the sediments and their porewaters, as well as in the calculation of rates of exchange between the sediments and lake water.

1.4. Site Description

1.4.1. Emerald Lake

Emerald Lake is located in a glacial cirque at an elevation of 2780 m, on the west slope of the Sierra Nevada, in Sequoia National Park (see Table 2 for location and summary of properties). The lake has an area of 2.85 ha and a maximum depth of 10.5 m. The surrounding watershed, which is approximately 113 ha in area, is extremely steep and dominated by granodiorite

Parameter and units	Lake		
	Eastern Brook[a]	Emerald[b]	Mosquito[c]
Latitude	37°25′52"N	36°35′49"N	38°30′58"N
Longitude	118°44′48"W	118°40′30"W	119°54′36"W
Elevation (m)	3170.	2800.	2454.
Watershed maximum elevation (m)	3780.	3416.	2536.
Watershed area (ha)	250.	120.	34.
Percent of the watershed that is			
Unvegetated (rocky)	50.	90.	70.
Vegetated	50.	10.	30.
Lake area (ha)	4.4	2.8	1.2
Lake area to watershed area ratio (percent)	1.8	2.3	3.5
Lake volume (m3)	130.	160.	22.
Average depth (m)	2.9	5.6m	1.8
Maximum depth (m)	9.0	10.5m	4.5
Typical summer alkalinity (μeq L^{-1})	125.	30.	50.

Notes:

a. Information from personal communication, Lanny Lund, University of Califonia, Riverside; personal communication, Carl Chen, Systech Engineering, Inc., Lafayette, California; USGS 7.5′ topographic quadrangle "Mt. Morgan".

b. Information from personal communication, Dr. Kathy Tonnessen, California Air Resources Board; Melack et al. 1987; USGS 7.USGS 15′ topographic quadrangle "Triple Divide Peak".

c. Information from our survey; USGS 7.5′ topographic quadrangle "Pacific Valley".

Table 2. Summary of the characteristics of the three lakes.

bedrock. Where it exists, the soil of the watershed is poorly developed and shallow (Huntington and Akeson, 1987), supporting stands of western white pine (*Pinus monticola*), red fir (*Abies magnifica*), and other typical Sierran subalpine vegetation (Rundel et al., 1986). The lake water is poorly buffered, with a typical summer alkalinity of ~ 30 ueq/l and pH of about 6.3 (Melack et al., 1985; 1987).

1.4.2. Eastern Brook Lake

Eastern Brook lake is located at 3170 m on the eastern side of the Sierra Nevada (Table 2). The lake has an area of approximately 4 ha and a maximum depth of 13 m. The watershed, which is approximately 250 ha in area, is bounded on the east by the steep, talus slope of a lateral moraine. The remainder of the watershed is a mosaic of outcrops of granitic bedrock, forested soils, and subalpine meadows. The lake water is higher in alkalinity than that of Emerald lake, with a mean summer alkalinity of 125 ueq/l and pH of 6.8.

1.4.3. Mosquito Lake

Mosquito lake is located near the crest of the central Sierra Nevada at 2451 m (Table 2). It is accessible by California State Highway 4, less than 1 km from Pacific Grade Summit. The lake has been modified at some time in the past by the addition of a small (1 m tall) dam between east and west portions of the lake. Our study was conducted in the lower, eastern portion, which had an area of approximately 1.2 ha and a maximum depth of

4.5 m (mean depth = 2 m). The watershed is gently to steeply sloping and is mantled by forested soils with occasional rock outcrops. Bedrock of the watershed is dominated by granodiorite, although Tertiary intrusive andesitic and Tertiary extrusive rocks outcrop in the area. The lake water has an alkalinity of about 50 ueq/l and a pH of 6.6 in the summer.

1.5. References

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Chapter 2

CHEMICAL, PHYSICAL, AND MINERALOGICAL PROPERTIES OF THE SEDIMENTS IN THREE SUBALPLINE SIERRAN LAKES

2.1. Introduction

A knowledge of sediment properties as a function of depth is essential to our objectives (flux calculations and identification of weathering mechanisms) in that:

1. sediment solids are a large reservoir of chemical elements which are subject to dissolution by the pore waters and to transport to the overlying lake,

2. since sediments increase with age with increasing depth, variations in properties with depth provide potential clues to the important chemical reactions taking place in the pore waters or to important depositional events in the lake's history.

The purpose of this chapter is to compare selected physical, chemical, and mineralogical properties of the solid phase of sediments in three subalpine lakes in the Sierra Nevada. An understanding of these properties is necessary to understand and model the chemistry of their interstitial waters and to determine their effect on the long-term chemistry of these sensitive aquatic systems.

2.2. Methods and Equipment

2.2.1. Short Sediment Cores

Twenty cores of about 20 cm in length were taken from the deeper portion of each lake using a gravity corer (Wildco Model

2424-A25). The core tubes were clear acrylic plastic about 4.9 cm in internal diameter.

Cores were extruded by placing the corer in a vertical position and by applying pressure to a rubber stopper at its base. As the rubber stopper was driven upward through the corer, displacing the sediment, the displaced sediment was pushed up into a 2 cm ring. When the sediment filled the 2 cm ring, the ring was separated from the core and its contents were deposited in a plastic bag. Twenty cores were collected and sectioned in 2 cm intervals, and composited in order to obtain enough sample for mineralogical analysis.

Water content of the sediment was determined by subtracting the dry weight from the wet weight of the sediments. Analytical error in water content results primarily from differences in drying time and oven temperature. The actual measurement, which consists of weighing on a Mettler balance, is not a significant source of error in this measurement. Gardner (1986) indicates that 0.5 % is a conservative coefficient of variation for the determination of water content by oven drying.

Porosity was calculated from water content by assuming a dry density of 1.1 g cm^{-3} for organic solids and 2.6 g cm^{-3} for mineral solids. Since porosity is derived from percent water, the coefficient of variation resulting from analytical measurements (drying and weighing) is also assumed to be 0.5 %. Another uncertainty results from assumptions about the density of dry solids, but in high porosity sediments like ours, porosity is relatively insensitive to the density of dry solids. Varying the dry densities from 1.1 (organic matter) and 2.0 (minerals) to 1.6 (organic matter) and 3.0 (minerals) only changed the mean porosity of the short cores from 90.7% to 93.5%, and the mean porosity of the long cores from 78.3% to 83.3%. We estimate the coefficient of variation of porosity at 3%.

2.2.2. Long Cores

Piston corers (Livingston corers) were used to obtain long cores. Eastern Brook and Emerald cores were obtained in the summer of 1986 with the help and equipment of the Indiana University team, directed by Mark Whiting, who was conducting a study of the biostratigraphy of Sierran lakes. The Mosquito lake core was taken in the fall of 1986 using the equipment of Roger Byrne of U.C. Berkeley.

The procedure for obtaining long cores was as follows. A stable raft, large enough to support three or four people, was secured over the sampling site with intersecting shore anchors to prevent horizontal movement. Distance to the bottom was measured with a Secche disk. A casing of pipe larger than the corer was then lowered to the bottom through a hole in the floating platform, gently pushed into the sediment, and secured to the raft. The corer (about 1 m in length) was then lowered through the casing to a depth 10 cm above the bottom. The piston cable of the corer was secured to the raft (rendering the piston incapable of vertical movement) and the push rods were raised to the top of the corer tube, rotated, and locked. The rod was pushed downward, driving the corer into the sediment, while the piston remained stationary. The core tube, with the piston now at its top, was pulled into the raft, disconnected from the piston, and stored. The presence of the casing allowed the corer to be reinserted in the same hole on the next drive. While the casing protected the hole from disturbance between drives, it was inevitable that some material fell into the hole between drives and that the top of each successive core contained some contamination. In addition, the bottom of each drive can become diluted and partially removed by lakewater as the core is pulled up through the water column.

Cores were extracted from the tubing in the field by extruding them onto aluminum foil. At this time, morphological descriptions were made and depth measurements of stratigraphic features were made. The extruded cores were sectioned either by pre-selected depth increments (usually 10 cm) or by lengths determined by stratigraphic features such as gravel lenses or volcanic ash layers. Sectioned samples were stored in plastic bags and returned to the lab. Determinations of water content and porosity were made by the methods described above.

2.2.3. Sediment Traps

Sedimentation rates in the 3 lakes were measured using *in situ* sediment traps (J. Melack, per. comm.). Traps consisted of four, vertically oriented PVC cylinders mounted on a PVC support rack. Spring-loaded rubber caps were made to cover the open, upper end of the cylinders. The entire apparatus, with the spring-loaded rubber caps in an open position, was lowered to a depth of 1 to 2 m above the sedients. A buoy, connected to a support rope, was used to suspend the traps. The bottoms of the traps were connected to a rope that extended to an anchor at the sediment surface, which prevented the traps from moving. The suspended traps were then allowed to remain in place for periods ranging from several weeks to several months. At the time of collection, a weighted messenger was used to release the spring-loaded rubber caps and close the tops of the collection cylinders. The traps were then raised out of the lake, the cylinders were removed from the apparatus, and the entire contents of the cylinders were transferred to large plastic bottles.

The sediment content of the cylinders was determined by removing the water by centrifugation, filtration, and evaporation and determing the weight of the remaining solids. The mass of solid in a similiar volume of lake water was subtracted from the mass in the traps to correct for initial solid content of the lake water.

The four separate sampling cylinders on the trap provided a measure of the variance produced by the sampling and analysis procedure. Pooled standard deviations with 20 degrees of freedom were 1.9 mg cm^{-2} yr^{-1} for total sedimentation rate, 5.6% for organic matter content, and 1.2 mg cm^{-2} yr^{-1} for mineral sedimentation rate.

2.2.4. Laboratory Methods

The uncertainties for the solid phase analyses described below are presented in Table 1. Where possible, they were determined from replicate analyses and therefore include subsampling error as well as analytical error.

Table 1. Solid phase analyses: summary table of uncertainties

Parameter (units)	Pooled standard deviation	Degrees of freedom for pooled std. dev.	Coefficient of variation (%)	Method
water content[a] (weight % of total sediments)			0.5	dry & weigh
porosity[b] (volume % of total sediments)			3.	
org matter (weight % of dry sediments)	3.2	40		combustion
% org C (weight % of dry sediments)	0.47	107		Walkley-Black
% org N (weight % of dry sediments)	0.076	30		Kjeldahl
Fe oxides (weight % of dry sediments)	0.060	41		AA
Mn oxides (weight % of dry sediments)	0.00080	14		AA
Chemical composition of mineral clays[c] (weight % of dry mineral clays)				Digestion & AA
Ca			3	
Mg			3	
Si			9	
Al			7	
Fe			7	
sand, silt, and clay[d] (weight % of dry sediments)			5	

a. Replicates not run; estimated from Gardner 1986
b. See text.
c. Based on the standard deviations for AA analysis (see Chapter 3, Table 1)
d. Replicates not run; estimated from Gee and Bauder 1986

The total organic matter content of the dried sediment samples was determined by ashing pre-weighed samples at 425 °C for 24 hrs, cooling, re-weighing and determining the weight loss. This temperature was chosen to avoid the destruction of any carbonate minerals which may have been present (Davies, 1974).

The organic C content of the sediments was determined using the Walkley-Black method (Nelson and Sommers, 1982). Sediment samples were digested in a $K_2Cr_2O_7/H_2SO_4$ mixture and then titrated to determine the amount of the dichromate which was reduced by the C.

Total N in the sediments was determined using a modified Kjeldahl method (Bremner and Mulvaney, 1982). Samples and reagents were digested and diluted. The N concentration in the solution was determined on a Lachat autoanalyzer using N standards which had the same background matrix as the samples.

The iron oxide (hematite, goethite, ferrihydrite, lepidocrocite, as well as poorly defined Fe hydroxides) content of the samples was determined with the dithionite-citrate-bicarbonate (DCB) method outlined by Kunze (1965). Samples were placed through a series of digestions, centrifugations, and decantations in order to remove all soluble oxides of iron. The supernatants were combined and brought to volume. The iron concentration in these solutions was then determined by atomic absorption spectroscopy.

Manganese oxides in the sediment samples were measured by the hydroxylamine hydrochloride method of Chao (1972). Following the extraction steps, the manganese in the supernatant was determined by atomic absorption spectroscopy and the manganese oxide present in the original sample calculated.

The particle size distribution of sediment samples was determined during their preparation for mineralogical analysis. Organic matter was first removed using sodium hypochlorite (Anderson, 1961). Iron oxides were removed by the methods described above. Following these pretreatment steps, the organic matter-free samples were passed through a 2 mm diameter sieve to remove gravel. A portion of the less-than-2-mm fraction was then added to water in which a dispersing agent (sodium metasilicate) had been added, and was shaken. The dispersed suspension was then passed through a 50 micron sieve and the > 50 um fraction (i.e. sand) was dried and weighed. The < 50 um fraction was then placed through a series of sedimentation/centrifugations. The material remaining suspended (< 2 um, i.e. clay) was decanted and saved for mineralogical analysis. The > 2 um fraction (silt) was collected, dried, and weighed. The clay concentration was then determined by difference.

The mineralogical composition of the clay fraction collected above was determined semiquantitatively by X-ray diffraction analyses. First the clay in an aliquot of the suspension was oriented on a glass slide using the filter-membrane peel technique of Dreever (1973). The technique consists of filtering an aliquot of clay suspension through a Millipore filter. The retained clay is then saturated with either Mg^{2+} or K^{+} chloride salt solutions and is then rinsed with deionized water. The filter, with the retained clays, is then removed and placed clay side down on a glass slide, rolled with a tube, and the filter is then peeled off, leaving the clay film on the glass slide. Subject to X-raying, the following treatments are made:

- a) K-saturated samples
  - i. air dried
  - ii. heated to 300 °C
  - iii. heated to 550 °C
- b) Mg-saturated samples
  - i. placed in a dessicator at 54 % r.h.
  - ii. placed in contact with ethylene glycol at 60 °C

Subsamples of a given clay sample, placed through the above treatments, must be X-rayed in order to distinguish the various clay minerals which are normally present in soils or geologic samples. Prepared clay samples were then X-rayed on a Rigaku Geiger-flex diffractometer. Measures of the relative abundance of individual minerals were made by measuring the height of their major peaks.

The chemical composition of the clay fraction of selected sediment samples was made using the method of Lim and Jackson (1982). Weighed, oven-dried samples were placed in 250 ml polypropylene bottles. Aqua regia and HF were then added to the samples. Following digestion, H_3BO_3 was added, and the samples were allowed to stand prior to being brought to volume. The SiO_2, Al^{3+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, K^+, and Na^+ concentrations in the solution were determined by atomic absorption spectrophotometry using standards with the same background as the samples.

2.3. Results

2.3.1. Sedimentation Rate

Sedimentation rate (SR) is here defined as the mass of mineral solids which accumulates per cm^2 each year. This definition is chosen because of the very slow diagenesis of mineral solids, resulting in a constant "burial rate" at all depths in the sediments if the mineral deposition rate at the surface is relatively constant. If SR is assumed to be constant over time, it can be used in conjunction with cumulative mineral solids to calculate age, and with the concentration of mineral solids to calculate the conventional burial rate (cm/yr). Since organic matter undergoes considerable decomposition with depth, the burial rate changes with depth.

The Pb-210 dating of Emerald Lake sediments was performed on the core designated Mid-2 by Melack et al. (1987). Robert Holmes from UC Santa Barbara did the core sectioning and measured wet weights, dry weights, and ignition losses on cores Mid-2, Right-1, and Left-1. Half-cm intervals were sampled down to 5 cm and one-cm intervals below that. Douglas Hammond of UCLA measured total disintegrations per minute (dpm) on 11 of the 25 core sections of core Mid-2, subtracted the background of 12.3 dpm due to Ra-226 in the sediments, and multiplied the result by 1.047 to correct for the year and a half between collection and counting (Table III-1, p.135; Melack et al., 1987). The hardcopy listing of the data was provided by Robert Holmes. One of us (H. Michaels) regressed the corrected dpm data (CDPM) against the cumulative mass of the mineral fraction (CMMINMB) of the sediment as calculated from Holmes' data. The following is the regression equation:

$$CDPM = C_o e^{-(DC)(CMMINMB)/SR}$$

where DC = 0.03114 is the disintegration constant for PB-210 (based on a 22.26 year half life) and SR is sedimentation rate in g/cm^2 yr. Assumptions inherent in this regression are 1) a constant deposition rate of mineral solid, 2) no dissolution of mineral solid, 3) no bioturbation, and 4) a constant concentration of Pb-210 in freshly deposited sediments. The mineral solid, rather than total solid, was chosen as a regression parameter because, as was previously mentioned, the organic fraction is subject to significant loss. The regression was performed using the SAS non-linear regression procedure NLIN. The result of this regression is a calculated sedimentation rate of 30 mg of mineral solid/cm^2 yr, with a SAS-generated standard error of 4.3 mg and a 95% confidence interval of 20-40 mg. A plot of the data and the model are shown in Fig. 1. As a measure of the similiarity between Holmes' cores and ours, the cumulative mineral mass of the UC Santa Barbara and UC Berkeley cores were plotted against depth in Fig. 2.

The age at any depth can be calculated as the accumulated mineral matter, CMMINM, down to that depth divided by the sedimentation rate. The burial rate at any depth is sedimentation rate divided by the concentration of mineral solids, CMIN (g/cm^3). The burial rate decreases with depth due to compaction.

The physical analysis of our cores results in a measured concentration of mineral matter at each depth. Due to real irregularities in sedimentation, if the measured CMIN is applied directly to calculate burial rate, the result will be a burial

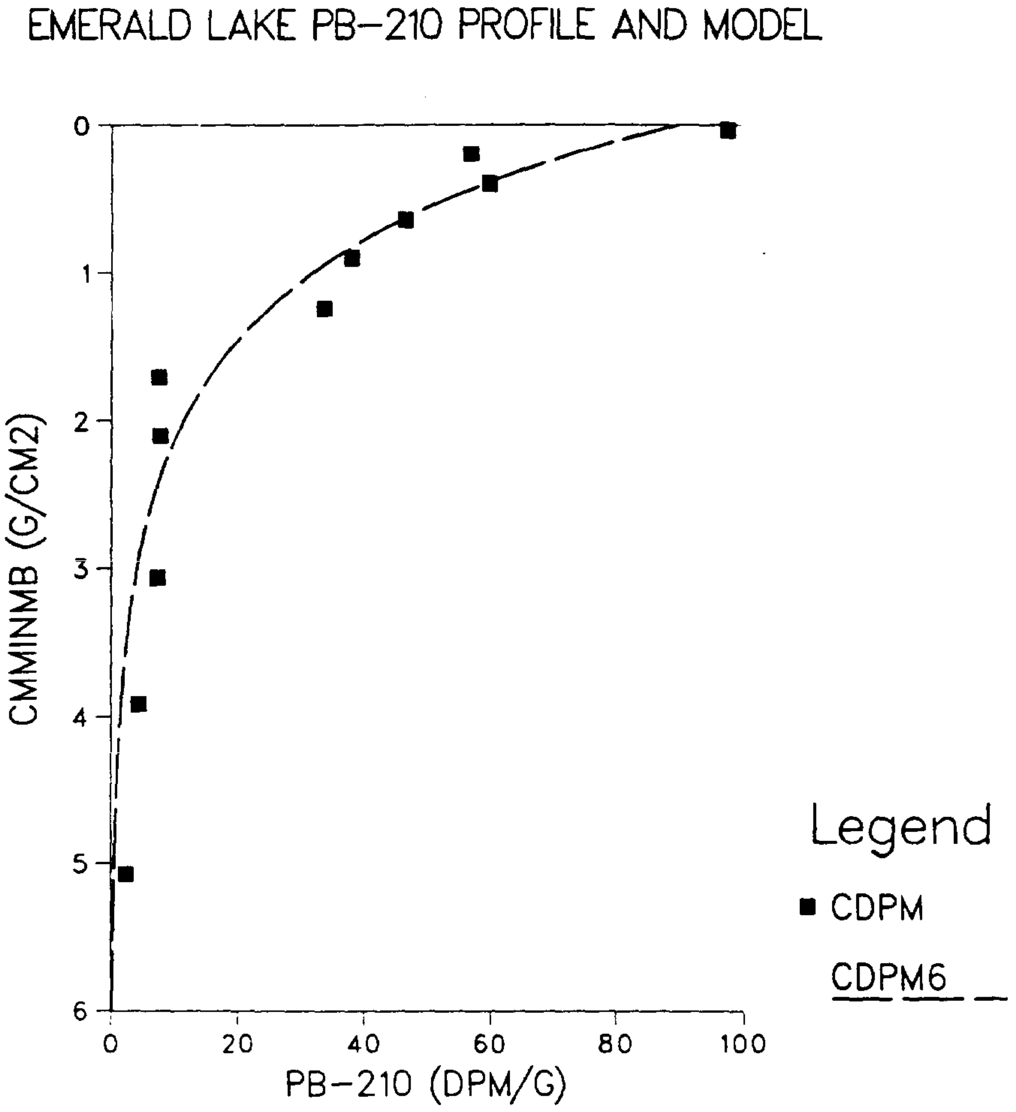

Figure 1. The Pb-210 activity vs. cumulative mass of minerals in Emerald Lake core Mid-2. Data from Melack et al. (1987).

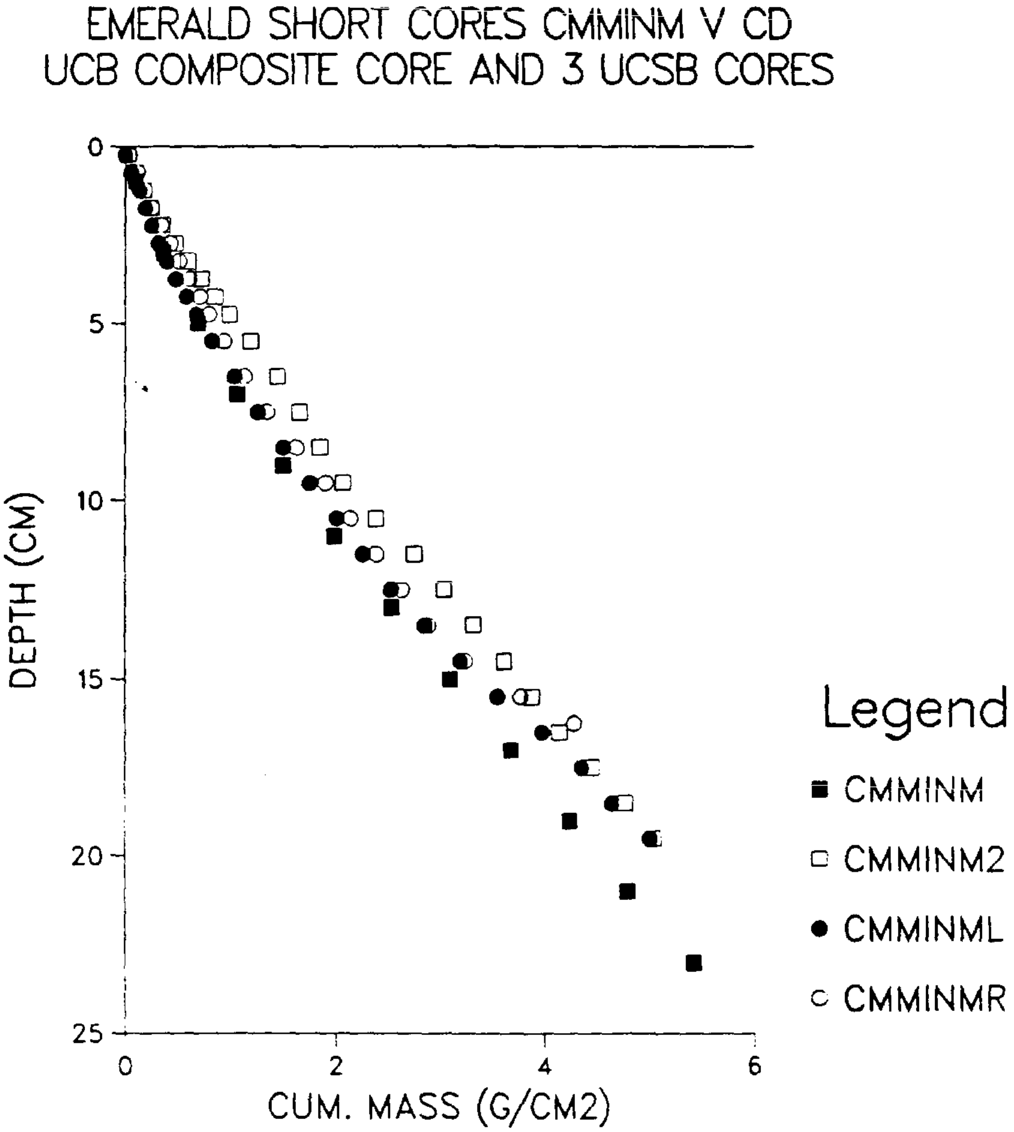

Figure 2. A comparison of cumulative mineral mass vs. sediment depth for a UCB composite core (CMMINM) and three UCSB cores. The UCSB data from Melack et al. (1987).

rate which may occasionally increase with depth. This is physically impossible since it would imply inverse compaction. Therefore, an equation was used to fit CMIN (actually 1/CMIN) to depth:

$$\mathrm{CMIN} = C - Ae^{-BX}$$

where C represents CMIN at the depth where the compaction rate is nearly zero, and X is depth. While the physical situation is too complex to justify this equation mechanistically, it appears to fit the data rather well. An equation for CMMINM as a function of depth was derived by integrating the equation for CMIN. The equation-generated values are referred to as CMIN25 and CMMINM25 to distinguish them from the measured values. CMMINM25 is shown plotted with the real data, CMMINM, in Fig. 3 (short core), in Fig. 4 (long core), and Figure 5 (both cores). For modeling purposes, solid burial rate and age are then calculated using SR plus these two equations.

In comparing the Pb-210 SR value with sedimentation rates obtained from in-situ traps, the traps show values which are far too low (Table 2). For example, the rate of mineral sedimentation indicated by the traps ranged between 3 to 7 mg/m^2 yr, compared with 30 mg/m^2 yr by Pb-210 dating. One explanation is that the Pb-210-derived rate measures average annual rates, which include major sedimentation events such as occur during high runoff, avalanches, and slides, whereas most traps were set during a quiet two-week period when runoff was low. The Emerald trap which overwintered during the large avalanche event in the 1985-1986 winter gave a sedimentation rate nearly twice the rate derived from Pb-210 dating (55 mg/m^2 yr).

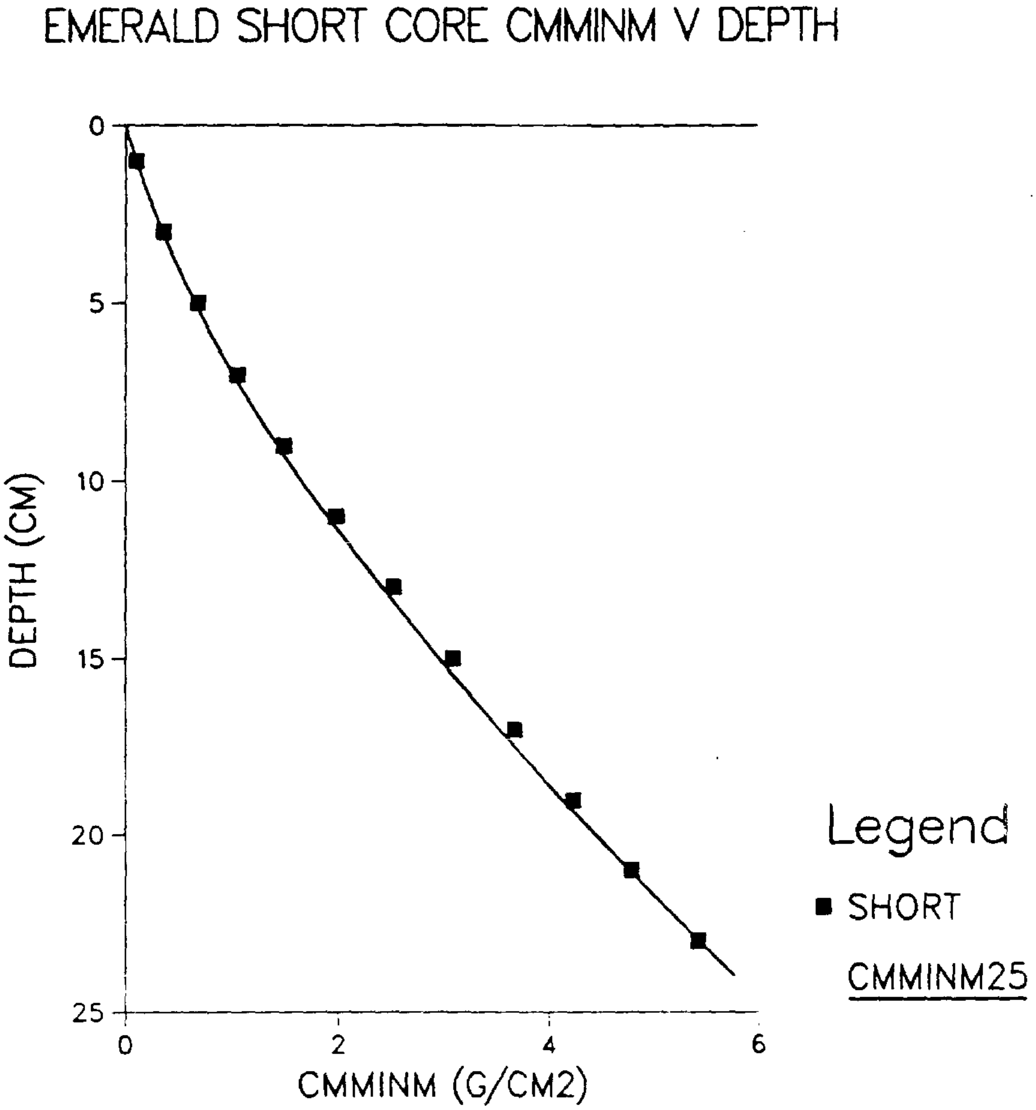

Figure 3. The measured (short) and modeled (CMMINM25) cumulative mineral matter vs. sediment depth for Emerald Lake short cores.

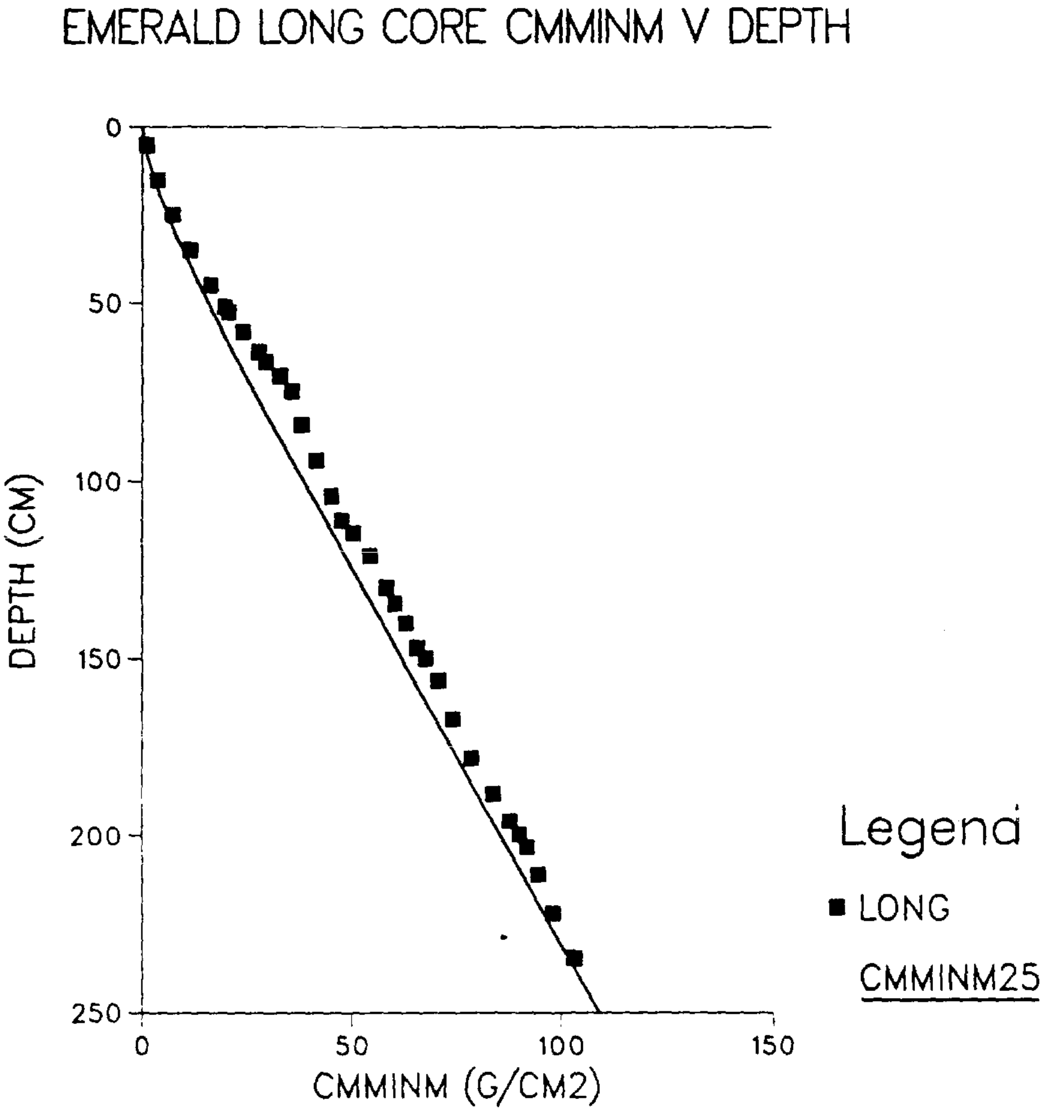

Figure 4. The measured (long) and modeled (CMMINM25) cumulative mineral matter vs. Sediment depth in the Emerald Lake long core.

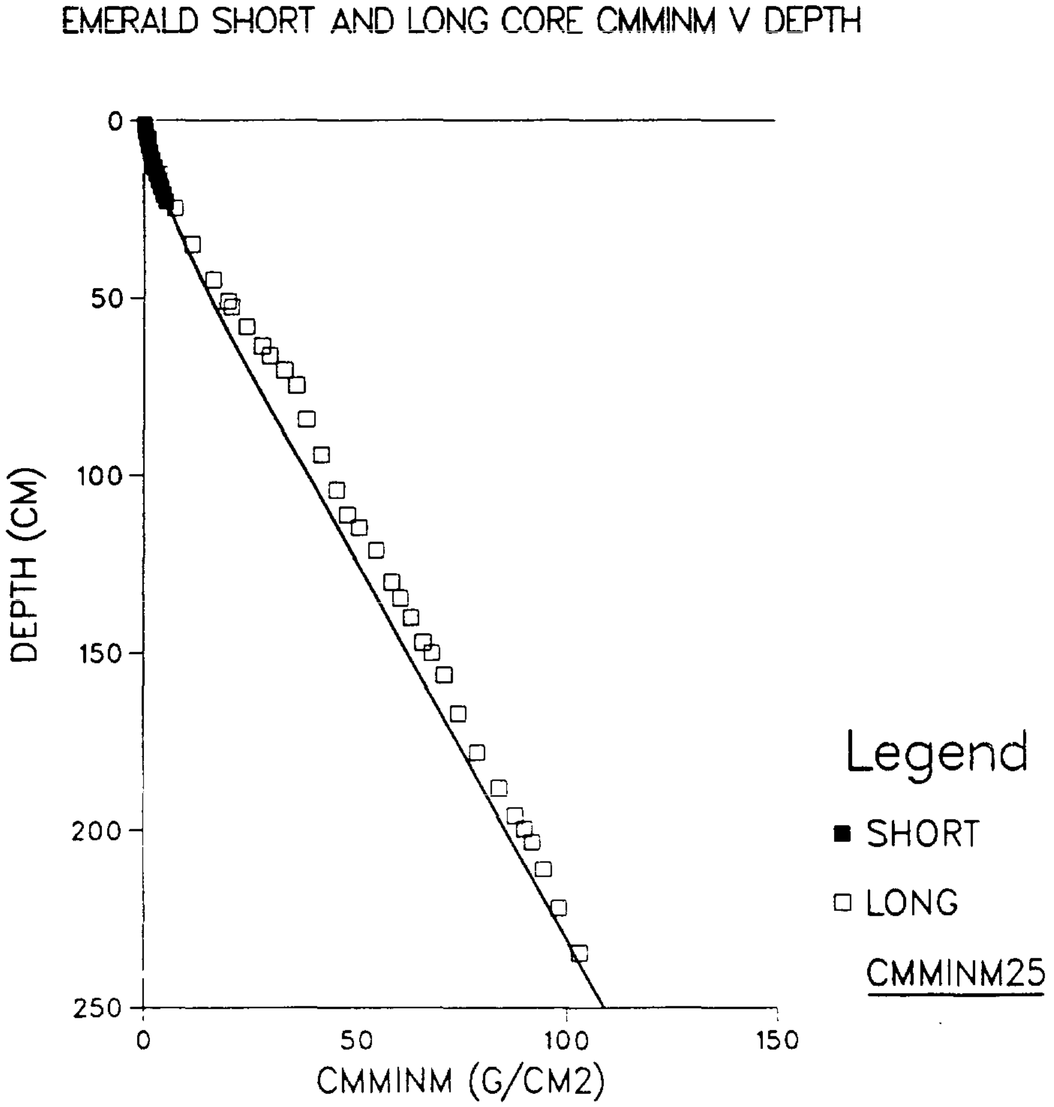

Figure 5. The measured (short and long) and modeled (CMMINm25) cumulative mineral matter vs. Sediment depth for Emerald Lake short and long cores.

Table 2. Measured sedimentation rates in the three lakes.

Lake	Date Deployed	Date Collected	Total Days	*n*	Total Sed. Rate (mg $cm^{-2}yr^{-1}$)	Organic Matter (%)	Mineral Sed. Rate (mg $cm^{-2}yr^{-1}$)
Eastern Brook	8/14/85	9/26/85	44	4	10.3±0.9	42.8±0.8	5.9±0.6
Eastern Brook	7/10/86	7/29/86	19	4	10.0±1.1	53.9±2.3	4.7±0.7
Emerald	9/5/85	10/2/85	27	4	5.6±0.7	38.5±5.9	3.4±0.2
Emerald	10/2/85	7/31/86	302[a]	4	71.9±0.8	23.4±0.2	55.1±0.6
Emerald	7/31/86	8/19/86	19	4	10.1±1.1	51.0±3.3	5.0±0.8
Mosquito	9/17/85	8/25/86	342	4	14.9±1.2	54.9±0.9	6.7±0.6
Mosquito	8/25/86	9/23/86	29	3	52.3±0.6	63.1±0.7	19.3±0.6

a. An avalanche occurred during this period.

Plus and minus numbers refer to one standard error of the listed means. Since the number of replicates (*n*) is four at most, pooled standard deviations were also calculated, with 20 degrees of freedom. They were 1.9 mg $cm^{-2}yr^{-1}$ for total sedimentation rate, 5.6% for percent organic matter, and 1.2 mg $cm^{-2}yr^{-1}$ for mineral sedimentation rate. Based on pooled standard deviations, the standard errors for the means of four samples are then 0.9 mg $cm^{-2}yr^{-1}$, 2.8%, and 0.6 mg $cm^{-2}yr^{-1}$; the standard errors for the means of three samples are 1.1 mg $cm^{-2}yr^{-1}$, 3.2%, and 0.7 mg $cm^{-2}yr^{-1}$.

2.3.2. Sediment Core Descriptions

2.3.2.1. Short Cores

In general, the short cores from the three lakes showed a high degree of morphological similarity. The surface of the cores had very low densities and were essentially a slurry. Since the cores were collected in the summer during oxygenated conditions, the cores from all lakes had at least a small amount of reddish brown precipitate at the immediate surface. This material, presumably an iron hydroxide, was most prominant in Mosquito lake. With increasing depth, the cores became denser and more consolidated with occasional gravels or twigs found randomly with depth.

2.3.2.2. Long Cores

The long cores, which represent extremely long time intervals relative to the 25 cm short cores, had a number of important strata. Morphological descriptions of the long cores collected from each lake are given below in Tables 2 to 4.

2.3.3 Laboratory Results

2.3.3.1. Porosity

The average porosities of short cores from Eastern Brook and Mosquito lakes were greater than that of Emerald (92 to 98 % vs. 83 to 95 %)(Fig. 6). In contrast, the long core data indicate that at greater depths, the Eastern Brook and Mosquito sediments were somewhat more compact than the Emerald sediments (as low as

Table 2. Morphological description of the Emerald lake long core.

Collection date:	9/23/86
Collected by:	Judy Charles, Bob Wise, Don Schwartz, Ron Amundson
Described by:	Ron Amundson

Section	Section Depth (cm)	Total Depth (cm)	Comments
A	0-10	0-10	high H_2O, high OM
	10-20	10-20	less H_2O, high OM
	20-30	20-30	less H_2O, high OM
	30-40	30-40	less H_2O, high OM
B	0-2	40-42	less H_2O, high OM
	2-3	42-43	indistinct ash
	3-13	43-53	low H_2O, high OM
	13-14	53-54	clean ash
	14-18.5	54-58.5	low H_2O, high OM
	18.5-22	58.5-62	clean ash
	22-27	62-67	low H_2O, high OM
	27-28	67-68	gravel
	28-39	68-79	low H_2O, high OM
	39-49	79-89	low H_2O, high OM
	49-59	89-99	low H_2O, high OM
	59-63	99-103	low H_2O, high OM
C	0-5	103-108	gravel
	5-13	108-116	low H_2O, high OM
	13-21	116-124	low H_2O, high OM
	21-22	124-125	gravel
	22-32	125-135	low H_2O, high OM
	32-36	135-139	low H_2O, high OM
	36-38	139-141	gravel
	38-48	141-151	low H_2O, high OM
	48-60	151-163	low H_2O, high OM
D	0-10	163-173	low H_2O, high OM
	10-20	173-183	low H_2O, high OM
	20-25.5	183-188.5	low H_2O, high OM
	25.5-27.5	188.5-190.5	indistinct ash
	27.5-33	190.5-199	low H_2O, high OM
E	0-10	199-209	low H_2O, high OM
	10-22	209-221	low H_2O, high OM
F	0-13	221-234	low H_2O, high OM

Table 3. Morphological description of Eastern Brook long core #2. Collected 7/13/86.

Section	Section Depth (cm)	Total Depth (cm)	Comments
A	0-3	0-3	mush
	3-8	3-8	very soggy
	8-13	8-13	mod. soggy
	13-18	13-18	a little soggy
	18-23	18-23	quite unconsolidated
	23-28	23-28	
	28-33	28-33	
	33-38	33-38	contains a 0.5 cm ash layer
	38-43	38-43	
	43-48	43-48	
B	0-83	48-131	- at 17.5 to 20 cm was an ash layer - core is dark brown
C	0-19	131-223	medium brown
	19-23		ash marbled with black
	23-32		dark brown
	32-32.5		dark band
	35.7-36.2		dark band - all organic parts have a greenish tinge
D	0-22	223-307.5	dark brown with hair at base
	22-33.5		lighter gray
	33.5-36		light gray band split by dark band
	36-55		medium gray
	55-64		slightly darker-gray brown
	64-84		medium gray
E	0-90	307.5-397.5	collected upper 69.5 cm

Section	Section Depth (cm)	Total Depth (cm)	Comments
F	0-4	397.5-447.0	mushy, gray and brown-gray
	4-10		gray
	10-27		brownish gray
	27-28.5		lighter gray
	28.5-28.7		thin, gray band
	28.7-30.7		thin, gray band
	31-31.5		gray, fine clay
	31.5-34.5		clayey, gray
	34.5-35		coarser, gray, sandy
	35-36.5		fine, gray, clayey
	36.5-37.5		very coarse sand layer
	37.5-46.5		fine clay and silt, gray
	46.5-48		coarser and darker than above
	48-49.5		fine
G	0-3	447-462	clay
	3-6.5		fine sand and silt
	6.5-8		clay
	8-9		coarse sand
	9-10.5		clay
	10.5-12		sand
	12-bottom		silt and fine sand

- All samples from Section G were gray

Table 4. Morphological description of Mosquito lake core #2.

Section	Section Depth (cm)	Total Depth (cm)	Comments
A	0-2.8	0-85.5	watery mush
	28-37.5		dark, greenish brown high in organisms
	37.5-47		lighter gray, high in OM
	47-48		dark band
	48-74		uniform, indistinct bands
	74-77		courser texture than above
	77-79		dark greenish brown with sand
	79-82		gray sandy
	82-83		lighter gray than above
	83-85.5		even lighter gray, sandy

- below 80 cm, fine varves 1-2 mm were present

- a second core section could not be taken

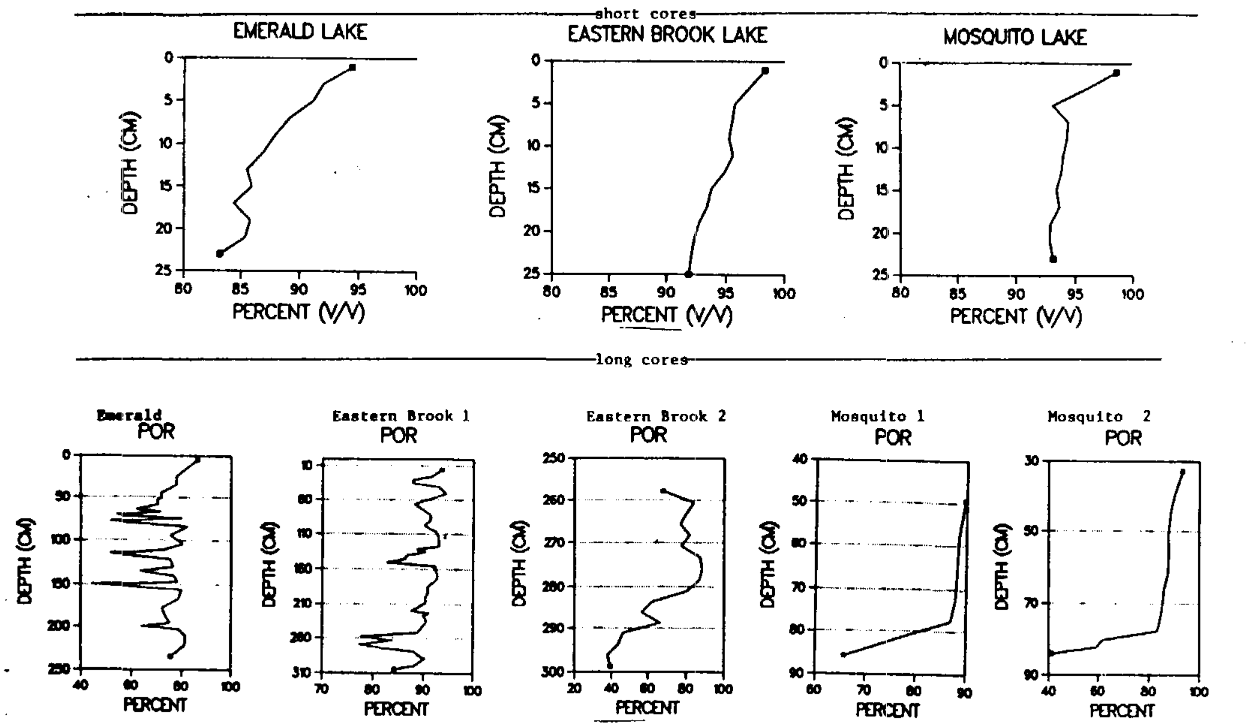

Figure 6. Sediment porosites of the short and long cores taken from the three lakes. The data are reported in % volume.

40% vs. about 75%)(Fig. 6). However, the variability in porosity that existed between long cores from the same lake indicate that these trends might be fortuitous.

2.3.3.2. Organic Matter

The total organic matter in the short cores was lowest in Emerald lake (~ 12 %) and highest in Mosquito lake (~ 20 %) (Fig. 7). In all lakes, the organic matter concentration decreased slightly with depth, indicating that decomposition processes are steadily removing C with increasing time.

The trends in total organic matter with depth in the long cores were more difficult to discern (Fig. 7). For Emerald and Eastern Brook cores, the OM concentration decreased with depth in the upper 50 cm of the sediments, but below that depth, sudden changes in OM appeared to occur randomly. Many of the sharp changes occur in conjunction with gravel lenses or ash layers (compare Fig. 8 to Fig. 7). Between these major stratigraphic breaks, it sometimes appeared that the OM decreased with depth although this trend did not hold true in every case. In Mosquito lake, and Eastern Brook lake core #1, the OM approached 0 % in the "glacial flour" which lies beneath the accumulated sediment. This flour, derived from outwash of the last alpine glaciation of the Sierra, dates back to the Pleistocene/Holocene boundary.

The organic C content of the long cores follows the same irregular patterns with depth as the OM content (Fig. 9). Since these two parameters were determined by separate analyses, they help substantiate that these patterns are real. Although some

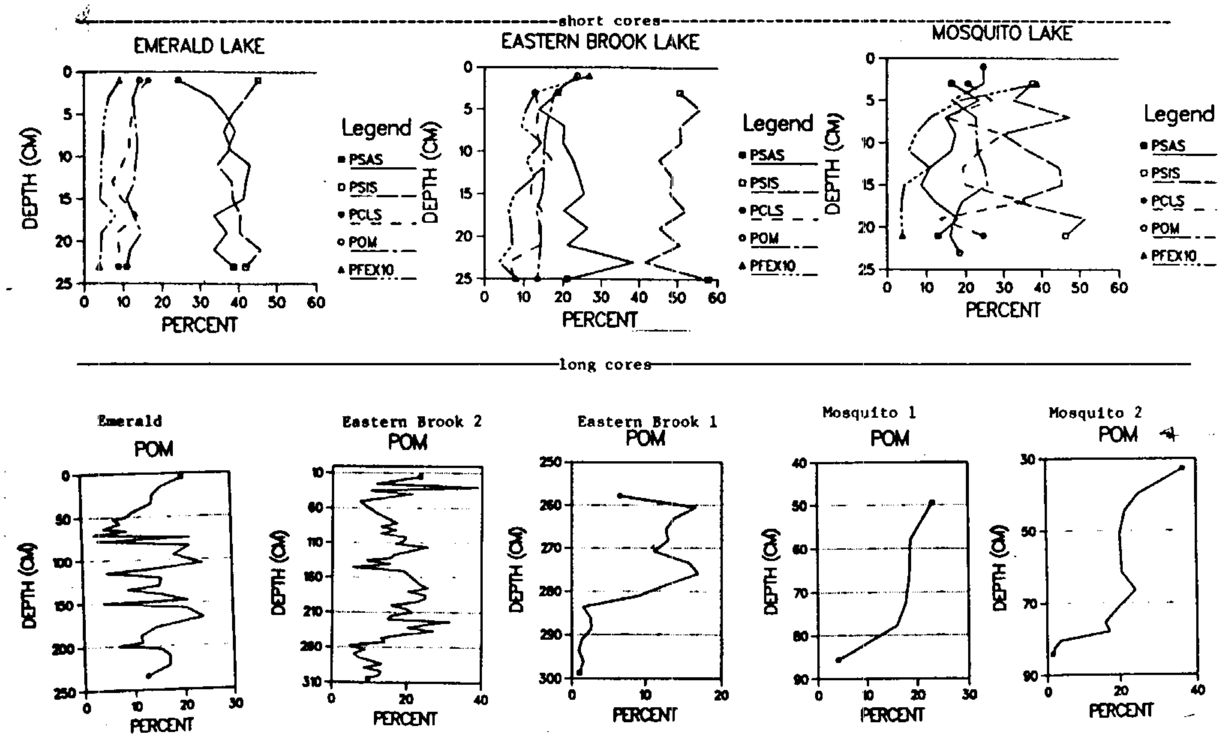

Figure 7. The total organic matter (POM) in the short and long cores from the three lakes. The legend for the short cores is PSAS = % sand, PSIS = % silt, PCLS = % clay, POM = % organic matter, and PFE x 10 = % Fe oxide x 10.

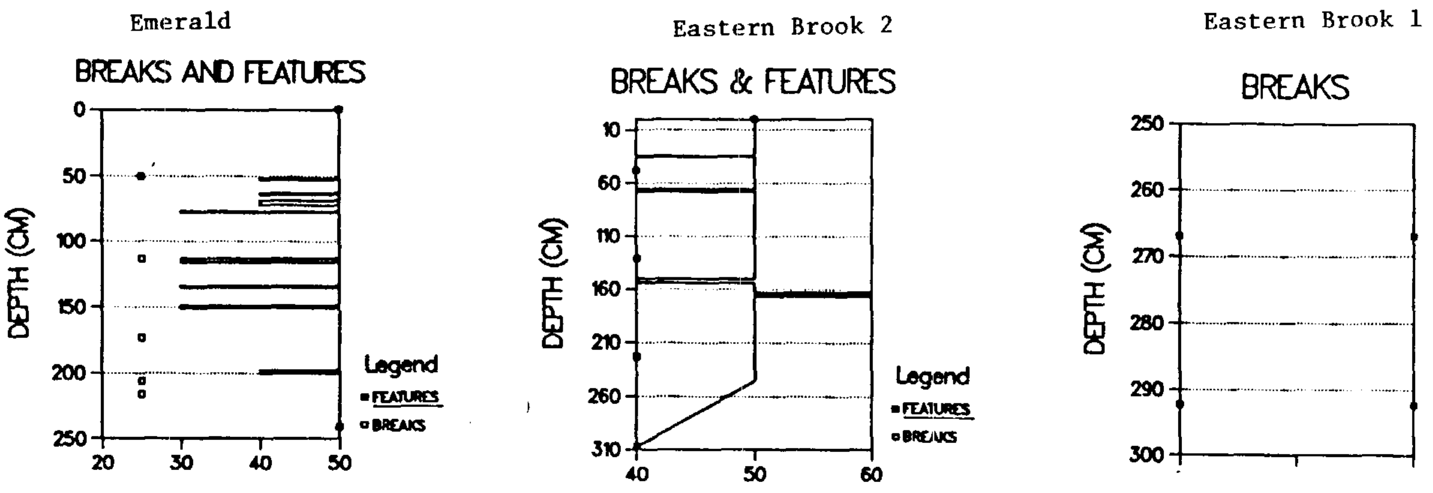

Figure 8. The breaks between core sections, and features (gravel lenses or volcanic ash), in long cores from Emerald and Eastern Brook lakes.

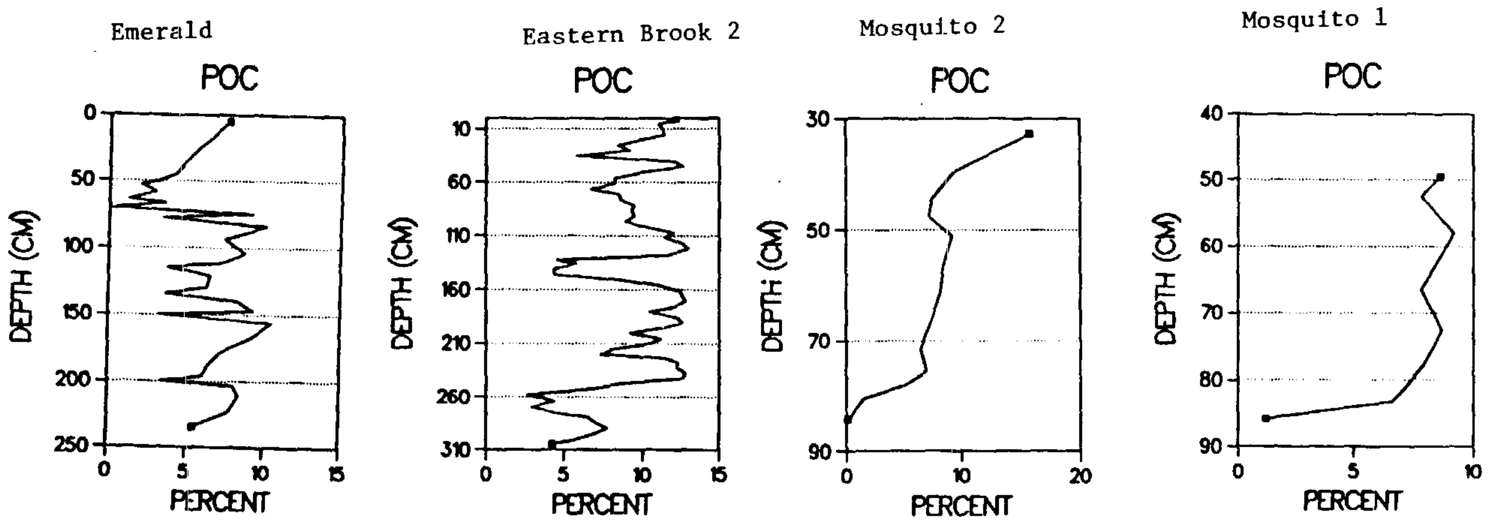

Figure 9. The organic carbon content (POC) of long cores from the three lakes.

scatter exists, it appears that the OM contains approximately 50 % C (Fig. 10).

As with organic C and OM, the organic N content of the cores decreased somewhat irregularly with depth although, in the upper portions of the cores, the concentration generally decreased with increasing depth (Fig. 11). In most cores, the C/N ratio ranged between 15 to 20 although in Eastern Brook lake, the deepest sediments had C/N ratios near 10 (Fig. 12).

The solid phase analyses do not have a neat unifying conservation principle which can serve as an indicator of analytical quality the way that charge balance serves as such an indicator for water analyses. However, the relationships just described between organic matter, organic carbon, and organic nitrogen do provide some internal checks of consistency. The similarity of the patterns with depth of organic matter and organic carbon, which were determined independently, is one such check, although there is no accepted criterion for deciding how similar they are or should be. Another indicator is the consistency of the carbon to nitrogen ratio in organic matter, since carbon and nitrogen were determined independently. While, again, there is no simple measure of how these ratios relate to the quality of analysis, they provide reassurance that gross systematic errors in analysis have not been made. They are also within the expected range for aquatic organic matter, as is the percent carbon of organic matter. The subsampling and analytical error for these and other measurements was based on replicate samples and is presented in Table 1.

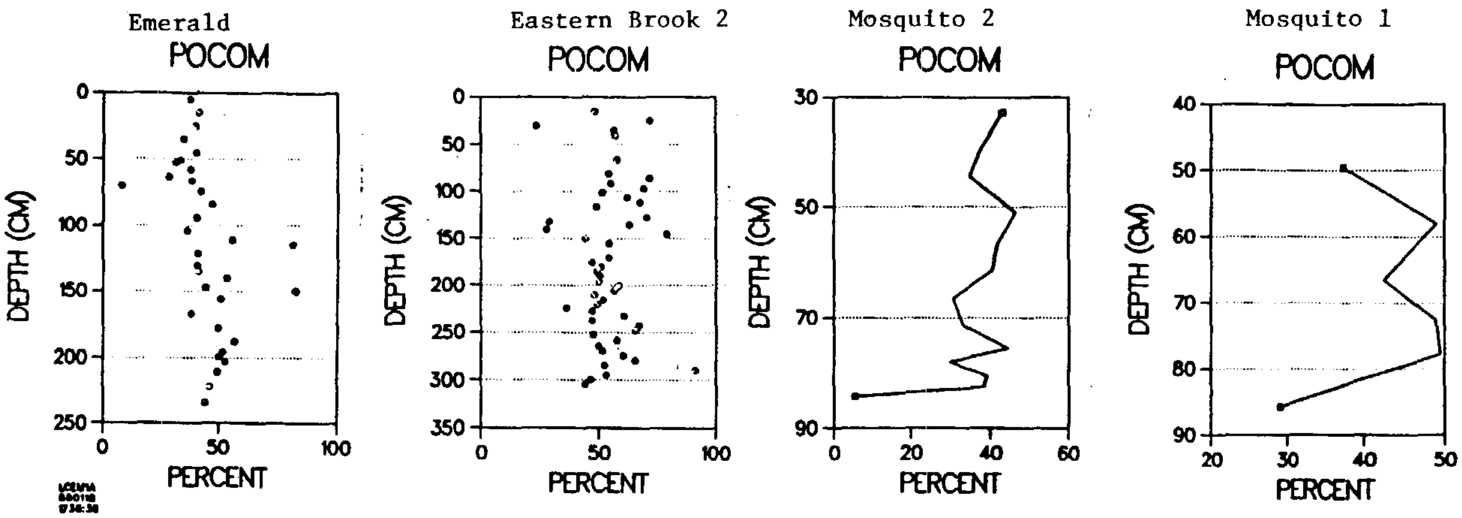

Figure 10. The ratio of organic carbon to total organic matter (POCOM) in long cores from the three lakes.

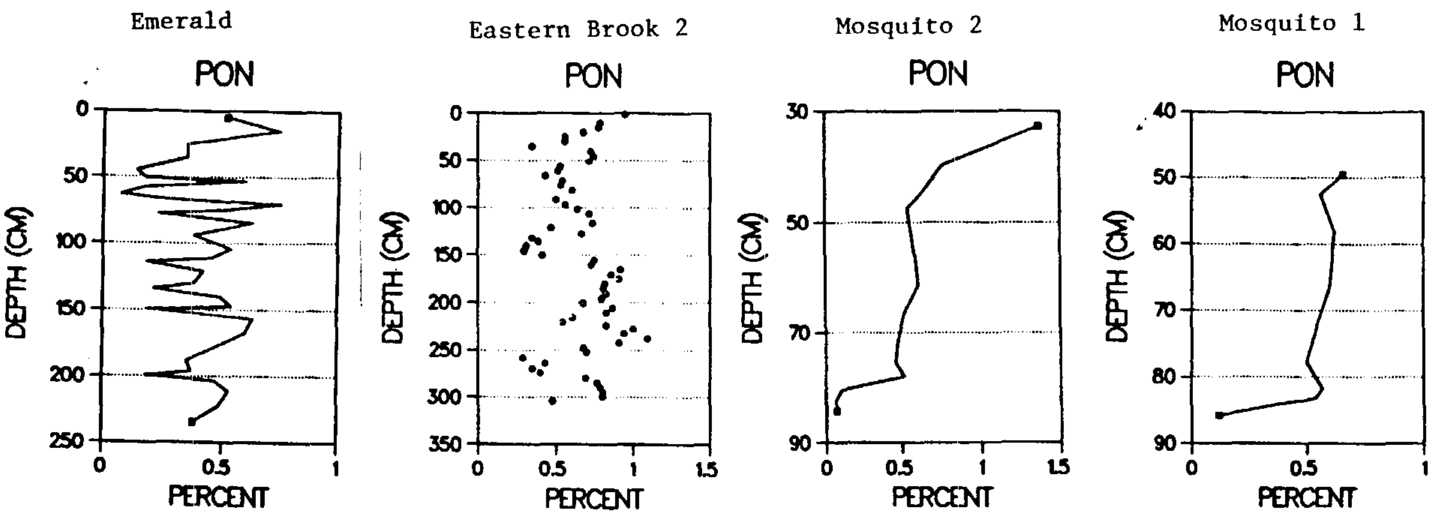

Figure 11. The organic nitrogen content (PON) in long cores from the three lakes.

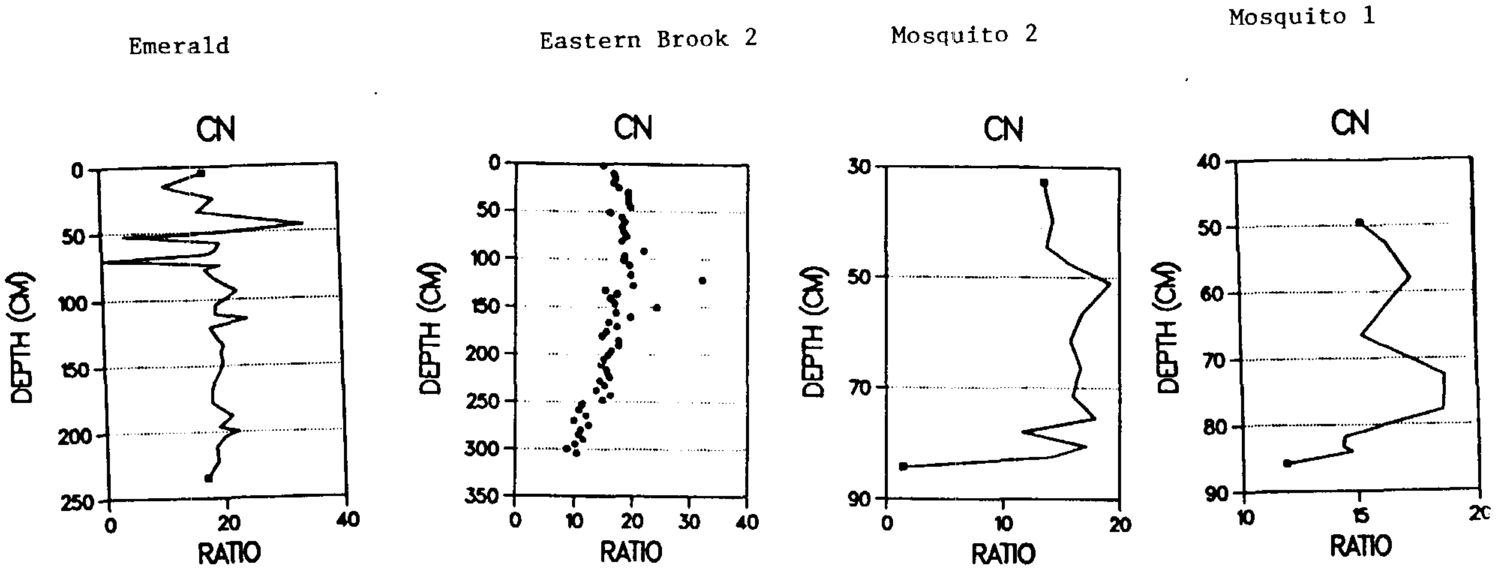

Figure 12. The carbon to nitrogen ratio (CN) of the long cores from the three lakes.

2.3.3.3. Iron and Manganese Oxide Content

In general, the iron oxide content of the short cores decreased with increasing depth (Fig. 7). In all 3 lakes, the concentration at 25 cm depth was about 0.5%. However, Mosquito had iron oxide contents up to 4.0 % at the sediment surface while Emerald lake, in contrast, had about 0.9%. These data correspond to visual observations made in the field which indicated that Mosquito lake had an extremely prominant layer of reddish brown precipitate at the sediment surface. This material was least visible in Emerald lake, corresponding to the iron data.

The iron oxide content of the long cores varied with depth in a manner which closely followed that of the organic C and OM (Fig. 13). Thus, it appears that much of the iron may be organically bound or in a mineral form closely associated with organic matter. In general, the actual range in concentrations with depth was small (about 0.8 %) but the highest concentrations were found near the surface (0.6 to 1.0 %) and the lowest concentrations were found near the base of the sediments (0.2 to 0.5 %).

Manganese oxide was present in extremely low quantities in the long core sediments (Fig. 14). In Eastern Brook long core #2, for which the most complete set of Mn analyses was obtained, the concentration decreased irregularly with depth from about 0.005 % near the surface to about 0.003 % near the bottom of the core. The limited number of samples, and high variability, in other cores make general trends difficult to discern.

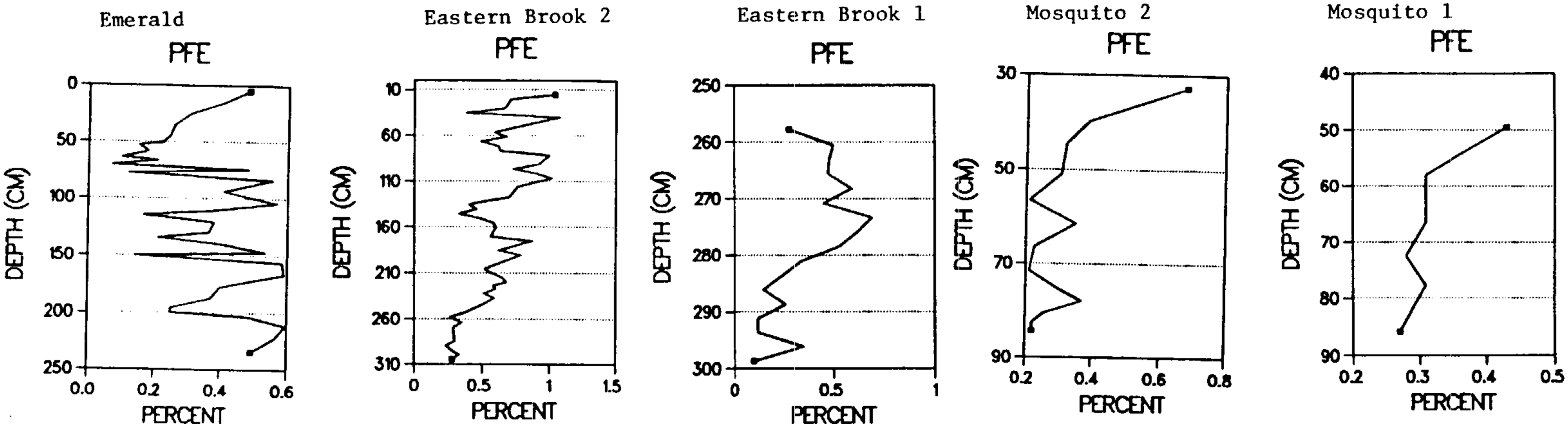

Figure 13. The iron oxide content (PFE) of the long cores from the three lakes.

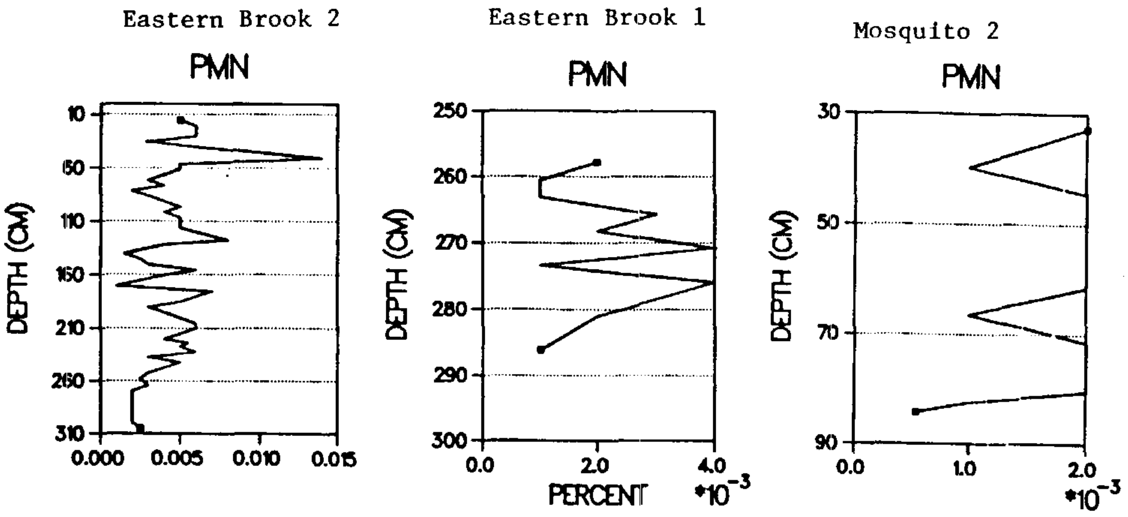

Figure 14. The manganese oxide (PMn) content of selected long cores.

2.3.3.4. Silicate Mineralogy of the Clay Fraction

The mineralogy of the clay fraction is of interest in weathering studies because this fraction generally contains the greatest abundance of weathering products in a given sample. The types of weathering products present indicate the intensity of the weathering environment while the relative amounts indicate how much weathering has occurred. In order to assess the effect of weathering from clay mineralogy studies, the original mineralogical composition of the sample must be known. In lake sediments, the minerals are ultimately derived from the soils of the watershed, which at least partially bear the imprint of their weathering environment.

In general, the clay fraction in the Emerald lake short cores was dominated by smectite and quartz, with kaolinite, mica, and vermiculite present in decreasing amounts, respectively (Fig. 15). It is interesting to note that the relative abundance of minerals near the top of the sediment column, which should represent the most recent contribution from the watershed, is about the same as at the lowest depth, indicating that measureable clay mineral alteration or additions are not occuring in the time span represented by the short cores (approximately 200 years). Even though the mineralogy does not reflect extensive weathering, it does indicate that the relative proportions of minerals added through sedimentation, with the exception of one point, has varied little over that time.

Quartz, which is one of the most abundant minerals in the

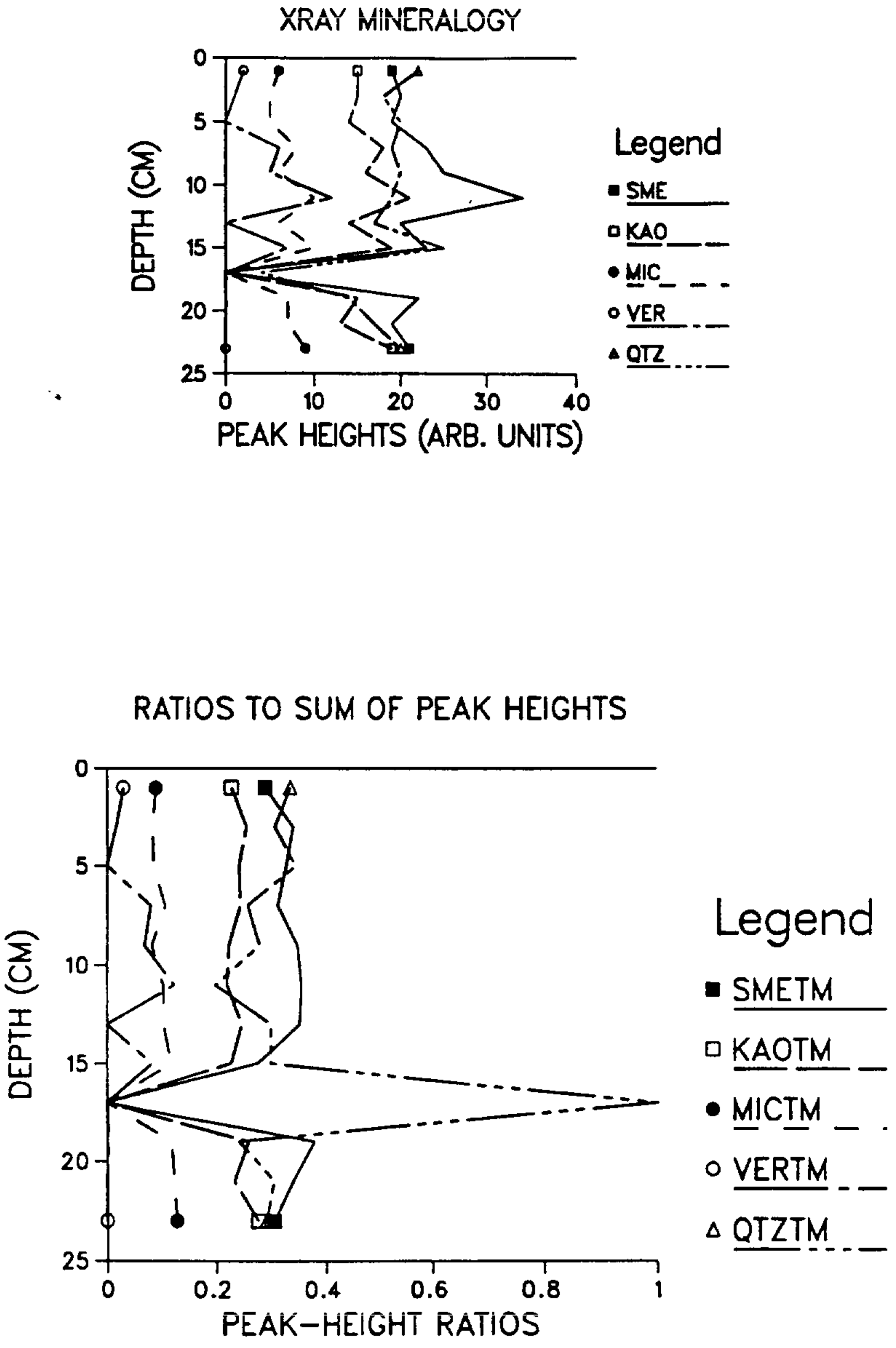

Figure 15. The silicate minerology of the clay fractions of the Emerald Lake short cores reported as the ratio of a given mineral to the total. SMETM = smectite, KAOTM = kaolinite, MICTM = mica, VERTM = vermiculite, and QTZTM = quartz.

sediments, must be derived from the bedrock of the watershed since it is not a weathering product. Since the watershed is dominated by intrusive igneous rock, which has relatively large crystals, some physical weathering has occurred to reduce the quartz to clay size particles (< 2 um). Smectite, which is a secondary mineral, is not derived from the bedrock and is probably the weathering product of plagioclases and primary micas (Borchardt, 1977). Kaolinite, which is also a weathering product, is lower in Si and cations than smectite and is usually associated with more intensive leaching and weathering than is smectite. The mica in the clays is derived from the bedrock and has undergone some physical weathering to reduce its particle size to that of the clay fraction. The mica is undoubtedly biotite or a slightly weathered form of that mineral. Vermiculite is commonly found as a weathering product of mica (biotite) in soils of the Sierra Neavada (Barshad, 1966). The alteration step usually involves the oxidation and partial removal of structural Fe and the partial loss of K from layers between mineral platelets.

Although the mineralogical assemblage appears to be typical of Sierran soils, the relative abundance is somewhat unusual (Barshad, 1966). For Sierran soils receiving precipitation similar to that of the Emerald lake area, kaolinite rather than smectite should be the dominant secondary soil mineral. Mica and vermiculite have been found in relatively similar proportions. The large relative abundance of smectite in Emerald lake sediments therefore might be an artifact of the selective transport of smectites from the soils to the sediments.

In general, the chemical composition of the clay fraction from short cores of the three lakes was similiar (Fig. 16). Silica (not shown on the diagrams) dominated the chemistry since the clay was dominated by silicate minerals and also because of the presence of diatom fragments in the samples. Aluminum comprised approximately 4 % of the samples while Fe, Ca, and Mg were found in order of decreasing abundance. As with X-ray mineralogy, there was little evidence of consistent change in chemistry with depth as a result of mineral weathering processes.

2.4. Discussion

2.4.1. Organic matter decomposition

Organic matter is the one solid phase parameter which appeared to change rapidly enough to measure the change with depth. Figure 17 shows percent OM of mineral matter (POMM) against CMMINM25, which is a surrogate for time. POMM is used instead of COM (concentration of organic matter in wet sediments (g/cm^3)) or POM (percent organic matter of total solids), because it is the parameter which 1) is not affected by compaction (unlike COM which actually tends to increase with depth due to compaction) and 2) changes in direct proportion to the change in mass of organic matter in a unit of sediment (unlike POM whose change depends on the relative amounts of mineral and organic matter). The following equations clarify these definitions and relationships:

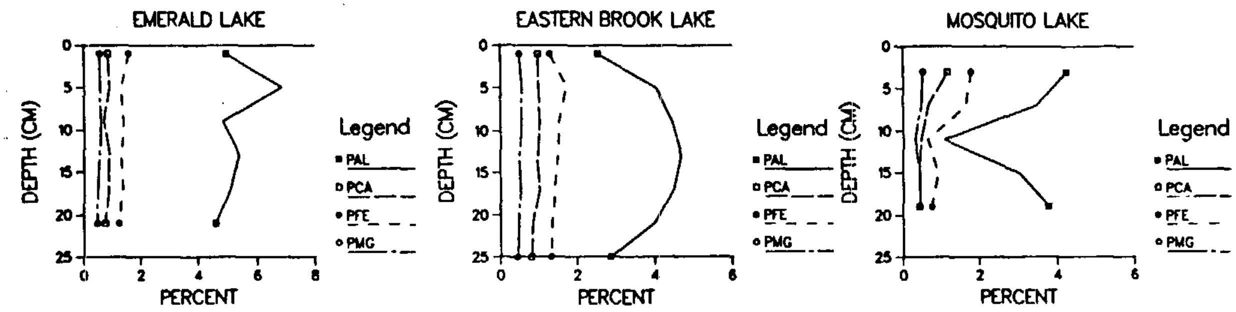

Figure 16. The chemical composition of the clay fractions in short cores from the three lakes.

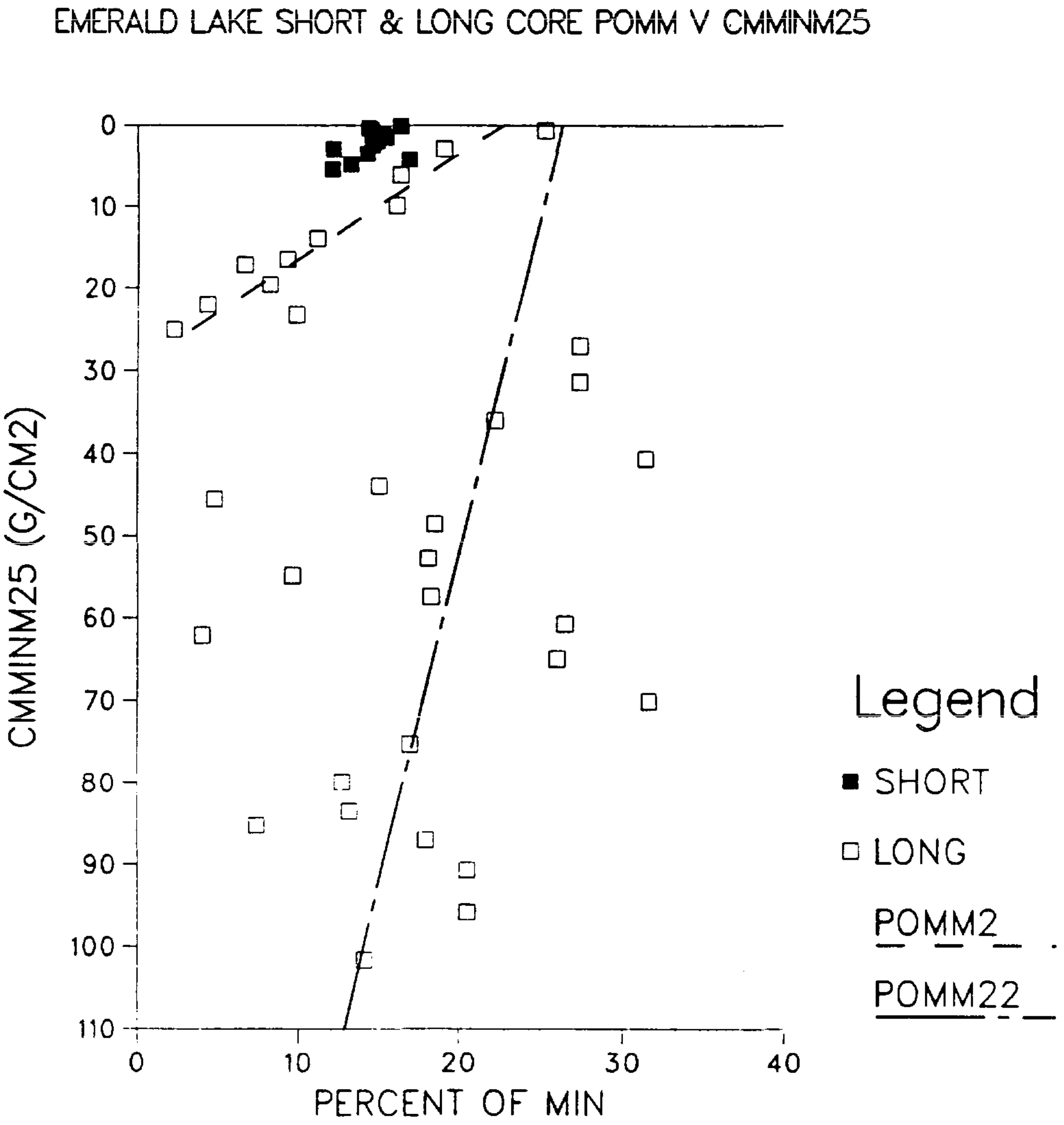

Figure 17. The percentage of organic matter in the mineral fraction (percent of min) vs. the cumulative mineral accumulation of Emerald Lake sediment cores.

POM = 100 x COM/(CMIN + COM)

POMM = 100 x COM/CMIN

The data in Figure 17 show a rather confusing rate of change for organic matter. Above 72 cm, POMM changes rapidly with depth, with a zero order rate constant of 0.77 POMM per CMMINM. Multiplying this by the SR of 0.030 g/yr, the rate constant is 0.02319 POMM per year. Since POMM starts out at about 31%, organic matter should totally disappear from the sediments in about 1,300 years. Indeed, from the data in Fig. 17, the organic matter does almost disappear by that time but, at greater depths, the organic matter concentration increases.

The irregular pattern of C beneath 72 cm is probably good evidence for a nonconstant deposition rate over the history of the lake. It is also possible that different decay rates prevail at different depths due to differences in the character of the OM. The C/N ratios of OM, along with lignin content, is one of the most important factors controling the decomposition of organic matter (Tate, 1987). As the data in Fig. 12 indicate, there is very little evidence for a dramatic difference in the C/N ratios, and presumably the decomposability, of the OM through the entire length of the sediment core. Therefore, it seems unlikely that the unexpected distribution of OM with depth is the result of differences in the decomposability of the OM. While differences in the rate of decomposition may vary with depth, they would not be expected to result in the rather irregular change in OM with depth. The most probable explanation is that the organic matter variability with depth is largely a result of random depositional events and unknown variations in lake productivity.

Predicted OM concentrations using a steady state computer model were compared to the measured data (Fig. 17). The model used COM rather than POM. The model was run assuming a constant deposition rate and using the previouly derived burial rates (SR/CMIN25) and a decomposition rate calculated from the OM in the upper 72 cm of the core (0.77 POMM x SR/CMMINM25). The results for CMIN, POR, and COM are shown in Figures 18, 19, and 20, respectively. The model calculations fit the actual organic matter data well for the upper 72 cm but beneath that depth suggest continual decrease with depth until nothing is left (Fig. 20).

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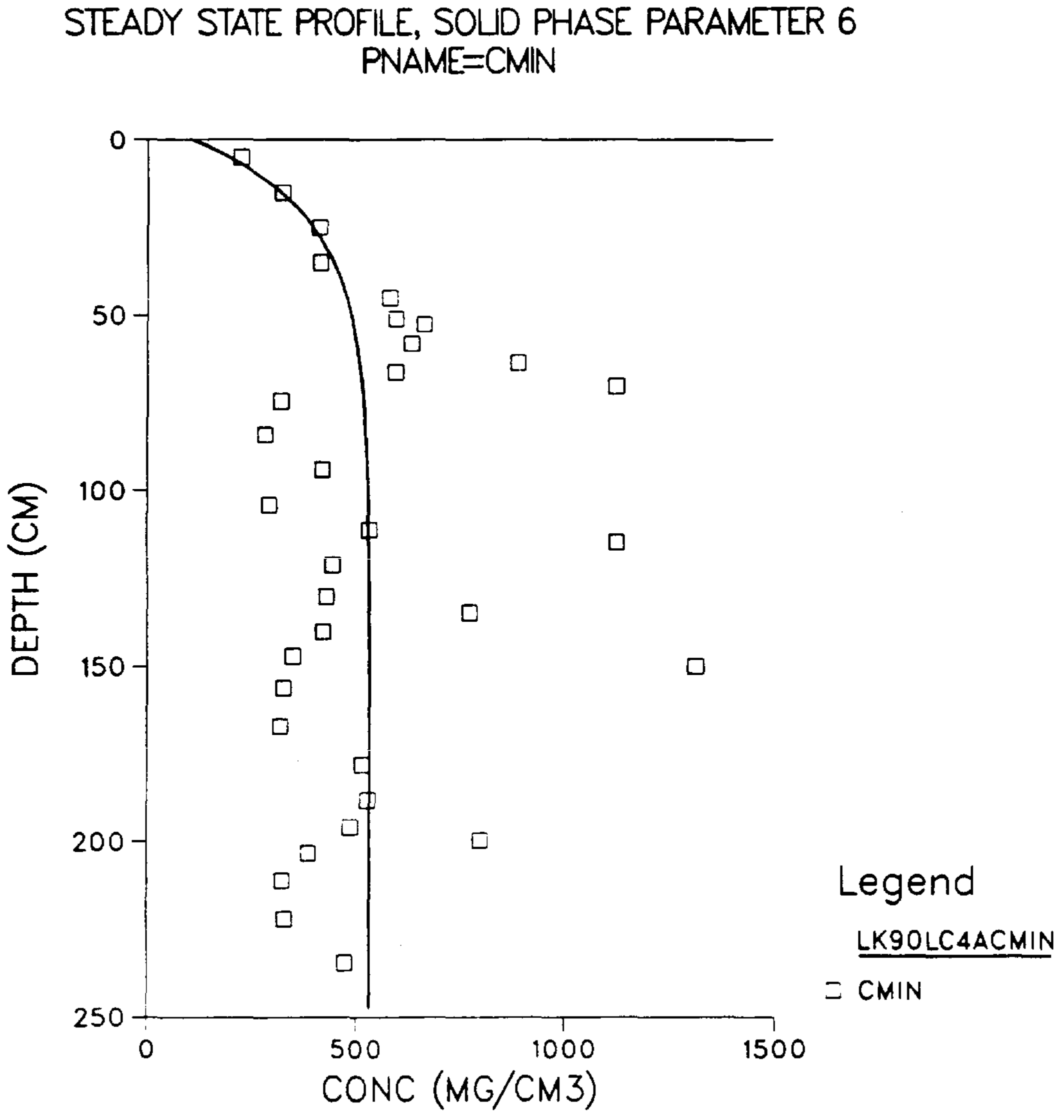

Figure 18. The measured (CMIN) and modeled concentration of mineral matter (CONC) vs. depth in the Emerald Lake long core.

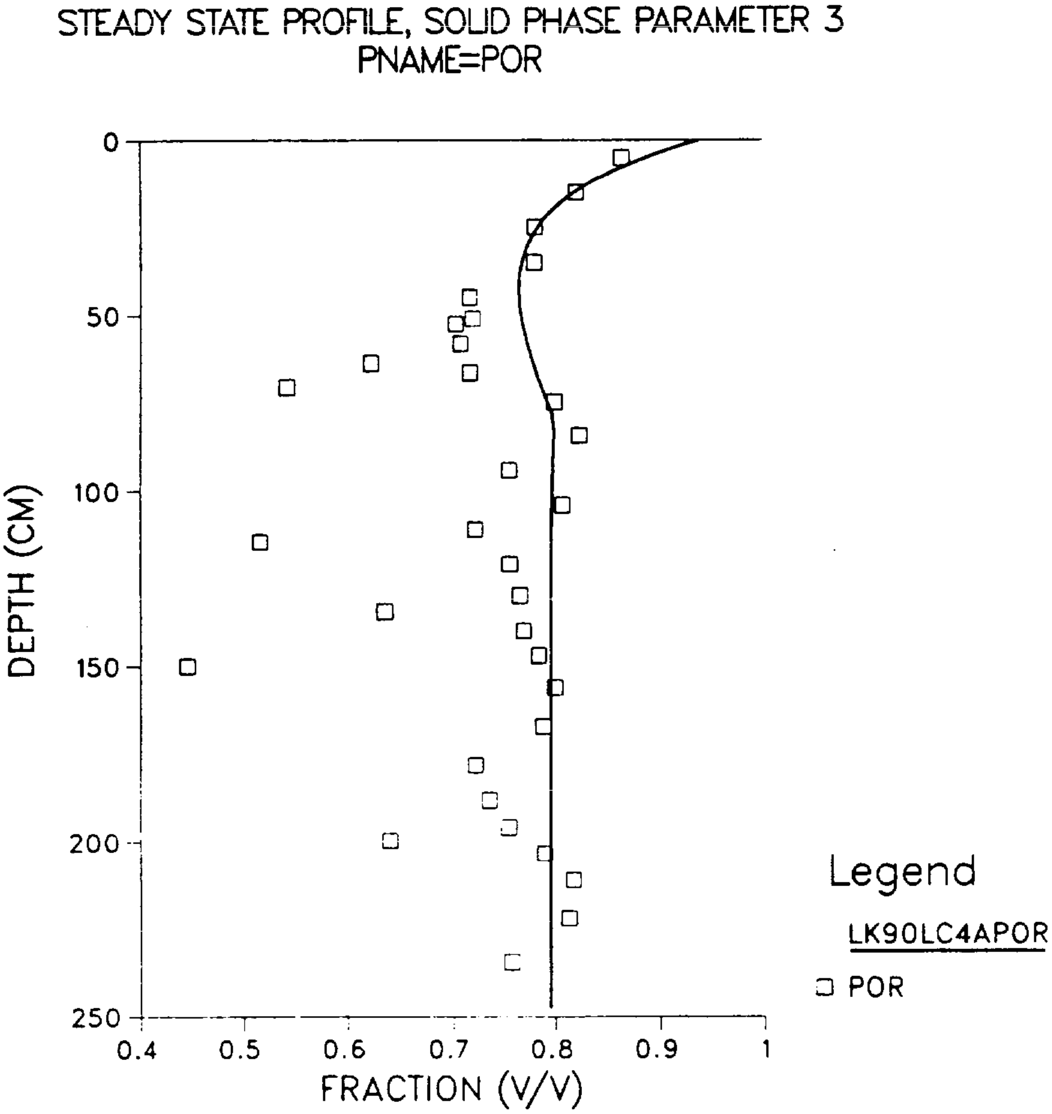

Figure 19. The measured (POR) and modeled porosity (fraction) vs. depth in the Emerald Lake long core.

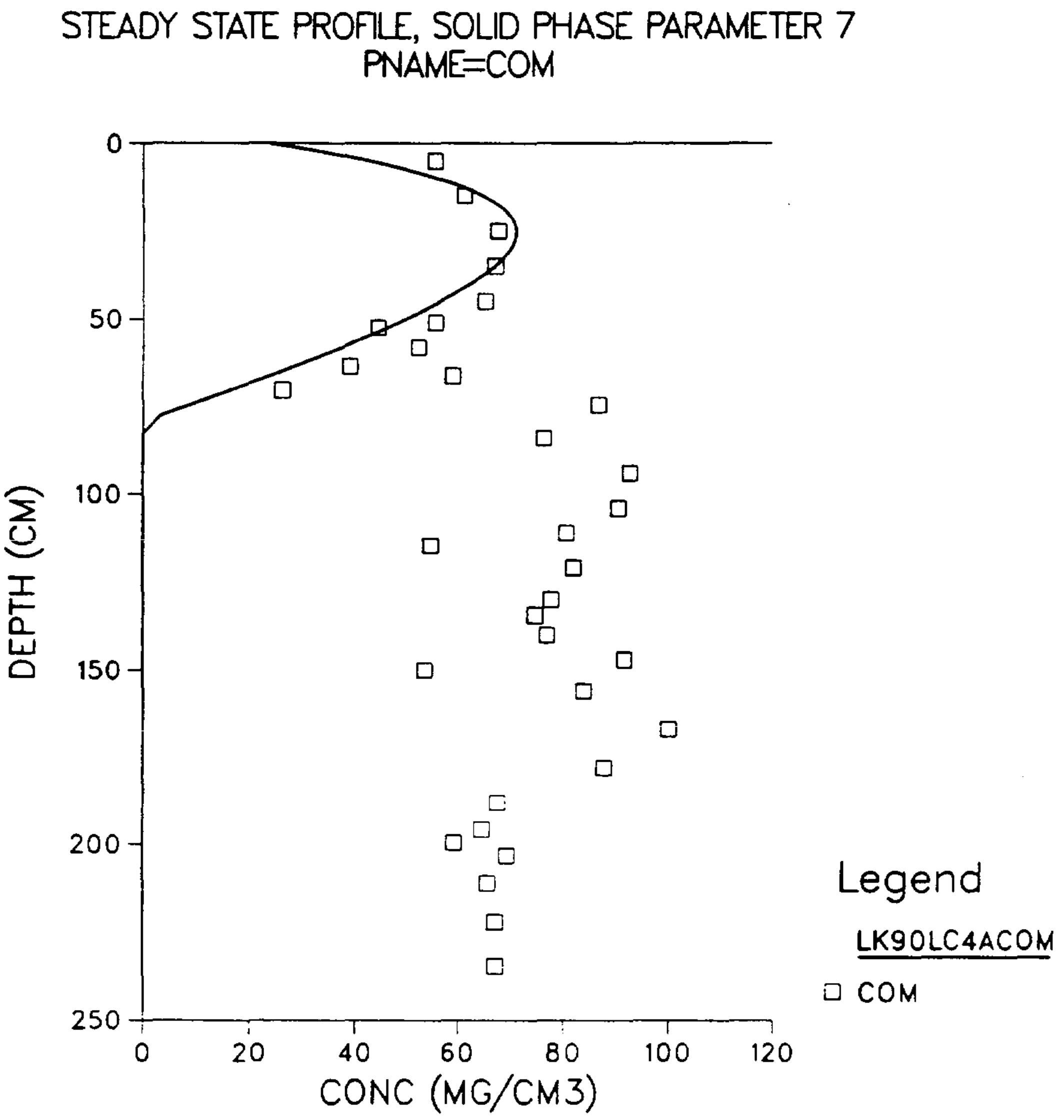

Figure 20. The measured (COM) and modeled concentration of organic matter vs. depth in the Emerald Lake long core.

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