ROLE OF CALCIUM CARBONATE PRECIPITATION IN LAKE METABOLISM

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W. Sedgefield White

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Major professor
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O-7639

ABSTRACT

ROLE OF CALCIUM CARBONATE PRECIPITATION IN LAKE METABOLISM

By

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During a two year period analyses were made every other week on seston collected at three depths in a small hard-water lake in southwestern Michigan. The seston was analyzed for total dry weight, organic material, calcium carbonate, and ash content. During the second year seasonal changes in sestonic particulate organic carbon, Kjeldahl nitrogen, and total phosphorus were assayed.

Organic material and ash content of the seston was similar both years, but the calcium carbonate content was five times greater in the second year than in the first. The dissimilarity in calcium carbonate precipitation between the two years was related to degree of vernal circulation and calcium ion concentration in the water column when the ice broke up. During the study an improved sediment trap was designed and constructed. The trap had replicated, discrete upper and lower sections, which permitted correction for attached and non-sedimenting matter.

Investigation of calcium ion concentration by flame atomic absorption and a calcium ion electrode revealed an average of 36.7 mg 1^{-1} of colloidal calcium was suspended in the lake during 1973.

W. Sedgefield White

Measurements on total phosphorus content in the seston showed there was a marked displacement of phosphorus out of the epilimnion into the metalimnion during July and August. The displacement of phosphorus, among other factors, stimulated algal growth in the metalimnion.

Laboratory experiments suggested the availability of iron and vitamin B_{12} to algae were related to the precipitation of calcium carbonate in hard-water lakes. Iron was not adsorbed directly onto particulate calcium carbonate; instead, the availability of iron may be regulated as calcium carbonate precipitates natural chelator compounds from the trophogenic zone. In contrast, a significant proportion of available vitamin B_{12} was removed in association with the precipitating calcium carbonate.

ROLE OF CALCIUM CARBONATE PRECIPITATION IN LAKE METABOLISM

By

W. Sedgefield White

A THESIS

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Dr. Ellis willingly gave constructive advice and help in the x-ray diffraction analyses, thermal analysis, surface area determinations, and calcium electrode determinations.

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Figure Page

Figure Page

I. INTRODUCTION

A. Sedimentation in Lakes

Initial investigations on lake sediments by Heim (1900) stimulated a more detailed consideration of this topic, and a number of studies were undertaken after Nipkow (1920) disclosed and successfully reconstructed conditions that led to stratified sediments in Zurichsee. These studies have provided valuable information on the physicochemical quality, as well as the quantity of seston reaching the bottom of lakes (Reissinger, 1932; Scott and Miner, 1936; Wilson, 1936; Rossolimo, 1937; Pechlaner, 1956; Hohne and Olrich, 1966; Ludlam, 1967; Heinemann, Rausch and Campbell, 1968; Emery, 1973). Rates of seston mineralization and nutrient release from the sediment has received attention (Mortimer, 1941-1942; Kleerekoper, 1953; Hayes, 1964; among others). Biological investigations of the sedimenting seston and sediment have given attention to both algae (e.g. Conger, 1942; Järnefelt, 1955; Tutin, 1955) and zooplankton (e.g. Frey, 1960). Although the resulting profusion of ecological information deduced from seston and sediment core analysis has revealed valuable information about past production rates, close study has not been accorded factors controlling contemporary production.

In contrast, Thomas (1950, 1951, 1955a, 1955b, 1956) used a specially designed sediment pan to collect and investigate sedimenting seston during short periods of time. His investigations demonstrated phytoplankton mineralization rates, settling rates of particulate matter, and the removal of nutrients from the trophogenic zone influenced the productivity of lakes. These studies inferred seston can function in a regulatory manner in the total operation of an aquatic ecosystem.

When a detrital food chain was proposed (Odum, 1962, 1963; Odum and de la Cruz, 1963), additional importance of detritus in the structure and function of an ecosystem was implied. Many limnologists were already aware of seasonal variations in the quantity and quality of dissolved and particulate organic detritus in lakes, and studies on seston expressed this awareness (e.g. Lawacz, 1969, 1970; Moss, 1970). The wealth of new information about dissolved and particulate organic detritus in seston prompted an IBP-UNESCO symposium on detritus in Pallanza, Italy during 1971. Although considerable diversity existed among the data presented at this meeting, there was general agreement on two major points. First, there is an important detritus pathway, parallel to the grazing pathway, in which energy from dead animal and plant material is transferred to microorganisms. Second, energy partition in an aquatic ecosystem can be influenced and/or regulated by the detritus component of seston.

Sedimentation is the major mechanism for transport of detrital organic matter; accordingly, sedimentation determines the distribution of metabolism within the aquatic system, and is one method by which the components of the aquatic ecosystem can be influenced and/or regulated.

Sedimentation rates of particular seston components are explored in the present work. The sedimentation of calcium carbonate is especially important here, since it is a major fraction of the inorganic component of seston in hard-water lakes. Detrital organic compounds and metabolically important nutrients in the seston can be absorbed and coprecipitated with calcium carbonate as it precipitates from the trophogenic zone.

B. Sedimentation of Calcium Carbonate in Hard-Water Lakes

Investigations by Ohle (1934) on hard-water lakes in northern Germany, have demonstrated that concentrations of calcium and bicarbonate in the epilimnion exceed what would be anticipated at equilibrium and normal atmospheric partial pressures of carbon dioxide. This apparent supersaturation with calcium carbonate exists in Lawrence Lake, a small hard-water lake of southwestern Michigan, and has been reported in other studies as well (Steidtmann, 1935; Brunskill, 1969; Wetzel, 1973).

Special significance is assigned to the particulate and colloidal carbonate when supersaturation exists, since biochemical reactivity and adsorptive capacity is a function of surface area. One must acknowledge coprecipitation and adsorption both proceed in a complicated manner; nevertheless, calcium carbonate sedimentation can coprecipitate important nutrients e.g. iron, phosphorus (Otsuki and Wetzel, 1972; Wetzel, 1972) and adsorb dissolved organic compounds e.g. lipids, yellow humic acids, amino acids (Suess, 1968, 1970; Meyers and Quinn, 1971; Wetzel and Allen, 1972; Otsuki and Wetzel, 1973).

Hard-water lakes are well buffered at pH 8.0-8.4 and alkalinity varies between 2 - 5 meq liter^{-1}. Concentrations of metabolically important nutrients such as iron and phosphorus, are markedly low in hard-water lakes; however organic and inorganic nitrogen may occur at high levels (Manny, 1971). Indirect evidence would indicate (Schelske, 1962) that the low levels of naturally occurring chelating agents e.g. dissolved organic matter, in marl lakes may be one factor limiting productivity. Wetzel (1965, 1966a, 1966b, 1968, 1972, 1973) has given evidence that particulate and colloidal calcium carbonate can effectively inactivate certain labile organic compounds, reducing bacterial metabolism and subsequently disrupting the regeneration of organic and inorganic material which ultimately results in reduced productivity. The high concentration of calcium carbonate in the sedimenting seston of Lawrence Lake (Rich, 1970a; Miller, 1972; Wetzel et al., 1972) offered the opportunity to investigate the alleged relationship with sedimenting seston, and to determine the temporal sequence in which nutrients are utilized by the phytoplankton and/or precipitated from the trophogenic zone.

C. Description of Lawrence Lake

Lawrence Lake is situated along the southern boundary of Barry County in southwestern Michigan and is located about 2.1 km east of Hickory Corners.

The local topography that is part of the southern outwash apron of the Kalamazoo moraine (Leverett and Taylor, 1915) and the morphometry of the lake basin indicate that Lawrence Lake is a kettle lake. Lawrence Lake is a small (4.96 ha), deep (12.6 m), hard-water

lake surrounded by a watershed roughly 7 times larger than the surface area of the lake. Glacial deposits upon the outwash apron contain deposits rich in limestone, thus calcium is the predominate cation in the drainage to the lake. Two small spring-fed brooks and several submerged springs along the shoreline supply drainage to the lake. A single outlet is located in the south by southwest corner of the lake and drains through a marsh into Augusta Creek.

Lawrence Lake has a mean depth of 5.89 m, a volume of 292,000 m^3, and a shore development of 1.29. An extensive marl bench exists along the littoral zone, and has been dredged in the past for lime kiln and agricultural use (Rich, 1970b).

The lake water is well buffered at a pH of 8.0 to 8.5 by the CO_2 - HCO_3^- - CO_3^{2-} equilibrium system. Divalent cation concentrations are high, especially calcium ion, which varies between 50 to 90 mg $liter^{-1}$. In contrast, monovalent cation concentrations are very low. The alkalinity ranges from 2 to 5 meq $liter^{-1}$, and the specific conductance varies between 300 and 600 µmhos cm^{-1} (25C).

Phytoplankton production rates are moderate to low, indicating the relative oligotrophic state of Lawrence Lake (_cf_. Wetzel, _et al_., 1972).

D. Objectives of Study

Elementary goals in this study were to establish seasonal variations in the quantity and precipitation rates of organic matter, calcium carbonate, and ash during a two year period. The investigation of calcium carbonate precipitation rates included a determination of colloidal calcium carbonate, measured by differences between dissolved alciu

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calcium (ionic) and total calcium. These goals were strengthened by differential thermal analysis, x-ray diffraction, and scanning electron micrographs of the sedimenting seston.

Correspondingly, the content of organic matter, calcium carbonate, ash, particulate organic carbon, Kjeldahl nitrogen, and total phosphorus was assayed in the sedimenting seston during the second year to ascertain the dynamics by which metabolically important compounds are removed from the trophogenic zone.

A collateral goal in this study was to conduct laboratory experiments on the association of iron and vitamin B_{12} with calcium carbonate to corroborate field observations on nutrient interactions with precipitating calcium carbonate.

II. MATERIALS AND METHODS

A. Sampling Schedule

Sedimentation traps were placed at 2, 6, and 10 meter intervals on a cable between an anchor and surface buoy, located at the central depression (Station A) in Lawrence Lake (Figure 1). These depths were chosen since each was located in the epilimnion, metalimnion, and hypolimnion, respectively. All collections were taken biweekly, except for the spring of 1972 and 1973, when collections were made weekly.

B. Sediment Traps

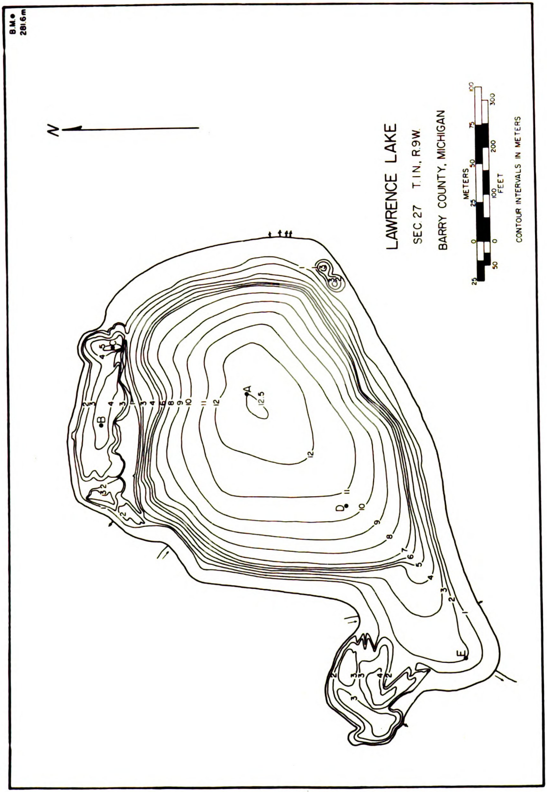
The sediment traps used in this study are described in detail elsewhere (White and Wetzel, 1973). The collection chambers were made from Schedule 80 polyvinylchloride (PVC) pipe (Figure 2). Upper and lower chambers were formed when each threaded end of the PVC pipe was turned into a PVC coupling, which contained two rubber stoppers inserted between acrylic plastic disks. The suspension rack was made from acrylic plastic, two support bases (Flexaframe Foot, Fisher Sci. Co.), an aluminium support rod, and two Flexaframe hook connectors.

The rack was placed upon a support cable by a hook connector attached to the support rod, which firmly presses the support cable against the support rod when it is tightened. The lower spring clip rests on a line clamp attached to the suspension cable.

Before the traps were removed from the lake, No. 10 rubber stoppers were inserted into the bottom of each collecting chamber. The

Figure 1.--Morphometric map of Lawrence Lake, Barry County, Michigan. Sediment traps were located at Station A.

Figure 1


B.M. 281.6m
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SEC 27 T.1N., R.9W.
BARRY COUNTY, MICHIGAN
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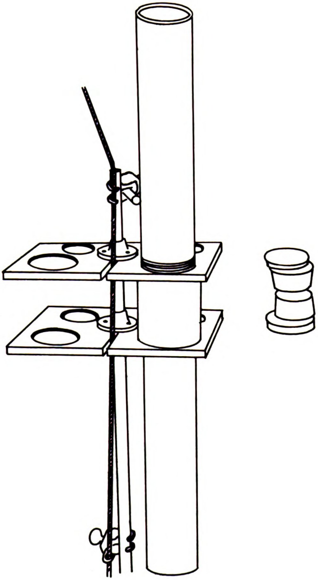
Figure 2.--Diagram of sediment traps showing construction and method of attachment.

Figure 2



water and sediment in the collecting chamber were poured into containers and transported back to the laboratory for analysis. Corrections for attached and non-sedimenting total phosphorus, Kjeldahl nitrogen, particulate organic carbon, and loss on ignition, were made by subtracting the quantity in the lower chamber from the quantity contained in the upper chamber. This correction was particularly significant in the total phosphorus and Kjeldahl nitrogen determinations.

C. Physicochemical Characterization of Seston

The sedimented seston from the traps was filtered onto precombusted (525C) glass fiber filters (984 H Reeve Angel) of 0.3-0.5 μm porosity (Sheldon, 1972) for all the chemical analyses. Throughout this study, the word seston is used according to Kolkwitz (1912) and includes both living and non-living particulate components.

During 1972, sedimenting seston was collected from each of four upper and lower chambers of the traps. The total dry weight of seston was determined after filtering the contents of each upper and lower chamber onto individually weighed, precombusted glass fiber filters. The filters were placed into separate precombusted (950°C), weighed combustion boats; dried at 105°C for 24 hours; cooled under desiccation and then weighed to ± 0.05 mg. Each sample was heated at 550°C for one hour, cooled under desiccation, and reweighed to determine loss on ignition for an estimate of organic weight. Finally, each sample was heated at 950°C for 3 hours, cooled under desiccation, and reweighed to determine the calcium carbonate content from the loss of carbon dioxide. The quantity of calcium carbonate was determined by multiplying the carbon dioxide loss by 2.274. The ash content was determined

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by subtracting the combined weights of calcium carbonate and organic matter from the total dry weight of the seston.

Ignition temperatures were selected after differential thermal analysis (DTA) was performed on seston collected in the traps and sediment retrieved from the lake bottom. The water content of sedimenting seston (Figure 3) is removed between 50° and 200°C. Some of this water content may have been water of hydration, thus it was not removed until the temperature was above 100°C. Organic material was decomposed between 200° and 600°C, and the more refractory calcium carbonate decomposed between 750° and 900°C. In comparison, water content in sediment (Figure 4) is lower and is removed between 75° and 150°C. The area under each curve shows quantitative information on the materials of interest and differences are notable between the two samples. The organic content in the sediment is much less and is decomposed between 200° and 550°C. The more refractory compounds in the sediment, primarily calcium carbonate, decomposes between 550° and 1050°C. The DTA information when coupled with the chemical characteristics of the compounds of interest, provided the basis for the temperatures chosen for ignition techniques.

In 1973, only one of the collecting tubes, comprising an upper and lower chamber, was used to determine the total dry weight of seston, organic matter, calcium carbonate, and ash. The seston within the three remaining traps was used in additional chemical analyses.

The particulate organic carbon content of the seston was determined from 8 January 1973 to 8 January 1974. The material from 2, 6, and 10 meters was filtered onto precombusted glass fiber filters

Figure 3.--Differential thermal analysis curve showing decomposition of seston from the 10 m sediment trap in Lawrence Lake. Decomposition took place in air and arrows indicate changes in recording resistance.

Figure 3

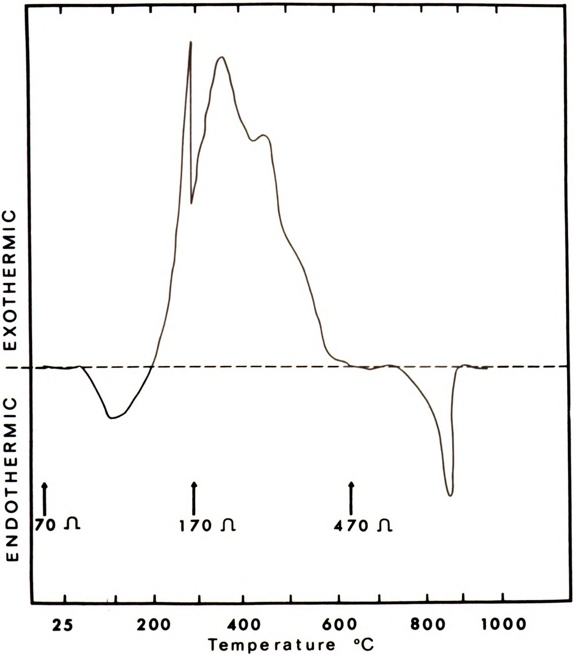
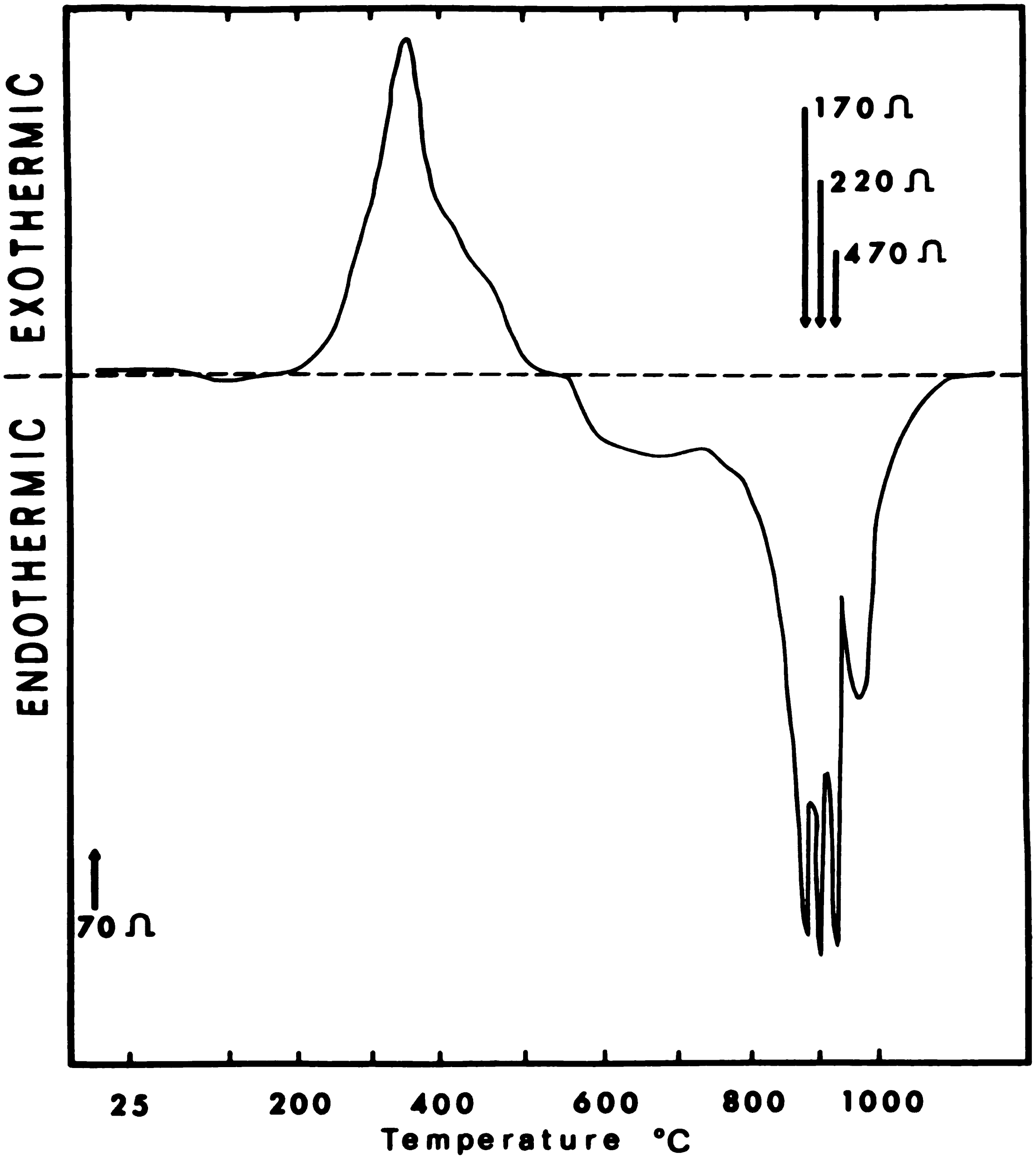

EXOTHERMIC
ENDOTHERMIC
70 Ω
170 Ω
470 Ω
25
200
400
600
800
1000
Temperature °C

Figure 4.--Differential thermal analysis curve showing decomposition of sediment from the lake bottom in Lawrence Lake. The decomposition took place in air and arrows indicate changes in recording resistance.

Figure 4


EXOTHERMIC
ENDOTHERMIC
170 Ω
220 Ω
470 Ω
70 Ω
25
200
400
600
800
1000
Temperature °C

and processed by sulfuric acid-potassium dichromate oxidation (Strickland and Parsons, 1972). Each batch of acid dichromate was calibrated against a 3 mg 1^{-1} standard glucose solution and the results are expressed as glucose equivalents.

The total nitrogen content of the seston was determined by Kjeldahl digestion (McKenzie and Wallace, 1954) followed by distillation (Markham, 1942). Before digestion, the sample was allowed to stand overnight with 4 ml of concentrated H_2SO_4 and 150 mg salicylic acid in a 30 ml Kjeldahl flask (Brinkhurst et al., 1972). Next day, 300 mg of $Na_2S_2O_3$ was added to the Kjeldahl flask, then the flask was heated on a Kjeldahl apparatus for 5 minutes. Finally, 150 mg HgO red, 3 g K_2SO_4 and one Hengar granule was added to the Kjeldahl flask and digestion was continued on the Kjeldahl apparatus. The heat was increased very slowly to minimize foaming. Foaming usually ceased after 45 to 60 minutes, then the heat was increased gradually. After the sample cleared, heating was continued an additional 45 minutes. Three hours were generally required for complete digestion. A 274 μg tryptophan sample showed that 99.3% of the nitrogen was recovered by this method. The nitrogen standard used in all determinations was 0.4 ml of a 5 g 1^{-1} L-(-)-tryptophan solution.

Perchloric acid digestion (Strickland and Parsons, 1972) was used to determine the total phosphorus content of the sedimenting seston. Samples filtered onto glass fiber filters were placed into 100 ml volumetric flasks and the total solution volume in all cases was 50 ml. Slow digestion insured that all the phosphorus was released. Samples were held at the boiling temperature for 20 minutes, then allowed to boil vigorously until the total volume was about 2 ml and

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droplets of perchloric acid refluxed down the sides of the flask. Centrifugation of the samples for 2 minutes at high speed was necessary to remove all the glass fiber particles before the color was developed.

The surface area of calcium carbonate, precipitated from filtered Lawrence Lake water, was determined by a nitrogen adsorption method. The continuous flow method (Nelson and Eggertsen, 1958) was used with a Perkin-Elmer Shell Model 212 B Sorptometer.

Untreated seston samples were used in x-ray diffraction analyses. Diffraction of x-rays by crystals can be used to identify crystalline materials, because the atoms of crystalline materials, such as calcite, are arranged in a regular manner and definite phase relationships exist between the scattered rays from the atoms. X-rays incident upon a crystal mounted upon a rotating table allows the glancing x-ray angle to be varied, thus constructive interferences of scattered radiation will result. In these analyses, deflections of copper radiation were recorded with a scanning goniometer that utilized a Geiger-Muller counter tube.

Sedimenting seston samples, collected during August 1973, were subjected to scanning electron microscopy. The photographs were used to evaluate the particle size, shape, and surface structure of the material collected on Nuclepore filters (Nuclepore Corp.).

D. Physicochemical Characterization of Lake Water

Total alkalinity was determined as titratable base, according to Standard Methods (American Public Health Association, 1971). Lake water pH was determined electrometrically with a Beckman Expandomatic

(Model 76-A) pH meter and temperature was measured in situ by an electrical resistance thermister thermometer (Yellow Springs Corp., Yellow Springs, Ohio). Oxygen values were determined by the Alsterberg modification of the Winkler titration (American Public Health Association, 1971), and silica was determined by the Rainwater and Thatcher method (1960).

Total calcium was determined by flame atomic absorption (Jarrell Ash Model 82-700). To prevent calcium carbonate precipitation during storage, 0.3 ml of concentrated nitric acid was added to each 125 ml lake water sample. Before calcium concentrations were determined, 5 ml of La_2O_3 solution (5% La^{3+} in 25% HCl v/v) was added to each 25 ml lake water sample to prevent anion and cation interferences. The ionized (free) calcium was estimated by a calcium ion electrode, Model 92-20 (Orion Research, Inc.). Two drops of 1 M KNO_3 were added to the calcium electrode standards and lake water samples to avoid any differences in total ionic strength. Calcium electrode standard solutions were mixed to reflect the ionic composition of the lake samples. Response of the calcium electrode to changes in calcium activity was rapid when placed in any of the standard solutions, although some drift did occur when the electrode was placed into the lake samples. To avoid any drift complications, all readings were timed and the electrode was allowed to equilibrate for two minutes in a 10^{-3} M Ca^{2+} solution between each lake water sample reading. The calcium electrode was stored in air between use and was placed into a 10^{-3} M Ca^{2+} standard solution for one hour before use.

E. Biological Data

Chlorophyll a determinations on the lake water were conducted using spectrophotometric techniques (Talling, 1971).

III. VARIATIONS IN SEDIMENTATION AMONG THE SESTON COMPONENTS

A. Introduction

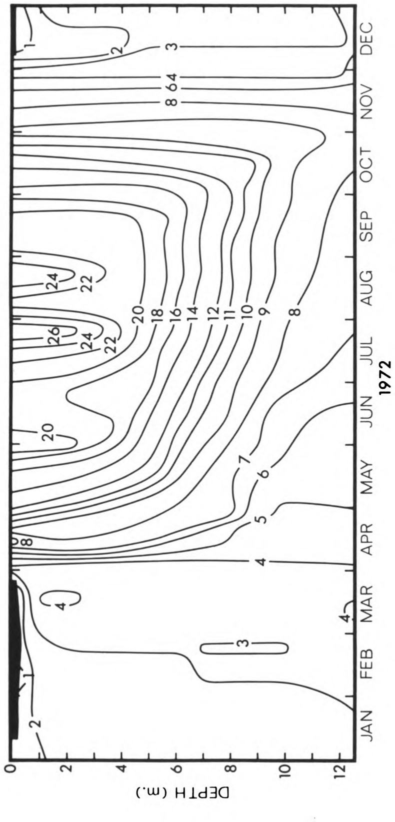
All collection of sedimenting seston was made at the central depression, Station A, thus extrapolation of this data to circumstances occurring within the littoral zone must be done with care.

The number of depths sampled was restricted by the tensile strength of the tiller cable and physical strength required to retrieve the traps. Basic information on Lawrence Lake has shown practical locations within the epilimnion, metalimnion and hypolimnion occur at 2, 6, and 10 meters respectively (Figure 5 and Figure 6). Resuspension of sediments in dimictic lakes occurs during spring and fall circulation (Davis, 1973), thus increased amounts during this period are impossible to avoid. Collection of resuspended material in the hypolimnion of Lawrence Lake during summer and winter was avoided by suspending the lower trap at 10 m, about 2 m above the bottom. While depths chosen for this study conformed to physical limitations, they nevertheless allowed the collection of relevant information in the thermally partitioned zones of the lake.

Frequent collection reduced problems associated with living material growing on the sampler. In addition, the contents of the lower chamber were subtracted from the quantity of material in the upper chamber, allowing for correction for non-sedimenting material. The results are expressed as weight m^{-2} day^{-1}.

Figure 5.--Isotherms of temperature (^{O}C) at Station A in Lawrence Lake, 1972. Opaque areas at the surface represent ice cover.

Figure 5


DEPTH (m.)
0
2
4
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8
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12
JAN
FEB
MAR
APR
MAY
JUN
JUL
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SEP
OCT
NOV
DEC
1972
1
2
3
4
4
4
4
8
5
6
7
20
26
24
22
24
22
20
18
16
14
12
11
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9
8
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6
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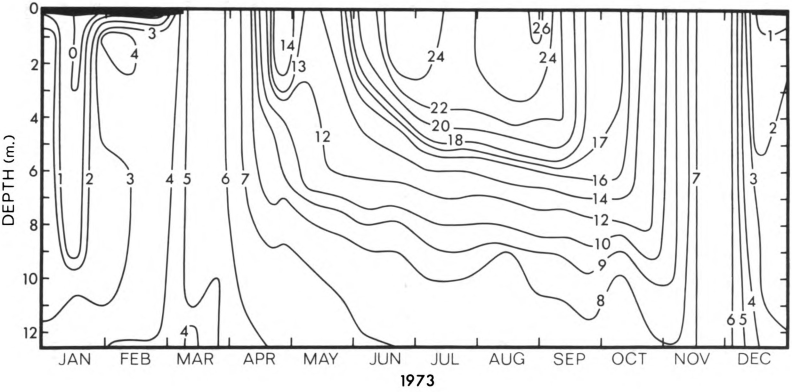
Figure 6.--Isotherms of temperature (^{o}C) at Station A in Lawrence Lake, 1973. Opaque areas at the surface represent ice cover.

Figure 6


DEPTH (m.)
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JAN
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18
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24
17
16
14
12
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9
8
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1
2
3
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6
5

B. Total Particulate Seston

Seasonal variation in total seston for 1972-1974 is illustrated in Figures 7 and 8. It is important to note two breaks that exist in these data. During the spring of 1972, as the ice broke up, the buoy became trapped in the ice and the anchor was moved so that the 10 m trap touched bottom. Thus, data from 18 March to 31 March was omitted for this depth. In 1973, data for the period from 6 March to 22 March was lost after the tiller cable broke and all the traps were lost to the bottom of the lake. The traps were replaced on 23 March, 1973.

Lesser amounts of seston were collected during 1972 than during 1973 (Table 1). The differences between spring circulation in 1972 and circulation in 1973 are important. A long cold spring in 1972 extended the period of circulation, whereas warm weather and less severe winds allowed the water to stratify rapidly in 1973. The duration of circulation and stratification for the annual cycles 1972-1974 is given in Table 2. A comparison of Figures 5 and 6 suggest a circulatory pattern of incomplete mixing after the ice broke up on 6 March 1973. Incomplete circulation during the spring of 1973 is further illustrated by comparing dissolved oxygen (Figures 9 and 10), alkalinity (Figures 11 and 12), hydrogen-ion (Figures 13 and 14), and calcium-ion concentrations (Figures 15 and 16) during the vernal period of each year. Temporary spring meromixis has been observed previously in Lawrence Lake (Wetzel *et al.*, 1972) and its occurrence is discussed in Wetzel (1966b). The effect of temporary spring meromixis on seasonal variation among the seston components will be discussed later.

Figure 7.--Seasonal variation in total dry weight of seston ($g\ m^{-2}\ day^{-1}$) collected in sediment traps suspended at 2, 6, and 10 meter depths. Traps were located at Station A in Lawrence Lake from 8 January 1972 to 8 January 1973. Bars equal ± S.E. Where no bars appear, the S.E. was less than the thickness of the line.

Figure 7

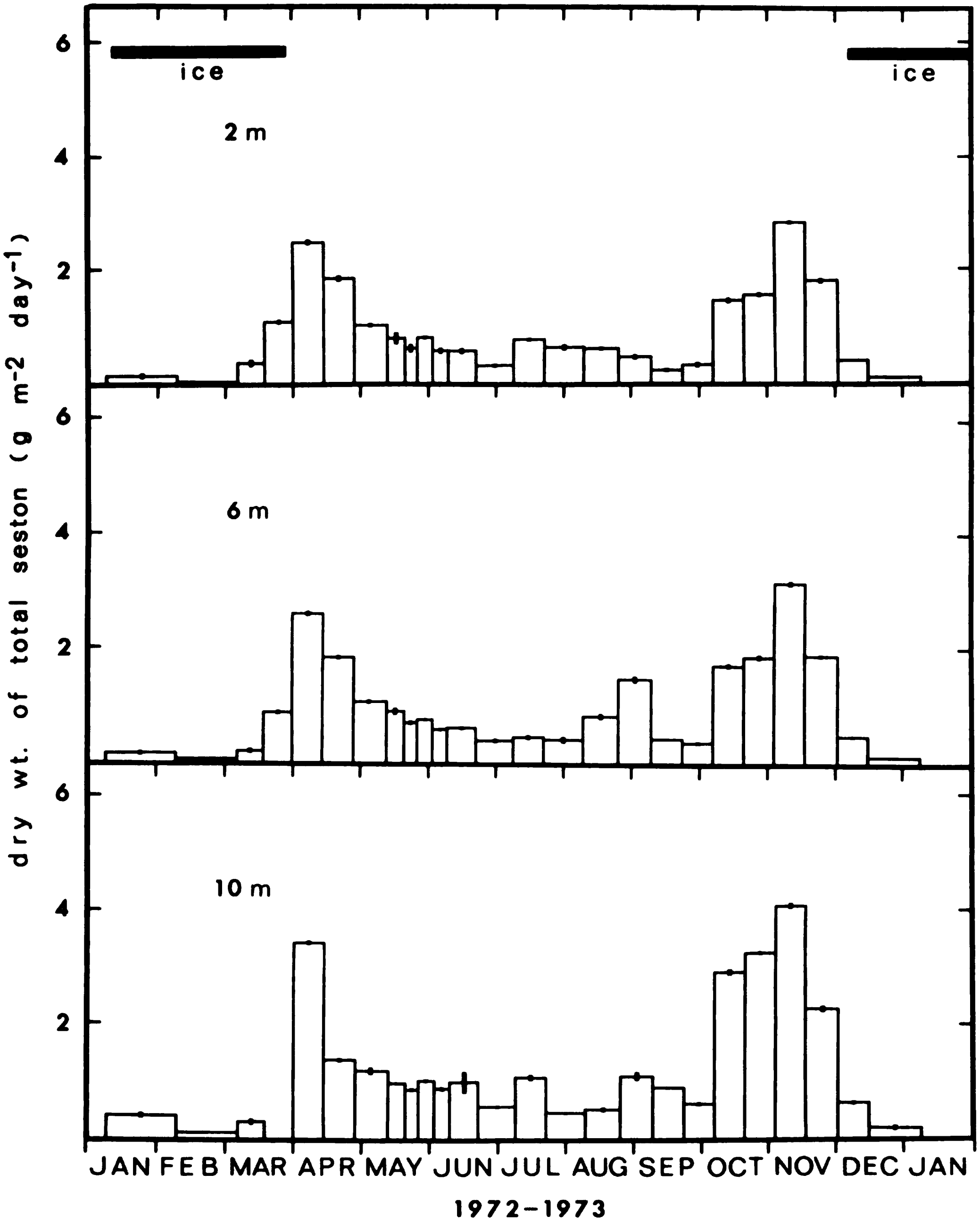

ice
ice
2 m
6 m
10 m
dry wt. of total seston (g m^{-2} day^{-1})
6
4
2
6
4
2
6
4
2
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1972–1973

Figure 8.--Seasonal variations in total dry weight of seston (g m^{-2} day^{-1}) collected in sediment traps suspended at 2, 6, and 10 meter depths. Traps were located at Station A in Lawrence Lake from 8 January 1973 to 8 January 1974.

Figure 8

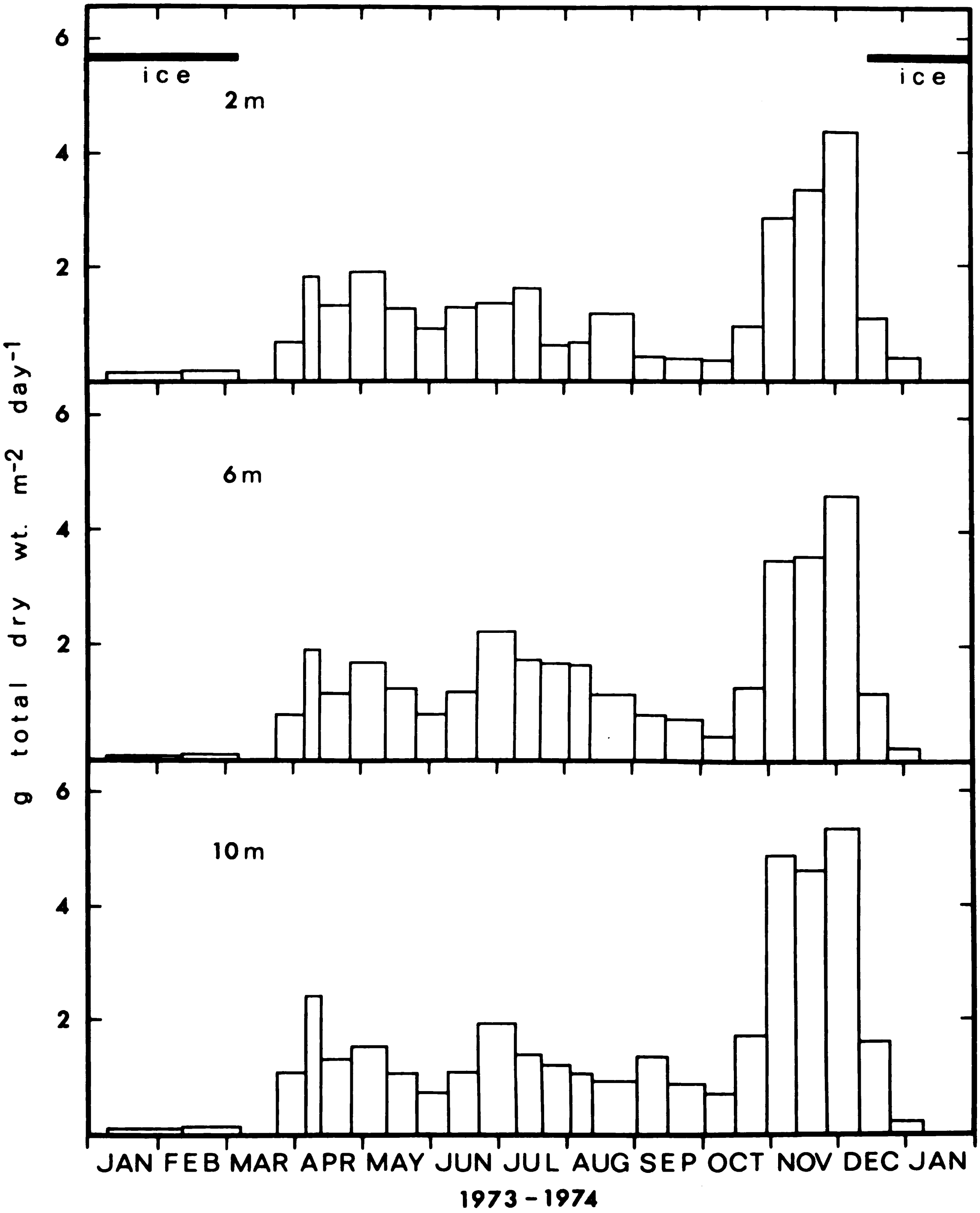

ice
ice
2m
6m
10m
6
4
2
g total dry wt. m^{-2} day^{-1}
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 - 1974

TABLE 1.--Sedimentation rate of total seston collected during 1972 - 1974 in Lawrence Lake. Quantity is expressed as mg m^{-2} day^{-1}.

		Total Seston			
Year	Depth	Winter	Spring	Summer	Fall
1972	2m	7.87	119	42.7	141
	6m	5.47	118	56.6	151
	10m	10.6	262	66.7	229
1973	2m	6.57	126	69.2	277
	6m	8.44	135	89.4	232
	10m	7.92	185	87.0	294

TABLE 2.--Sedimentation rates of components of seston collected during 1972 - 1974. Quantity is expressed as mg m^{-2} day^{-1}.

	Total Seston								
	Organic Matter			$CaCO_3$			Ash		
	2m	6m	10m	2m	6m	10m	2m	6m	10m
1972									
Winter Stratification (83 days)	1.77	1.18	2.56	0.50	0.59	1.73	4.09	2.65	4.27
Spring Circulation (42 days)	47.0	44.7	58.8	69.1	66.3	100.8	36.6	40.6	44.7
Summer Stratification (147 days)	18.7	22.6	30.0	4.86	6.73	9.65	19.1	27.3	27.0
Fall Circulation (56 days)	32.2	32.5	45.4	79.3	95.4	145	29.3	23.0	38.4
1973									
Winter Stratification (95 days)	1.74	1.93	1.60	2.68	5.09	4.05	2.15	1.42	2.27
Spring Circulation (37 days)	31.1	29.7	67.7	35.0	90.6	75.6	60.0	15.0	41.2

TABLE 2.--(continued)

	Total Seston								
	Organic Matter			$CaCO_3$			Ash		
	2m	6m	10m	2m	6m	10m	2m	6m	10m
Summer Stratification (200 days)	21.5	29.9	31.8	25.6	38.9	36.0	22.1	20.6	19.2
Fall Circulation (56 days)	105	49.7	56.8	137	137	176	35.0	44.9	61.4
1974									
Winter Stratification (15 days, to end of study)	14.8	7.18	5.80	2.00	1.71	1.56	9.50	7.41	7.55
	Average Values								
Winter Stratification	6.34	3.63	3.61	1.92	2.80	2.82	5.69	4.12	5.17
Spring Circulation	33.9	32.2	54.7	44.4	71.1	73.5	44.2	23.3	36.4
Summer Stratification	20.1	26.3	30.9	15.2	22.8	22.8	20.6	24.0	23.1
Fall Circulation	68.6	41.1	51.1	108	116	160	32.2	34.0	49.9
Annual Average	32.2	25.8	35.1	42.4	53.2	64.8	25.7	21.4	28.6

There was an increase in total seston during summer stratification in 1973 (cf. Figures 7 and 8). A comparison of the relative percentage composition of seston during summer stratification 1973-1974 (Figure 17) indicates that the content of calcium carbonate was noticably higher, and the content of organic matter was somewhat reduced.

As one would expect, seston collection is very low after the ice forms. Reduced light and lower temperatures decreased phytoplankton and zooplankton growth during this period. There is also reduced allochthonous input to the lake (Otsuki and Wetzel, 1974).

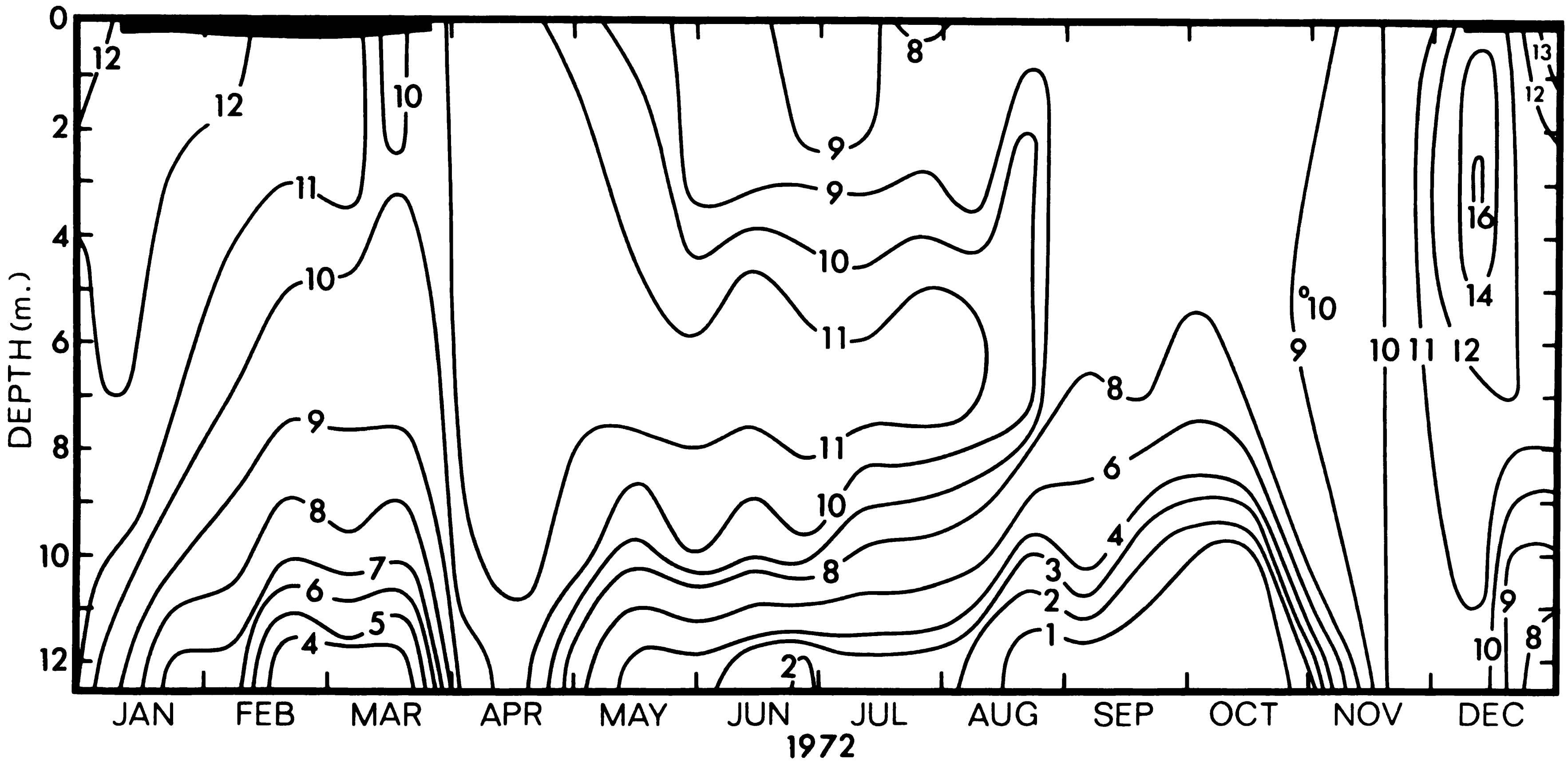
The seston collected during August (12 August - 1 September), 1973 was investigated by scanning electron microscopy. Equal volumes of water, containing resuspended seston from upper sediment chambers, were filtered onto Nuclepore filters (Nuclepore Corp.). The material was air dried, mounted upon stubs, coated with gold, and then scanned to evaluate the particulate matter.

The scanning electron micrograph of the seston from the 2 m trap (Figure 18a) contained various species of diatoms and a number of zooplankton filtering appendages. Clumps of white debris scattered over the surface of the filter contained calcium carbonate and organic material (Figure 19b). The amount of the debris increased with depth (cf. Figures 18a, 18b, and 19a).

Material from the 6 m trap (Figure 18b) consisted of diatoms, primarily Cyclotella sp. and Fragilaria sp. A rotifer lorica (Keratella) is located in the upper right of the photograph. Zooplankton filtering appendages were observed at this depth; however, none are included on this photograph.

Figure 9.-- Isopleths of oxygen concentration (mg l^{-1}) at Station A in Lawrence Lake, 1972.

Figure 9


DEPTH (m.)
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NOV
DEC
1972
12
12
11
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9
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11
10
8
2
8
8
6
4
3
2
1
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14
16
13
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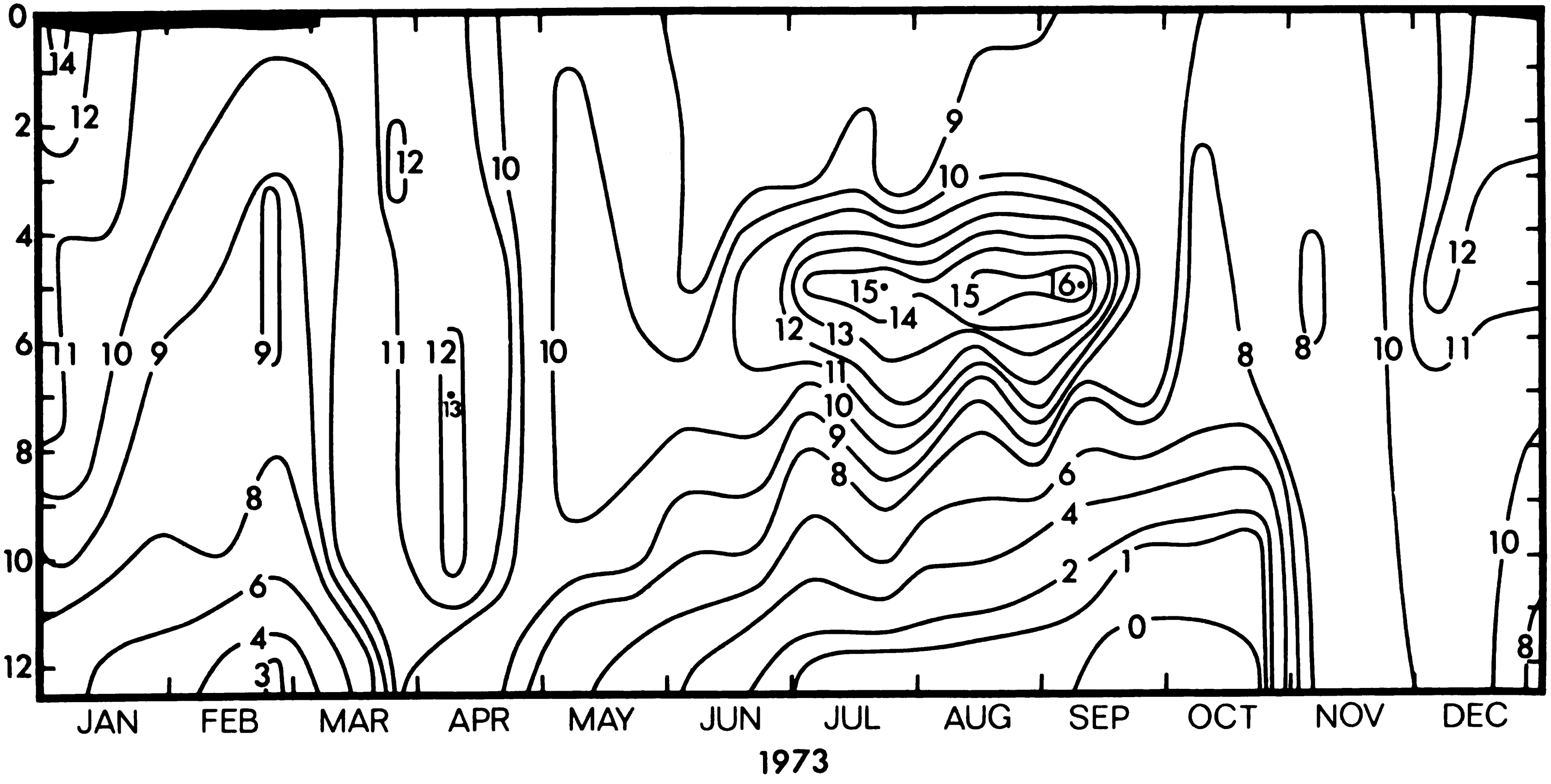
10
8

Figure 10.--Isopleths of oxygen concentration (mg l^{-1}) at Station A in Lawrence Lake, 1973.

Figure 10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12
14
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9
9
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3
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10
10
9
10
12
13
11
10
9
8
15
14
15
16
6
4
2
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JAN
FEB
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APR
MAY
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JUL
AUG
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OCT
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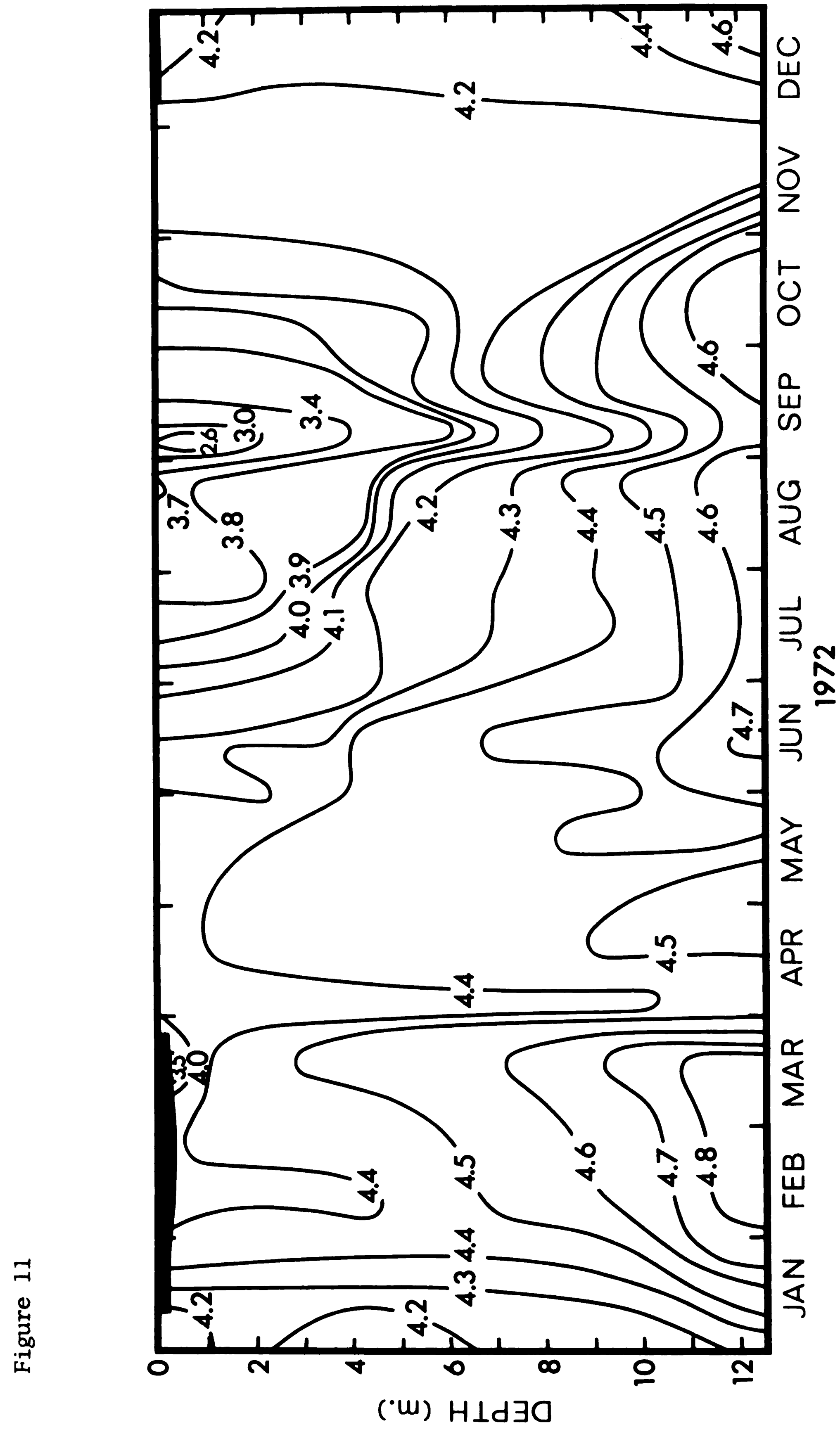
DEC
1973

Figure 11.--Isopleths of alkalinity (meq 1^{-1}) at Station A in Lawrence Lake, 1972.

Figure 11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DEC
1972
4.2
4.2
4.3
4.4
4.4
4.5
4.6
4.7
4.8
3.5
4.0
4.4
4.5
4.7
3.7
3.8
3.9
4.0
4.1
4.2
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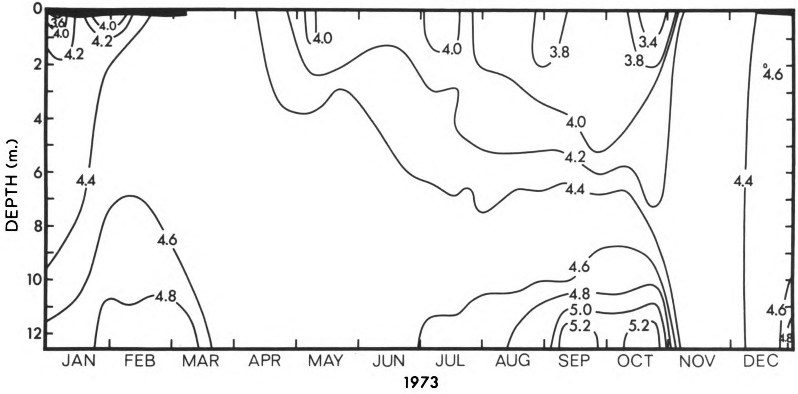
4.4
4.5
4.6
2.6
3.0
3.4
4.6
4.2
4.2
4.4
4.6

Figure 12.--Isopleths of alkalinity (meq 1^{-1}) at Station A in Lawrence Lake, 1973.

Figure 12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DEPTH (m.)
JAN
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AUG
SEP
OCT
NOV
DEC
1973
3.6
4.0
4.0
4.2
4.2
4.4
4.6
4.8
4.0
4.0
3.8
4.0
4.2
4.4
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5.0
5.2
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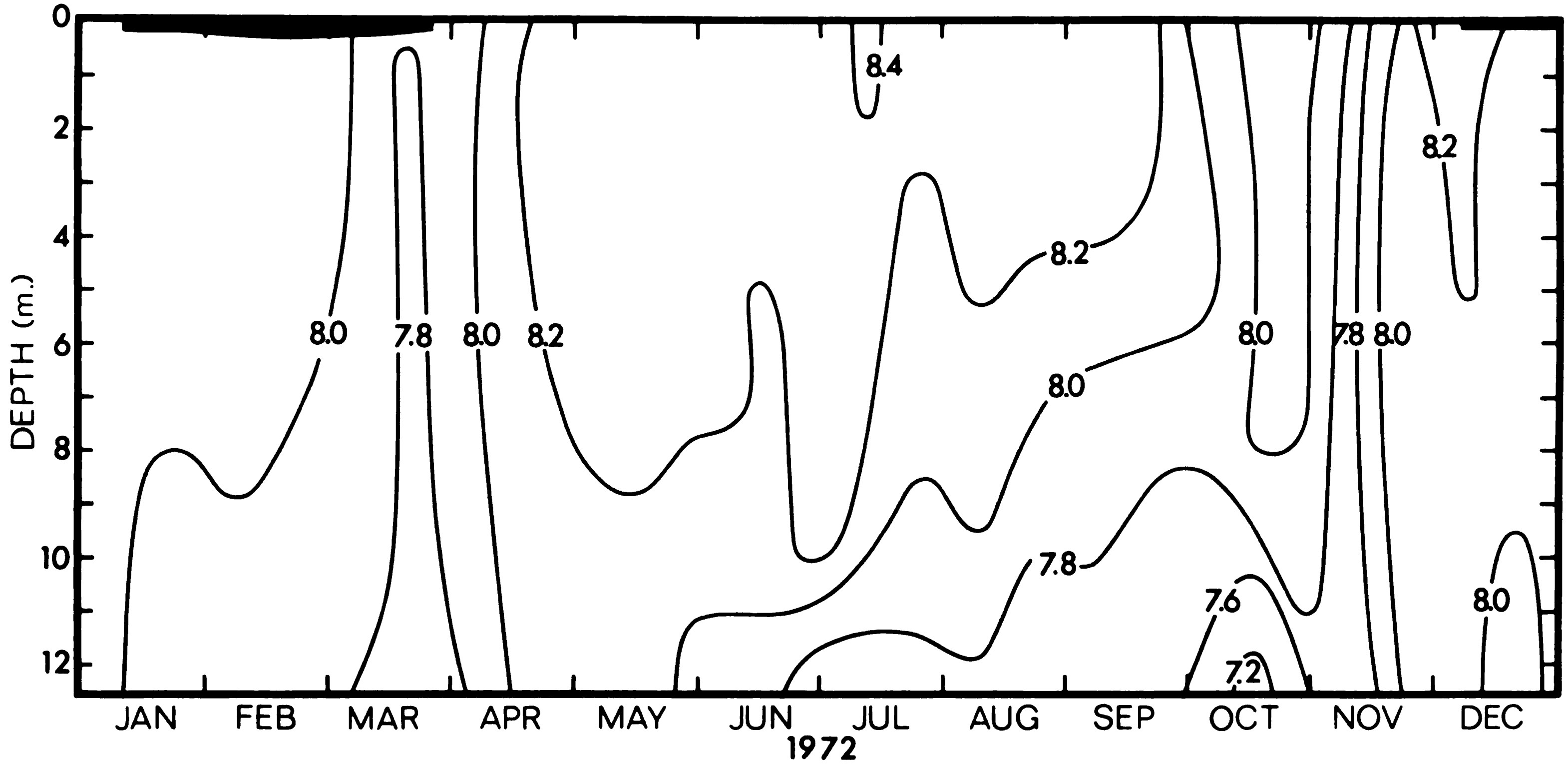
3.8
5.2
°4.6
4.4
4.6
4.8

Figure 13.--Isopleths of pH at Station A in Lawrence Lake, 1972.

Figure 13


DEPTH (m.)
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1972
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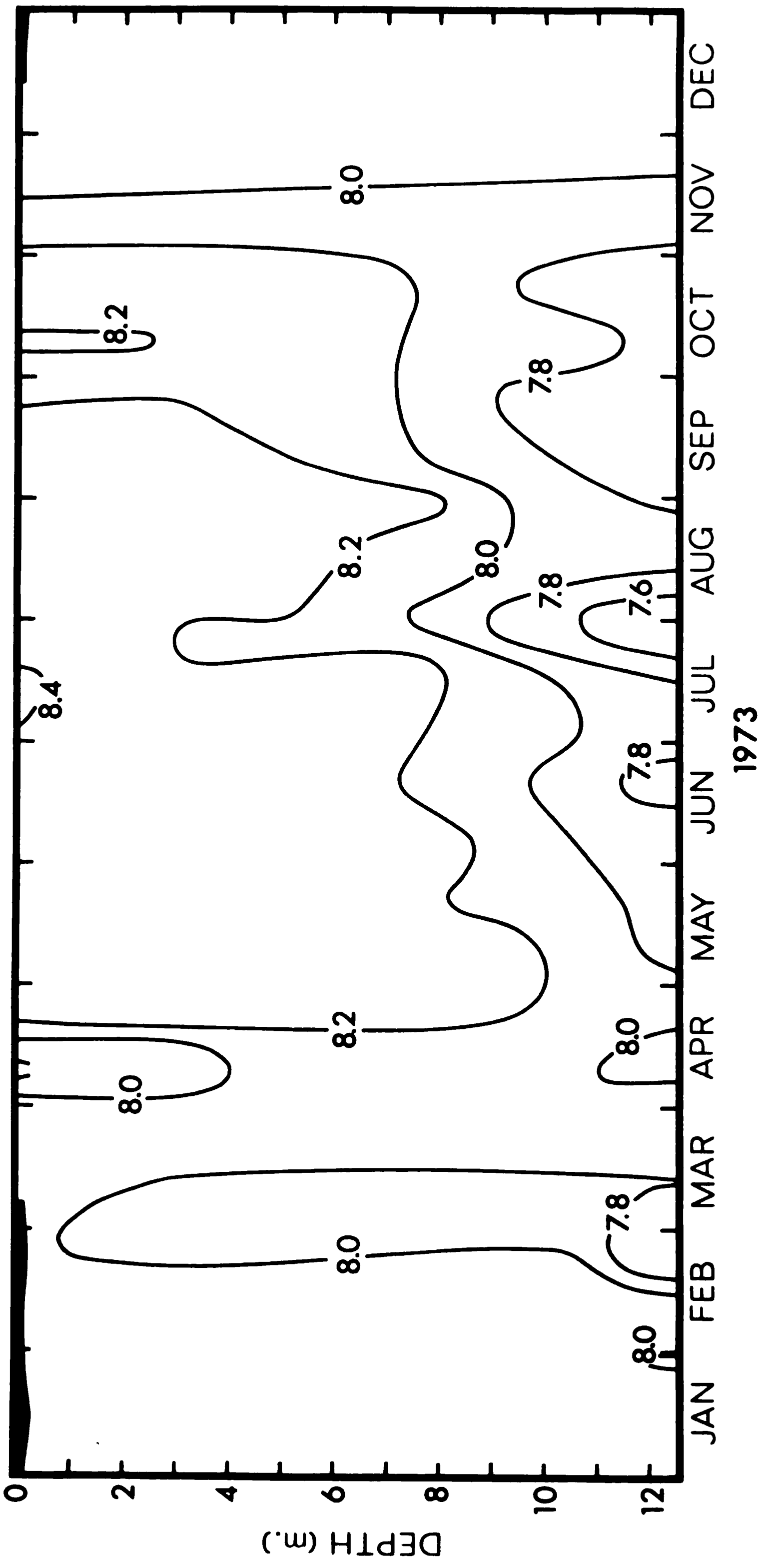
7.8
8.0
8.2
8.4
8.2
8.0
7.8
7.6
7.2
8.0
7.8
8.0
8.2
8.0

Figure 14.--Isopleths of pH at Station A in Lawrence Lake, 1973.

Figure 14


DEPTH (m.)
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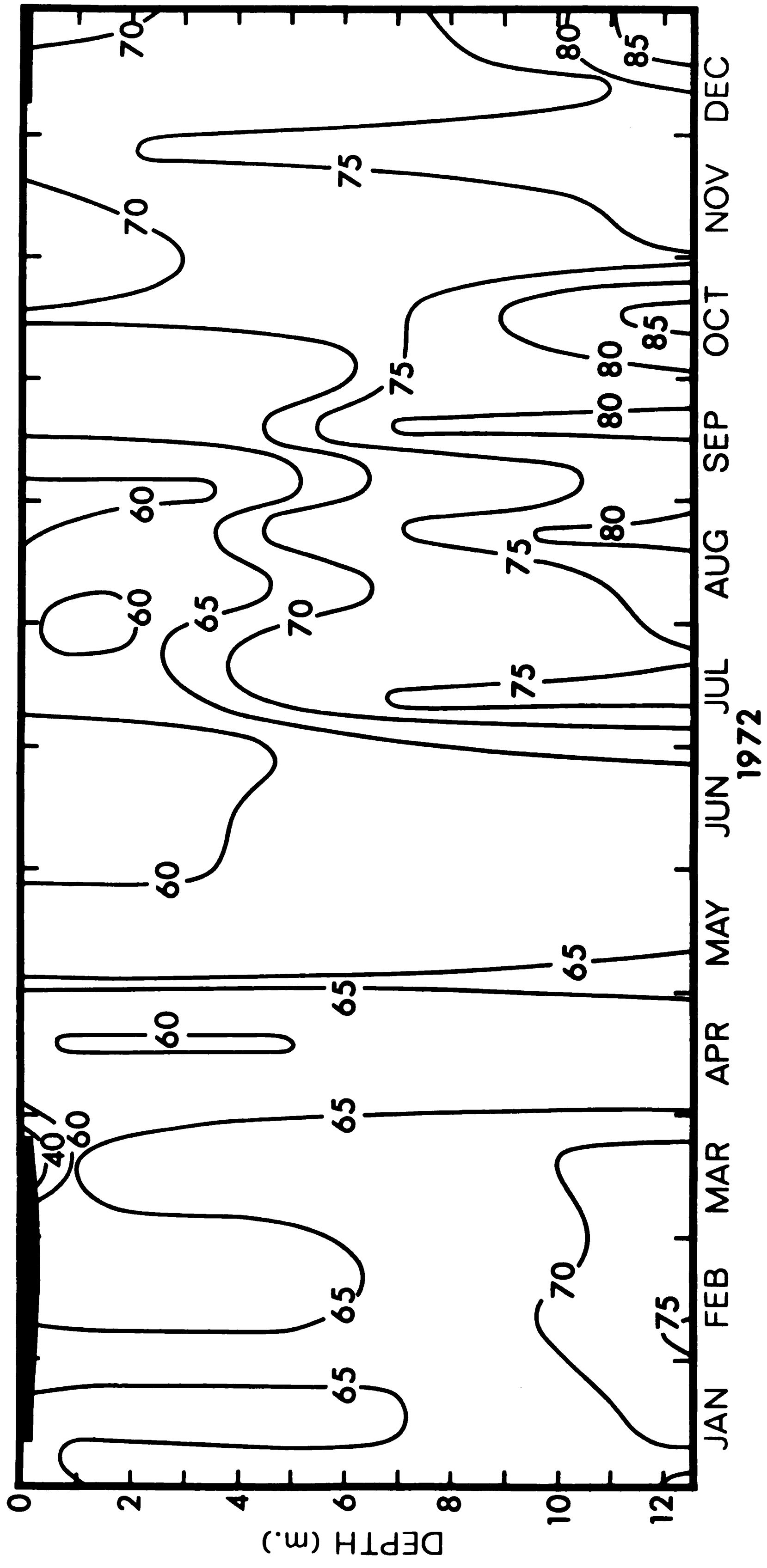
OCT
NOV
DEC
1973
8.0
8.0
7.8
8.0
8.0
8.2
8.4
8.2
8.0
7.8
7.6
7.8
8.2
7.8
8.0

Figure 15.--Isopleths of Ca^{2+} concentration (mg 1^{-1}) at Station A in Lawrence Lake, 1972.

Figure 15


DEPTH (m.)
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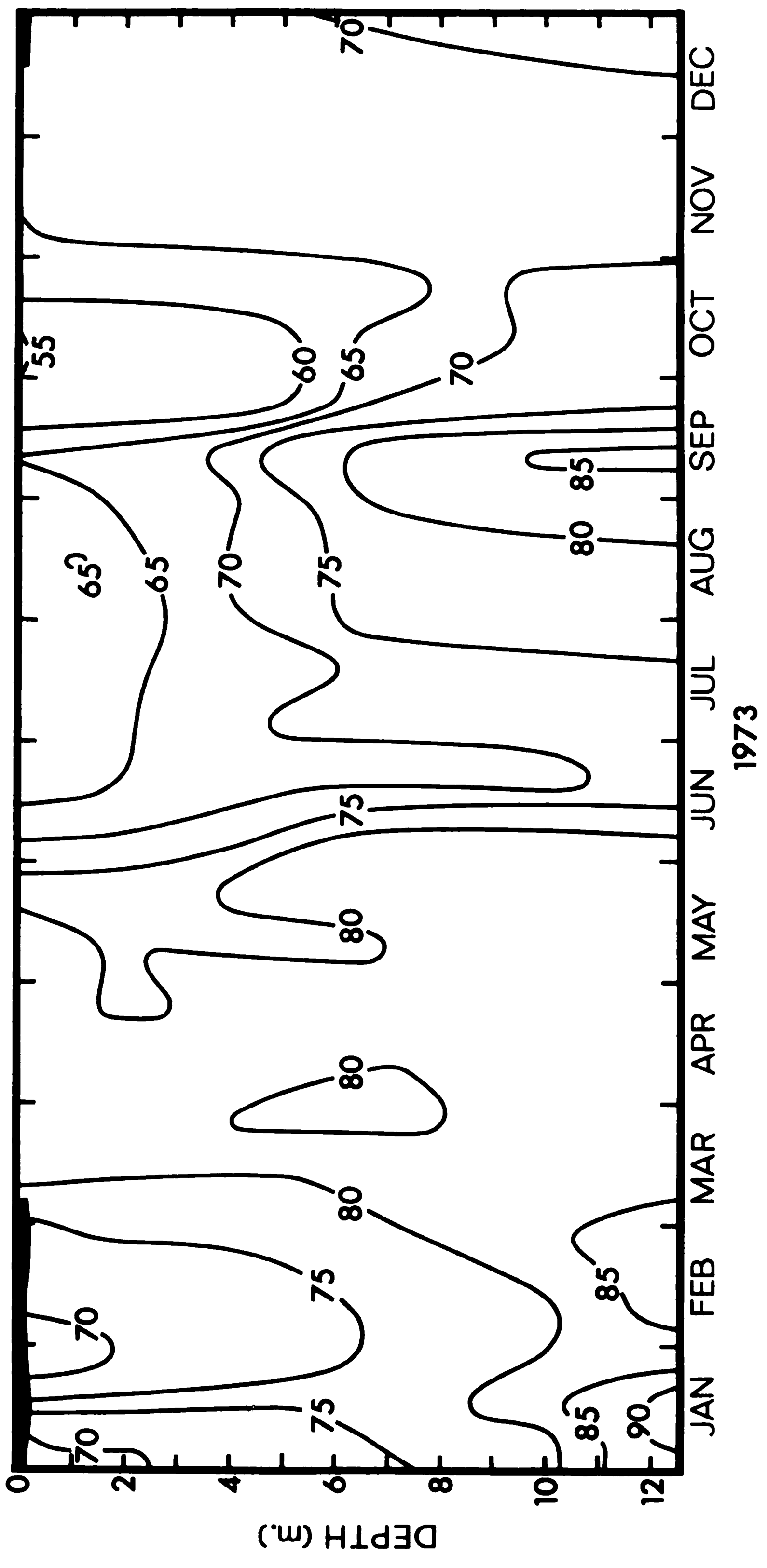
SEP
OCT
NOV
DEC
1972
40
60
65
70
75
80
85

Figure 16.--Isopleths of Ca^{2+} concentration (mg l^{-1}) at Station A in Lawrence Lake, 1973.

Figure 16


DEPTH (m.)
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12
JAN
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MAR
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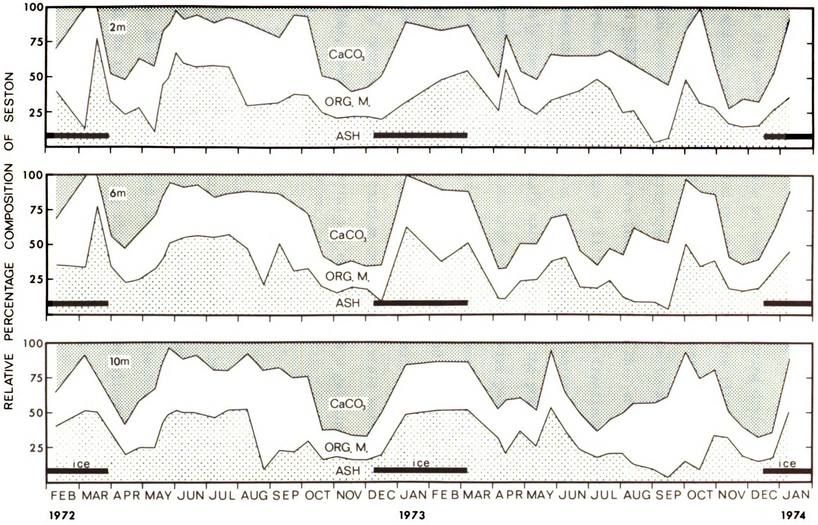
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1973
70
75
85
90
70
75
80
85
80
80
75
65
65?
70
75
80
85
55
60
65
70
70

Figure 17.--Relative percentage composition of calcium carbonate, organic matter, and ash in seston collected from 8 January 1972 to 8 January 1974, in Lawrence Lake.

Figure 17


RELATIVE PERCENTAGE COMPOSITION OF SESTON
100
75
50
25
2m
6m
10m
CaCO$_3$
ORG. M.
ASH
ice
FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1972
1973
1974

At 10 m the seston contained very small particles in an organic matrix (Figure 19a). This micrograph showed that the fine material formed a film over the surface of the filter. During drying, cracks formed and the material lifted up and away from the filter. Only 10 ml of the material was filtered onto the filter; nevertheless, in the upper mid-section of the micrograph it is possible to see that plugs of material pulled out of the pores in the filter. This evidence would cast some suspicion on the use of filters to size fractionate particulate materials especially when larger volumes of water are filtered. Apparently the fine particulate material clogged the pores and reduced the amount and size of material that would otherwise pass through. The material in the seston at 10 m (Figure 19a) was mechanically broken down and well decomposed by the time it reached 10 m. Resistant diatom frustules were the only recognizable biological material present. Clumps of debris containing calcium carbonate crystals were present on the filter, however all material was covered with a gelatinous like coating.

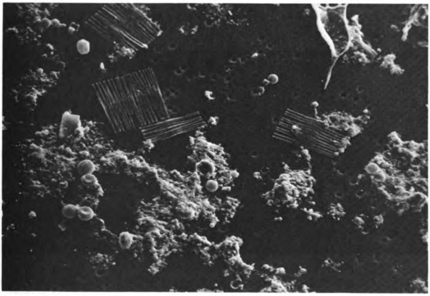
C. Organic Matter

Analyses of the organic matter content in the seston showed the quantity of organic matter increased during spring and fall circulation (Figures 20 and 21). This indicated a considerable amount of organic material was resuspended during this period. Some allochthonous organic material was introduced during autumn after vegetation was killed by frosts and carried from the littoral areas by fall rains (Wetzel and Otsuki, 1974). Flooding of these areas during the spring again transported more organic materials into the lake.

Figure 18.--Scanning electron micrographs of seston caught in sediment traps during August 1973 and filtered onto 8 μ Nuclepore filters. a: Material collected in sediment traps suspended in epilimnion, 2 meters (200X). b: Material collected in sediment traps suspended in the metalimnion, 6 meters (200X).

Figure 18

a



b

Figure 19.--Scanning electron micrographs of seston collected during August, 1973. a: Seston collected from 10 meters showing the fine particulate material and gelatinous organic matrix (500X). b: Enlargement of detritus showing crystals of calcite and fragments of diatom frustules in an organic matrix (5000X).

Figure 19

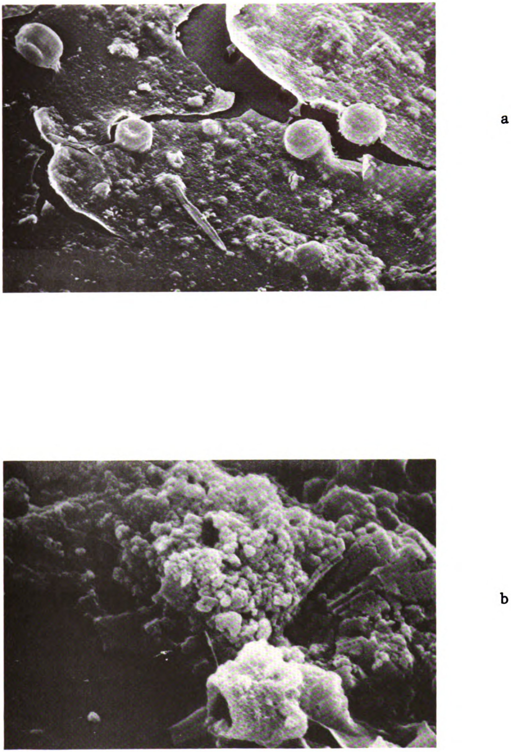


Figure 20.--Seasonal changes in the organic component of seston (g m^{-2} day^{-1}) collected in traps at 2, 6, and 10 meter depths. Traps were located at Station A in Lawrence Lake from 8 January 1972 to 8 January 1973. Bars equal ± S.E. The S.E. was less than the thickness of the line where no bars appear.

Figure 20

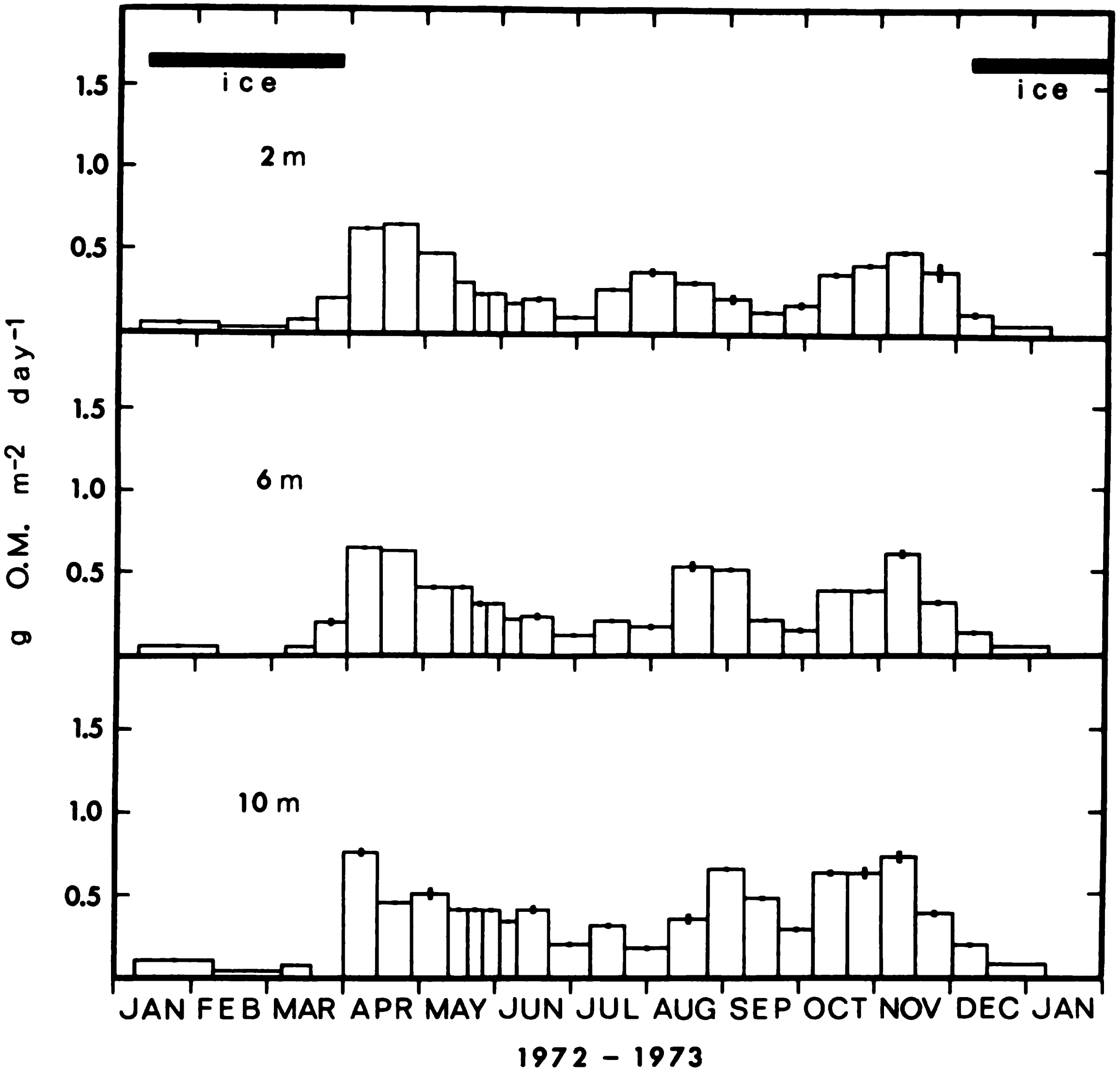
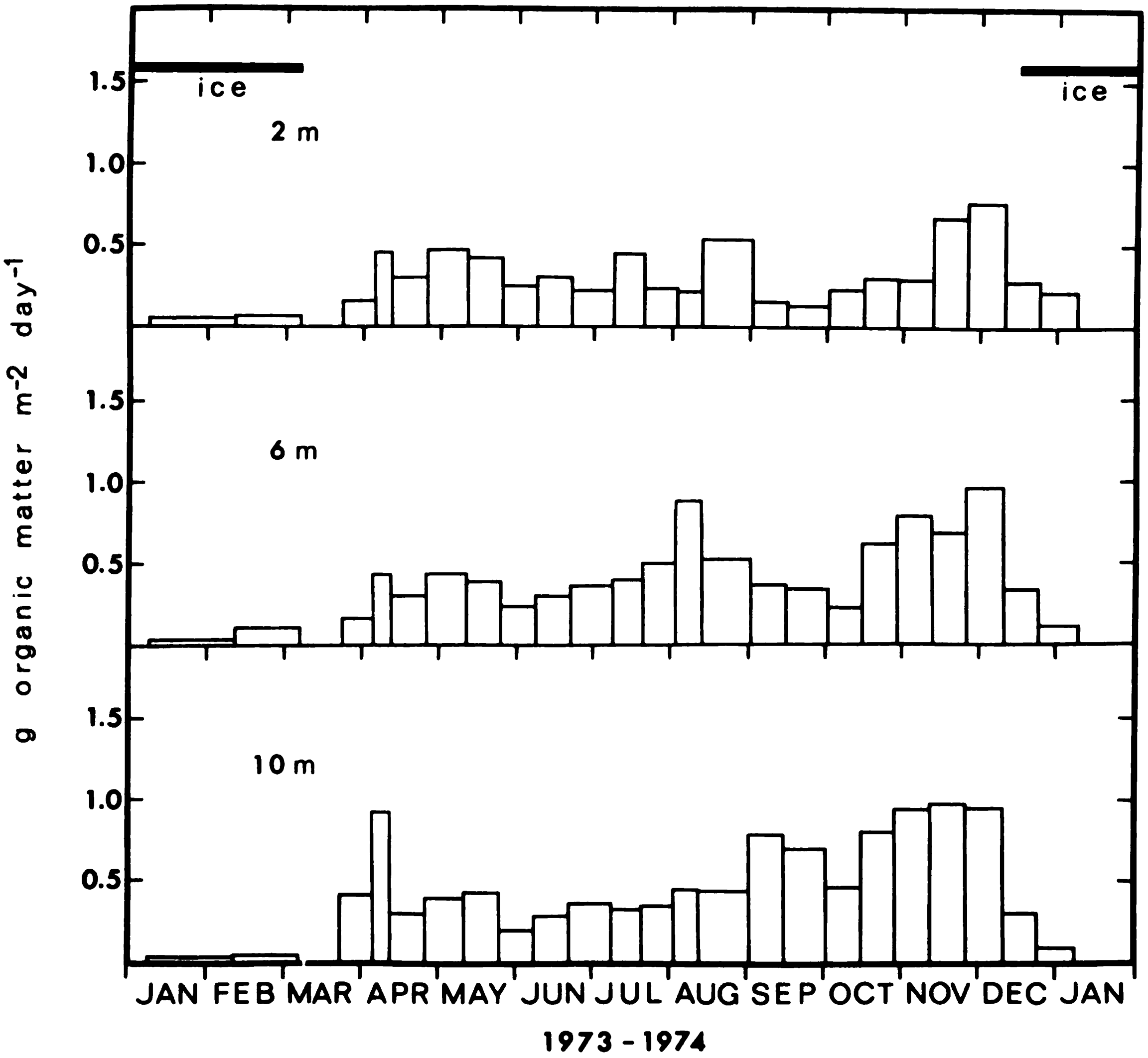

ice
ice
2 m
6 m
10 m
1.5
1.0
0.5
g O.M. m-2 day-1
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1972 - 1973

Figure 21.--Seasonal changes in the organic component of seston (g m^{-2} day^{-1}) collected in traps at 2, 6, and 10 meter depths. Traps were located at Station A in Lawrence Lake from 8 January 1973 to 8 January 1974.

Figure 21


ice
ice
2 m
6 m
10 m
1.5
1.0
0.5
g organic matter m-2 day-1
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 - 1974

During summer stratification in 1972 - 1973 the organic content of the seston was at times much lower than in 1973 - 1974 (e.g. June and July), however, the average amounts of organic matter during summer stratification were similar (Table 2).

During 1972 organic matter content increased at 2 m during late July and August. This increase was also noted at 6 m during August and September. These observations agree with an increase in algal growth as evidenced by the amount of corrected chlorophyll a found at these levels (Figure 22). It is reasonable to suggest the settling rate of phytoplankton responsible for this increase in organic matter (Figure 20) took about two weeks, since the maximum level at 2 m occurred at the end of July and the first of August. The peak at 6 m occurred in mid-August through early September, indicating further growth took place at this level. At 10 m the maximum level of organic matter occurred in late August and early September then levels were reduced by mid-September.

During 1973 a similar production of organic matter by phytoplankton was observed during August (Figure 23). The maximum growth of phytoplankton took place at 6 m in the metalimnion and is represented by the seston caught in the 6 m trap (Figure 21) during early August.

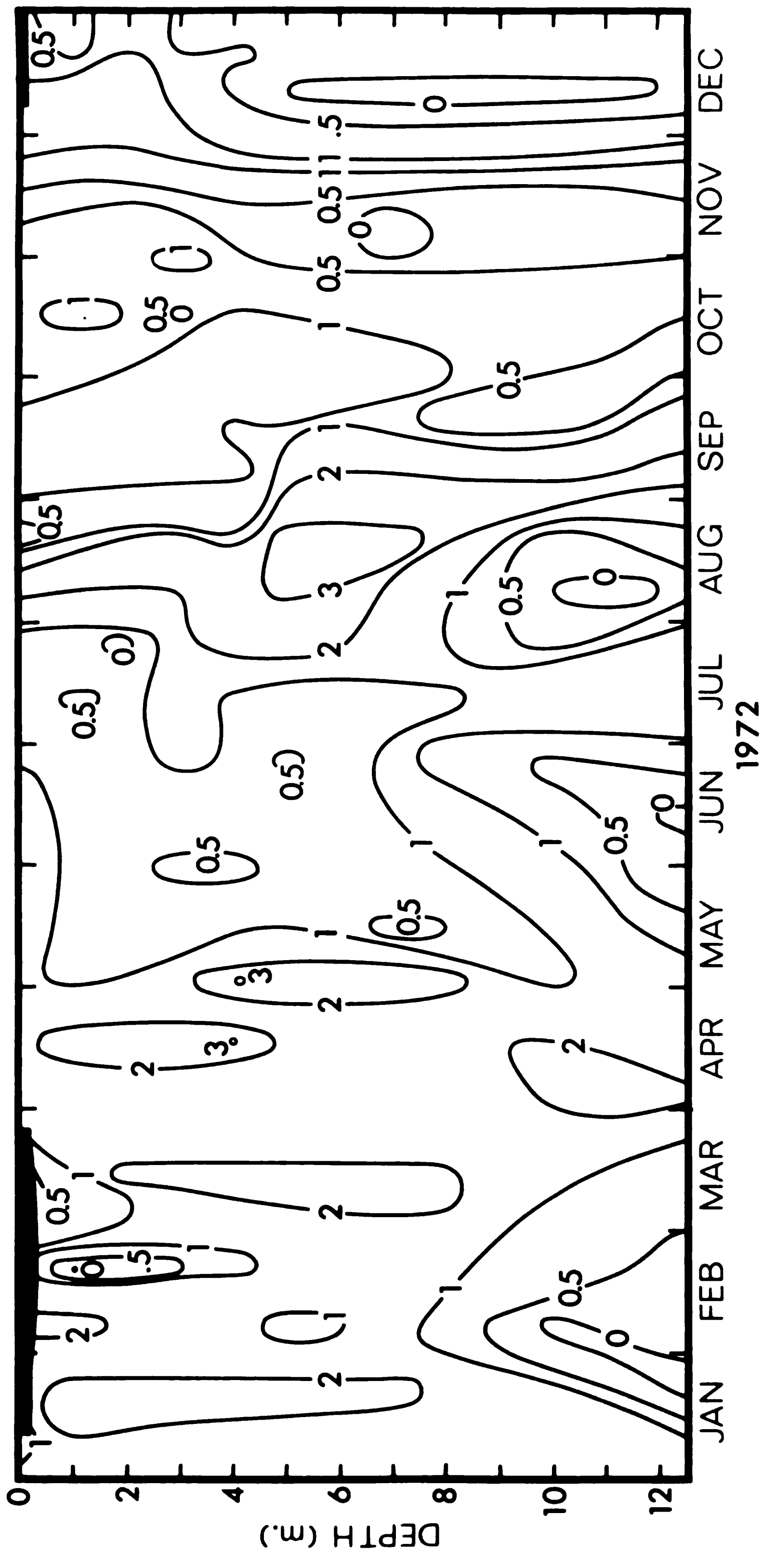
D. Calcium Carbonate

1. Solubility of Calcium Carbonate

The apparent solubility of calcium carbonate in natural water is related to the partial pressure and solubility of carbon dioxide at any given temperature (Johnson, 1915; Johnston and Williamson, 1916). The

Figure 22.--Isopleths of corrected Chlorophyll *a* (μg 1^{-1}) at Station A in Lawrence Lake, 1972.

Figure 22


DEPTH (m.)
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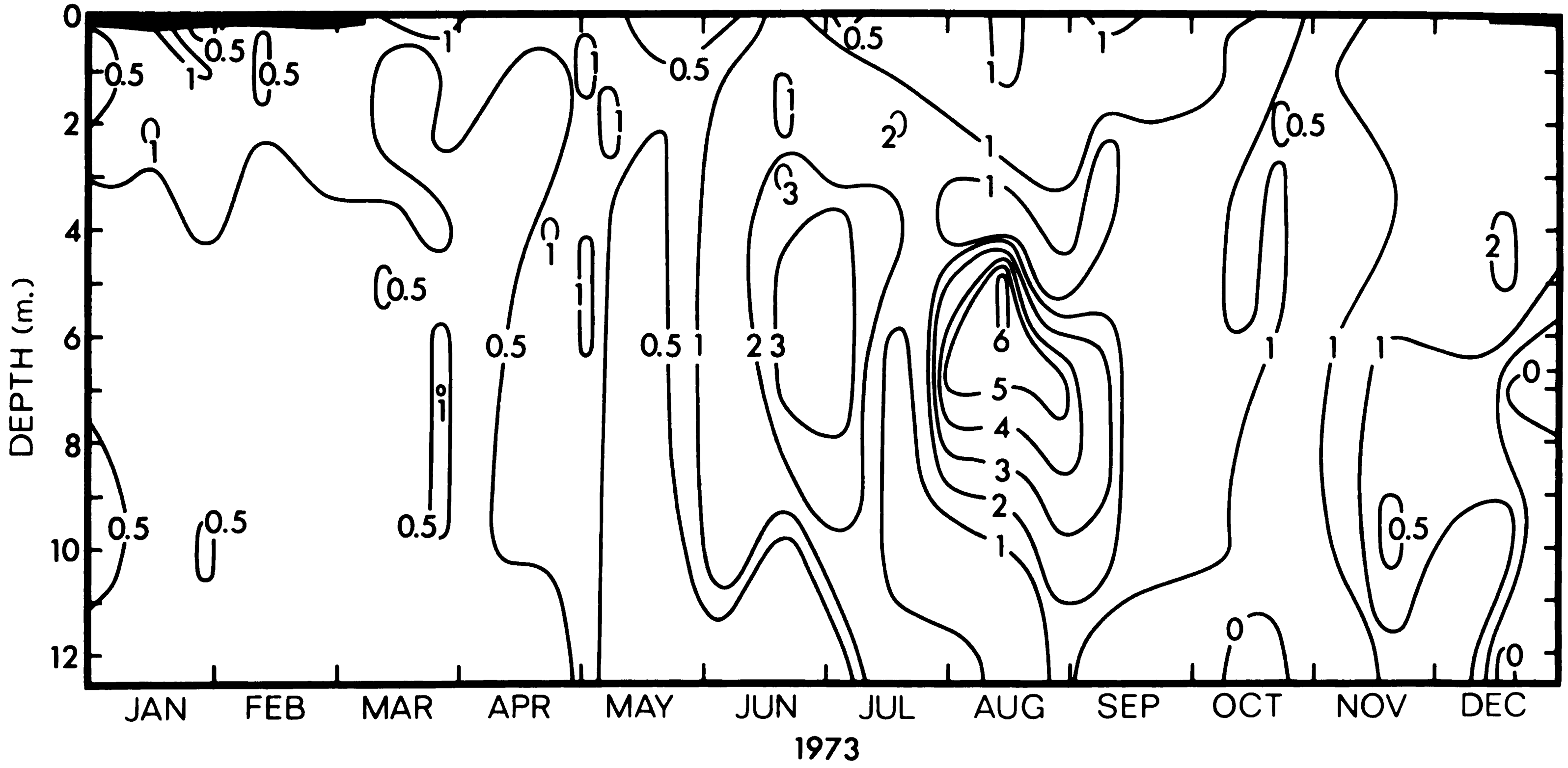
SEP
OCT
NOV
DEC
1972
0.5
1
2
3
0

Figure 23.--Isopleths of corrected Chlorophyll a ($\mu g\ l^{-1}$) at Station A in Lawrence Lake, 1973.

Figure 23


DEPTH (m.)
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NOV
DEC
1973
0.5
1
0.5
0.5
0.5
1
0.5
1
0.5
1
1
0.5
1
0.5
0.5
1
0.5
1
2
3
3
2
1
1
1
6
5
4
3
2
1
1
0.5
1
1
1
0
0.5
2
0
0
0.5

formation of H_2CO_3 and its subsequent dissociation into H^+ and HCO_3^- ions determine to a large degree the solubility of calcium carbonate. A practical definition of calcium carbonate solubility is based upon the dissolution of calcite suspended in pure water (Hutchinson, 1957). In an open system, calcite will dissolve until an equilibrium is established, based upon the interdependence of these solute species: CO_2, $H_2CO_3^-$, CO_3^{2-}, H^+, HCO_3^-, and OH^-. At this point, further dissolution of calcium carbonate does not occur unless the partial pressures of CO_2 increases. The solubility of calcium carbonate under different carbon dioxide pressures and temperatures in pure water are based upon the work of Frear and Johnston (1929) and are given in Hutchinson (1957). All calculations in this work are based upon these values.

Berner (1965) used two equations to describe precipitation of calcium carbonate in sea-water and these equations are used to describe calcium carbonate precipitation in Lawrence Lake. When an increase in pH occurs the following equation describes subsequent changes among the involved ionic species:

$$Ca^{2+} + 2HCO_3^- \rightleftarrows CaCO_3 + CO_2 + H_2O \qquad (1)$$

Whenever the pH decreases the following changes occur:

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3 \qquad (2)$$

pH changes in lake water are related to the concentration of H^+ ion and this parameter is ultimately related to the partial pressure of CO_2 and chemical enhancement of CO_2 diffusivity (Wood, 1974). The H_2CO_3 in turn determines the proportion of HCO_3^-, CO_3^{2-}, and OH^- present.

Figures 13 and 14 show isopleths of pH change in the water column during 1972 and 1973, respectively. These changes indicated that an increase in pH does occur through the summer in the epilimnion and metalimnion; although, the pH does not rise above 8.4. The change in pH means calcium carbonate precipitation would proceed in accordance with equation (1). The initiation of calcium carbonate precipitation in the hypolimnion would take place by equation (2); since, there is a decrease of pH in the hypolimnion.

Changes in alkalinity during 1972 and 1973 (Figures 11 and 12) indicate the values decreased in the epilimnion and metalimnion during summer stratification.

A corresponding change in the isopleths of Ca^{2+} concentration is observed during the above mentioned period (Figures 15 and 16). The Ca^{2+} concentration was progressively reduced in the trophogenic zone, while an increase occurred in the hypolimnion. These data all indicate a considerable precipitation of calcium carbonate was taking place.

2. X-ray Diffraction Analysis of Seston

Preliminary samples of seston were collected at 10 m in Lawrence Lake during 1970 to determine what crystalline polymorph was present. X-ray diffraction investigation of this material revealed calcite was the only crystalline material present in the sample. It is supposed this crystalline form precipitates out of Lawrence Lake; although, it is plausible the calcium carbonate may form an amorphous matrix with the organic material as well (Figure 19a).

3. Calcium Carbonate Content in Seston

Calcium carbonate content in the sedimenting seston had vernal and autumnal maxima in 1972 (Figure 24). In 1973 (Figure 25) an autumnal maximum is obvious; however, the vernal maximum is less pronounced. These maxima correspond to periods of circulation and are caused by resuspension of material from the bottom sediments. The short period of circulation (cf. page 36) during the spring of 1973 raised less material from the bottom sediments. Autumnal circulation in 1973 (Figure 25) resuspended perceptibly more calcium carbonate presumably because of two factors: (1) fall winds were stronger; and (2) more calcium carbonate was precipitated during the preceeding summer season.

One of the unmistakable differences between the two annual patterns (Figures 24 and 25) is the larger quantity of calcium carbonate that precipitated out during summer stratification in 1973. Approximately 5 times more calcium carbonate precipitated in 1973 than in 1972 (Table 2). A shorter circulation period and elevated concentrations of Ca^{2+} (cf. Figures 15 and 16) during the spring of 1973 were directly related to this dissimilarity.

The lowered amount of calcium carbonate precipitation during ice cover was anticipated, insofar as lower temperatures increased the solubility of CO_2 and reduced metabolic activity to very low levels.

4. Cause of $CaCO_3$ Precipitation

The precipitation of calcium carbonate can be divided into three broad categories: (1) abiogenic precipitation; (2) precipitation by freshwater bacteria and plants; and (3) precipitation by animals (Pia, 1933).

Figure 24.--Seasonal changes in calcium carbonate content of seston (g m^{-2} day^{-1}) collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1972 to 8 January 1973. Bars equal ± S.E. Where no bars appear the S.E. was less than the thickness of the line.

Figure 24

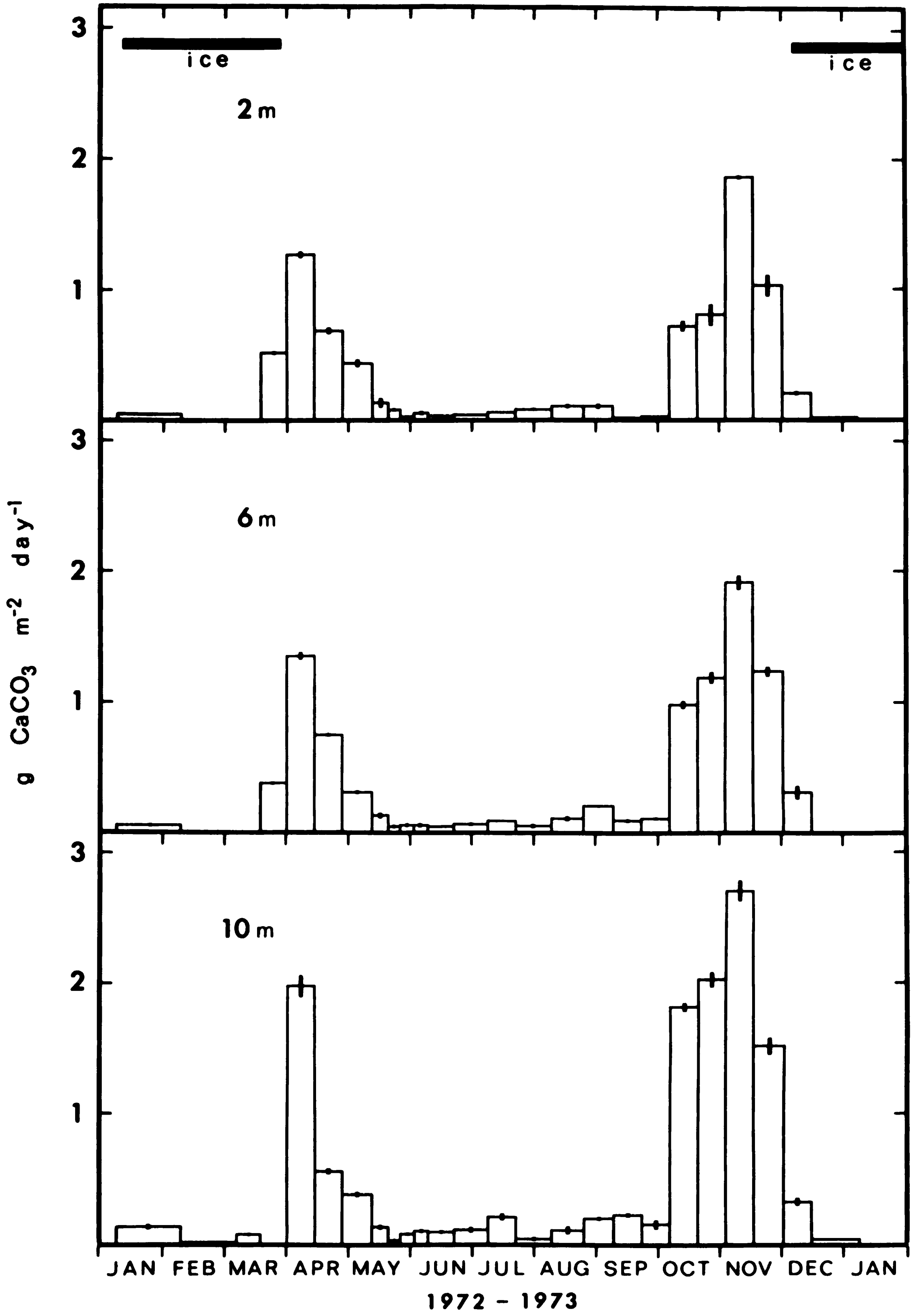
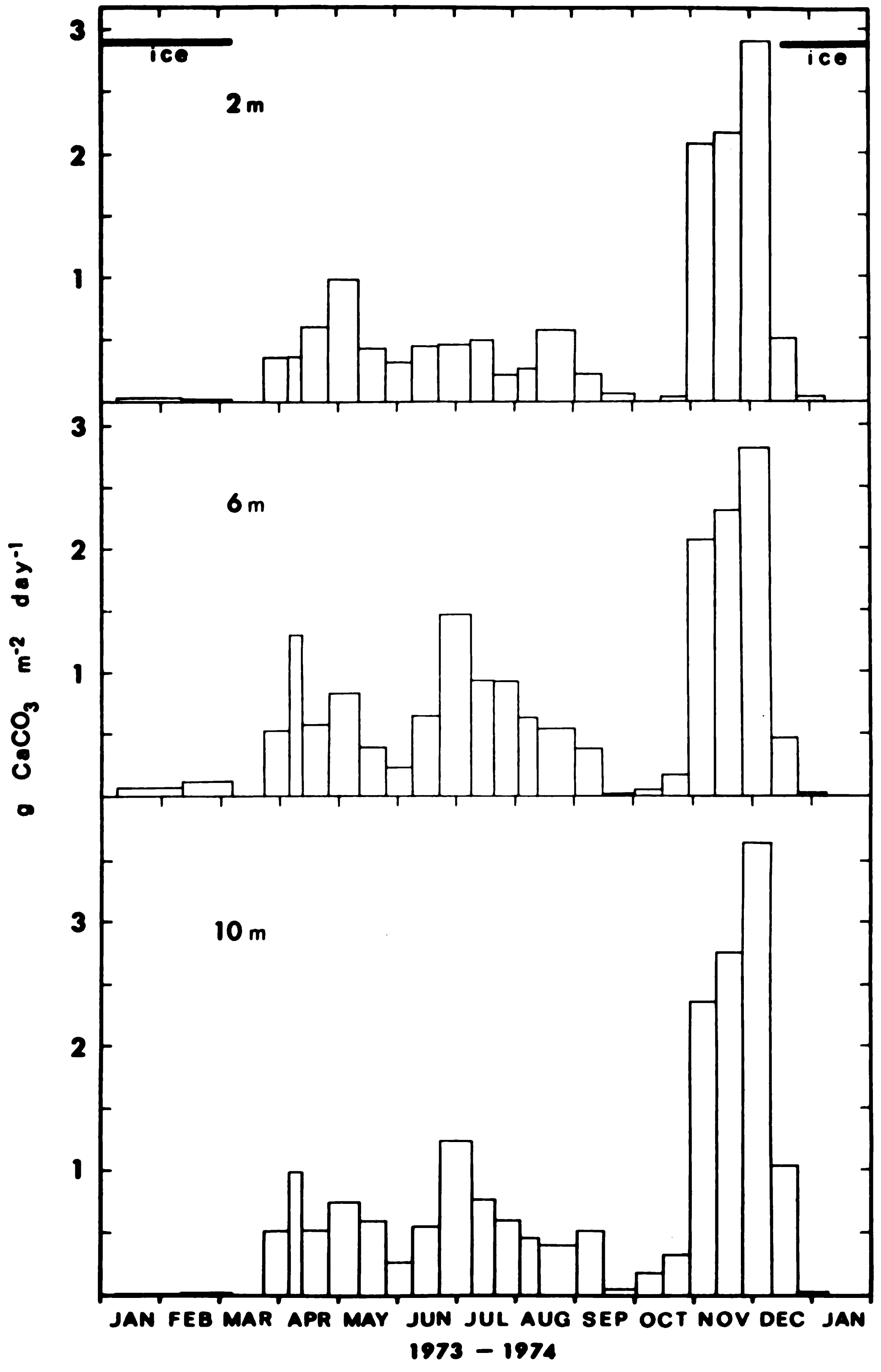

3
2
1
ice
ice
2 m
3
2
1
6 m
3
2
1
10 m
g CaCO$_3$ m^{-2} day^{-1}
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1972 - 1973

Figure 25.--Seasonal changes in calcium carbonate content of seston (g m^{-2} day^{-1}) collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974.

Figure 25


2m
ice
ice
6m
10m
3
2
1
3
2
1
3
2
1
g CaCO$_3$ m^{-2} day^{-1}
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 — 1974

Abiogenic precipitation of calcium carbonate in Lawrence Lake may be caused by changes in temperature and loss of carbon dioxide to the atmosphere. Otsuki and Wetzel (1974) found the groundwater and inlet water from two small streams flowing into Lawrence Lake contained elevated concentrations of calcium (ca. 90 mg l^{-1}) and total alkalinity (ca. 5.5 meq l^{-1}) as compared to average values of calcium concentration and total alkalinity at Station A (68 mg l^{-1} and 4.4 meq l^{-1}, respectively). Since the inlet water and lake water were already saturated, it is possible some free or equilibrium CO_2 was lost to maintain equilibrium values. This reaction should proceed according to equation (1) with an attendant precipitation of calcium carbonate and release of free CO_2 to establish equilibrium conditions. However, photosynthetic activity of submersed macrophytes in the littoral zone and their attached microflora would induce calcium carbonate precipitation (Wetzel, 1960, 1970; Rich _et al._, 1971; Wetzel _et al._, 1972) and tend to overshadow this abiogenic process. Moreover, the surface waters of Lawrence Lake are supersaturated with respect to calcium carbonate, so the dissolved CO_2 is not in equilibrium with the atmosphere and this would indicate loss of CO_2 to the atmosphere does not play a primary role in calcium carbonate precipitation in this study, especially in the open water.

Temperature change has been implicated as the causal factor in the initiation of $CaCO_3$ precipitation (Brunskill, 1969) and a time lag of one month was observed between the onset of calcium carbonate precipitation and a decrease in total CO_2. Otsuki and Wetzel (1974) indicated temperature was not the direct causal factor in the initiation of calcium carbonate precipitation based upon outlet water and surface lake water of Lawrence Lake. In this work, a careful examination of temperature (Figures 5 and 6), alkalinity (Figures 11 and 12), Ca^{2+} concentration (Figures 15 and 16), and calcium carbonate content in the seston (Figures 24 and 25) indicated that all these parameters were closely interrelated in calcium carbonate precipitation. Increases in temperature and light intensity, coupled with an abundant nutrient supply, promote rapid algal growth in spring (Figures 22 and 23). Likewise, considerable calcium carbonate is precipitated during this period (Figures 24 and 25). This information indicated calcium carbonate precipitation results from both increasing temperature and photosynthetic activity. A comparison of Figure 6, Figure 23, and Figure 25 at the 6 m depth over the period June, July, and August clearly show increases in temperature, chlorophyll a, and calcium carbonate content in seston are closely correlated.

While it is unclear what factor or factors initiated calcium carbonate precipitation, it is clear that photosynthesis facilitated calcium carbonate precipitation when free CO_2 and/or bicarbonate ions were utilized.

Phosphate combines with the seston to form colloidal phosphorus (Lean, 1973). Some of the colloidal phosphorus may be hydrolyzed directly to phosphate; however, some of the colloidal phosphorus becomes biologically unavailable and is precipitated out of the trophogenic zone. The reduced collection of phosphorus at the 6 m depth during June and July indicated phosphorus was tied up in growing organisms (Figure 26). Later, during August and September, considerable quantities of phosphorus were collected, presumably as dead algal and zooplankton remains. During this same period of intense algal growth in

Figure 26.--Seasonal variation in total phosphorus content (mg m^{-2} day^{-1}) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974.

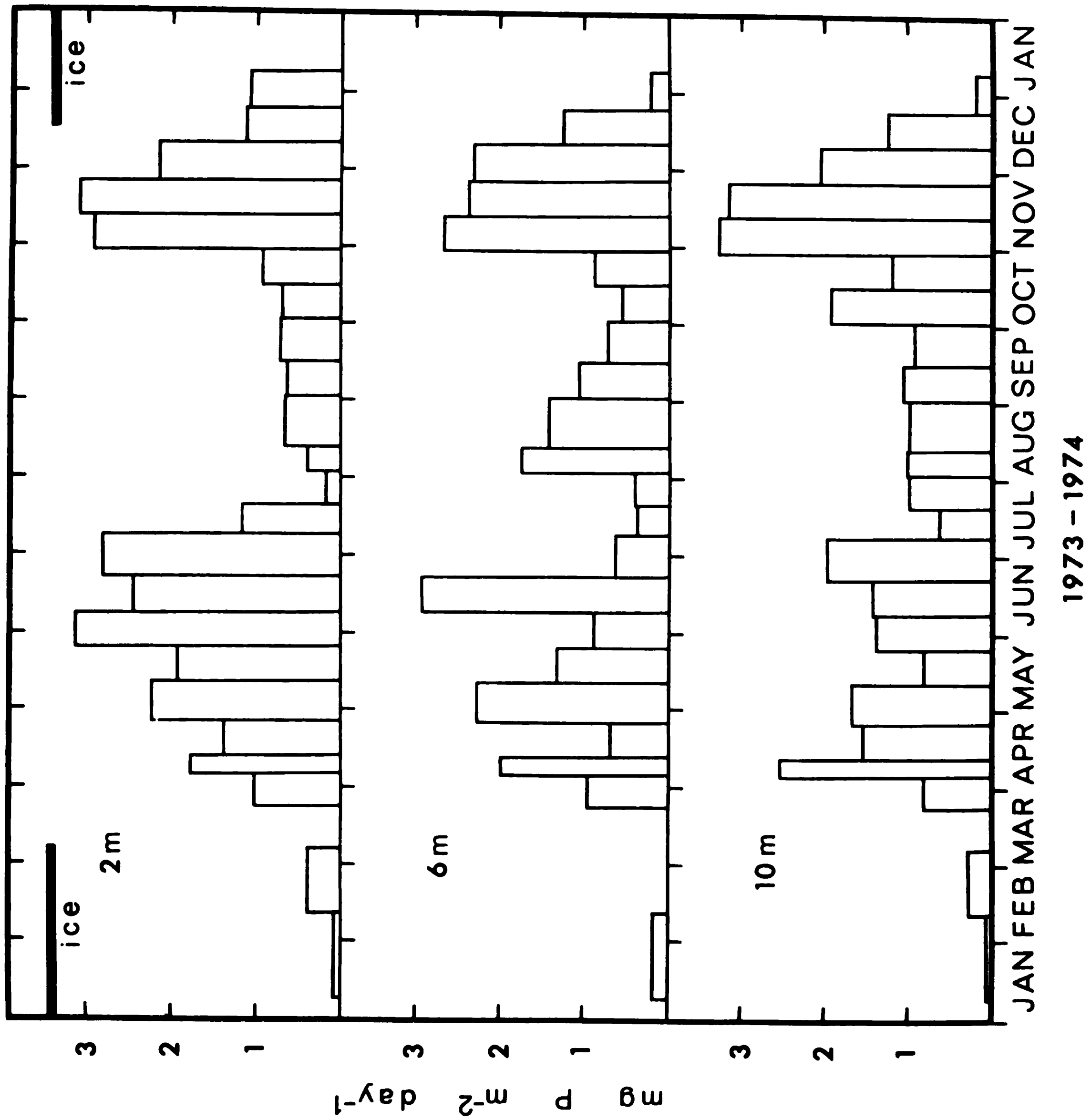

ice
ice
2m
6m
10m
3
2
1
3
2
1
3
2
1
mg P m-2 day-1
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 - 1974

Figure 26

June, July, and August (Figure 23), large quantities of calcium carbonate were precipitated (Figure 25). This observation supports the contention photosynthesis does play an important role in decalcification of water in the trophogenic zone. The assimilation of free CO_2 and/or bicarbonate ions by aquatic plants and resulting calcium carbonate precipitation has been observed and well studied in natural waters (Ruttner, 1921, cited by Ruttner, 1963; Gessner, 1959; Schelske and Callender, 1970).

Bacteria play a minor role in inducing calcium carbonate precipitation; however, they are involved in forming larger crystals in the sediment (Kusnezow, 1966). It is unlikely that bacterially induced precipitation is an important process in Lawrence Lake, since, large (e.g. 8 cm diam.) calcium carbonate crystals are not found.

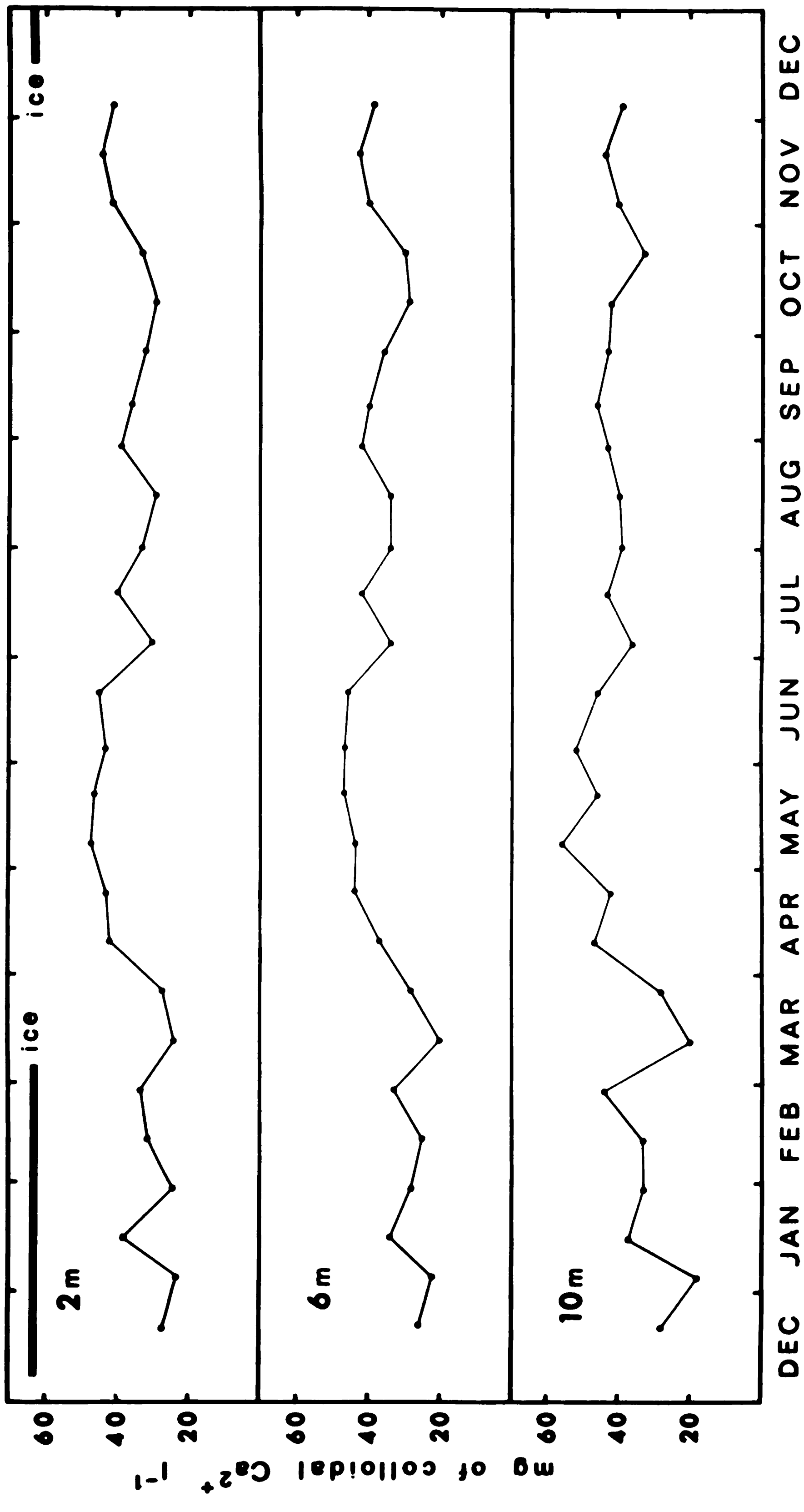
Likewise organisms such as fresh water clams and snails are not considered important here; because, they do not initiate calcium carbonate precipitation in the pelagic zone.

5. Supersaturation with Calcium Carbonate

The apparent supersaturation with calcium carbonate in Lawrence Lake was investigated during 1973. As described in the methods section, total calcium was determined by flame atomic absorption and the ionized (free) calcium was determined by a calcium ion electrode. Total calcium and ionized calcium determinations were sumed and averaged over these depths: 0, 1, 2; 3, 4, 5, 6; and 7, 10 meters. The mass in mg of suspended or colloidal Ca^{2+} l^{-1} during 1972 - 1973 was obtained by subtracting the ionized calcium determinations from the total calcium values (Figure 27).

Figure 27.--Variations in colloidal calcium (mg Ca^{2+} l^{-1}) suspended in Lawrence Lake at Station A. Quantity of suspended calcium is given for 2, 6, and 10 meter depths.

Figure 27


ice
ice
2m
6m
10m
60
40
20
60
40
20
60
40
20
mg of colloidal Ca^{2+} l^{-1}
DEC
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC

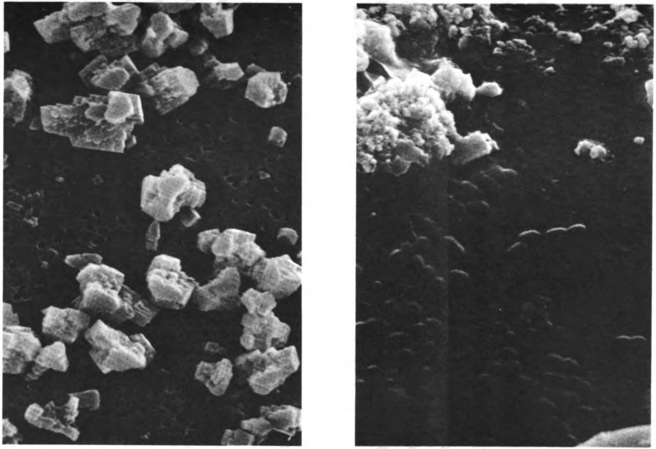
During the annual cycle of colloidal calcium carbonate there was an average of 37 mg Ca^{2+} l^{-1} suspended in the lake water. There was no period when the lake was undersaturated. The level of colloidal calcium was less during spring circulation (6 March - 26 April). The lower spring values were related to an increase in ionized calcium which indicated calcium carbonate was redissolving. A rapid increase in colloidal calcium content occurred after stratification until June, July, and August when the levels dropped. The drop in colloidal calcium during this period is related to elevated levels of algal growth in the metalimnion (Figure 23) and precipitation of calcium carbonate (Figure 25).

6. SEM Photos of Calcite Crystals

Water samples collected at 6 m during May 1973 were filtered onto a 0.4 μ Nuclepore filter after the water was first filtered through a series of larger Nuclepore filters. The size of these crystals (Figure 28a) are larger than ordinarily occur in the water; since, vacuum filtering can remove CO_2 from the water (Felfoldy and Kalke, 1957) and cause crystal nucleation and growth to occur. The crystals range from 1 μ to 6 μ in length and show a dendritic growth pattern. Dendritic development occurs when solvent molecules are unable to rapidly diffuse away from the crystal surface where growth is occuring; thus corners located in less severely blocked areas continue to grow at a more rapid rate (Walton, 1967). Impurities are also suggested as playing an important role in causing dendritic growth. Dendritic crystals provide a surface prone to entrap surface adsorbed compounds and this mechanism may be important in coprecipitation.

Figure 28.--Scanning electron micrographs of material collected from Lawrence Lake. a: Calcite crystals filtered onto a 0.4 μ Nuclepore filter from water collected at 6 meters, May 1973 (2000X). b: Seston collected from 10 meters showing bacteria in the foreground with calcite crystals embedded in an organic matrix in the background (2000X).

Figure 28



a

b

E. Ash

The most obvious characteristic in the annual pattern of ash content in the seston during 1972 (Figure 29) and 1973 (Figure 30) was an increase during spring and fall circulation when resuspension of the bottom sediment occurred.

Ash content in seston was higher during the months of May, June, and July then tapered off during late summer (Figures 29 and 30). This sedimentation pattern suggested diatoms were primarily involved and agrees with data from Manny (1971) and unpublished algal data (Wetzel, personal communication) on Lawrence Lake. Their data showed larger diatom populations during late spring and early summer, as well as late fall and winter. Annual patterns of SiO_2 content (Figures 31 and 32) in lake water also showed a more rapid utilization of silica during May, June, and July than other periods of the year.

Examination of seston by light microscope and scanning electron microscopy showed large numbers of diatom frustules were present on the filters (Figures 18a, 18b; and 19a, 19b) during most of the season. Ash content in seston may have been increased somewhat by clay particles, but most observations supported the contention that diatom frustules were the major component.

Figure 29.--Seasonal variation in ash content (g m^{-2} day^{-1}) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1972 to 8 January 1973.

Figure 29

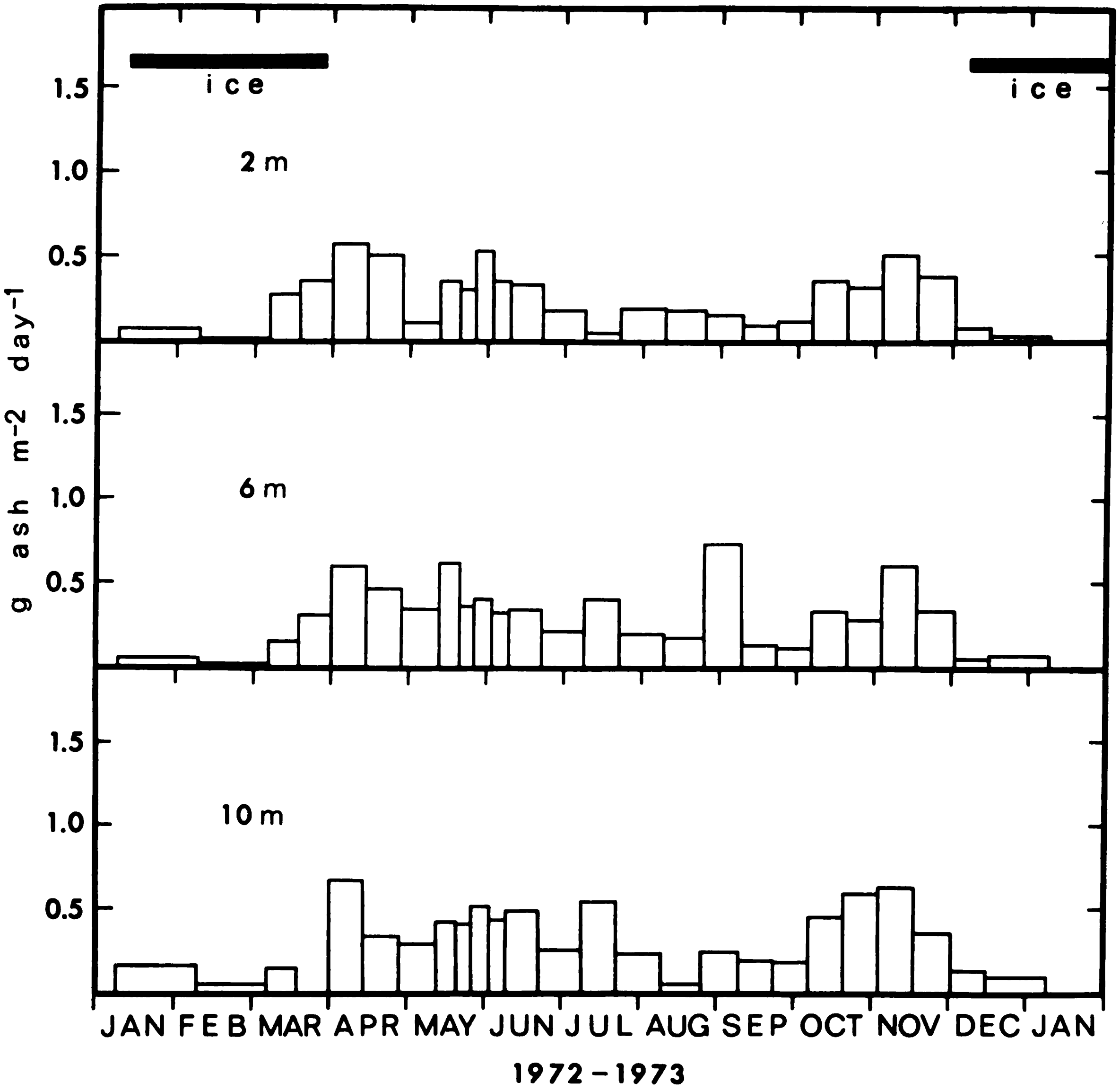

ice
ice
2 m
6 m
10 m
1.5
1.0
0.5
g ash m-2 day-1
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1972 – 1973

Figure 30.--Seasonal variation in ash content (g m^{-2} day^{-1}) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974.

Figure 30

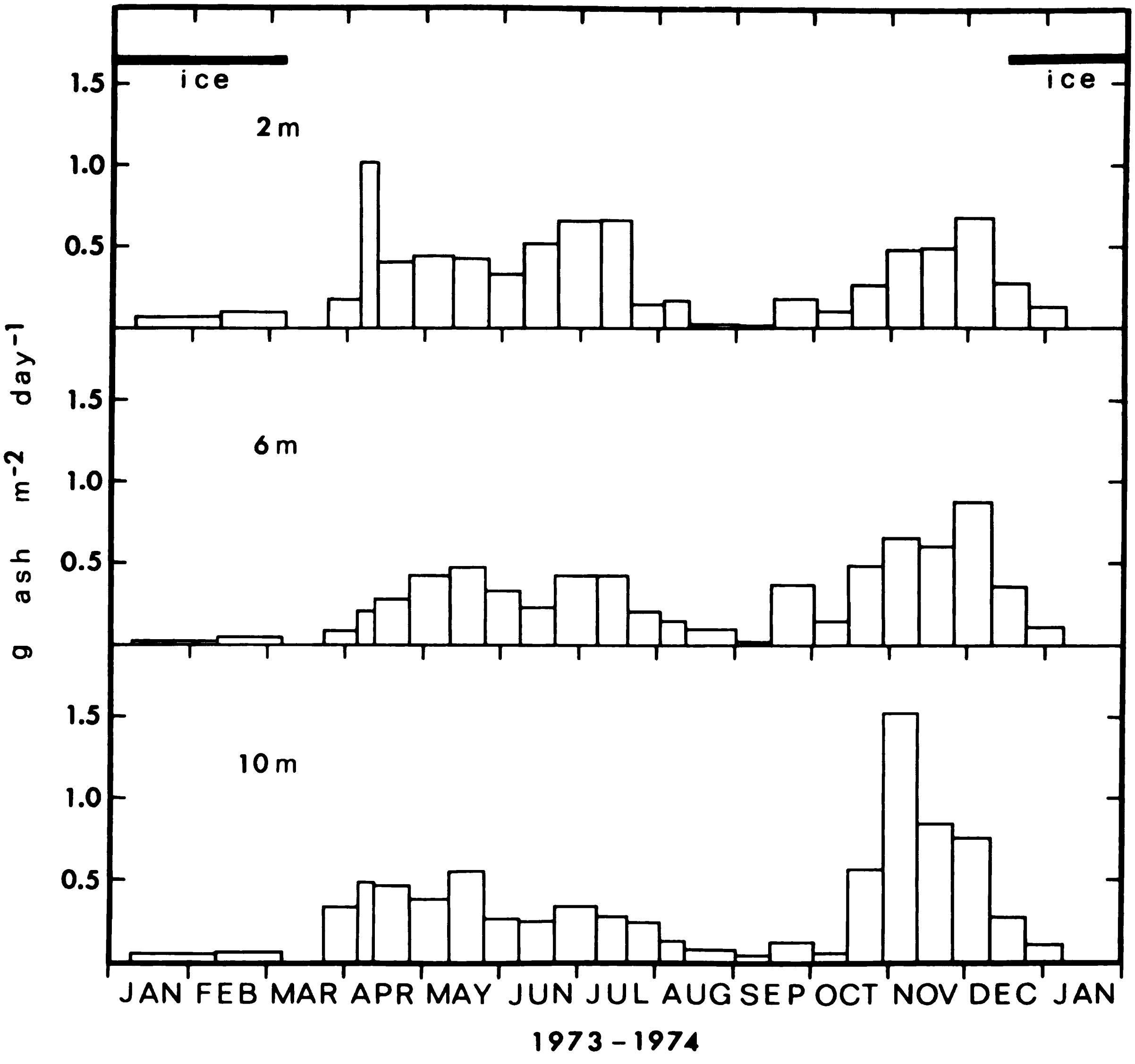

ice
ice
2 m
6 m
10 m
1.5
1.0
0.5
g ash m-2 day-1
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 - 1974

Figure 31.--Isopleths of SiO_2 (mg l^{-1}) at Station A in Lawrence Lake, 1972.

Figure 31

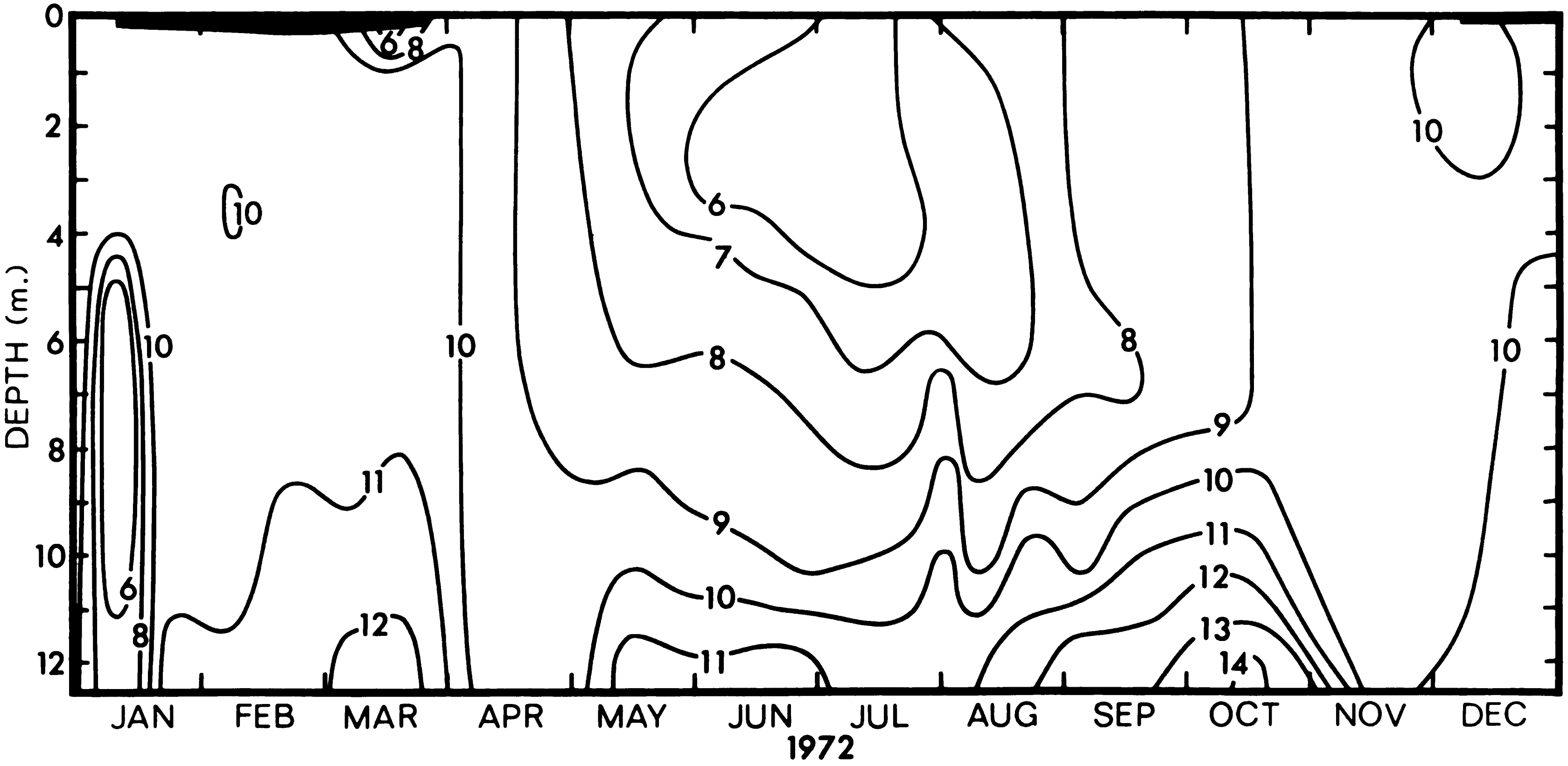
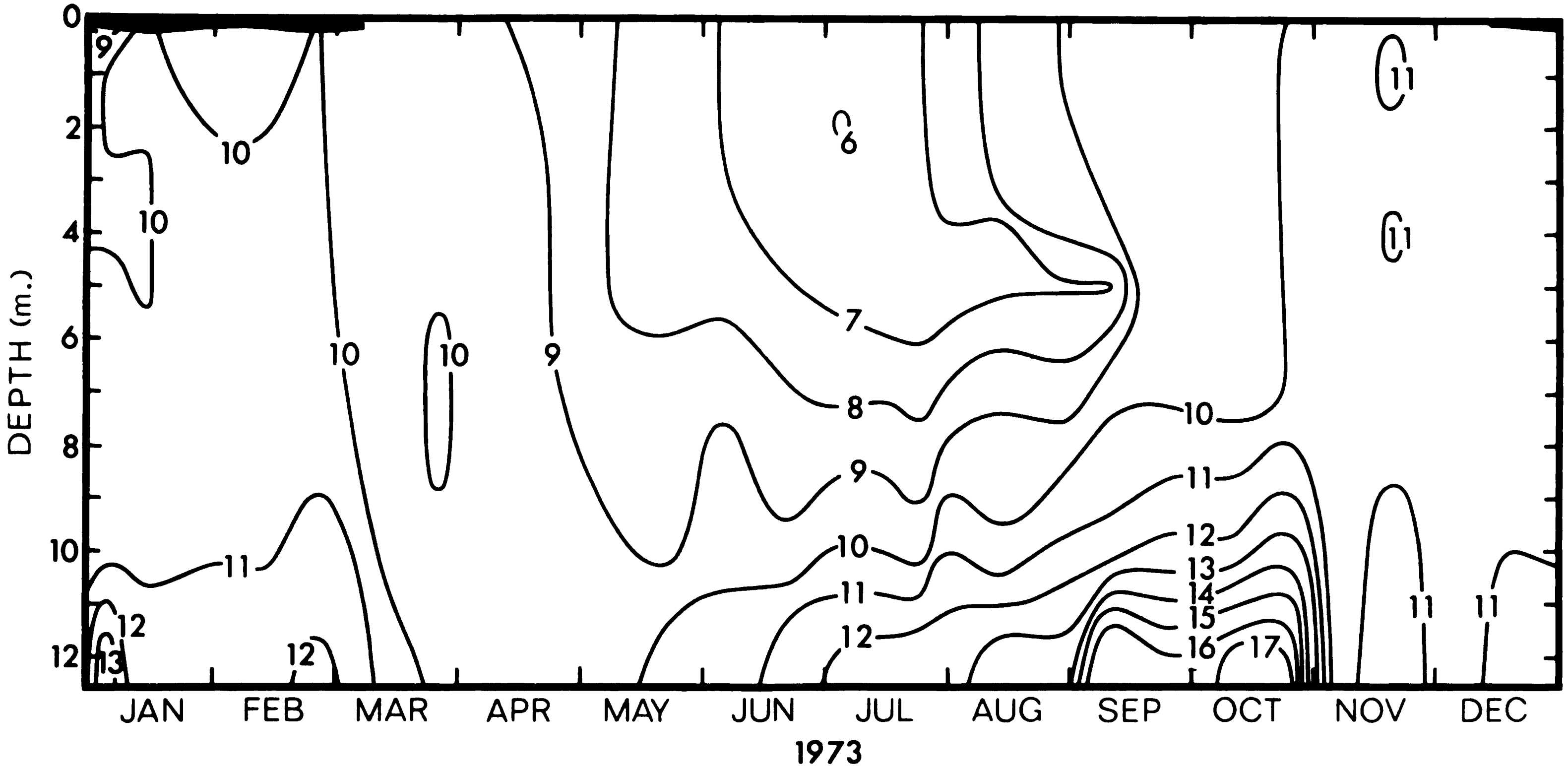

DEPTH (m.)
0
2
4
6
8
10
12
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1972
10
6
8
11
12
6
7
8
9
10
11
12
13
14

Figure 32.--Isopleths of SiO_2 (mg l^{-1}) at Station A in Lawrence Lake, 1973.

Figure 32


DEPTH (m.)
0
2
4
6
8
10
12
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
1973
9
10
10
10
10
9
6
7
8
9
10
11
12
10
11
12
13
14
15
16
17
11
11
11
11
11
12
12
13

IV. SEDIMENTATION OF METABOLICALLY IMPORTANT PARTICULATE MATERIAL FROM THE TROPHOGENIC ZONE

A. Particulate Organic Carbon

The annual cycle of particulate organic carbon (POC) content of seston revealed precipitation of POC was relatively low throughout summer stratification and was further reduced under ice cover (Figure 33; Table 3). The correspondence between chlorophyll a distribution in the lake (Figure 23) and POC content of the seston (Figure 33) during 1973 implies dead and/or living algae were a major component of the organic seston. Increased algal growth in the metalimnion is clearly reflected in POC sedimentation at 6 and 10 meters during July and August.

Spring circulation POC values were 2.7 times higher than fall circulation values (Table 3). Higher spring POC values suggest the resuspended organic material contained more oxidizable carbon than seston collected during fall circulation.

A comparison of the annual cycle of POC (Figure 33) and the organic matter cycle (Figure 21) shows the heterogeneity of the organic material in the seston. General similarities are noted between the two carbon determinations, but the organic matter values are considerably higher throughout the season. The disparity between these two values are related in part to the dissimilar methods used. Organic matter content was determined by loss of weight upon ignition at 550°C for one hour; whereas, POC was determined by acid-dichromate oxidation based upon glucose carbon equivalents. The ignition method would include

Figure 33.--Seasonal variation in particulate organic carbon (g POC m^{-2} day^{-1}) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974.

Figure 33

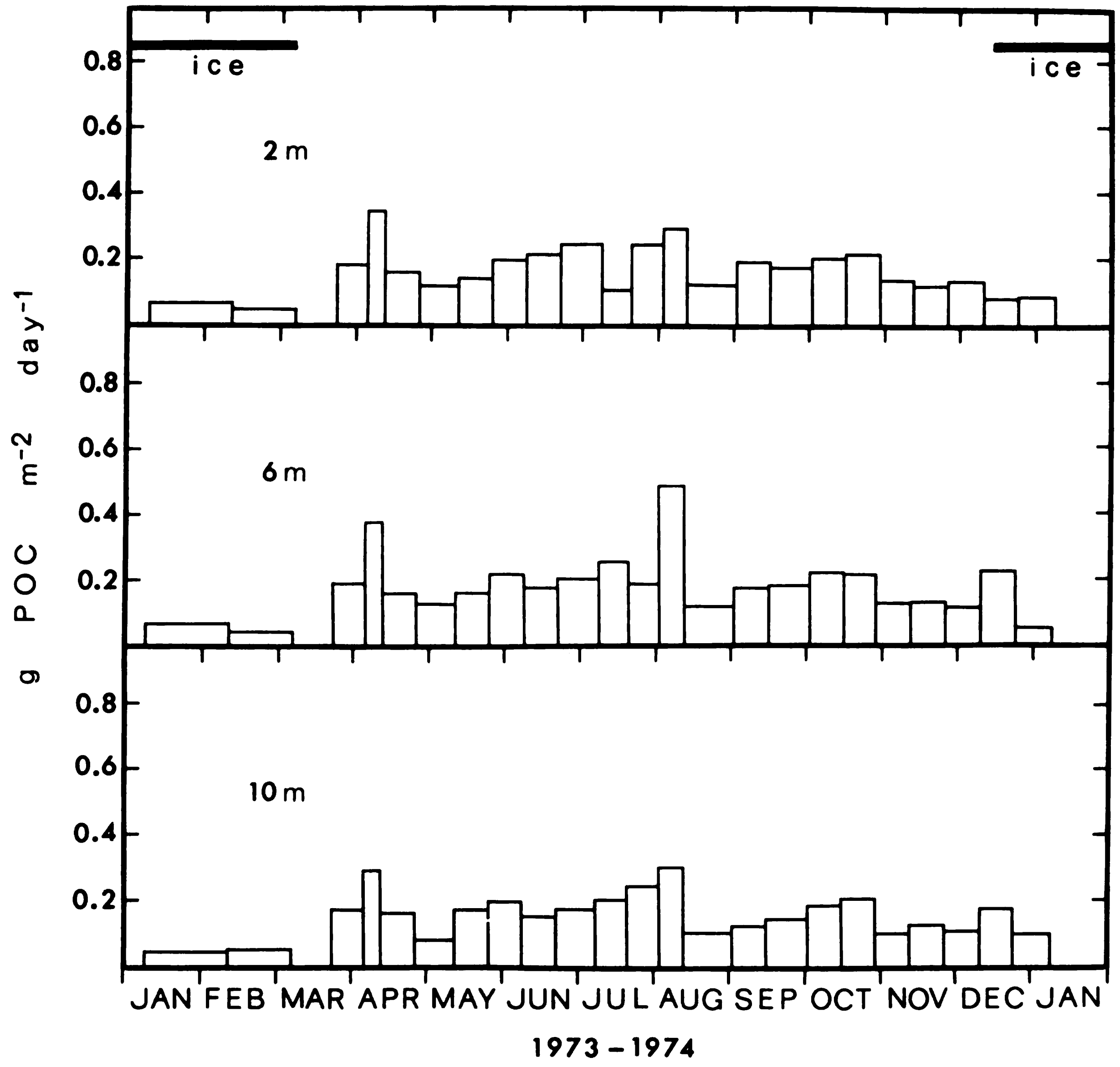

ice
ice
2 m
6 m
10 m
0.8
0.6
0.4
0.2
g POC m^{-2} day^{-1}
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 - 1974

TABLE 3.--Sedimentation rates of particulate organic carbon (POC), Kjeldahl nitrogen, and total phosphorus in the seston of Lawrence Lake during 1973-1974. Particulate organic carbon and nitrogen are expressed as mg m^{-2} day^{-1}. Phosphorus is expressed as μ g m^{-2} day^{-1}.

	POC			Nitrogen			Phosphorus		
	2m	6m	10m	2m	6m	10m	2m	6m	10m
1973									
Winter Stratification (57 days)	2.03	1.95	1.77	.326	.243	.238	.0163	.00317	.00577
Spring Circulation (20 days)	26.3	26.5	23.4	9.75	11.0	13.9	.140	.147	.167
Summer Stratification (200 days)	13.2	14.4	12.4	8.98	9.84	9.65	.0970	.0803	.0878
Fall Circulation (56 days)	8.34	10.4	9.15	15.8	16.6	20.0	.167	.155	.173
1974									
Winter Stratification (15 days, to end of study)	5.85	3.34	6.55	.961	1.88	1.03	.0720	.0144	.0116
Annual Average	11.1	11.3	10.7	7.16	7.91	8.96	.0985	.0800	.0890

the more refractory carbon compounds, while acid-dichromate oxidation may exclude some of these materials. These data indicate less than half of the total organic matter is composed of the more oxidizable particulate organic carbon.

B. Kjeldahl Nitrogen

Nitrogen levels are high in Lawrence Lake and nitrogen accumulates in the hypolimnion (Manny, 1971); epilimnetic productivity is not inhibited by lack of nitrate.

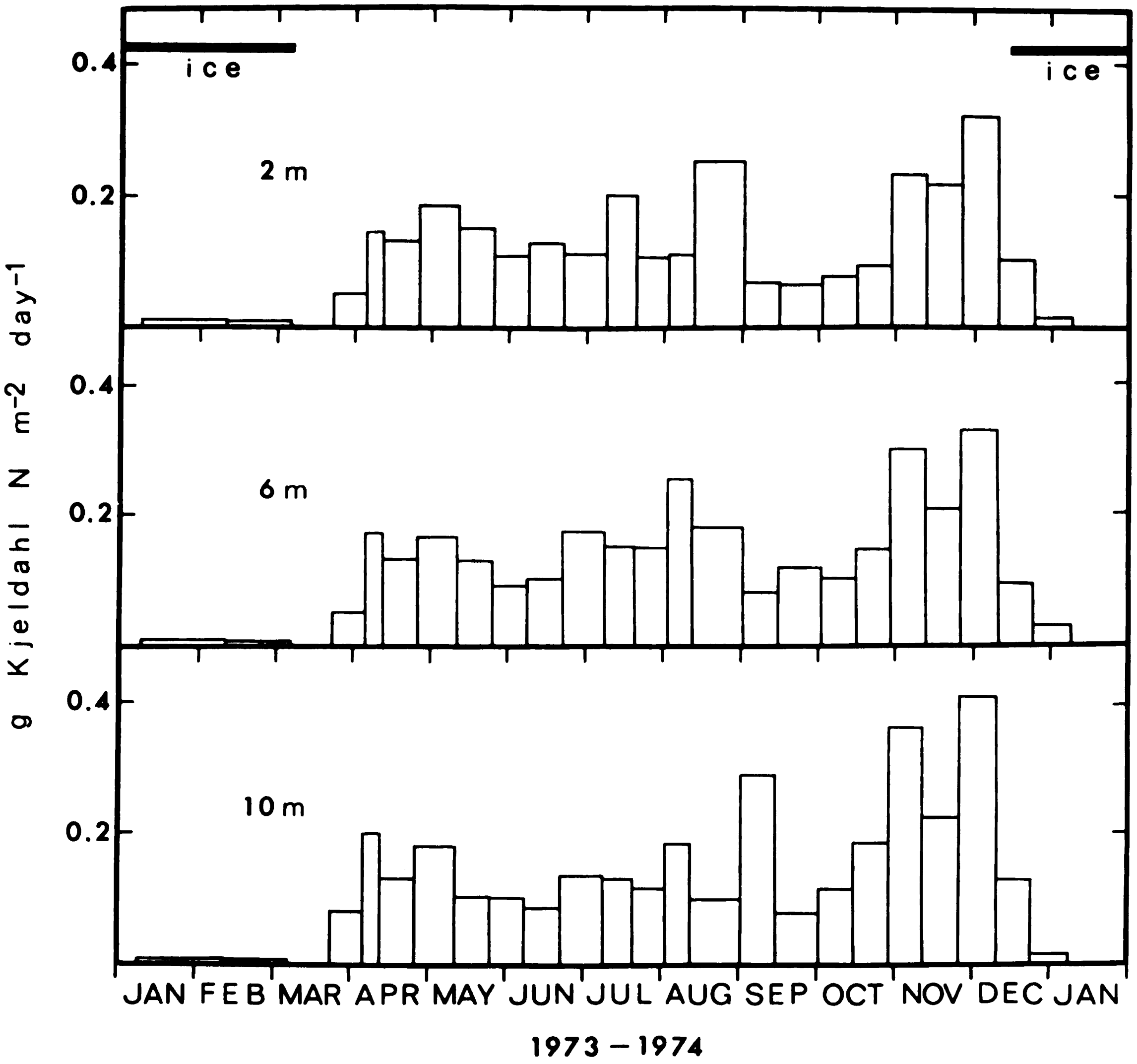
Under the ice, Kjeldahl nitrogen content of seston was very low (Figure 34). Reduced levels of seston sedimented during this period and probably some of the nitrogen was stored in the cells of non-sedimenting organisms.

The nitrogen content of seston during fall circulation was 1.5 times greater than that of spring circulation (Figure 34; Table 3). Bacterial decomposition of the sediment during ice cover may account for a lowered nitrogen content in the vernally resuspended sediment; however, partial mixing during spring circulation in 1973 may have resuspended less nitrogenous material.

Variations in Kjeldahl nitrogen sedimentation during summer stratification are closely related to periods of fluctuations in phytoplankton growth (Figure 23). During and after periods of increased algal growth, sedimenting seston contained large numbers of dead and live cells, and was correlated with increased nitrogen content. Some nitrogen was certainly decomposed and released as dissolved nitrogen before the detritus reached the sediment trap, but most of the nitrogen accumulates in the hypolimnion (Manny, 1971).

Figure 34.--Seasonal variation in Kjeldahl nitrogen (g m^{-2} day^{-1}) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974.

Figure 34


ice
ice
2 m
6 m
10 m
0.4
0.2
0.4
0.2
0.4
0.2
g Kjeldahl N m-2 day-1
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 – 1974

Kjeldahl nitrogen content of seston was similar at all depths measured. The slight differences in quantity were related to the time required for the material to reach the hypolimnion. During August the elevated quantity of Kjeldahl nitrogen found at 2 and 6 meters appeared two weeks later in the 10 meter trap.

C. Total Phosphorus

Annual changes in total dissolved phosphorus have been measured in Lawrence Lake (e.g. Wetzel, 1972, Figure 1 and 2), and variation between depths has not been great. The pool of dissolved total phosphorus appears to be relatively constant. A uniform level of total dissolved phosphorus yields no information on turnover rates and availability of phosphorus in the trophogenic zone. Phosphorus content in the seston; however, does give indirect evidence of availability and factors that may regulate availability.

Considerable amounts of phosphorus were resuspended during spring circulation (Figure 26 and Table 3). Levels of total dissolved phosphorus were not appreciably increased during spring circulation (Wetzel, 1972). The resuspended phosphorus was either not soluble or rapidly taken up and stored by phytoplankton. Large quantities of resuspended $CaCO_3$ during spring circulation (Figure 25) may have reduced the total dissolved phosphorus. Much of the resuspended phosphorus may have adsorbed to colloidal and particulate calcium carbonate (Ohle, 1935, 1937; Gessner, 1939). Otsuki and Wetzel (1972) have shown that more than 74% of phosphate ion was found to precipitate with calcium carbonate as the pH was raised to 9.5 - 10.

The rate of phosphorus removal at 2 m remained high until early July (Figure 26). The elevated rate of phosphorus precipitation during this period was correlated directly to the annual pattern of chlorophyll a (Figure 22), which showed phytoplankton activity was also high until early July. After July, the rate of phosphorus precipitation at 2 m remained low until fall circulation occurred in late October.

Rates of phosphorus removal at 6 m were very erratic until July. The fluctuation between high and subsequently reduced levels reflect periods of rapid phytoplankton growth, followed by periods of phytoplankton death. In August much of the epilimnetic phosphorus was displaced into the metalimnion where it perhaps contributed to the stimulated phytoplankton growth at 6 m (Figure 23). After August, successively lower levels of phosphorus were collected at 6 meters until fall circulation occurred.

The quantity of total phosphorus retained in the 10 m traps was higher whenever substantial phytoplankton reduction occurred in the trophogenic zone. The 10 m seston also reflected lower amounts of total phosphorus when rapid growth and storage of phosphorus occurred (cf. Figures 23 and 26).

The rate of phosphorus removal was much reduced during winter, because phytoplankton growth is very low under ice and snow cover.

V. ASSOCIATION OF IRON AND VITAMIN B_{12} WITH CALCIUM CARBONATE

A. Iron Experiments

1. Introduction

Additions of iron to Lawrence Lake water are immediately precipitated by inorganic compounds and are ineffective in stimulating algal C^{14} uptake (Wetzel, 1972). Wetzel (1972) found chelator compounds such as nitrotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) consistently stimulated algal growth when added in the proper ratios. The photosynthetic rate doubled within 4 hours. Additions of NTA were in the ratio of approximately 100 μg liter^{-1} iron : 100 μg liter^{-1} NTA; however, greater concentrations of EDTA were required (500 μg liter^{-1}). Natural amino compounds also complexed iron and stimulated phytoplankton growth. Experiments on iron availability by Schelske (1962) have shown similar results.

It is unlikely that trivalent iron is analytically detectable in alkaline lakes (Hutchison, 1957). Iron is retained in lake water as colloidal ferric hydroxide, adsorbed onto particulate matter, and in complexes with natural chelator compounds. Dissolved organic matter has been considered to function as a chelator of metals in lakes (Saunders, 1957).

Laboratory experiments demonstrated the complex nature of iron removal during calcium carbonate precipitation.

2. General Procedures

Water was collected from 6 meters in Lawrence Lake on 18 April 1973, filtered (984 H Reeve Angel), and stored at 15°C for three weeks before use. Triplicate samples of lake water were removed and allowed to equilibrate for 2 hours at 25°C before each experiment was started. Initial iron, calcium, and pH determinations were made, finally iron was added to give 1000 μg $liter^{-1}$. The sample flasks were placed on magnetic stirrers for one half hour after which subsamples were removed, filtered, and examined for iron and calcium content in solution and on the filters. Calcium precipitation was induced by adding 0.2 M NaOH to each flask whereby the pH was raised by increments of 0.5 each time NaOH was added. Samples were stirred one-half hour after each addition of NaOH. Subsequently, subsamples were removed to determine iron and calcium content on filters and in solution. This procedure was repeated until the pH reached 9.5.

The experiments were first done without any additions of chelator compounds, then repeated with EDTA and yellow organic acid extracted from <u>Scirpus subterminalis</u> Torr. (Otsuki and Wetzel, 1973).

Changes in calcium concentration were monitored by flame atomic absorption (Jarrell Ash Model 82-700). pH was determined electrometrically with a Beckman Expandomatic (Model 76-A) pH meter. Total iron concentrations were determined colorimetrically (Golterman, 1969). Iron samples were digested 15 minutes in a hot 10% $NH_2OH \cdot HCl$ and 4 N HCl solution, after which bathophenanthroline was added to develop a red-colored iron complex. The complex was subsequently extracted into hexanol and assayed spectrophotometrically (Lee and Stumm, 1960).

3. Results

Experiments on iron and calcium carbonate interactions demonstrated iron was substantially removed when the pH was increased to 9.0 (Table 4). More iron was contained in Lawrence Lake water at pH 9.5 than one would expect if pure solution chemistry was involved. This increase in iron content under these conditions may have been related to two conditions; equilibrium had not been reached and a longer lapse of time before sampling would have lowered this value, or naturally occurring organic compounds in Lawrence Lake water may have chelated some of the iron. When either EDTA or yellow organic acid was added, some iron remained in the solution after the pH had been increased to 9.5. Apparently, the chelator compounds were able to complex metabolically significant amounts of iron and keep it in solution.

Addition of EDTA and yellow organic acid reduced the rate of $CaCO_3$ precipitation (Table 4). When no chelator compound was added, 21% of the $CaCO_3$ precipitated at pH 9.0, and 50% at pH 9.5. When EDTA was added only 3.7% of the $CaCO_3$ precipitated when the pH was increased to 9.0 and 54% at pH 9.5. Additions of yellow organic acid lowered the rate of $CaCO_3$ precipitation at 9.0 to 2.2% of the total amount in solutions and to 57% at pH 9.5. These data suggest $CaCO_3$ formed a complex with the chelator compounds at pH 9.0 and when precipitation did occur (pH 9.5) the chelate was removed. Calcium was able to compete with iron for chelating ligands. Such a mechanism would prevent, or at least

TABLE 4.--Amount of iron and calcium carbonate precipitated as pH is increased.

	No Chelator Compound				EDTA (100 ug 1^{-1})				Yellow Organic Acid (5.37 mg 1^{-1})			
	Total Fe (ug 1^{-1})		Ca^{2+} (mg 1^{-1})		Total Fe (ug 1^{-1})		Ca^{2+} (mg 1^{-1})		Total Fe (ug 1^{-1})		Ca^{2+} (mg 1^{-1}	
pH	Sol'n	Filt'r	Sol'n	Filt'r	Sol'n	Filt'r	Sol'n	Filt'r	Sol'n	Filt'r	Sol'n	Filt'r
Start (8.30)	928	---	71.8	---	1110	---	68.9	---	1270	---	62.8	---
8.5	9.42	---	71.4	---	1060	---	68.7	---	1290	---	61.7	---
9.0	trace	949	58.7	15.6	14.6	1240	68.5	2.56	31.5	1170	61.7	1.36
9.5	2.51	1.54	39.0	36.2	22.7	14.8	31.3	37.0	15.1	39.8	28.4	36.1

reduce, chelation of iron. Work by Otsuki and Wetzel (1973, Figure 1, Table 1) demonstrated that more than 30% of yellow organic acids were removed from a solution when $CaCO_3$ precipitated.

Although a distinct coprecipitation mechanism was not obvious between iron and calcium on the basis of these experiments, conditions may prove otherwise in nature. Under natural conditions, the pH in Lawrence Lake water rarely rises above 8.4 (Figure 13 and 14), and thus, $CaCO_3$ nucleation and crystal growth is much slower than the rapid nucleation induced in these experiments. Colloidal $CaCO_3$ is present in Lawrence Lake (Figure 27) and it is possible adsorption of iron onto $CaCO_3$ may occur under natural conditions. This would involve adsorption of complexed iron at the liquid-solid interface, rather than simple adsorption of ferric hydroxide.

B. Experiments With Vitamin B_{12}

1. Introduction

Vitamin B_{12} is a growth factor that is required by many algae (Droop, 1962; Provasoli, 1963). Menzel and Spaeth (1962) suggested vitamin B_{12} was the growth promoting substance that produced a diatom maximum in the Sargasso Sea. Although most data on vitamin B_{12} are concerned with marine algae, vitamin B_{12} is also required by many freshwater algae. *Euglena gracilis* is often used in the bio-assay of vitamin B_{12}. Wetzel (1972, Figure 20) found with bioassays of *in situ* phytoplankton in Lawrence Lake that vitamin B_{12} caused a significant increase in carbon fixation. Similar results were found in hard-water lakes of northeastern Indiana (Wetzel, 1965, 1966).

Direct adsorption of organic nutrients, such as vitamin B_{12} onto particular $CaCO_3$ would reduce photosynthetic rates in Lawrence Lake. Thus, laboratory experiments were designed to study interaction between vitamin B_{12} and particulate $CaCO_3$.

2. General Procedures

Lyophilized tritium-labeled vitamin B_{12} (250 µCi, Cyanocobalamin-H3(G), Amersham Searle) was dissolved in 85 ml of glass distilled water under sterile conditions, filtered through a 0.22 µm GS filtration unit, and ampoulated by auto-syringe into sterile ampoules.

Radioassay of the vitamin B_{12} stock solutions were determined on a Beckman LS-150 scintillation counter and expressed as counts per minute. Ten µl of the vitamin B_{12} solution were radioassayed directly in a 1:1 (v/v) mixture of water and Insta-Gel (New England Nuclear; Boston, Mass.). Ten µl of vitamin B_{12} solution was also injected into a filter and the radioactivity of the evolved gas was determined after combustion on a Packard Tritium-Carbon oxidizer in 20 ml of scintillation mixture which consisted of PPO/bis-MSB/toluene (15g, 1g/l). Counting efficiency was calculated using external standard ratios. All samples were corrected for memory loss by adding counts min^{-1} in blanks assayed between each sample.

Lake water was collected from 6 m in Lawrence Lake, filtered through HA Millipore filters, and stored three weeks at 15C. All experiments were performed at 25C. Filtered lake water (215 ml) was placed into triplicate 300 ml Erlenmeyer flasks, fitted on the bottom with rubber septa sample ports. Two levels at less than 0.01 µg per liter of tracer vitamin B_{12}, 1 ml (3.2 µCi) and 2 ml (6.4 µCi), were added to separate sets of triplicate flasks. Before the flasks were fitted with a rubber stopper, initial pH and vitamin B_{12} activity and calcium concentrations were determined and a test tube containing 5 ml of 0.5 N NaOH was suspended inside the flask. The flasks were placed on magnetic stirrers. Calcium carbonate precipitation was induced as CO_2 was absorbed into the NaOH solution. Calcium concentration and pH were determined every 24 hours over a period of 240 hours. When the experiment was ended, the amount of vitamin B_{12} in the lake water was radioassayed directly in 10 ml of lake water and 10 ml of Insta-Gel mixture on a Beckman LS-150 scintillation counter. The precipitated $CaCO_3$ was filtered onto HA Millipore filters, combusted on a Packard Tritium-Carbon oxidizer, and counted on the Beckman LS-150 scintillation counter.

Distilled water samples containing vitamin B_{12} showed significant quantities of vitamin B_{12} were not retained on filters.

The second experiment was conducted in a similar manner to the first; however, there were two major changes. First, additions of 0.2 M Na_2CO_3 were used to increase the pH by increments of 0.5 which caused the $CaCO_3$ to precipitate very quickly. Second, after each increase in pH, samples were removed from each experimental flask and filtered onto HA Millipore filters to monitor the association of vitamin B_{12} with precipitating calcium carbonate. Calcium ion concentration was determined after each pH increase. Radioassays of vitamin B_{12} activity in the solution and on the millipore filters were determined by the same methods used in the previous experiment. Triplicate flasks were stirred magnetically during the entire experiment and 15 minutes separated each addition of 0.2 M Na_2CO_3.

3. Results

The results of the first experiment on vitamin B_{12} and $CaCO_3$ interactions are summarized on Table 5. When 1 ml of vitamin B_{12} solution was added, 15% of the counts were recovered on the filter with the calcium carbonate. In contrast, 12% of the counts were recovered with the precipitated calcium carbonate when 2 ml of the vitamin B_{12} was used. The solution in the flask contained 88% of the counts at this concentration level.

The vitamin B_{12} may have been taken up by bacterial populations; however, more of the vitamin B_{12} would be utilized when 2 ml of vitamin B_{12} solution was used, providing the bacterial needs were not already satisfied.

The calcium concentration dropped throughout the experiment and at the termination of the experiment, 87% of the $CaCO_3$ had precipitated (Table 5). Vitamin B_{12} concentration is low in Lawrence Lake (Wetzel, 1972) and a similar 12-15% reduction of vitamin B_{12} availability in Lawrence Lake, as shown during the ten day period of this experiment, would significantly influence metabolism in the lake. Any reduction in vitamin B_{12} concentration means it would be unavailable for bacterial or phytoplankton utilization.

A summary of the second experiment on vitamin B_{12} association with calcium is given in Table 6. Average values of the triplicate samples are given for the radioassay of vitamin B_{12} in solutions and collected on HA Millipore filters. In this experiment, the pH was raised from 8.30 to 9.50 during a period of 45 minutes.

Since there was variation among the triplicate samples, it was not immediately obvious if the changes in vitamin B_{12} counts min^{-1} were

TABLE 5.--Loss of vitamin B_{12} and calcium ion from lake water as $CaCO_3$ precipitated.

Time	Treatment							
	1 ml B_{12} added				2 ml B_{12} added			
	pH	% Ca^{2+} lost	counts min^{-1} (sol'n)	counts min^{-1} of filtered material	pH	% Ca^{2+} lost	counts min^{-1} (sol'n)	counts min^{-1} of filtered material
Start	8.43		74,766 ± 523		8.43		151,577 ± 450	
29 hr 45 min	8.43	44			8.43	36		
53 45	8.43	66			8.44	62		
74 05	8.45	72			8.42	67		
98 05	8.49	77			8.48	72		
122 05	8.52	80			8.55	77		
146 05	8.79	82			8.84	79		
170 05	8.78	83			8.86	81		
194 05	8.67	--			8.75	--		
218 05	8.86	85			8.88	83		
240 45	8.85	87	63,802 ± 1940	6,857 ± 150	8.97	85	133,012 ± 422	12,715 ± 176

TABLE 6.--Interaction between B_{12} and $CaCO_3$ when the pH was raised rapidly with 0.2 M Na_2CO_3.

	1 ml of B_{12} sol'n added			2 ml of B_{12} sol'n added		
		Counts min^{-1}			Counts min^{-1}	
pH	% Ca^{2+} lost	Sol'n	Filter	% Ca^{2+} lost	Sol'n	Filter
Start (8.30)	---	68,620	4,430	---	135,748	8,813
8.50	9.1	68,541	3,826	8.3	140,446	7,241
9.00	18	69,374	3,301	36	138,391	6,662
9.50	94	69,108	3,468	96	137,662	6,825

significant (Table 6). A nested analysis of variance computation was determined on the data. This design was used, because four treatment levels were subdivided into randomly chosen triplicate sample flasks (Sokal and Rohlf, 1969). An analysis of variance determined if the observed differences among the counts $\min^{-1}$ were due to variation among the triplicate samples or actual changes in vitamin B_{12} concentrations.

Analysis of variance on the change in vitamin B_{12} in solution (counts $\min^{-1}$) was not significant at the 5% level (Table 7), when either 1 ml or 2 ml of vitamin B_{12} solution was used. It would have been necessary to obtain a 4.07 critical value of the F-distribution to be significant at the 5% level. This means there was essentially no change in the amount of vitamin B_{12} in the solution as the pH was increased.

Table 8 contains analysis of variance data on the concentration of vitamin B_{12} (counts $\min^{-1}$) retained on the filter with $CaCO_3$ after the pH was increased. A critical value of the F-distribution was 7.59 at the 1% level and the data was significant for both concentrations of vitamin B_{12}. Vitamin B_{12} was retained on the filter with $CaCO_3$ at each pH level; however, less was retained as the pH reached 9.5 (Table 6). The percentage of vitamin B_{12} removed on the filter with $CaCO_3$ at each pH level was the same whether 1 ml or 2 ml of vitamin B_{12} solution was added (6.5%, 5.6%, 4.8%, 5.1% and 6.5%, 5.3%, 4.9%, 5.0%, respectively). The surface area of $CaCO_3$ was the same in each flask. The same quantity of vitamin B_{12} was adsorbed, regardless of the concentration of vitamin B_{12} used. This indicated there was an excess of adsorption sites.

The largest percentage of vitamin B_{12} was removed at pH 8.30 before the pH was increased (Table 6). Suspended calcium carbonate

TABLE 7.--Analysis of variance table of data on vitamin B_{12} content in lake water after pH was raised rapidly from pH 8.30 to pH 9.50. The data is given for two concentrations of vitamin B_{12}.

	1 ml of B_{12} sol'n used				2 ml of B_{12} sol'n used			
Source	DF	SS	MS	F	DF	SS	MS	F
Total SS	35	174882816.	---	---	35	466485248.	---	---
Trt. SS	3	4292608.	1430868.	.15	3	101449728.	33816576.	3.84
Rep. SS	8	76087296.	9510912.		8	70385664.	8798208.	
Det. SS	24	95502912.	3937621.		24	294649856.	12277078.	

F is not significant at the 5% level

TABLE 8.--Analysis of variance table of data on vitamin B_{12} content on filters after the pH was raised rapidly from pH 8.30 to pH 9.50. The data is given for two concentration levels of vitamin B_{12}.

	1 ml of B_{12} sol'n used				2 ml of B_{12} sol'n used			
Source	DF	SS	MS	F	DF	SS	MS	F
Total SS	35	9931072.	---	---	35	46528768.	---	---
Trt. SS	3	6741312.	2247104.	25.47	3	27506432.	9168810.	9.35
Rep. SS	8	705728.	88216.		8	7848704.	981088.	
Det. SS	24	2484032.	103501.		24	11173632.	465568.	

F is significant at the 1% level

was already present in the lake water and thus vitamin B_{12} was adsorbed to the existing $CaCO_3$ particles before filtration. The rapid precipitation of $CaCO_3$ (15 min between each increase in pH) removed less vitamin B_{12} from the solution than when $CaCO_3$ precipitation was induced by CO_2 removal over a period of 10 days (cf. Tables 5 and 6).

VI. DISCUSSION

A. Sedimentation of Seston Components

The amount of seston and its rate of sedimentation are closely correlated with the morphometry (Pennington, 1974) and net primary production within the pelagic zone of a lake. The intensity of sedimentation depends in part upon the nutrient conditions within a lake. For example, one would expect the ecological classification of a lake (i.e. the degree of oligotrophy and eutrophy) to be reflected in the quality and quantity of organic and inorganic components in the seston. The chemical composition of seston from a particular lake integrates the effects of a variety of physical, chemical, and biological processes acting concurrently.

The total dry weight of seston (g m^{-2} day^{-1}) shows considerable seasonal and annual variation in Lawrence Lake (Table 1). Much of the seasonal and annual variation is closely related to duration and completeness of spring and fall circulation.

A conspicuous increase in the $CaCO_3$ content of the seston during 1973 accounted for the larger quantity of seston caught in the traps during 1973 (Table 1 and Figure 17). Two major factors caused the rate of $CaCO_3$ to increase during 1973. First, the concentration of calcium in the water column during spring circulation in 1973 was at least 15 mg l^{-1} higher than it was in 1972 (cf. Figures 15 and 16). However, by mid-June the concentration of calcium had dropped to 65 mg l^{-1} in the epilimnion and metalimnion. During 1972 the calcium concentration remained between 60 and 65 mg l^{-1} and showed no dramatic drop in concentration after spring circulation. Second, the duration of spring circulation during 1973 was very short and mixing was incomplete. A longer period of circulation would have suspended larger quantities of $CaCO_3$ and resuspended $CaCO_3$ would provide surface area upon which further $CaCO_3$ crystal growth may have taken place. Crystal growth would have lowered the concentration of calcium throughout the entire water column.

The sedimentation rate of $CaCO_3$ in Lawrence Lake reported in this study contrasts sharply with that reported by Miller in Lawrence Lake (1972). Miller (1972) reported the sedimentation rates of $CaCO_3$ were 397.5 mg m^{-2} day^{-1} and 538.1 mg m^{-2} day^{-1} for 5 m and 10.5 m, respectively. This study found the annual average precipitation rate of $CaCO_3$ to be 53.2 mg m^{-2} day^{-1} and 64.8 mg m^{-2} day^{-1} at 6 m and 10 m, respectively. It is plausible this disagreement resulted from the dissimilar methods utilized. In this study, loss upon ignition at 950C was used to determine $CaCO_3$ content. Miller (1972) acidified his sample with 3% H_3PO_4 in a 400 cc chamber and nitrogen was used as a carrier gas. The amount of CO_2 released during four minutes was measured with a Beckman CO_2 non-dispersive infrared gas analyzer. A method (Bundy and Bremner, 1972) similar to that employed by Miller was tried and rejected in this study, after initial tests showed that 3 times as much $CaCO_3$ was found in sediment samples as was known to actually be present. On the basis of these tests, it seemed probable decarboxylation of organic matter in the sediments increased the release of CO_2 when acid was added. The precipitation rates determined by Miller may be elevated for this reason.

The 1.22 g m^{-2} day^{-1} $CaCO_3$ precipitation rate calculated by Otsuki and Wetzel (1974) was based upon the difference between calcium concentration in the inlet water and outlet water, thus their value is an average value for the whole lake and does not represent the pelagic value. This high average value for the whole lake suggests that up to 19 times more $CaCO_3$ is precipitated in the littoral zone than the pelagic zone each year. The presence of extensive marl beaches along the shore of Lawrence Lake (Wetzel et al., 1972) adds credence to these data.

The average sedimentation rates for organic matter and ash content during summer stratification in 1972 were not significantly different than those in 1973 (Table 2). This similarity may not have been expected, since a sizeable increase of $CaCO_3$ may have coincided with an increase in production. Chlorophyll a data (Figures 22 and 23) were similar both years and primary productivity data suggest no great dissimilarity between 1972 and 1973 (Wetzel, personal communication). This evidence suggests particulate $CaCO_3$ is very effective in adsorbing and/or removing important metabolic compounds and annual variations in $CaCO_3$ formation and subsequent precipitation does not significantly reduce primary productivity once a critical level has been attained.

The presence of an organic coating on carbonate particles (Suess, 1968; Chave and Suess, 1970; Suess, 1970) may have inactivated much of the increased $CaCO_3$ surface area during 1973. Particulate $CaCO_3$ is very rapidly coated by organic compounds in sea water (Chave, 1970) and freshwater (Wetzel and Allen, 1972; Otsuki and Wetzel, 1973). Organic coatings on particulate $CaCO_3$ would reduce the interaction between $CaCO_3$ and metabolic compounds (e.g. phosphorus, iron, and organic micronutrients). The refractory dissolved organic carbon (DOC) pool has a mean value of 5.6 mg C l^{-1} in Lawrence Lake, and there is an unvarying level in the DOC pool (Wetzel, et al., 1972). A constant source of DOC may deactivate the surface properties of particulate $CaCO_3$ to some extent and thus removal of important metabolic compounds is inhibited. Arguments from this point of view would contend the increased amount of $CaCO_3$ particles during 1973 were quickly coated with organic humic compounds, and the quantity of metabolically important compounds adsorbed were similar for 1972 and 1973.

B. Significance of Suspended $CaCO_3$

The average amount of colloidal calcium in Lawrence Lake during 1973 was 36.7 mg l^{-1} (Figure 27). This quantity of calcium represents a considerable amount of surface area where biochemical reactions and adsorption may take place. In the summer of 1972, water was removed from 6 m, filtered, and placed into a flash evaporator flask. The surface area of the powdered calcium carbonate was determined by the BET method (Brunauer, Emmett, and Teller, 1938). The average surface area of two samples was 5.17 m^2 g^{-1}. This value does not represent the actual surface area of the suspended calcium in the lake water. Before physical treatment of the water, the actual surface area was much larger, because any attempt at filtering or flash evaporation caused the crystals to grow considerably larger with reduced surface area (Figure 28a). Based upon filtration of Lawrence Lake water through Nuclepore filters, it is estimated the diameter of suspended

$CaCO_3$ is less than 0.2 μ.

The annual pattern of total phosphorus content in the seston (Figure 26) shows a noteworthy decrease after the middle of July at 2 meters. This decline is also reflected in the reduction of phytoplankton activity at 2 meters. It seemed apparent from these data the displacement of phosphorus into the metalimnion was directly related to the phytoplankton maximum at 6 m (Figure 23). The increased phytoplankton growth during July and August in the metalimnion occurs annually in Lawrence Lake (Wetzel, *et al.*, 1972). Displacement of phosphorus out of the epilimnion may cause this consistent development of algal populations in the metalimnion during July and August of each year.

Studies by Golterman (1972) have shown phosphate is rapidly released after autolysis. In culture Golterman found that 80% of the particulate phosphorus reappeared in solution but under natural conditions this phosphorus would be utilized by populations of organisms present. The residence time of dissolved phosphorus is considerably shorter and any model of the phosphorus cycle must include the concept of rapid exchange kinetics. Zooplankton fecal pellets are considered a major method of phosphorus loss from the trophogenic zone and it has been estimated 12.6% of the total phosphorus is daily turned into feces (Peters and Rigler, 1973). Scanning electron micrographs did not show zooplankton fecal pellets were a major component in the seston of Lawrence Lake. Lean (1973) demonstrated that phosphorus movement within the epilimnion involves colloidal phosphorus and a labile form of phosphorus (XP) and both forms are negatively charged. It is suggested in this study the positive calcium

ion and colloidal $CaCO_3$ bind to these negatively charged forms of phosphorus, making it biologically unavailable. It is further suggested this is an important method of phosphorus removal in Lawrence Lake. The continued presence of colloidal $CaCO_3$ and precipitation (Figure 25), during summer stratification, may provide the mechanism for the effective phosphorus removal shown in Figure 26.

$CaCO_3$ precipitation may function as a scavenger of iron complexed with yellow organic acids (Shapiro, 1969; Wetzel, 1972). Interaction between iron and precipitating $CaCO_3$ did not suggest a direct adsorption of iron to $CaCO_3$ in this study, but rather that precipitating $CaCO_3$ can lower the complexing capacity of lake water by removing natural organic ligands such as yellow organic acids. A reduction in the abundance of complexing ligands in a body of water would regulate the availability of trace metals (Chau, 1973) such as iron. Laboratory experiments on iron and $CaCO_3$ interaction showed chelator compounds do influence the precipitation rate of both iron and $CaCO_3$ (Table 4).

Vitamin B_{12} interaction with $CaCO_3$ showed a more direct relationship between $CaCO_3$ precipitation and vitamin B_{12} removal from solution. In both of the experiments similar amounts of vitamin B_{12} were removed when either 1 ml or 2 ml of vitamin B_{12} was added. This implied bacterial utilization was not responsible for vitamin B_{12} removal, but rather some other mechanism was in operation. Since no significant adsorption of vitamin B_{12} onto the membrane filters was found, vitamin B_{12} must have been associated with the $CaCO_3$ precipitated from the lake water.

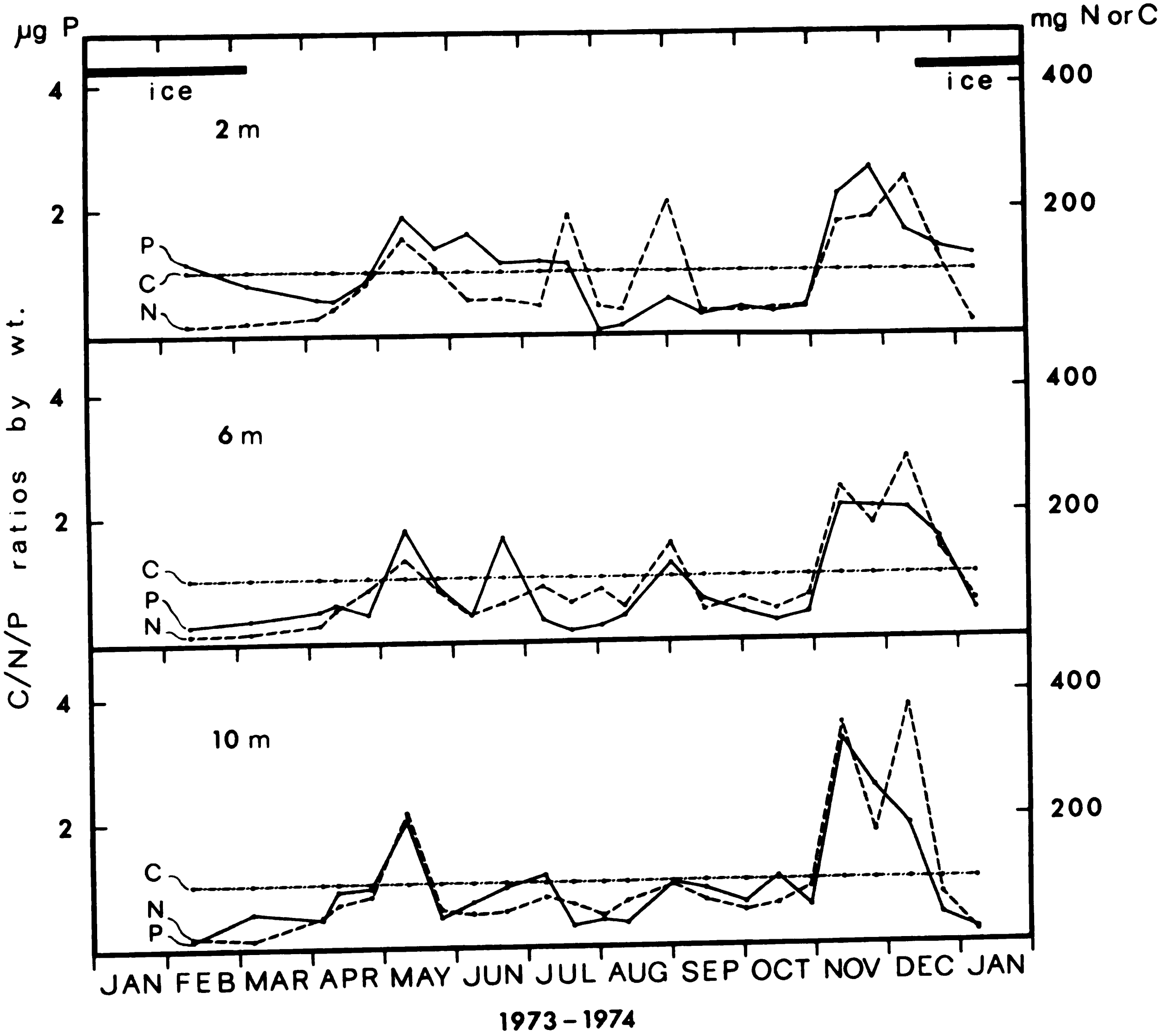
C. Carbon, Nitrogen, and Phosphorus Ratios

Although this study is concerned primarily with particulate matter, it is important to stress the flux between dissolved and particulate components. Seston, which includes dead organic matter of both plant and animal origin as well as inorganic components, is transformed by microbiological activity so the morphological, physicochemical, and biochemical characteristics are constantly changing (Rodina, 1967; Sushenya, 1968; Olah, 1972; Wiebe and Pomeroy, 1972). Bacteria were observed on scanning electron micrographs (Figure 28b) in this study. The bacteria were about 2.0 μ in length and associated with the fresh particulate matter collected in the sediment trap positioned at 6 m in Lawrence Lake. The presence of bacteria among the sedimenting seston demonstrated the possibility of rapid recycling of nutrients in the trophogenic zone. Rapid rates of mineralization have been suggested as the main factor controlling algal primary production in lakes (Golterman, 1972). Mineralization rates are reflected to some extent in the carbon, nitrogen, and phosphorus ratios of lakes.

The relationship between carbon, Kjeldahl nitrogen, and total phosphorus in seston indicated considerable variation during the season (Figure 35). Carbon content was maintained at 100 mg m^{-2} day^{-1} and the nitrogen and phosphorus values were calculated in compliance with carbon levels. During spring circulation, the nitrogen and phosphorus values were low at 2, 6, and 10 meters. In comparison, the nitrogen and phosphorus were considerably higher during fall circulation. This difference showed the constituents of seston were dissimilar during spring and fall. A considerable quantity of nitrogen and phosphorus

Figure 35.--Seasonal changes in carbon:nitrogen:phosphorus ratios (by weight) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974. Particulate organic carbon and nitrogen are expressed as mg m^{-2} day^{-1}. Phosphorus is expressed as μg m^{-2} day^{-1}.

Figure 35


µg P
mg N or C
C/N/P ratios by wt.
ice
ice
2 m
6 m
10 m
P
C
N
C
P
N
C
N
P
4
2
4
2
4
2
400
200
400
200
400
200
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC JAN
1973 - 1974

were contained within living organisms during spring circulation, therefore it was not collected in the sediment traps. Incomplete spring circulation also reduced nitrogen and phosphorus levels in the seston. During autumnal circulation, considerable quantities of nitrogen and phosphorus were resuspended from the bottom sediments and quickly resedimented back into the traps.

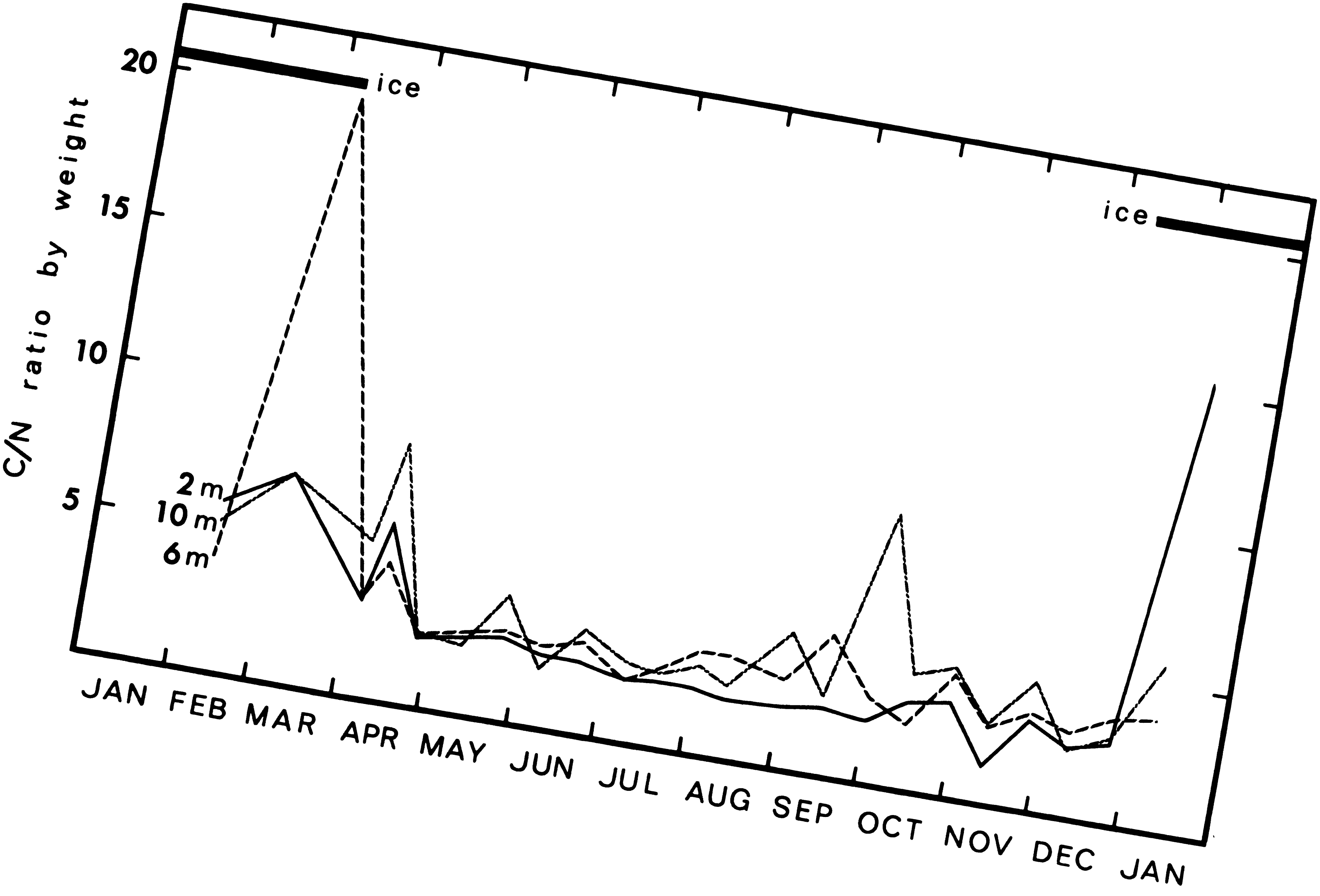
At 2 m the phosphorus value was rather high in early May, but this value continued to drop until it reached a very low level in early August. The rapid decrease in phosphorus was related to the displacement of phosphorus into the metalimnion. Higher values of nitrogen occurred after peaks in phytoplankton growth (Figure 23).

Values of nitrogen and phosphorus were much lower at 10 m and a rather constant pattern developed during summer stratification with only minor peaks.

Carbon:nitrogen ratios of the seston were higher under ice cover and during spring and autumnal circulation (Figure 36). The low ratios during spring circulation indicated higher nitrogen content of the seston and thus a slower release of nitrogen from the seston. This relationship also suggests most of the particulate organic material was autochthonous in origin, since allochthonous organic material would give a much higher carbon:nitrogen ratio (Pennington, 1974). The high values under ice cover showed the nitrogen content in the seston was lower while the carbon content remained very high. The carbon:nitrogen ratio was lower at 2 m in comparison to 6 and 10 m during most of the year, which indicated that nitrogen was being released more slowly from the seston by bacterial degradation. The carbon:nitrogen ratio at 10 m

Figure 36.--Seasonal changes in carbon:nitrogen ratio (mg m^{-2} day^{-1}) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974.

Figure 36


C/N ratio by weight
20
15
10
5
ice
ice
2 m
10 m
6 m
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
JAN

was generally higher than the 2 and 6 m values and also displayed more fluctuation. The higher 10 m carbon:nitrogen values were probably related to rapid nitrogen release by bacterial degradation.

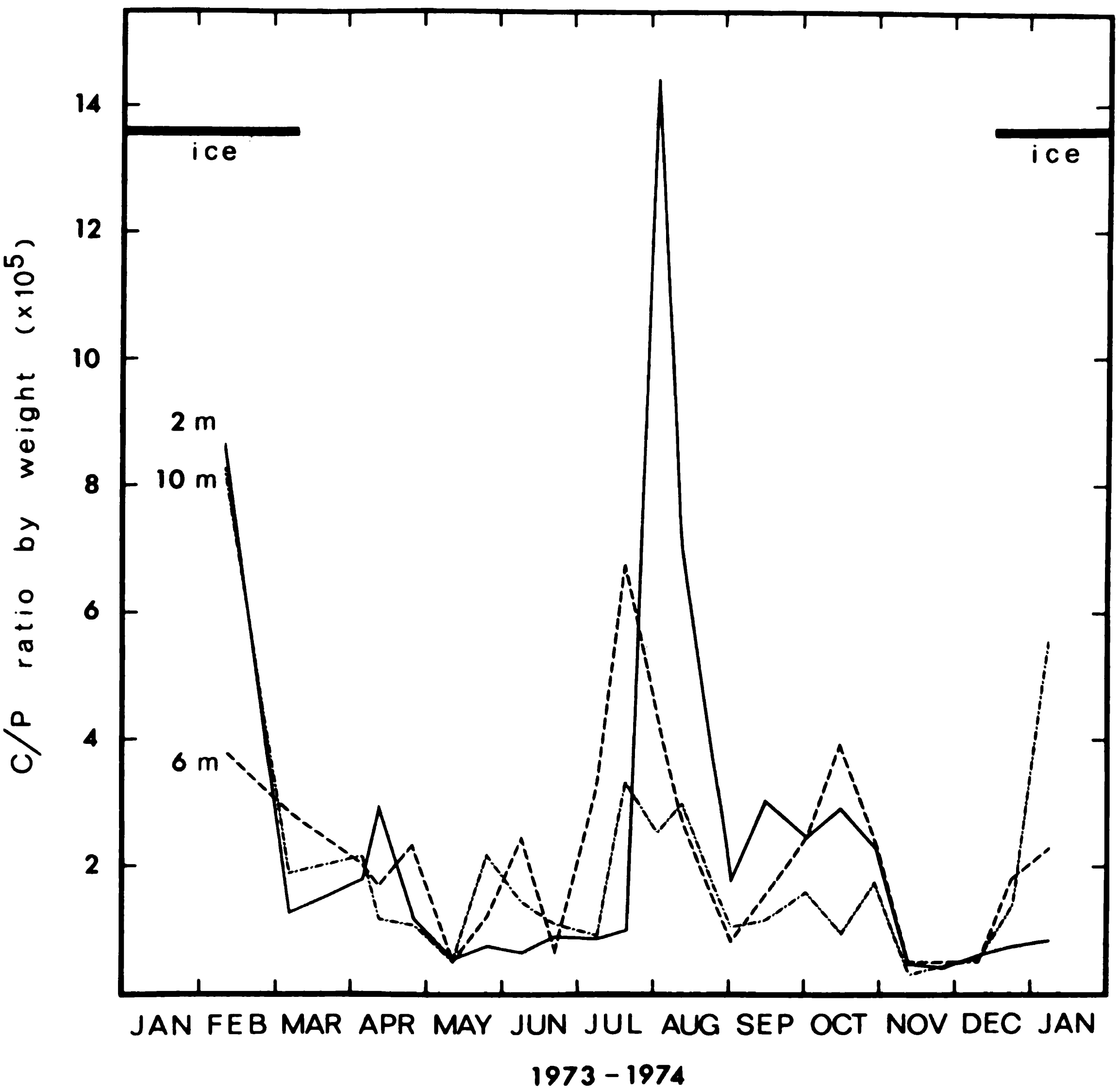
The carbon:phosphorus ratios of the seston showed very rapid changes and considerable variation throughout the year (Figure 37). The 2 m values were high under the ice because the phosphorus content of seston was low. Just before spring circulation the ratio dropped rapidly, indicating an increase in the phosphorus content of the seston. This increase was related to diatom growth under the ice (Wetzel, unpublished data). The ratio remained low until late July, then it increased sharply. This sharp increase marked the rapid displacement of phosphorus into the metalimnion. The carbon:phosphorus ratio remained somewhat elevated until fall circulation occurred in late October.

The 6 m carbon:phosphorus ratio was lower under the ice than either the 2 m or 10 m value. Phosphorus was being precipitated and not utilized. The ratio increased rapidly at 6 m in mid-July; however, it declined as phosphorus was displaced from 2 m into the metalimnion. Considerable phytoplankton growth took place in the metalimnion during this time (Figure 23). By late October the ratio increased once again until fall circulation rapidly lowered the ratio.

At 10 m changes in the carbon:phosphorus ratio were less dramatic; however, they reflected changes that were taking place in the trophogenic zone.

Figure 37.--Seasonal changes in carbon:phosphorus ratio by weight (x 10^5) of seston collected at Station A in Lawrence Lake. Traps were located at 2, 6, and 10 meter depths from 8 January 1973 to 8 January 1974. Particulate organic carbon is expressed as mg m^{-2} day^{-1}; whereas, phosphorus is expressed as μg m^{-2} day^{-1}.

Figure 37


C/P ratio by weight ($\times 10^5$)
14
12
10
8
6
4
2
ice
ice
2 m
10 m
6 m
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
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JAN
1973 - 1974

VII. SUMMARY AND CONCLUSIONS

Sedimenting seston was collected into improved sediment traps during a two year period and analyzed for total dry weight, organic material, calcium carbonate, and ash content in Lawrence Lake. During the second year particulate organic carbon, Kjeldahl nitrogen, and total phosphorus content of seston were examined to illustrate when metabolically important compounds are removed from the trophogenic zone. Conclusions reached were:

1. Sedimentation rates of organic material and ash were similar during the two year period; however, the rate of $CaCO_3$ precipitation was 5 times greater in 1973 than 1972.

2. Colloidal calcium was present during the entire year in Lawrence Lake and the average quantity of suspended $CaCO_3$ was 36.7 mg l^{-1}.

3. Scanning electron micrographs of seston collected at 10 meters showed that an organic matrix covered all material and the organic material clogged pores in the filters.

4. Sedimentation of total phosphorus showed a marked displacement into the metalimnion and hypolimnion when severe decalcification occurred in the epilimnion.

5. Material is resuspended from the bottom of Lawrence Lake and the quantity resuspended varies with the strength and duration of vernal and autumnal winds.

6. Sedimentation rates of nitrogen and particulate organic carbon were comparatively constant throughout the season and were closely related to phytoplankton activity in the trophogenic zone.

7. Laboratory experiments on interactions between $CaCO_3$ and iron suggested no direct adsorption of iron onto $CaCO_3$ particles; however, $CaCO_3$ and iron precipitation rates were influenced by the presence of organic compounds.

8. Investigations on vitamin B_{12} and precipitating $CaCO_3$ relationships suggested vitamin B_{12} was removed in association with precipitating $CaCO_3$.

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