



The role of the bottom sediments in the eutrophication of Georgetown Lake, Montana
by Paul Jackson Garrison

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Botany

Montana State University

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Abstract:

Georgetown Lake is a relatively small reservoir located in southwestern Montana. It receives much recreational use all year round being the most heavily fished lake in the state for its size. The present study was part of a larger limnological project to evaluate the limnology of the reservoir. This particular study was undertaken to determine the extent to which the sediments may provide nutrients to the overlying waters. During the ice free period Georgetown Lake did not exhibit chemical stratification. During the ice cover period at the deep water station oxygen declined until the bottom waters became anaerobic and the water column became chemically stratified. At this time certain elements such as ortho-phosphorous, ammonia, iron, silica, bicarbonate, etc. were released into the bottom waters from the sediments. With the advent of ice-out and the reintroduction of oxygen, the stratification disappeared and iron and manganese precipitated causing some phosphorus to be precipitated. As a result of turbulent mixing orthophosphorus and iron appeared to be suspended in the bottom waters during the summer.

In the sediments iron oxides, aluminum oxides, exchangeable manganese, exchangeable zinc, inorganic phosphorus, and exchangeable ammonia decreased during the ice cover period but increased at ice out. Only exchangeable manganese followed this trend at the shallower station. At the deep water station iron oxides and aluminum oxides appeared to be associated with the same particles. At the shallower station where macrophytes were present, aluminum oxides and iron oxides were associated with different particles, probably because of iron accumulation by the plants.

The proportion of the initial volatile solids attributable to organic carbon varied with the season because of the rate of benthic decomposition. During the ice cover period organic phosphorus regulated the total phosphorus because of detrital deposition the previous autumn. During the ice free period inorganic phosphorus determined total phosphorus trends because of macrophytic uptake. There was a potential for much phosphorus to be released into the water under the right conditions as exchangeable phosphorus makes up 14 to 25% of the sediment inorganic phosphorus.

Although organic nitrogen makes up the majority of the total nitrogen, it was less important than reported in the literature. This was a result of the shallow depth of the lake which makes the bottom environment more conducive to microbial mineralization. This is supported by the C:N which was 31:1.

Because of the deep-water withdrawal of the dam, much nitrogen and phosphorus was discharged during anaerobic conditions in the bottom waters. This is indicated by the C:N:P of 469:31:1. This results in an annual loss of both total nitrogen and total phosphorus from the lacustrine ecosystem.

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Date August 5, 1976

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by

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A thesis submitted in partial fulfillment
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ABSTRACT

Georgetown Lake is a relatively small reservoir located in southwestern Montana. It receives much recreational use all year round being the most heavily fished lake in the state for its size. The present study was part of a larger limnological project to evaluate the limnology of the reservoir. This particular study was undertaken to determine the extent to which the sediments may provide nutrients to the overlying waters.

During the ice free period Georgetown Lake did not exhibit chemical stratification. During the ice cover period at the deep water station oxygen declined until the bottom waters became anaerobic and the water column became chemically stratified. At this time certain elements such as ortho-phosphorous, ammonia, iron, silica, bicarbonate, etc. were released into the bottom waters from the sediments. With the advent of ice-out and the reintroduction of oxygen, the stratification disappeared and iron and manganese precipitated causing some phosphorus to be precipitated. As a result of turbulent mixing ortho-phosphorus and iron appeared to be suspended in the bottom waters during the summer.

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INTRODUCTION

For its size Georgetown Lake is the most heavily fished lake in Montana. The Montana Fish and Game Department estimates that the lake sustains 81,000 fishermen days per year. This is just under four per cent of the total fishing pressure for the state (Georgetown Lake Pre-Study, 1973). In addition the lake is used for boating, swimming, and water skiing. The drainage basin is used for horseback riding, camping, snowmobiling, and permanent and summer residences, with many of the residences being located along the lake shore. The water from the lake is also used for power development, irrigation, and the reduction works at Anaconda.

Concerned for the status of the lake caused by the increasing and potential development of the watershed, the county commissioners and conservation districts from Deer Lodge and Granite Counties have undertaken a study to develop an overall land use plan for the area. One aspect of a general investigation evaluating land use in the Georgetown Lake drainage basin was a limnological study. It was initiated in July 1973 to characterize the lake and assess the roles of the various components of the lacustrine environment. The study of the lake was divided into projects to study the water chemistry, sediment chemistry, phytoplankton, macrophytes, periphyton, and zooplankton. My study was undertaken to investigate the role of the sediments in the lake ecosystem. A report has already been published concerning the water and sediment chemistry as well as the phyto-

plankton ecology (Knight et al., 1976). My thesis includes some of the water chemistry discussed in the aforementioned report and all of the sediment chemistry as well as an expanded discussion of the nutrient sediment chemistry.

The possibility of a winter fish kill has been of concern because of the low oxygen concentrations during part of the ice cover period. These low oxygen tensions result from the use of oxygen in respiratory processes as well as oxidative decomposition coupled with the long period of ice cover (generally six months). During the ice cover period oxidative decomposition is important because of the moderately high production during the previous summer. During reducing conditions sediments may liberate nutrients into the overlying water which may be utilized in the succeeding year's primary production. Therefore the sediment study was undertaken to determine the potential and actual release of nutrients from the bottom sediments.

DESCRIPTION OF THE STUDY AREA

Georgetown Lake is located in the Clark Fork River drainage near the divide between Flint Creek and Warm Springs Creek (Figure 1). The lake was formed from the impoundment of Flint Creek by a dam which is about 27.4 km (17 miles) west of Anaconda, Montana.

In 1885, a small earthen dam was built across Flint Creek at the present dam site by the Montana Water, Electric, and Power Company to produce power for the Bi-Metallic Mining Company. The area flooded was a large hay meadow which was virtually free of timber. The dam was purchased in 1901 by the Anaconda Copper Mining Company who built a masonry dam to an elevation of 6424.5 feet above mean sea level. In 1919, the dam was raised to its present level of 6429.5 feet above mean sea level. The Montana Power Company, which had acquired the dam in 1925, strengthened the dam with concrete and built a two-lane highway across it in 1967 (Beal, 1953 and Georgetown Lake Pre-Study, 1973).

The dam has a crest length of 94.5 m, a top width of 2.2 m, and a maximum base width of 10.0 m. The lake has a storage capacity of $5.9 \times 10^7 \text{ m}^3$ (47,924 acre feet), and floods an area of 1479.2 ha (2990 acres).

At maximum pool elevation, the lake has a length of 7.1 km (4.4 mi.) and a maximum and mean breadth of 3.6 km (2.3 mi.) and 1.7 km (1.1 mi.) respectively. Mean depth is 4.9 m (16.0 ft.); however, it reaches a maximum depth of 10.7 m (35.0 ft.) directly upstream from the dam. Morphometric data for Georgetown Lake is summarized in

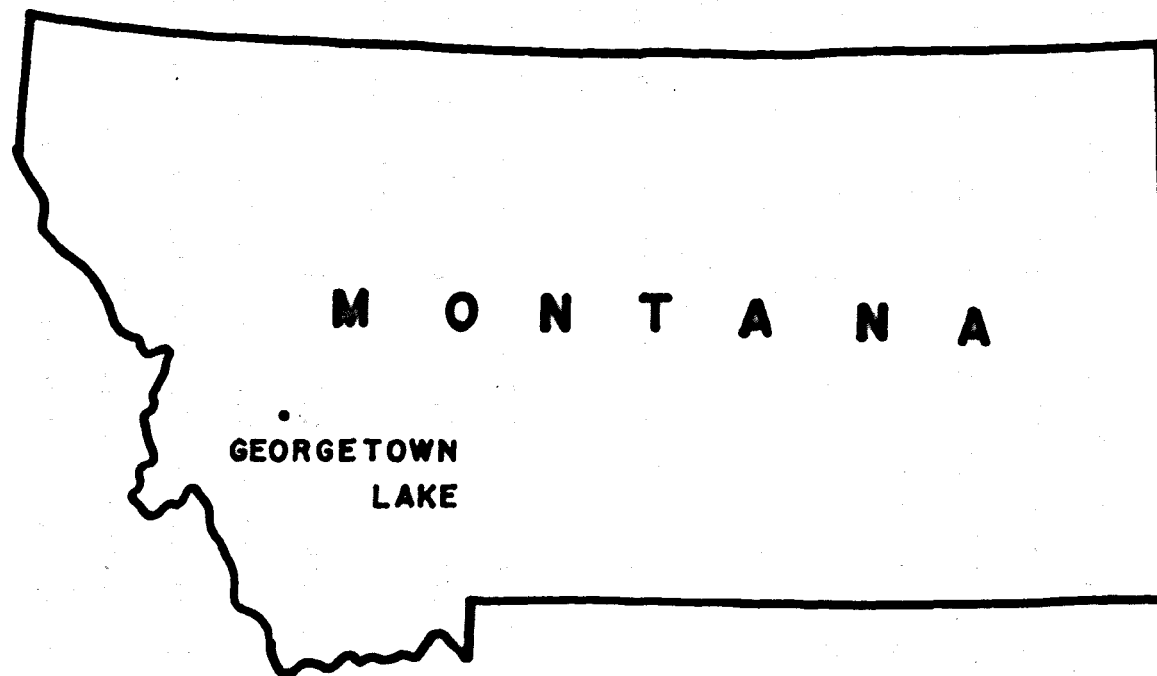


Figure 1. A map of the state of Montana showing the location of Georgetown Lake.

Table 1.

The reservoir has a drainage area of 13,728 ha (33,920 acra), which is mostly upland terrain. The two major streams that enter the lake, North Fork Flint Creek and Stuart Mill Creek, make up 36% and 31% of the total drainage area, respectively. The remaining area presumably discharges groundwater into the lake. In addition to these sources, backflow water also may enter from Silver Lake via Hardtla Creek. Georgetown Lake annually receives about 18 inches of precipitation in the form of rain and snow. Snowfall averages about 130 inches annually.

A general geological description of the study area can be found in Alt and Hyndman (1972). The principal soil type in the drainage area is gravelly loam.

Five permanent sampling station were established within the lake (Figure 2). Station I was located near the dam. This station was located in the deepest part of the lake (8 m) and was in the limnetic zone. Stations II, III, and IV were all located in the littoral zone, the depth being about 6 m. Station IV differed from Stations II and III because it was more protected from wind. Station V was also located in the littoral zone but its depth was only 3 m. This station also differed from the other stations because Stuart Mill Creek discharges into this bay and it receives the greatest wind disturbance.

Table 1. Morphometric data for Georgetown Lake at maximum pool elevation (1959.7 m).

Maximum Depth	10.7 m (35.0 ft)
Mean Depth*	4.9 m (16.0 ft)
Maximum Length	7.1 km (4.4 mi)
Maximum Breadth	3.6 km (2.3 mi)
Mean Breadth*	1.7 km (1.1 mi)
Surface Area	1479.2 ha (2990 acres)
Volume	$5.9 \times 10^7 \text{ m}^3$ (47,924 acre-ft)
Length of Shoreline	30.4 km (18.9 mi)

* Definition of these parameters in Reid (1961).

Figure 2. A map of the study area. The locations of the sampling stations within Georgetown Lake are indicated by numbers I-V.

METHODS

Water Chemistry

Water samples were generally collected biweekly during the period 5 June 1974 through 24 September 1974 at all the stations whenever possible. During the periods 12 September 1973 - 25 April 1974 and 25 November 1974 - 13 January 1975, Station I was sampled on a monthly basis. During the period of 21 January 1974 - 25 April 1974 Stations IV and V were sampled monthly whenever possible.

Water samples, with the exception of those for dissolved oxygen, were collected with a 3-liter polyvinyl chloride Van Dorn type water bottle. Samples for analysis of dissolved oxygen were collected with a Labline Inc. BOD-sewage sampler. Water samples at Station I were collected at 2-meter intervals from the surface to the bottom. At all other stations, samples were collected at 3-meter intervals from the surface to the bottom. All sample bottles were rinsed with distilled-deionized water and sample water prior to the sample collections.

Immediately upon collection of a water sample a 300 ml BOD bottle was filled and fixed for Winkler dissolved oxygen determinations as described in Standard Methods (APHA, 1971). A 500 ml water sample was filtered through a Gelman type A glass fiber filter and the filtrate put in a 500 ml glass stoppered Pyrex bottle. A 250 ml glass stoppered Pyrex bottle was filled with unfiltered water for further analysis.

The conductivity was measured in the laboratory using unfiltered water. It is measured at a frequency of 1 KH_z with a Yellow Springs Instrument Co. AC conductivity bridge (Model 31) equipped with an Industrial Instruments Co. dipping cell (Model CEL-S2). Specific conductance was computed and reported as $\mu\text{mhos} \cdot \text{cm}^{-1}$ at 25°C .

Total phosphorus and soluble inorganic phosphorus were determined using the Single Reagent Method described by the Environmental Protection Agency (1971). Combined phosphorus was then computed as the difference between total and soluble inorganic phosphorus. Total phosphorus includes particulate, dissolved organic, and dissolved inorganic phosphorus. Combined phosphorus includes particulate and dissolved organic phosphorus.

Nitrate was determined by the method of Mullin and Riley, as described by Barnes (1959). Nitrite was determined using Hach Chemical Company's NitriVer^(R) reagent. The method of Strickland and Parson (1972) which includes amino acids was used for the ammonia determination and for the determination of total Kjeldahl nitrogen. Combined nitrogen was then computed as the difference between total Kjeldahl and the sum of the ammonia and nitrite nitrogen. Total Kjeldahl nitrogen does not include nitrate but does include particulate, dissolved organic, ammonia and nitrite nitrogen. Combined nitrogen includes particulate and dissolved organic nitrogen.

Total soluble iron was determined by the FerroZine method using

FerroZine^(R) provided by the Hach Chemical Company. Silica was determined using the molybdosilicate method (APHA, 1971). Total organic carbon was determined from unfiltered water using a Beckman Laboratory Carbonaceous Analyzer.

Sediment Chemistry

Sediment samples were collected from 12 September 1973 to 7 January 1975, generally at the same time and place as the water samples. Single grab samples were collected with an Ekman dredge. The sampler generally collected a sample to a depth of 8-10 cm. However at Stations II, III, IV, and V during periods of large macrophytic growth sampling was more difficult. At these times the dredge only penetrated the bottom sediment a few centimeters, therefore, 3-4 grab samples per station were composited into one sample.

Sampling error may be much greater when collecting sediments than when gathering water samples because water is generally more homogeneous horizontally than sediments. Since it was not possible to mark the stations with permanent markers, the samples were not always collected in the same exact place. Analyses were sometimes not comparable as a result of the great variability of the bottom sediments. Station I was generally sampled in the same area as it was located near a dock, although the station was moved approximately 50 meters on 5 June 1974. However, at the other stations the sampling area was much larger, thereby increasing the sampling errors.

After sediment samples were collected, they were dried in an oven at 60°-70°C and ground with a porcelain mortar and pestle to pass through a 100 mesh sieve.

Total, inorganic and organic phosphorus were determined by the sequential acid and alkali extractions of the sediment and analysis of total and inorganic phosphorus in the combined extracts (Mehta et al., 1954). Total phosphorus in the extract was converted to inorganic P with persulfate digestion (EPA, 1971). It was stated in Standard Methods (APHA, 1971) that perchloric acid digestion gives total P values slightly higher or equal to the values from persulfate digestion. However, for safety reasons persulfate digestion was used. The inorganic P solubilized was analyzed by the Single Reagent Method (EPA, 1971). The difference between the total P and inorganic P in the combined extracts was reported as total organic phosphorus.

The phosphorus extracted by this procedure as total P may not include all the phosphorus in the sample. The portion not extracted may be attributable to inorganic P that is tightly occluded within certain minerals. However, Wildung and Schmidt (1973) found that although the more rigorous Na_2CO_3 fusion method gave slightly higher total P results than the Mehta, et al. (1954) method, but there was no statistical difference between the two methods.

Total inorganic phosphorus was fractionated using the method of Chang and Jackson as modified by Frink (1969a). The inorganic

P in the neutralized NH_4Cl , NaOH, and HCl extracts was determined using the Single Reagent Method (EPA, 1971). The NH_4F and CDB extracted inorganic P was determined using the stannous chloride method as described by Frink (1969a).

Williams, et al., (1971a) reported that this fractionation scheme gives erroneously high phosphorus results in the NaOH fraction in calcareous sediments but not in noncalcareous sediments. From analysis of a few varied samples the sediments of Georgetown Lake proved to be noncalcareous, the CaCO_3 content being less than 10 per cent.

It should be pointed out that this entire phosphorus mineral fractionation scheme is based upon known solubilities of model compounds and that dissolution of discrete mineral forms by each extractant is probably not possible in the complex bottom sediment system. In fact, only apatite and possibly vivianite have been substantiated as discrete phosphorus compounds in sediments. With this in mind, it is still useful to know the relative chemical solubilities of these various mineral components.

The difference between the total inorganic phosphorus and the sum of the inorganic P fractions was reported as residual inorganic P. This fraction most likely included the inorganic P which was tightly occluded within certain minerals.

Total nitrogen was extracted using the Kjeldahl method and determined using steam distillation (Bremner, 1960). Exchangeable

ammonium-N and nitrate-N were extracted with 2N KCl and determined by the method of Bremner and Keeney (1965). Total Kjeldahl nitrogen does not include the oxidized nitrogen forms. Since from a few varied samples it was found that no nitrite-N was present, the nitrate-N was added to the total Kjeldahl N to give the total N concentration in the sediments.

Organic N was determined by the acid hydrolyzation method of Bremner (1965) in conjunction with steam distillation. The acid hydrolyzation method fractionates organic N into hexosamine and amino acid fractions. The amino acids described by this method only include amino acids with an α -amino group. The fraction of organic nitrogen not identified was reported as unidentified hydrolyzable nitrogen.

The difference between the total N and organic N was reported as total inorganic N. Inorganic N is present primarily as ammonium. The ammonium extracted by acid hydrolyzation (Bremner, 1965) is reported as hydrolyzable ammonium. The difference between hydrolyzable ammonium-N and exchangeable ammonium-N is reported as nonexchangeable ammonium-N. This includes nonoccluded ammonium-N. The difference between total Kjeldahl N and hydrolyzable ammonium-N is reported as nonhydrolyzable N. This fraction is not well understood but is believed to be part of the soil humin-N (Bremner, 1967).

Organic carbon was determined using the Walkley-Black method as modified by heating the sample to 150°C (Allison, 1965) which

actually estimates the chemical oxygen demand. Organic carbon was determined by multiplying by a correction factor of 1.12 as recommended for soils of western United States (Allison, 1965).

The initial volatile solids (IVS) were determined by weight loss after ignition at 600°C for one hour. Prior to combustion the samples were dried at 110°C. Initial volatile solids includes most organic matter as well as organic carbon.

Iron oxides were extracted using the sodium dithionite method of McKittrick and Hope (1963). Exchangeable iron was extracted with neutral 1 N ammonia acetate (Chapman, 1965). The iron extracted by these procedures was determined using the orthophenanthroline method of Olson (1965).

Aluminum oxides were extracted using the sodium dithionite method (McKittrick and Hope, 1963). Exchangeable aluminum was extracted with 1 N KCl as described by Syers, et al., (1971). The aluminum extracted by these methods was determined using the methylthymol blue method (Arshad, et al., 1972).

Exchangeable calcium, magnesium, manganese, and zinc were extracted with neutral 1 N ammonium acetate (Chapman, 1965). Concentrations of these cations were determined using atomic absorption spectroscopy as described by APHA (1971).

The hydrogen ion activity was determined with a Beckman Expanded Scale pH meter (Model 76) on the samples which had been frozen and then

thawed.

All colorimetric determinations for both the water and sediment chemistry were made with either a Klett-Summerson colorimeter or a Bausch and Lomb "Spectronic 20".

RESULTS AND DISCUSSION

The sediments of a lake can be influential in determining the concentrations of certain chemicals in the lake waters. Many workers, including Rittenberg, et al. (1955), Keeney (1973), Syers, et al. (1973), and Sanville, et al. (1974) have shown that sediments and interstitial water usually contain higher chemical concentrations than the overlying water and may partially regulate the chemical content of the lake waters by sediment-water interchange of elements. These higher concentrations may cause sediments to act as a buffer system in the lacustrine ecosystem.

The mud-water interface separates two very different domains of exchange. In all but the upper few centimeters of sediment, diffusion is controlled by motions on a molecular scale with correspondingly low diffusion rates. In the water, exchange is regulated by much higher and extremely variable turbulent diffusion rates (Mortimer, 1971).

Sediments can be divided into two layers. The bottom zone is the historical layer. This zone represents the older sediment deposited years earlier. It generally includes the area deeper than 20 cm below the mud surface where essentially no mixing takes place, therefore virtually no exchange occurs. Some molecular diffusion may occur but its contribution to sediment-water exchange is probably negligible. The top zone is the active deposition layer. This zone is in contact with the overlying water and contains the most recent sediment. This

layer experiences considerable mixing from physical, chemical, and biological sources. It is with this layer that sediment-water elemental interchange occurs.

The most important regulatory feature in the exchange processes is the mud-water interface and its oxygen content. The oxygen content is governed by three factors. The first is the biological oxygen demand arising primarily from the metabolism of bacteria, fungi, planktonic invertebrates that migrate to the interface, and sessile benthic invertebrates. The second is a chemical oxygen demand arising from such inorganic elements as Fe^{2+} and Mn^{2+} , that accumulate in the sediment from decomposing biological structures, accumulate in reduced form. Reduced iron and manganese also migrate upwards from deeper reduced sediment. The third is the diffusion of oxygen into the interface either passively or actively (Mortimer, 1971). Howeller and Boulder (1971) estimated that in undisturbed sediments, 50% of the oxygen consumption at the interface was a result of metabolic respiration and the rest was caused by chemical reduction. Most of the chemical reduction was attributed to immobile reduced compounds: only 3-16% being attributed to mobile reduced compounds.

During periods of high oxygen concentration at the interface, an oxidized microzone is maintained. Mortimer (1941, 1942) has shown that this is very important in controlling the exchange rates between the sediment and overlying water. This microzone is not completely

understood but is thought to consist principally of iron and manganese, possibly as precipitated hydroxides. There is some evidence that an organic constituent, possibly humic in nature, may be important in this complex. This was indicated by Mortimer (1941) who observed a rise in color and substances reducing permanganate after the mud surface became reduced. Iron and manganese in their oxidized form are very insoluble and readily adsorb certain elements, especially phosphorus.

Mortimer (1942) suggested that the oxidized microzone was a result of the slow diffusion of molecular oxygen into the surface sediments with the resultant oxidation of iron to $\text{Fe}(\text{OH})_3$. Gorham (1958) reported that the oxidized microzone is a result of turbulent mixing of the surface sediments into the overlying water, oxidation of iron, and a precipitation of the $\text{Fe}(\text{OH})_3$ onto the surface of the mud. The depth of oxidized microzone is dependent upon the degree of sediment mixing into the overlying water, but generally varies from 5-15 mm.

As the oxygen content of the mud surface decreases to near zero, concurrently with the immediate overlying waters, the oxidized microzone is destroyed. As a result of the disappearance of oxygen, the bottom environment changes from an oxidized to a reduced one. The ferric hydroxide or ferric hydroxide complexes then undergo reduction and the reduced iron and manganese become water soluble. The reduction destroys the adsorptive capacity of the oxidized microzone and allows

certain compounds to be liberated into the overlying waters. The majority of the liberated elements come directly from the interstitial water and not the soil particles.

The exchange rates of chemical constituents across the sediment-water interface are influenced by many factors. Some of these are the biological activity in the sediment, the turbulence within and over the distribution of chemical constituents in the sediment, various physiochemical parameters such as pH, redox potential, viscosity of the interstitial water, and the mineral composition of the sediment.

Water Chemistry

Figure 3b shows the oxygen isopleths at Station I in Georgetown Lake. During the summer the oxygen concentrations in the bottom waters were always great enough to maintain the oxidized microzone, never being less than 3.5 mg.L^{-1} . Although organic production was relatively high, the lake was shallow enough to allow general mixing of the entire water column. This was evidenced by the lack of thermal stratification (Knight, et al., 1976). However, during ice cover the oxygen concentration decreased and by 18 February 1974 oxygen was undetectable in the bottom waters. This was probably a result of sediment oxidative decomposition of detritus from the previous summer and fall and planktonic respiration in the water as well as some benthic respiration. Both of these processes were active during the summer but during the ice cover period general mixing of the water was greatly reduced, resulting in the depletion of the oxygen in the bottom waters.

Figure 3a illustrates the conductivity isopleths at Station I. During the summer the water is generally homogeneous with respect to conductivity, but conductivity was slightly higher in the bottom waters. This could be evidence of the surface sediment being suspended in the bottom waters by turbulent mixing. At the beginning of ice cover, this trend ceased, substantiating the contention that increased conductivity during the summer was due to suspended sediment. During ice cover the amount of mixing would be greatly decreased.

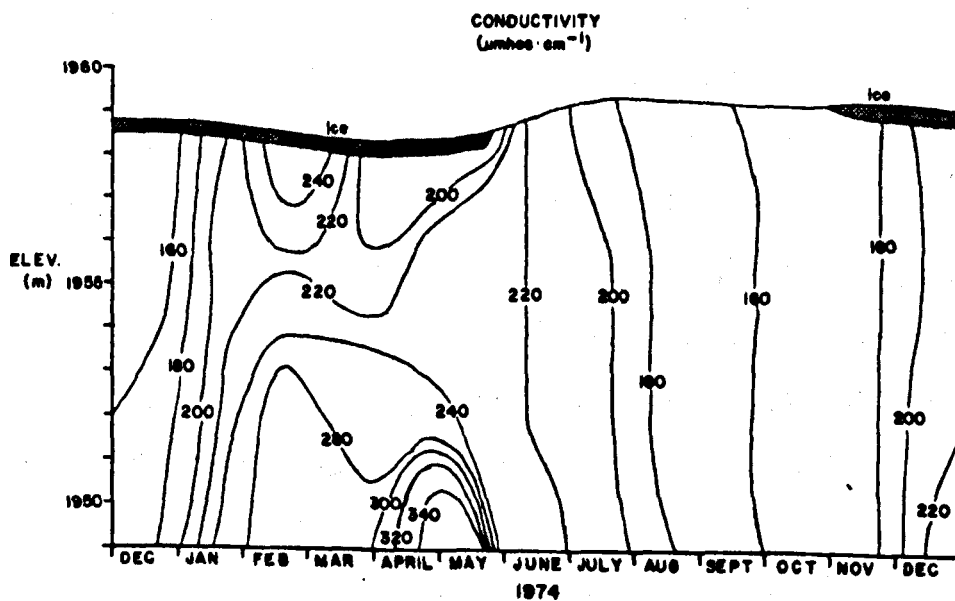


Figure 3a. Conductivity isopleths at Station I.

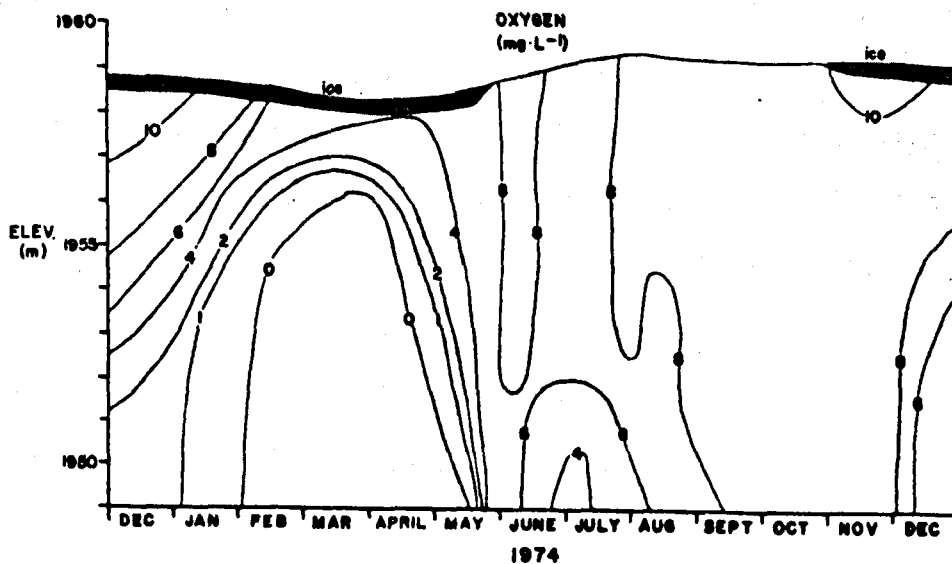


Figure 3b. Oxygen isopleths at Station I.

At Station I the lake began to stratify at the end of January and stratification becomes more pronounced through the remaining ice cover period. This period of stratification correlates well with the disappearance of oxygen in the bottom waters (Figure 3b).

Although the redox potential was not measured, Mortimer (1942) has shown that low oxygen levels are indicative of low redox potentials. He found that at an oxygen concentration of 0.5 mg.L^{-1} the redox potential (E_7) was 0.24 volts, which is approximately the potential at which iron is reduced.

The increased conductivity in the bottom waters during late winter appears to be a result of the breakdown of the oxidized microzone. When the microzone is destroyed certain chemical constituents are liberated thus increasing the conductivity in the overlying water. Released elements include Fe, Mn, Si, PO_4 , NH_3 , HCO_3 , among others. Mortimer (1941) observed that most of the increased conductivity was a result of an increase in the total alkalinity. This would include iron and ammonia combined with bicarbonate, as well as other bases. The increase in bicarbonate in the bottom waters during chemical stratification was illustrated by Knight, et al. (1976).

At the end of May, the stratification ceased as the ice cover disappeared and oxygen reentered the entire water column. The iron, and to some degree manganese, were oxidized to $\text{Fe}(\text{OH})_2^+$ and MnO_2 which then precipitated, removing with them adsorbed elements such

as phosphorus from the overlying waters. This formed the oxidized microzone which then removed other ions from the water thus reducing its conductivity. Some elements such as manganese do not precipitate immediately. Mortimer (1942) and Gorham and Swaine (1965) observed that manganese remains in the water for a period of time after oxygen has been reintroduced. This may partially explain why on 5 June 1974 the conductivity was higher in the bottom waters. This may also be a result of suspended sediment caused by turbulent mixing during overturn. Unfortunately the concentration of manganese was not determined in the water.

As shown in Figure 4a, total soluble iron at Station I followed the same seasonal trend as conductivity. During the summer iron concentrations were relatively low, generally ranging from 10-20 $\mu\text{g}\cdot\text{L}^{-1}$. Since the oxygen content was always above 3.5 $\text{mg}\cdot\text{L}^{-1}$ the iron would have existed in its oxidized form. Stumm and Morgan (1970) illustrated that total soluble ferric iron exists as $\text{Fe}(\text{OH})_2^+$ and at normal pH ranges should not exceed concentrations of 1 μg Fe per liter. However, it is well established that oxidized iron readily complexes with organic bases. At normal pH ranges, this colloidal iron is much more soluble.

The filters used to filter the sample water allowed colloids to pass through, therefore most of the observed iron was probably in colloidal form. The increase in iron to 44 $\mu\text{g}\cdot\text{L}^{-1}$ in the bottom

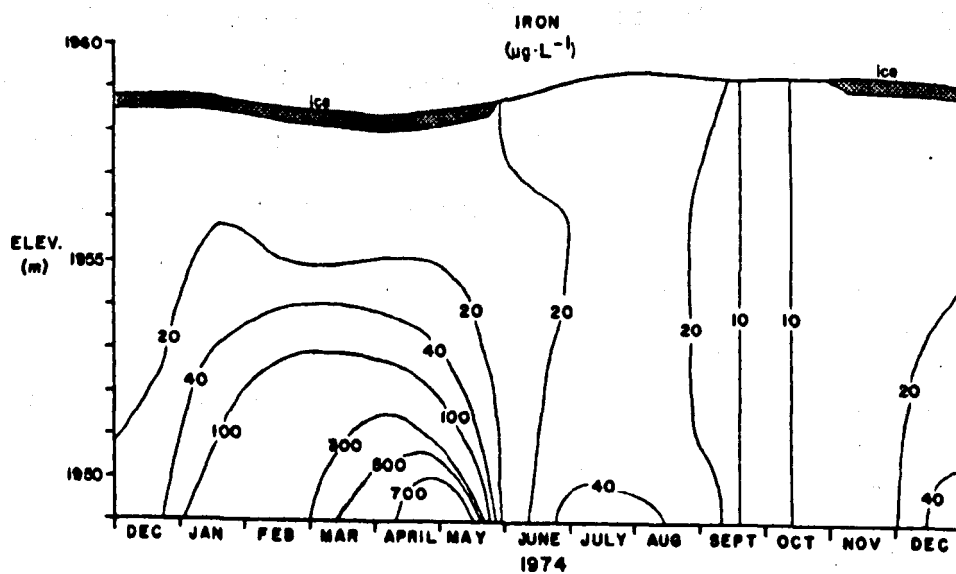


Figure 4a. Iron isopleths at Station I.

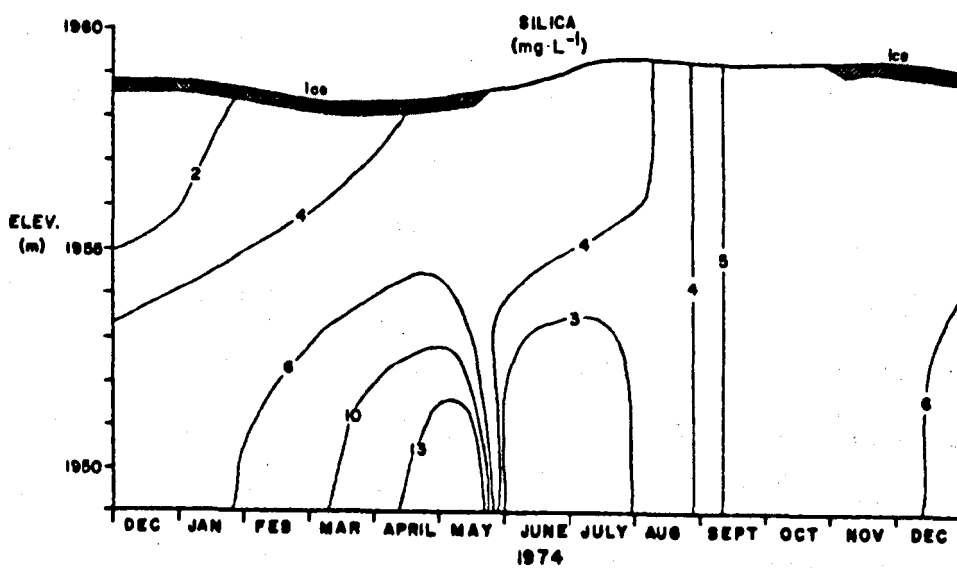


Figure 4b. Silica isopleths at Station I.

waters during July may have been associated with sediment suspended by turbulent mixing. This sediment would have contained more organic matter, some of which could be complexed with iron. Suspended sediments were also indicated by the aforementioned conductivity rise in the bottom waters during the summer.

During the latter part of ice cover in January, the iron in the bottom waters began to rise rapidly. As with conductivity this was caused by the breakdown of the oxidized microzone. Previous to this time the iron in the surface sediment had been present as insoluble ferric hydroxide. When the bottom waters were reduced sufficiently, the ferric iron was reduced to ferrous iron. Iron initially rose rapidly and on 21 January 1974 its concentration was $135 \mu\text{g}\cdot\text{L}^{-1}$. This initial rise was primarily due to the reduction of iron in the surface sediments, especially the oxidized microzone. Iron in the bottom waters continued to increase until it reached a high of $740 \mu\text{g}\cdot\text{L}^{-1}$ on the last sampling date during the ice cover period, which was 25 April 1974. The source of this iron after the initial rise was probably iron which diffused from the deeper sediments. Howeller and Boulder (1971), in undisturbed cores, observed that iron moved in the interstitial water at a rate of $0.29 - 0.73 \times 10^{-6} \text{ mg}\cdot\text{cm}^{-1}\cdot\text{sec}^{-1}$. The liberation of this mobile iron is very dependent upon the concentration gradient between the surface sediments and the water. The continued rapid increase of iron in the bottom waters through Febru-

ary, March, and April would indicate that the concentration gradient is large.

Following the destruction of the ice cover, the waters were completely oxygenated (Figure 3b). This caused the oxidation of ferrous iron to ferric iron. The iron then rapidly disappeared from the water as it precipitated to form the oxidized microzone.

Figure 4b also illustrates the silica isopleths. During the summer, silica concentrations ranged from $2.7 \text{ mg}\cdot\text{L}^{-1}$ to $5.7 \text{ mg}\cdot\text{L}^{-1}$. The water was generally homogeneous with respect to silica. However during the period of chemical stratification silica increased in the bottom waters while remaining nearly constant in the upper waters. Silica concentrations reached a high of $13.1 \text{ mg}\cdot\text{L}^{-1}$ on the last sampling trip during ice cover. This probably was due to the liberation of silica from the sediments during reducing conditions.

The release of silica during reducing conditions has not been as well documented as iron or phosphate. Mortimer (1942) observed a liberation of silica from the sediments during stratification. However, Kamp-Nielsen (1974) did not observe an influence of redox conditions upon silica exchange rates and did not attempt to explain why his results differed from those of Mortimer.

Although the release of silica from sediments is not well understood, some discussion in the literature can be found. Mattson (1935) suggested that in peaty podzols the adsorptive complex at the mud-

water interface is a ferri-silico-humate. Stumm and Morgan (1970) state that silica may be adsorbed on iron oxides. Since it has been well established that iron oxides make up part of the oxidized microzone in lake sediments, adsorbed silica may also be present. Silica in the bottom waters of Georgetown Lake did appear to increase slightly when the oxidized microzone was destroyed. This could be silica that was adsorbed on the iron oxides of the oxidized microzone. Silica did not appear to increase initially as fast as iron, phosphate, or ammonia (Figures 4a, 5a, and 5b); however, its rate of release seemed to increase later. This later increase was also observed by Mortimer (1942). Wetzel (1975) states that dissolved silica in the interstitial water is in equilibrium with chemically bound or adsorbed silica. Since silica concentrations in the bottom waters only increased slightly with the destruction of the oxidized microzone, adsorbed silica did not seem to be present in large amounts in the surface sediments. Since the amount of adsorbed silica is not large, the interstitial silica in the surface sediments may not be present in concentrations significantly greater than those in the overlying waters. In fact, Harriss (1967) observed that interstitial silica concentrations increased with the depth of the sediment in some lakes and rivers. He found that the interstitial silica concentrations in the surface sediments were similar to those found in the overlying waters. If this were true in Georgetown Lake, there

would not be a concentration gradient between the interstitial silica of the surface sediments and the overlying water; therefore, silica would not diffuse into the overlying water. When the oxidized microzone is destroyed, the silica system's equilibrium is consequently destroyed. This would cause the higher concentrated silica in the deeper sediments to diffuse towards the surface sediments and eventually into the overlying waters. The net result of this would be a delay in the appearance of silica in the overlying waters.

The exchange of phosphate in the sediments with the overlying waters has been intensively studied in the last ten years. It is still not known whether the sediments of a lake act as a sink in which the majority of the sediment phosphorus present is refractory, i. e., not available for exchange, or whether the sediments act as a buffer in which phosphate concentrations in the overlying water are controlled by sediment-water exchange reactions. Li, et al. (1972) observed that inorganic phosphorus in lake sediments had a high degree of exchangeability which ranged from 19-43% of the sediment inorganic phosphorus.

Figure 5a depicts the phosphorus isopleths at Station I. They exhibit the same seasonal trend as conductivity, iron, and silica. During the early part of the summer phosphorus was very low ($3 \mu\text{g}\cdot\text{L}^{-1}$) and undetectable at times but increased during August and September. During the later part of the ice cover period, phosphorus increased

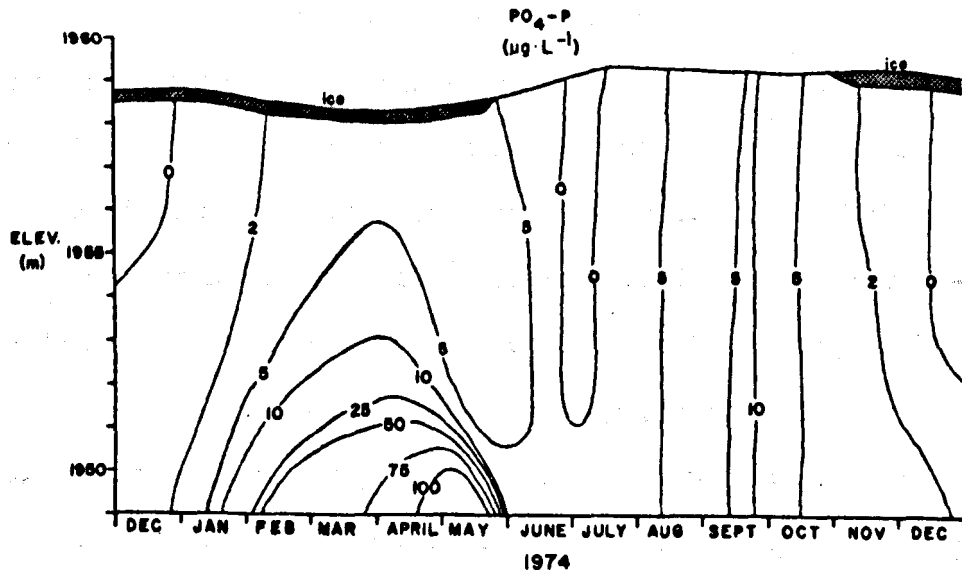


Figure 5a. Ortho-phosphate-P isopleths at Station I.

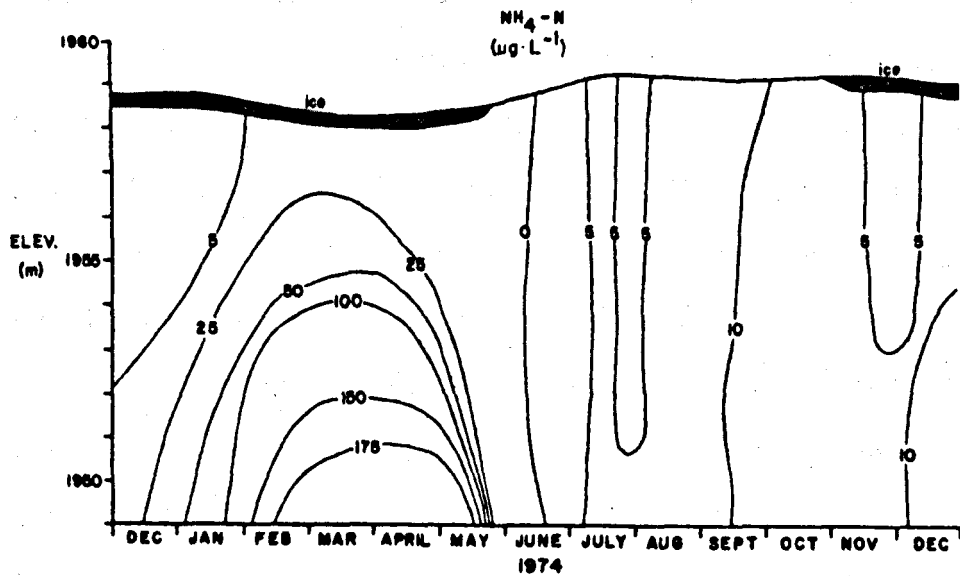


Figure 5b. Ammonium-N isopleths at Station I.

greatly in the bottom waters while anaerobic conditions existed.

During the ice free period, phosphorus was much lower than during the late winter because of the existence of the oxidized microzone.

The ability of the sediments to retain phosphorus beneath the oxidized microzone is related to several interacting factors. Much of the organic phosphorus which reaches the sediments is decomposed and hydrolyzed. Most of the sediment phosphorus then is inorganic, such as apatite and as phosphorus adsorbed onto clays, humus, and ferric hydroxides. Additionally, phosphorus can coprecipitate with iron, manganese, and carbonates (Harter, 1968). The oxidized microzone forms an efficient trap for iron and manganese as well as phosphorus which is adsorbed on and complexed with ferric oxides and hydroxides.

The initial increase of phosphate in August and September could be due to the recycling within the water column of combined phosphorus from planktonic production. Since the allochthonous loading of phosphorus is low during the summer (Knight, et al., 1976) it seems that the phosphorus must have earlier come from the lake sediments. It is well documented that some phosphorus may be released during aerobic conditions. Gahler and Sanville (1971) observed, in the extremely shallow Upper Klamath and Agency Lakes, that exchange of nutrients during aerobic conditions maintained eutrophic conditions.

From December to February total phosphorus in the water increases although combined phosphorus tends to decrease (Figure 6). Lee (1970)

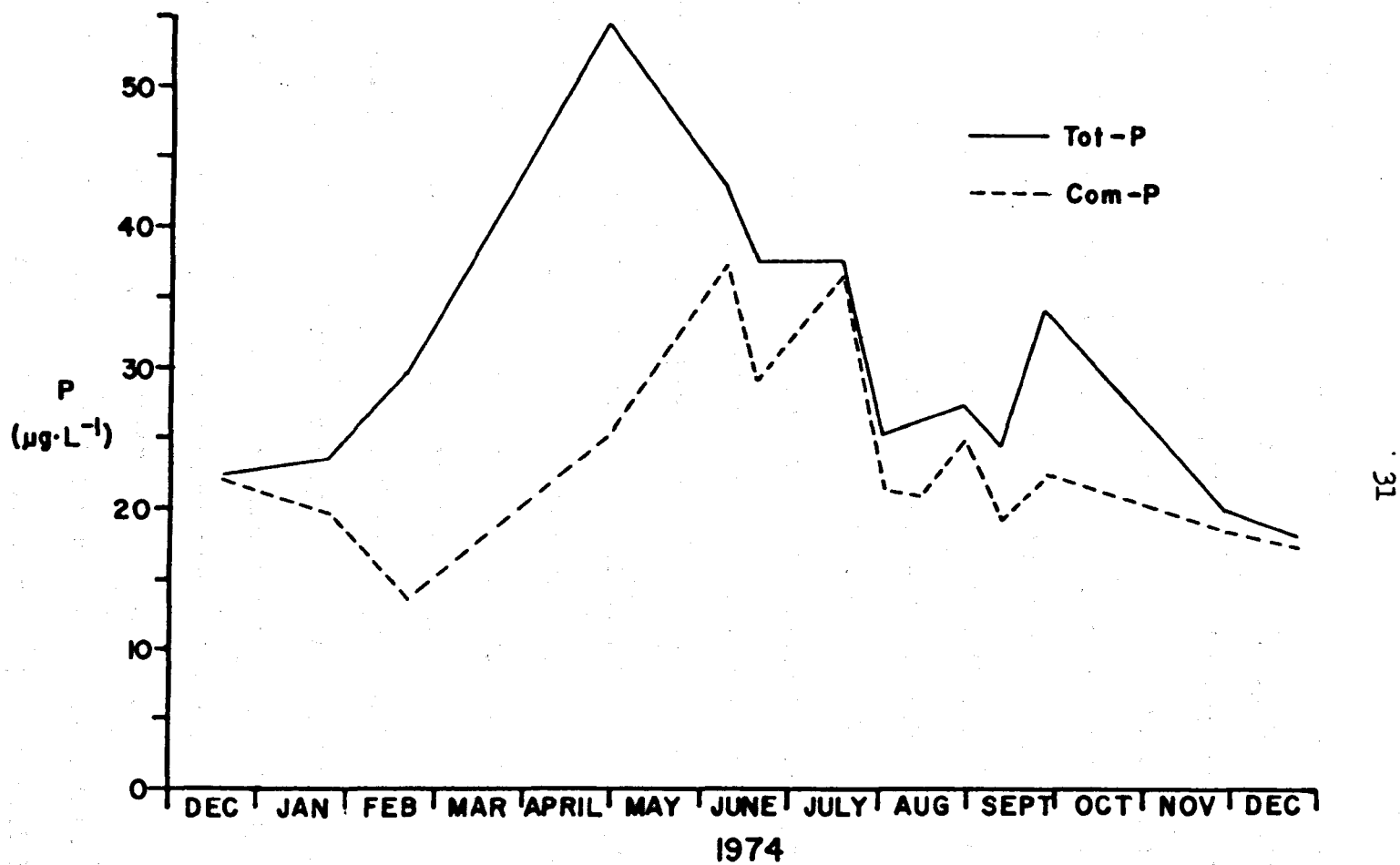


Figure 6. Seasonal trends of total phosphorus (Tot-P) and combined phosphorus (Com-P) at Station I.

stated that the hydrodynamics of the water and sediment is often the rate-controlling step in exchange reactions. Although diffusion may be important in the sediments, the oxidized microzone greatly reduces diffusion into the overlying waters. The most important method of releasing phosphorus into the water when an oxidized microzone is present is the suspension of sediments in bottom waters by turbulent mixing. Williams and Mayer (1972) observed that the bottom sediments, at a depth of 11 meters, in Lake Erie were disturbed by wind action. Surface sediments in Georgetown Lake were suspended during the summer as evidenced by increases in both conductivity and iron in the bottom waters. Phosphate did not show an increase in the bottom waters during the summer but this may have been a result of the rapid assimilation by the phytoplankton. Hayes (1953), Pomroy, et al. (1965), and Kamp-Nielsen (1974) found that, during aerobic conditions, phosphorus exchange was not important in undisturbed sediments but that, in disturbed sediments, rapid exchange occurred. Golterman, et al. (1969) demonstrated that algae, suspended in the water with various particulate inorganic compounds of extremely low solubility (e. g. phosphorus sorbed on suspended ferric hydroxides), were capable of extracting sufficient phosphorus for active growth. Therefore, it seems that during the summer surface sediment is being suspended, principally by wind-caused turbulence. Phosphorus is then immediately assimilated by the phytoplankton from the suspended particles. As

the phytoplankton standing crop decreases in late summer, the organic phosphorus is being mineralized to inorganic phosphorus and phosphate accumulates in the water column (Figure 6).

As shown in Figure 5a, phosphate in the water column decreased in the early part of the ice cover period. Since total phosphorus was also decreasing at this time, this phenomenon may have been caused by adsorption of phosphate by the sediments. It has been mentioned earlier that the oxidized microzone is capable of chemically extracting phosphate from water by adsorption reactions. It has also been shown that during aerobic conditions bacteria at the sediment interface can increase the microbial transport of phosphorus to the sediments significantly (Hayes, 1953, and Hayes and Phillips, 1958). This was probably happening during the entire summer but the suspension of sediment by turbulent mixing helped offset phosphate movement to the sediments. With the onset of ice cover, the turbulent mixing was greatly reduced, thereby causing a net movement of phosphate into the sediments.

Phosphate concentrations increased greatly during the latter part of the ice cover period in the bottom waters (Figure 5a). As with other ions, phosphate is liberated during reducing conditions when the oxidized microzone is destroyed. Stumm and Morgan (1970) state that phosphorus is readily adsorbed by ferric hydroxides. Although some of the liberated phosphorus is a result of the reduction of

iron in the surface sediments, most of it comes from deeper sediments. This is dissolved phosphorus in the interstitial water. Inorganic phosphorus associated with sediment particles regulates the inorganic phosphorus status of the associated interstitial water through inter-related adsorption-desorption and exchange processes. Inorganic phosphorus in the interstitial water in turn influences the dissolved inorganic phosphorus levels in the overlying waters. The magnitude and direction of the exchange is dependent upon the relative concentrations of dissolved inorganic phosphorus in the interstitial and overlying water. Inorganic phosphorus concentrations in the interstitial water generally exceed levels found in the overlying water (Syers, et al., 1973).

Lee (1970) stated that the interchange between interstitial and lake water was mainly regulated by mixing in both the sediments and overlying water. This may be true during ice free periods but not during ice cover periods. During the winter, sediment mixing caused by turbulent mixing of the overlying water would be very much reduced because of the absence of wind-caused turbulence. Also, biological action would be reduced because of the low temperatures and lack of oxygen. This contention is supported by laboratory studies showing the absence of bacterial mediation of exchange rates under anaerobic conditions (Hayes, 1963; Pomroy, et al., 1965; and Kamp-Nielsen, 1974). Exchange rates are not largely determined by mixing; however,

it may play a minor role in their regulation. Likens and Hasler (1962) using radioactive sodium observed that at the sediment interface there was significant current of several $\text{cm}\cdot\text{sec}^{-1}$ during an ice cover period.

Probably the most important mechanism in regulating exchange is diffusion. Gorham (1961) suggested that the driving force in diffusion may be ion exchange. He theorized that adsorbed ions may be replaced by hydrogen ions generated in the mud through the oxidation of carbon and sulfur compounds. Howeller and Boulder (1971) formulated a specific theory for phosphate diffusion. They thought that the reduced portion of the sediment may have a higher pH than the surface sediments. This would make phosphorus adsorbed on aluminum and iron unstable; thus, it would be released into the interstitial water. This would greatly increase the dissolved interstitial phosphate in the reduced sediments. Phosphorus is also increased in the interstitial water by the mineralization of organic phosphorus in the sediments. The net effect of these reactions would be to establish a concentration gradient between the sediments and the lake water. Hynes and Grieb (1970) observed that in undisturbed sediments phosphorus moved towards the surface sediments at a rate of 10 cm in 2-3 months.

As can be seen in Figure 5a, the phosphate concentration ($2 \mu\text{g}\cdot\text{L}^{-1}$) was low in the bottom waters just prior to the destruction

of the oxidized microzone. When the oxidized microzone was destroyed, phosphate readily moved into the overlying water. The concentration gradient was partially maintained by the currents caused by the deep-water withdrawal of the dam as reflected in the high concentrations of phosphate, iron, and ammonia in the outflowing water (Knight, et al., 1976). The continued rapid increase of phosphate in the bottom waters through February, March, and April indicated that the concentration gradient was indeed maintained.

The phosphate concentrations decreased rapidly when oxygen was reintroduced into the bottom waters (Figure 5a) causing iron and manganese to be oxidized. Some of the dissolved phosphate then coprecipitated with the iron and manganese. Apparently, a portion of the liberated phosphorus remained in the water column since the total phosphorus concentration did not return to levels experienced in December (Figure 6). Knight, et al. (1976) observed an increase in phytoplankton standing crop at about this same time. Apparently a portion of the liberated phosphate, which was not coprecipitated with the iron and manganese, was incorporated into planktonic biomass.

Whether the bottom sediments act largely as a sink or a reservoir for nitrogen is determined by the relative importance of four processes. Denitrification and mineralization remove nitrogen from the lacustrine system whereas nitrogen fixation and nitrogen release

from the sediments add nitrogen to the waters. Keeney (1973) noted that the concentration of nitrogen species in water is the net result of the rates of N immobilization, mineralization, nitrification, and denitrification.

Figure 5b depicts the ammonia isopleths at Station I. They exhibit the same general seasonal trend as phosphorus. During the ice cover period, ammonia was high while reducing conditions existed in the bottom waters. The high ammonia concentrations could not be accounted for by nitrate reduction. Part of the increase may result from the decomposition of plankton and deamination of organic nitrogen compounds, but most probably originates from the sediment. With the reoxygenation of the water column in May, the ammonia concentrations decreased to zero. Ammonia increased somewhat during the summer.

As with the other parameters discussed ammonia appeared to be released from the sediments during the ice cover period. When the oxidized microzone was destroyed, there was a rapid rise of ammonia in the bottom waters (Figure 5b). Since ammonium salts are freely soluble it seems that while the oxidized microzone existed, it adsorbed the ammonia that would have otherwise diffused into the overlying water. When the oxidized microzone is destroyed, the ammonia which it had held is liberated, and no further barrier to the free passage of dissolved ammonia produced in the mud is present.

Ammonia was liberated but at about the same time as iron. It

appears that ammonium ion is adsorbed on the surface sediments by the same complex as iron. This complex may be a colloid, which is known to adsorb cations such as ammonia and iron. Although the initial ammonia comes from the ferric complex, the majority of the ammonia liberated during reducing conditions comes from ammonia dissolved in the interstitial water. This dissolved ammonia is in equilibrium with exchangeable sediment ammonia. Since ammonia dissolved in the interstitial water is usually much higher than ammonia in the overlying water (Keeney, et al., 1970) the interstitial ammonia diffuses into the overlying waters. Ammonia concentrations continued to increase in the bottom waters following the destruction of the oxidized microzone until the ice melted.

With reintroduction of oxygen into the bottom waters at the end of May the ammonia concentrations decreased drastically to a low of $1 \mu\text{g}\cdot\text{L}^{-1}$ on 5 June. Mortimer (1941) also observed this in his studies but he was not able to explain this occurrence satisfactorily. Part of the decrease was probably a result of assimilation by phytoplankton as their standing crop increased from 25 April to 5 June (Knight, et al., 1976). Nitrate did not increase yet organic nitrogen only increased slightly. Apparently, part of the ammonia was adsorbed by the oxidized microzone.

Ammonia concentrations were low throughout the summer as a result of assimilation, although they did increase slightly from June to

September. This increase in late summer and early fall was probably attributable to a similar recycling as was observed with phosphate. Since the phytoplankton did not increase in November the ammonia decrease was probably caused by sediment adsorption coupled with a reduction of turbulent mixing with the onset of ice cover.

Sediment Chemistry

The sediments of Goergetown Lake are neutral to slightly acidic and noncalcareous. These sediments could be classified as gyttja, appearing soft and hydrous with a dark color in the fresh state. In the dry state they are lighter in color. The sediments are largely autochthonous, originating primarily as macrophytic or planktonic detritus. The organic carbon content is relatively high (16%) because the flooded area was originally a hay meadow and the lake presently supports considerable plant growth, both macrophytic and algal.

The sediments are very heterogeneous throughout the lake. This is mainly a result of the differential amounts of macrophytic growth in various parts of the lake. Additionally, prior to flooding, the area did not consist of a uniform substrate. This heterogeneity made representative sampling difficult and sometimes gave large sampling errors.

A weighted mean was calculated for each parameter to obtain a reasonable picture of the sediment characteristics for the whole lake. The areas represented by the five sampling sites were estimated in terms of their percentage of the total lake area. The means are sometimes biased because on some sampling trips, particularly during ice cover, only Station I was sampled and at other times only Stations I, IV, and V were sampled.

Cations

Table 2 gives the ranges and means of the cations in the sediments

TABLE 2. RANGES AND MEANS OF SOME CHEMICAL AND PHYSICAL PARAMETERS OF THE SEDIMENTS OF GEORGETOWN LAKE.

Parameters	Station I	Station II	Station III	Station IV	Station V	Weighted Mean of Lake
Fe_2O_3 ($\text{mg}\cdot\text{g}^{-1}$)	8.500 - 22.800 12.426	4.125 - 9.250 6.189	3.200 - 6.375 4.482	1.625 - 4.250 2.806	0.460 - 7.350 2.546	4.254 - 15.464 8.786
Al_2O_3 ($\text{mg}\cdot\text{g}^{-1}$)	0.047 - 0.164 0.116	0.045 - 0.120 0.082	0.037 - 0.091 0.0062	0.038 - 0.076 0.058	0.002 - 0.068 0.027	0.043 - 0.164 0.084
Ex-Ca ($\text{mg}\cdot\text{g}^{-1}$)	2.50 - 7.45 3.93	-	-	1.90 - 13.80 7.73	-	2.89 - 12.00 5.39
Ex-Mg ($\text{mg}\cdot\text{g}^{-1}$)	0.620 - 1.360 0.948	0.600 - 1.163 0.890	0.540 - 1.043 0.757	0.863 - 1.750 1.297	0.039 - 0.688 0.478	0.620 - 1.412 0.995
Ex-Mn ($\text{mg}\cdot\text{g}^{-1}$)	0.016 - 0.181 0.097	0.066 - 0.259 0.166	0.099 - 0.313 0.141	0.058 - 0.166 0.113	0.012 - 0.124 0.075	0.041 - 0.197 0.110
Ex-Fe ($\text{mg}\cdot\text{g}^{-1}$)	0.001 - 0.022 0.006	0.004 - 0.012 0.008	0.005 - 0.008 0.006	0.001 - 0.018 0.006	0.005 - 0.010 0.007	0.001 - 0.011 0.006
Ex-Al ($\text{mg}\cdot\text{g}^{-1}$)	0.004 - 0.019 0.011	0.004 - 0.017 0.010	0.005 - 0.021 0.010	0.007 - 0.020 0.010	0.005 - 0.010 0.007	0.004 - 0.019 0.011
Ex-Zn ($\text{mg}\cdot\text{g}^{-1}$)	0.016 - 0.114 0.055	0.011 - 0.121 0.057	0.006 - 0.086 0.039	0.004 - 0.060 0.039	0.001 - 0.069 0.034	0.008 - 0.096 0.049
pH	6.2 - 7.2 6.9	6.8 - 7.4 7.1	6.9 - 7.2 7.0	6.7 - 7.2 7.0	6.9 - 7.3 7.1	6.2 - 7.3 7.0

7

of Georgetown Lake.

At Station I, the concentrations of iron oxides (ranging from $8.500 \text{ mg}\cdot\text{g}^{-1}$ to $22.800 \text{ mg}\cdot\text{g}^{-1}$ with a mean of $12.426 \text{ mg}\cdot\text{g}^{-1}$) were generally twice as high as those found at the other stations. Aluminum oxide concentrations were also highest at Station I, although not as high as those for the iron oxides.

Frink (1969b) found iron oxides to be positively correlated with clay particles, which are typically finely grained particles that do not readily settle out of the water. Delfino, et al. (1969) have shown that total iron, which may also be associated with clay, was positively correlated with increasing water depth. They attribute this to current patterns and particle size differentiation. Davis (1968) showed that pollen grains were deposited 2-4 times before being buried deeply enough to escape further disturbance. He stated that apparently the sediments in the shallower areas are stirred up and resuspended. Since Station I is located near the dam, major currents probably would move towards this station because of the deep-water withdrawal at the dam. It appears that much of the Fe_2O_3 are associated with finely grained particles which tend to settle out in the deeper part of the lake, i.e. Station I. Since Al_2O_3 are highest at Station I it seems that they are also associated with finely grained particles.

The iron oxides and Al_2O_3 extracted by McKittrick and Hope's

(1963) sodium dithionite method are crystalline oxides, amorphous inorganic Fe and Al and organically complexed Fe and Al (McKeague, et al., 1971). The crystalline oxides of iron probably are goethite and those of aluminum are gibbsite. Iron oxides are positively correlated with aluminum oxides ($r = 0.96$) at Station I. This indicates that these two parameters are associated with similar sediment particles.

Although the iron and aluminum oxides appear to be associated with clay particles at Station I, this may not be the case at the other stations where the organic carbon content is higher. Oborn (1960) has shown that aquatic plants may concentrate iron by removing it from the water and sediments. Since Fe_2O_3 are positively correlated with organic C ($r = 0.87$) at Station IV it appears that most of this iron exists as organically complexed iron. However Al_2O_3 is not correlated with organic C. Aluminum oxide and Fe_2O_3 are not correlated and therefore appear to be associated with different sediment particles. The low concentrations of crystalline Fe_2O_3 are not surprising since organic compounds inhibit the crystallization of amorphous ferric hydroxides (Schwertmann, et al., 1968).

In the lake sediments as a whole, the iron oxides did not show any particular seasonal trends. Instead the concentrations remained relatively constant throughout the sampling period. However, at

Station I, which is the deep-water station where the bottom waters become anaerobic (Figure 3b), Fe_2O_3 was lower during the latter part of the ice cover period. When the ice melted and the oxygen concentration in the bottom waters increased, Fe_2O_3 increased, although not to the levels recorded earlier (Figure 7). When the sediment Fe_2O_3 was decreasing the dissolved iron in the bottom waters increased greatly (Figure 4a). Conversely, when the sediment iron increased in June the iron in the bottom waters decreased greatly. As will be discussed later, much of the iron released into the water was lost from the lacustrine ecosystem via the deep-water withdrawal of the dam. This may partially explain why the sediment iron did not increase in June to a level noted earlier.

Aluminum oxides exhibited a seasonal trend similar to Fe_2O_3 in the lake sediments as a whole. At Station I, the trend was also similar to the trend of Fe_2O_3 (Figure 7). During the latter part of ice cover Al_2O_3 decreased rapidly, but with the ice breakup, the Al_2O_3 increased and remained at approximately the same concentration throughout the summer, and decreased during the fall. Aluminum is not known to be liberated into the overlying water during reducing conditions. Unfortunately aluminum concentrations were not measured in the water.

Exchangeable iron was present only in low concentrations. In the lake it ranged from $0.001 \text{ mg}\cdot\text{g}^{-1}$ to $0.011 \text{ mg}\cdot\text{g}^{-1}$ with a weighted mean

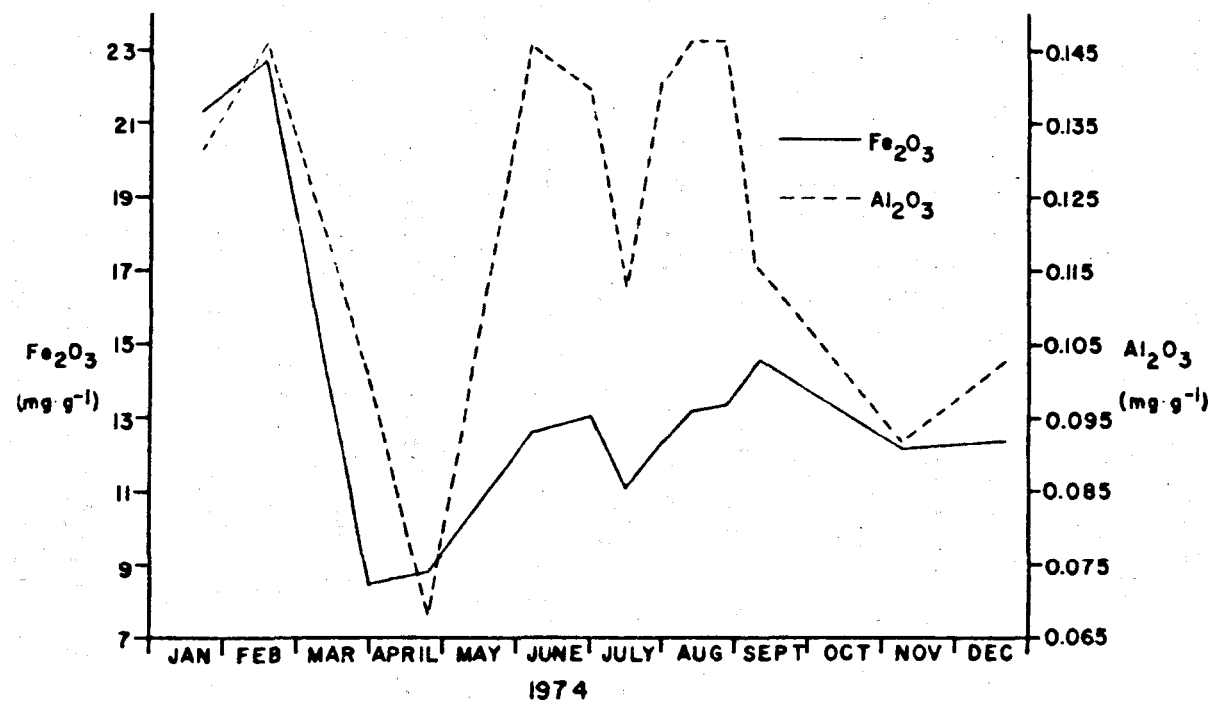


Figure 7. Seasonal trends and the relationship between iron oxides (Fe₂O₃) and aluminum oxides (Al₂O₃) at Station I.

of $0.006 \text{ mg}\cdot\text{g}^{-1}$. The low concentrations are not surprising because exchangeable Fe is present as ferrous iron which in the presence of oxygen is rapidly oxidized to $\text{Fe}(\text{OH})_3$. Since the samples after collection were not kept anaerobic the reduced iron may have been oxidized.

Exchangeable aluminum concentrations were also low ranging from $0.004 \text{ mg}\cdot\text{g}^{-1}$ to $0.019 \text{ mg}\cdot\text{g}^{-1}$. The weighted mean for the lake was $0.011 \text{ mg}\cdot\text{g}^{-1}$. Exchangeable aluminum contributes towards the exchangeable acidity of a soil. Since the average sediment pH was 7.0, little acidity would be expected. Mehlich (1964) has shown in muck soils at a pH of 7.0, that the permanent charge exchange sites are dominated by exchangeable bases which replace H^+ and Al. The exchangeable Al is then generally converted to gibbsite. The fact that these sediments have little exchangeable acidity was confirmed when exchangeable acidity was determined to be $0.010 \text{ meq}\cdot\text{g}^{-1}$ on a sample.

Exchangeable calcium was only determined at Station I and IV. Calcium was higher at Station IV than at Station I, the means being $7.73 \text{ mg}\cdot\text{g}^{-1}$ and $3.93 \text{ mg}\cdot\text{g}^{-1}$ respectively. The extractant used also partially extracts CaCO_3 (Heald, 1965). Oborn (1964) found that the symbiotic bacterium, Bacterium precipitatum, can precipitate calcite on aquatic plants. The higher exchangeable-Ca at Station IV may have been a result of this process. The higher Ex-Ca concentrations could also have been caused by the biogenic calcium carbonate precipitation

by the macrophytes themselves. As shown in Figure 8, Ex-Ca generally increased during the summer. This increase may partially be a result of CaCO_3 precipitation which occurs during the summer (Knight, et al., 1976).

Exchangeable magnesium exhibited the same distributional pattern as exchangeable Ca, being higher at Station IV than at Station I. The difference was not as great, the means being $0.948 \text{ mg}\cdot\text{g}^{-1}$ and $1.297 \text{ mg}\cdot\text{g}^{-1}$ for Stations I and IV, respectively. Exchangeable Mg tended to increase during ice cover period but fell drastically in June (Figure 8). Throughout the summer, Ex-Mg increased but it never reached the concentrations observed during the previous winter months.

Exchangeable manganese concentrations in the sediments ranged from $0.041 \text{ mg}\cdot\text{g}^{-1}$ to $0.197 \text{ mg}\cdot\text{g}^{-1}$ with a weighted mean of $0.110 \text{ mg}\cdot\text{g}^{-1}$. Oborn (1964) has found that aquatic plants concentrate manganese both intracellularly and extracellularly. The bacterium Micrococcus has been implicated in extracellular concentration. He found that aquatic plants may contain 30 times as much manganese as terrestrial plants. This concentration process may explain why exchangeable Mn is higher at the stations in the littoral zone, with the exception of Station V, even though Delfino, et al. (1969) observed a positive correlation with increasing water depth.

Dion and Mann (1946) have elucidated the manganese cycle in soils. Exchangeable manganese (Mn II), the form taken up by plants, is in

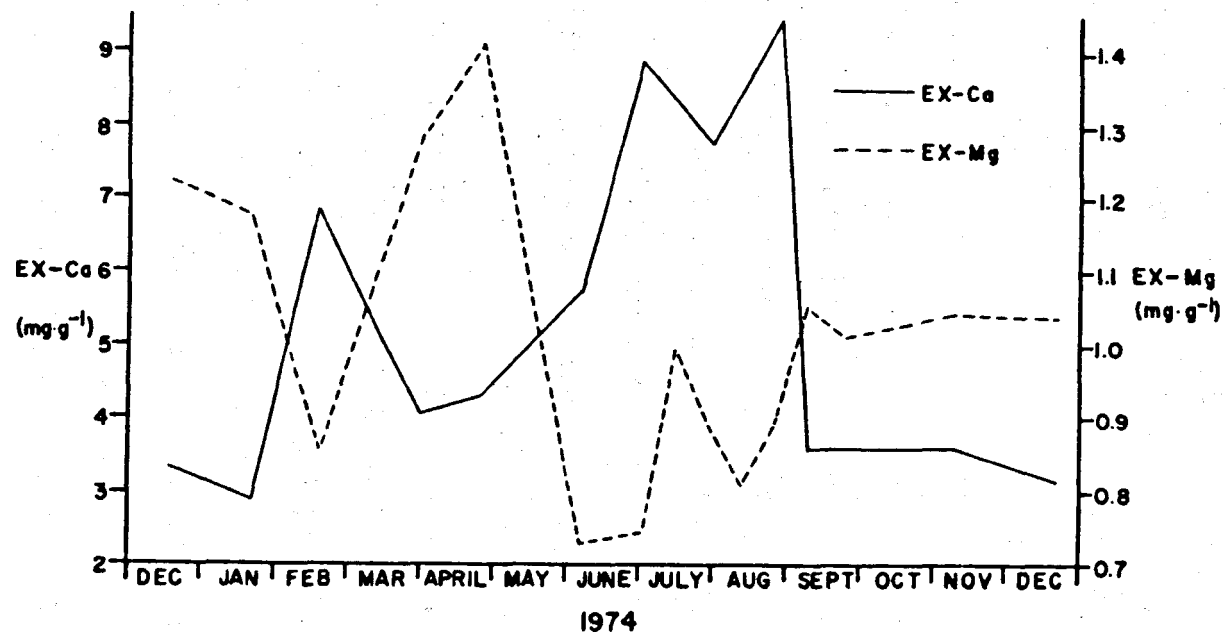


Figure 8. Seasonal trends of exchangeable calcium (Ex-Ca) and exchangeable magnesium (Ex-Mg) at Station I.

equilibrium with Mn_2O_3 (Mn III) and MnO_2 (Mn IV). Manganese II may be readily oxidized although the transformation of Mn II to Mn IV usually occurs only under alkaline conditions. Although the oxidation of Mn II is chemically controlled and rapid, the dismutation of Mn III to Mn II is bacterially mediated.

As shown in Figure 9b, exchangeable manganese decreased during the latter part of the ice cover period at Station I. However in the beginning of June, the exchangeable Mn increased drastically. This decrease coincides with the bottom waters becoming anaerobic (Figure 3b). Although manganese was not measured in the overlying waters, it has been well documented (Mortimer, 1941 and 1942; Hutchinson, 1957; Wetzel, 1975) that during reducing conditions, manganese is liberated into the water from the sediments. It appears that as the bottom waters become anaerobic, oxidized manganese is reduced. The reduced manganese, along with interstitial Mn II, is liberated into the overlying waters. Consequently there is a decrease in the sediment exchangeable Mn. Reduced Mn (Mn II) is the only form that is soluble in water. Manganese III is not dismutated to Mn II because the environmental conditions were detrimental to bacterial action. With the increase in oxygen content at ice out, the reduced Mn is oxidized and precipitates causing the exchangeable Mn to increase. Gorham and Swaine (1965) and Mortimer (1942) have shown that oxidized Mn remains in solution after recxygenation for a few days, which may

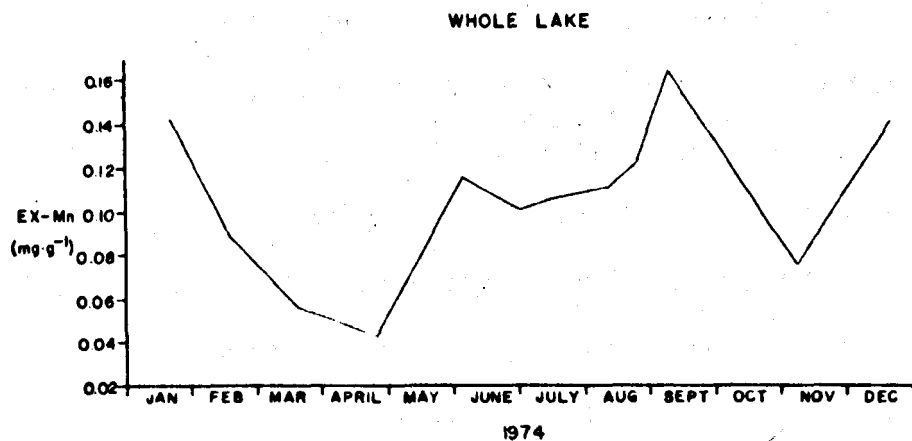


Figure 9a. Seasonal trends of exchangeable manganese (Ex-Mn) for the whole lake.

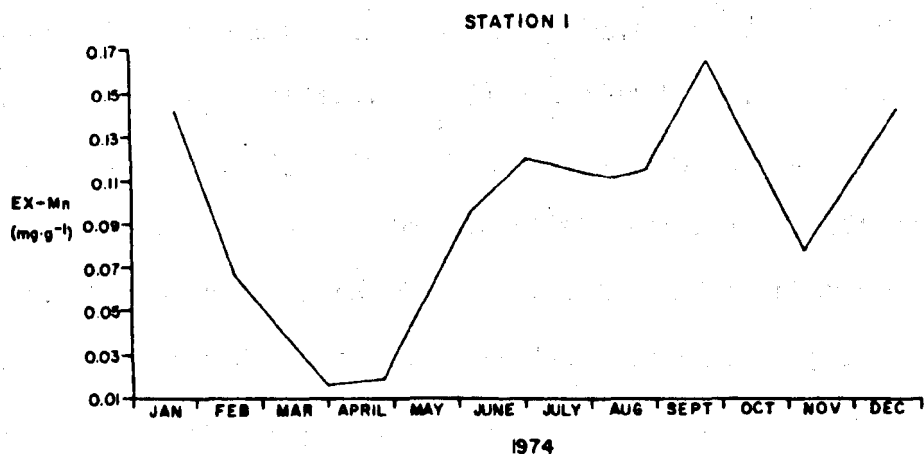


Figure 9b. Seasonal trends of exchangeable manganese (Ex-Mn) at Station I.

explain the increase in exchangeable Mn from 5 June to 1 July.

As with Station I, exchangeable Mn in the lake sediments as a whole decreased during the latter part of ice cover and increased at ice out (Figure 9a), although the Fe_2O_3 did not show this same trend. Stumm and Morgan (1970) have noted that Mn is reduced at a higher redox potential than iron. Since the rest of the lake, aside from Station I, contained more oxygen during January to May (Knight, et al., 1976), the bottom waters may not have become reduced enough to reduce iron. This was confirmed as dissolved iron in the water did not increase at Station IV during this period.

As shown in Figure 9a, exchangeable Mn increased during the summer. This is probably a result of biological concentration and sedimentation. The plants may be extracting Mn from the deeper sediments with a resultant sedimentation in the surface sediments. If this were true the manganese concentrations should decrease with sediment depth. Olsen, et al., (1967) observed this in sediments of Lake Washington, especially in the shallower water. The drastic increase in September was probably a result of the partial die off of aquatic plants. The decrease from 10 September to 24 September may be the result of the rapid oxidation of Mn II. The extremely low concentration on 8 November probably is a result of a sampling error.

Exchangeable zinc was present in low concentrations although it was in higher concentrations than either exchangeable iron or ex-

exchangeable aluminum. Exchangeable zinc ranged from $0.008 \text{ mg}\cdot\text{g}^{-1}$ to $0.096 \text{ mg}\cdot\text{g}^{-1}$ with a weighted mean of $0.049 \text{ mg}\cdot\text{g}^{-1}$. With the exception of Station II, Ex-Zn was higher in the deeper water. This same trend was also observed by Olsen, et al., (1967). As with Fe_2O_3 and Al_2O_3 , zinc may be associated with finely grained particles. As shown in Figure 10, exchangeable zinc at Station I decreased during the ice cover period. Although it is not well documented that zinc may be liberated during reducing conditions, Figure 10 shows that it may have been. If zinc were to be released, exchangeable Zn would be the form released. With the reoxygenation of the bottom water, exchangeable Zn increased in the sediment and continued to increase until the fall.

Organic Matter

The cycle of organic matter in lakes and reservoirs consists of two stages: the production of the organic matter from carbonic acid and minerals, and its destruction or mineralization. The bulk of the organic material in the waters is produced by the primary producers, i. e. phytoplankton and macrophytes, although some may come from allochthonous sources. Some production may occur in the sediments but the majority occurs in the water (Seki, 1968). The decomposition of the organic material occurs in the water column as well as in the sediments. Kuznetsov (1968) and Kajak, et al. (1970) indicate that only 0.8 to 30% of dead phytoplankton reach the sediments. The rest

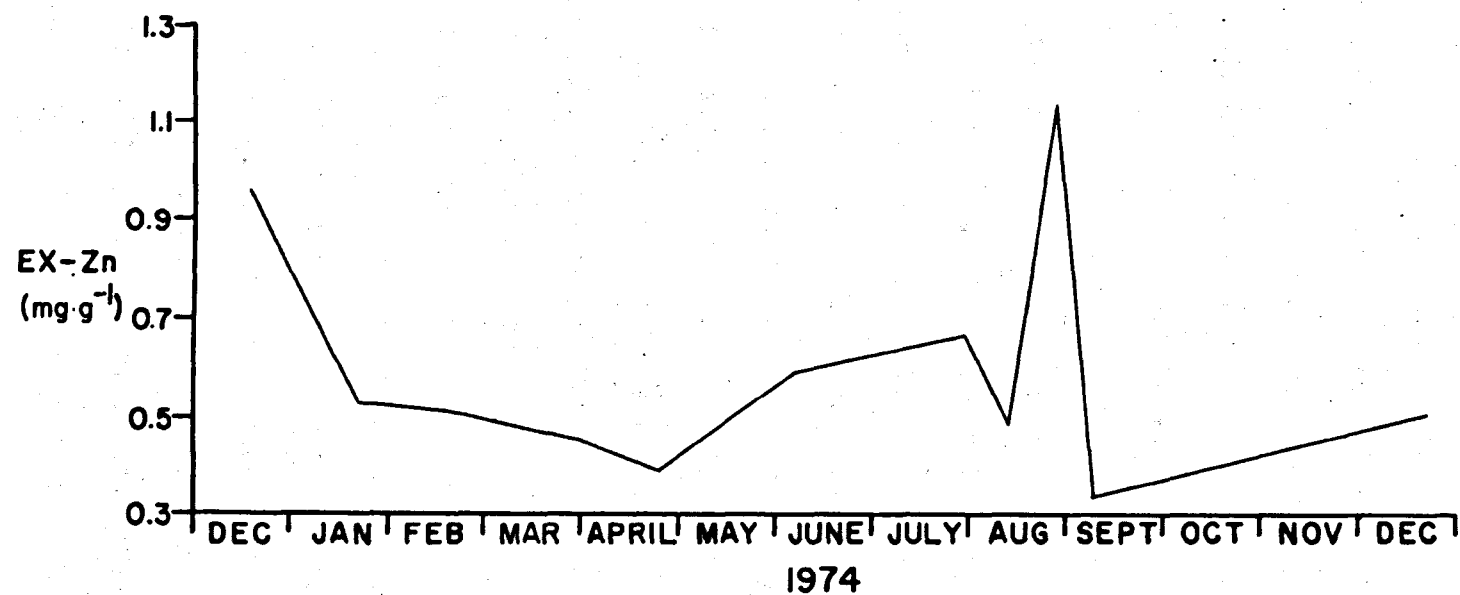


Figure 10. Seasonal trends of exchangeable zinc (Ex-Zn) at Station I.

are decomposed by bacteria and, to a small degree, fungi as they sink through the water column (Kerr, et al., 1973). Kuznetsov (1968) found that, in the water column, there was a direct relationship between destructive processes and the number of total bacteria.

The gross biological activity in and on the sediments is a sum of the metabolism of saprophytic, epiphytic, and free-growing organisms, whose growth is dependent in some way upon the metabolism of each of the other types of organisms. The principal organisms are probably heterotrophic bacteria. This mineralization of organic matter may proceed by either aerobic or anaerobic processes. Because of the lack of oxygen in the subsurface sediments, aerobic processes necessarily occur only on the surface sediments. During aerobic processes the organic matter is oxidized to carbon dioxide and water. However, during anaerobic decomposition the process is more prolonged, the organic matter being first converted to fatty acids and hydrogen, then to methane, and eventually to carbon dioxide. Reduced end products of anaerobic metabolism, near the sediment surface, are in a state of dynamic equilibrium between the rate of oxidation and the rate of formation. Below a few centimeters the reduced end products are no longer effectively oxidized. Instead they accumulate as shown by increases in concentrations with increasing sediment depth (Pamatmat and Jones, 1973). Hayes (1953) and Kerr, et al. (1973) reported higher bacterial activity on the surface sediments than in the deeper

sediments. This would seem to imply that aerobic decomposition is much more important than anaerobic breakdown. Romanenko and Kuznetsov (1972) and Gulaya and Tyuten'kova (1974) in Russia observed anaerobic decomposition rates that were 40-50% of the total rates.

Organic carbon and the initial volatile solids (IVS) were consistently highest at Station IV (Table 3). This is contrary to the findings of Frink (1969b) and Loring and Nota (1973) who found that organic C was positively correlated with increasing water depth. In Georgetown Lake the deepest station (Station I), with the exception of Station V, consistently had the lowest concentration of organic matter. The higher concentrations at Station IV apparently were due to the increased macrophytic biomass at this station. The importance of the macrophytes in influencing organic matter concentrations is suggested by the higher concentrations at the other two littoral zone stations (Stations II and III). Keeney (1973) noted that organic matter formed by macrophytes is more resistant to mineralization than organic matter formed by algae and zooplankton. Even though Station V had a high macrophytic biomass it had the lowest sediment organic matter content. This seems to be a contradiction of the previous statement. However, Station V was unusual because the substrate was much more gravelly than the other stations. Before the lake was formed this area was in the stream bed of Stuart Mill Creek. Since this stream originates in a spring close to the lake it never carries

TABLE 3. RANGES AND MEANS OF SOME CHEMICAL PARAMETERS OF THE SEDIMENTS OF GEORGETOWN LAKE.

Parameters	Station I	Station II	Station III	Station IV	Station V	Weighted Mean of Lake
Organic - C (mg.g ⁻¹)	56.7 - 187.8 125.5	120.1 - 227.6 165.9	75.8 - 211.0 149.7	202.1 - 352.7 276.5	44.3 - 138.6 91.0	56.7 - 268.9 161.4
IVS (mg.g ⁻¹)	132.17-312.43 207.86	176.08-325.21 264.05	167.81-325.16 243.47	342.99-669.33 493.22	78.08 - 224.43 161.71	132.17-423.30 270.29
Total - P (mg.g ⁻¹)	0.663 - 1.088 0.789	0.563 - 1.606 1.150	0.675 - 1.219 0.939	0.938 - 1.438 1.190	0.306 - 1.163 0.680	0.706 - 1.211 0.918
Inorganic-P (mg.g ⁻¹)	0.434 - 0.634 0.522	0.347 - 1.100 0.731	0.384 - 0.825 0.555	0.522 - 0.919 0.646	0.181 - 0.747 0.414	0.434 - 0.742 0.566
Organic - P (mg.g ⁻¹)	0.178 - 0.491 0.267	0.216 - 0.581 0.419	0.290 - 0.469 0.384	0.416 - 0.637 0.542	0.109 - 0.416 0.265	0.178 - 0.548 0.352
Total - N (mg.g ⁻¹)	4.69 - 13.72 9.02	9.57 - 19.52 13.48	9.00 - 15.92 12.12	16.84 - 24.84 21.18	3.85 - 10.86 7.49	4.69 - 20.40 12.25
Inorganic-N (mg.g ⁻¹)	0.98 - 2.34 1.55	1.33 - 2.49 2.07	1.23 - 2.33 1.81	2.19 - 3.63 3.04	0.72 - 1.65 1.16	0.98 - 3.05 1.85
Organic - N	3.709 - 11.396 7.571	8.24 - 17.033 11.357	7.766 - 13.674 10.310	14.652-21.212 18.397	3.086 - 8.405 5.704	3.709 - 17.352 9.947

much organic matter, even during spring runoff.

As shown in Figure 11, the seasonal trends of IVS and organic C for the lake sediments were similar and correlated ($r = 0.94$). This is not surprising since IVS estimates total organic matter. This organic matter includes carbohydrates, celluloses, lignins, fats, waxes, proteins, etc. Although organic C makes up the majority of these compounds, it is not the only constituent. Nitrogen, phosphorus, sulfur, etc. are also included in organic matter. Subsequently IVS was consistently higher than organic C.

Brady (1974) stated that the organic matter content is about 1.7 times the organic carbon content. This generally holds true for the sediments of Georgetown Lake. Since some constituents such as nitrogen and phosphorus decompose more rapidly than carbon (Nichols and Keeney, 1973), the IVS to organic C ratio may vary. This happened in the sediments of Georgetown Lake (Figure 11). From 17 December 1973 to 15 July 1974, organic C made up less of the IVS than during the period 20 July to 21 December 1974. Several workers, including Romanenko and Kuznetsov (1972), Gulaya and Tyuten'kova (1973), and Wetzel (1975), have noted that anaerobic decomposition is not as rapid as aerobic breakdown. Romanenko and Kuznetsov (1972) also noted that decomposition greatly decreased during low temperatures. During the ice cover period, the bottom waters of the lake were around 4°C and nearly anaerobic. Therefore, decomposition

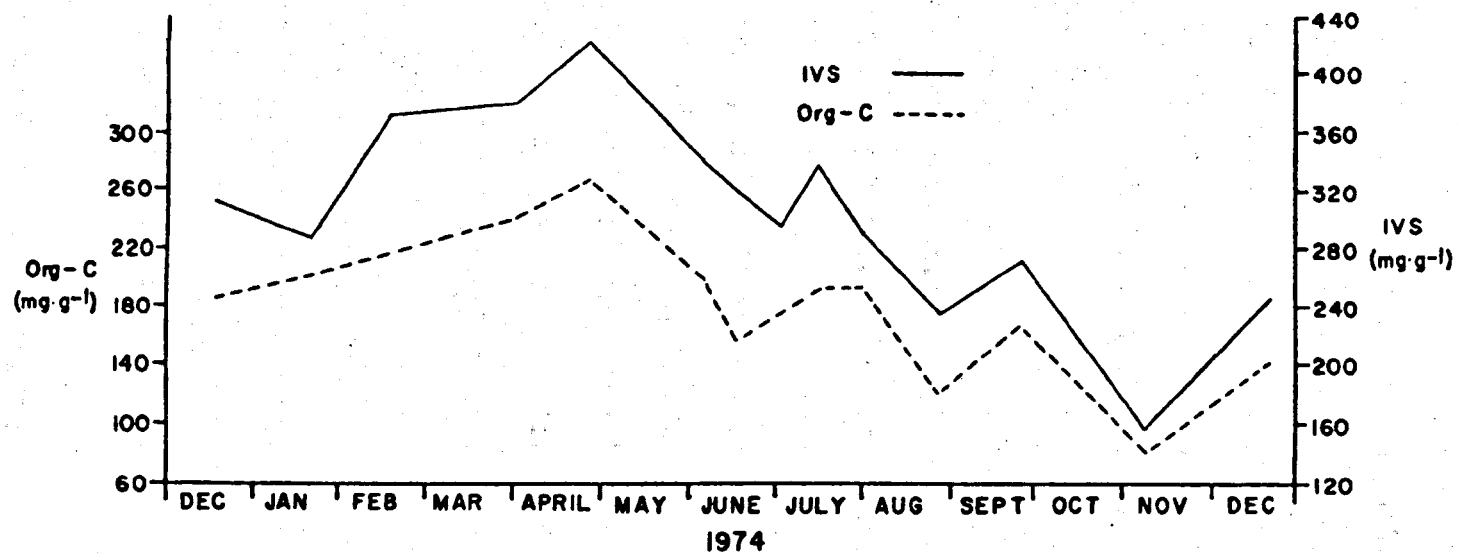


Figure 11. Seasonal trends and the relationship between initial volatile solids (IVS) and organic carbon (Org-C) in the whole lake.

was occurring at a reduced rate, causing the organic carbon to be less abundant in the IVS than in late summer and fall.

Figures 12a and 12b illustrate the relationship between IVS and organic C at Station I and IV. Throughout the sampling period at Station I organic C made up 60% of the IVS but at Station IV organic C only made up 56% of the IVS. The difference was probably a result of the nature of the sedimenting detritus. Station I contained predominantly phytoplankton whereas Station IV contained macrophytes as well as phytoplankton. Phytoplankton normally contain 2.3% ether extract (crude fats), 74% carbohydrates, and 24% protein (Hutchinson, 1957). Submerged aquatic macrophytes normally contain 3.6% ether extract, 51% nonfibrous carbohydrate, and 22% protein, as well as 35% cellulose (Boyd, 1968). Brady (1974) states that in soils carbohydrates and proteins are relatively easy to decompose whereas cellulose and fats are more difficult. At Station I, it would seem that the organic C percentage of IVS should be greater during the ice free period when the plankton population is largest. This is not true, probably because much of the planktonic detritus reaching the sediments is refractory and lower in organic nitrogen and phosphorus than fresh plankton. This is a result of bacterial breakdown of the easily decomposable fractions during sedimentation (Johannes, 1968).

At Station I, organic C made up a larger percentage of the IVS

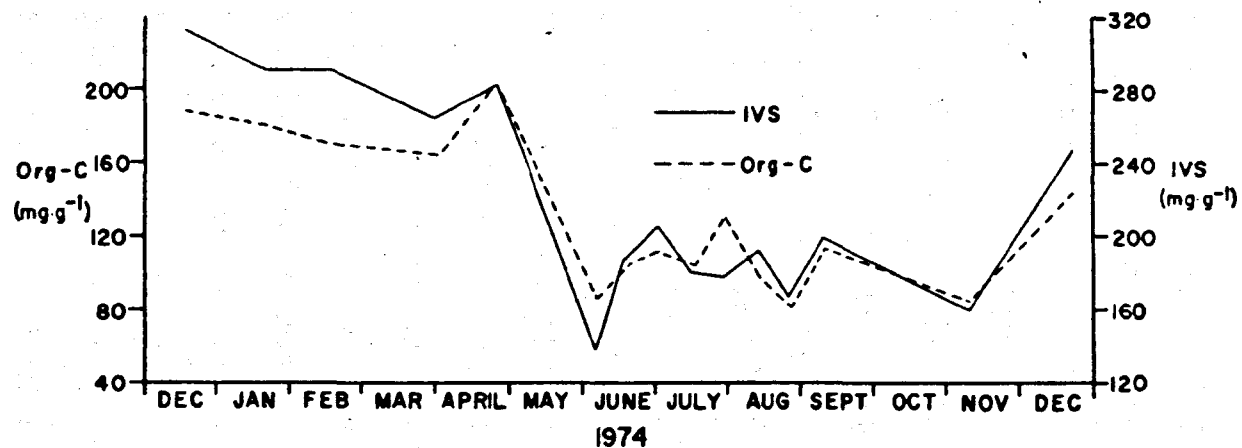


Figure 12a. Seasonal trends and the relationship between initial volatile solids (IVS) and organic carbon (Org-C) at Station I.

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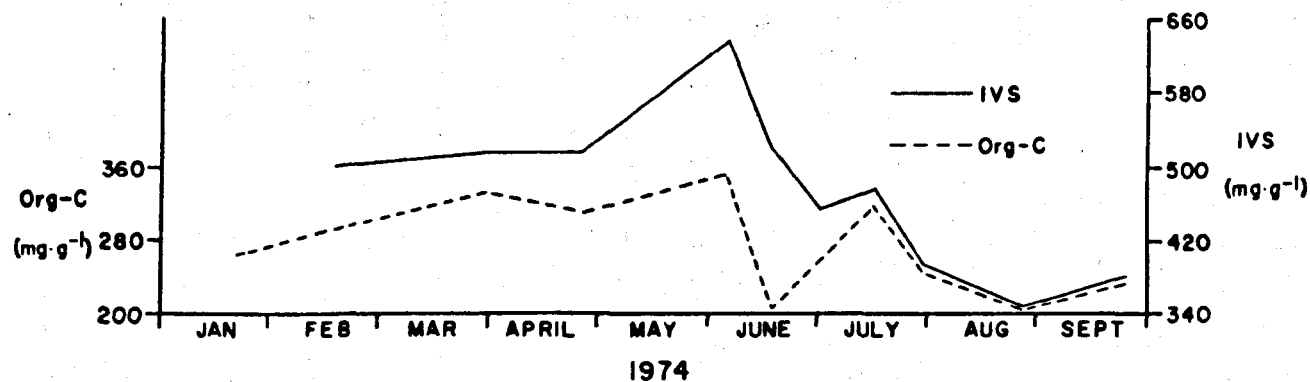


Figure 12b. Seasonal trends and the relationship between initial volatile solids (IVS) and organic carbon (Org-C) at Station IV.

during the summer than during the winter (Figure 12a). During the ice cover period the environmental conditions were not as conducive to microbial decomposition. Increased microbial activity could be expected during the summer months when the temperature was higher and oxygen present in the bottom waters. At Station IV the organic C content of IVS was less than at Station I until 29 July (Figure 12b). This probably reflects the higher percentage of resistant organics present at Station IV. By the end of July the rate of decomposition of macrophytes that had died the previous fall had apparently been stabilized. This trend continued until the end of September when sampling was terminated at this station.

Organic carbon was higher during the ice cover period and early summer than it was during the remainder of the sampling period (Figure 13). Some of this organic carbon probably originated from the die off of macrophytes the previous fall. Although some anaerobic decomposition may occur, Wetzel (1975) noted that when oxygen was low or absent the rate of carbon mineralization was slower than when oxygen was abundant. Also, when the sediment temperature is low, as during the winter, microbial activity is retarded. During the summer the organic C content decreased as it was mineralized. During the winter macrophytic production seemed to be low enough so that planktonic production would have been a more important contributor to sediment organic carbon. As shown in Figure 13, during the

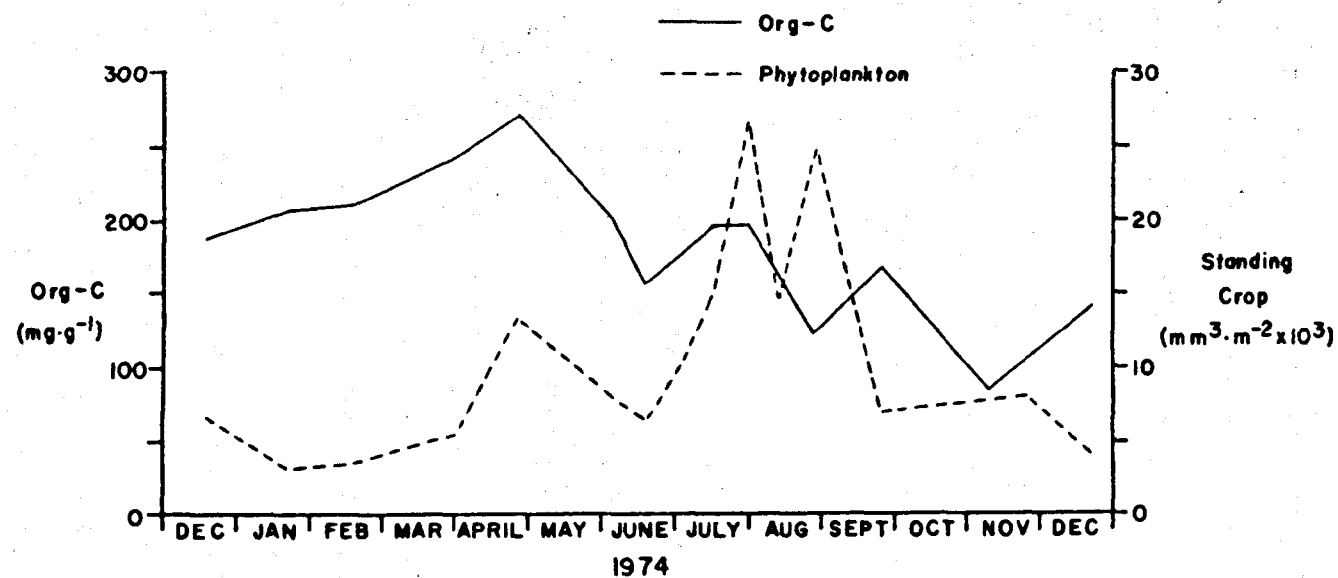


Figure 13. The relationship between organic carbon (Org-C) and the phytoplankton standing crop at Station I.

winter, the phytoplankton standing crop trend resembled that of organic C. The phytoplankton data was obtained from Knight, et al. (1976). However during the summer, the resemblance disappeared. This indicated that macrophytic production coupled with organic C mineralization had a greater influence on the sediment organic C at this time. Organic C did not appear to increase in the fall as might be expected with the macrophytic die-off. This was due to the fact that after 24 September only Station I was sampled. Organic C was determined in the water but its seasonal trend did not resemble that of sediment organic C.

Phosphorus

Total sediment phosphorus is composed of total organic phosphorus and total inorganic phosphorus. Organic P exists principally as organic esters of phosphoric acid (Williams, et al., 1971b). Inorganic P exists as orthophosphate ions which are dissolved in the interstitial water, adsorbed on the surfaces of phosphorus retaining compounds, absorbed within the matrices of phosphorus retaining compounds, and present in discrete phosphate minerals.

Although some of the adsorbed phosphorus is precipitated on the surfaces of soil particles with iron and manganese, the majority is present in a hydrous gel complex. Shukla, et al. (1971) and Williams, et al. (1971b) postulated that this gel complex largely consists of hydrated iron oxide along with organic matter, Al_2O_3 , and associated

Si(OH)_4 , and phosphorus. Shukla, et al. (1971) noted that in this complex, iron would form an isoelectric amorphous precipitate with organic matter and associated anions. Gorbunov, et al. (1961) demonstrated that an artificial iron oxide gel could absorb large amounts of inorganic P.

Little is known of the discrete phosphorus minerals that exist in lake sediments. Few minerals have actually been demonstrated in sediments. Stumm and Morgan (1970) list hydroxyapatite, fluorapatite, variscite, strengite, and wavellite as possible phosphorus minerals in sediments. Apatite, both hydroxyapatite and fluorapatite, is the most abundant phosphorus mineral. Apatite, a calcium phosphate, may form as a precipitate as a result of combining of calcite and phosphate, although the reaction is slow. Vivianite, an iron phosphate, has also been reported in lacustrine sediments (Syers, et al., 1973). It is thought that it is formed under strongly reducing conditions associated particularly with the decomposition of organic materials. Since strengite, an iron phosphate, and variscite, an aluminum phosphate, are unstable at pH values greater than 1.4 and 3.1, respectively, they are probably not present in the surface sediments of Georgetown Lake. Wavellite has also not been observed in lake sediments. The presence of only small amounts of phosphate minerals in the sediments is supported by the fact that most sediment P is associated with amorphous iron and therefore not in crystalline form (Harter, 1968; Shukla,

et al., 1971; and Williams, et al., 1971a and b).

Total phosphorus was generally higher at Station IV than at the other stations (Table 3). Station IV also had a large biomass of macrophytes and the greatest mean organic carbon concentration. The mean total P concentration at Station II was only slightly less than that at Station IV. However a larger percentage of the total P at Station II was inorganic P than at the other stations. Total P was lower at the deep water station, Station I, than at Stations II, III, or IV. This is contrary to the findings of Delfino, et al. (1969) and Frink (1969b) who found that total P was positively correlated with increasing water depth. Neel, et al. (1973) also found in Lake Sallie, a shallow eutrophic lake similar to Georgetown Lake, that total P was higher in the deeper waters. Although the general reverse trend was observed in Georgetown Lake, this may partially be a result of the greater macrophytic growth in the shallower waters. The major reason may be the removal of phosphorus associated with the deep water withdrawal. As will be discussed later, the sediments, especially at Station I, are losing phosphorus on an annual basis through the dam.

Throughout the year organic phosphorus accounted for 38% of the total phosphorus in the lake sediments and inorganic phosphorus accounted for 62%. Changes in total P for the sampling period were more closely correlated with organic P than inorganic P, $r = 0.88$ and $r = 0.78$, respectively. This demonstrates the influence of the heavy

macrophytic growth on the sediments. The high primary production in Georgetown Lake had an important influence on total P concentrations since it has been found in the literature that organic P is very poorly correlated with total P (Williams, et al., 1971b). If the sampling period is divided into ice cover periods and ice free periods different constituents become important. During the ice cover periods, total P was correlated much more closely with organic P ($r = 0.96$) than inorganic P ($r = 0.72$). However, during the ice free period, total P was more closely correlated with inorganic P than organic P, $r = 0.91$ and $r = 0.85$, respectively. This indicates that during the winter, organic P was more important than inorganic P in influencing the levels of total P. Apparently, organic P, resulting from the previous autumnal deposition of organic materials, was only slowly mineralized during the winter. During the summer, organic P was being mineralized more rapidly and inorganic P was being utilized by the macrophytes and the phytoplankton. Therefore, inorganic P was regulating the total P level in the sediments during the summer.

Seasonal trends of sediment phosphorus are illustrated in Figure 14. Total P increased during the ice cover period primarily because of organic P. Organic material accumulated in the fall and early winter as a result of the death of macrophytes and phytoplankton. During the summer the total P generally decreased as inorganic P was incorporated into macrophytic biomass as well as being suspended in

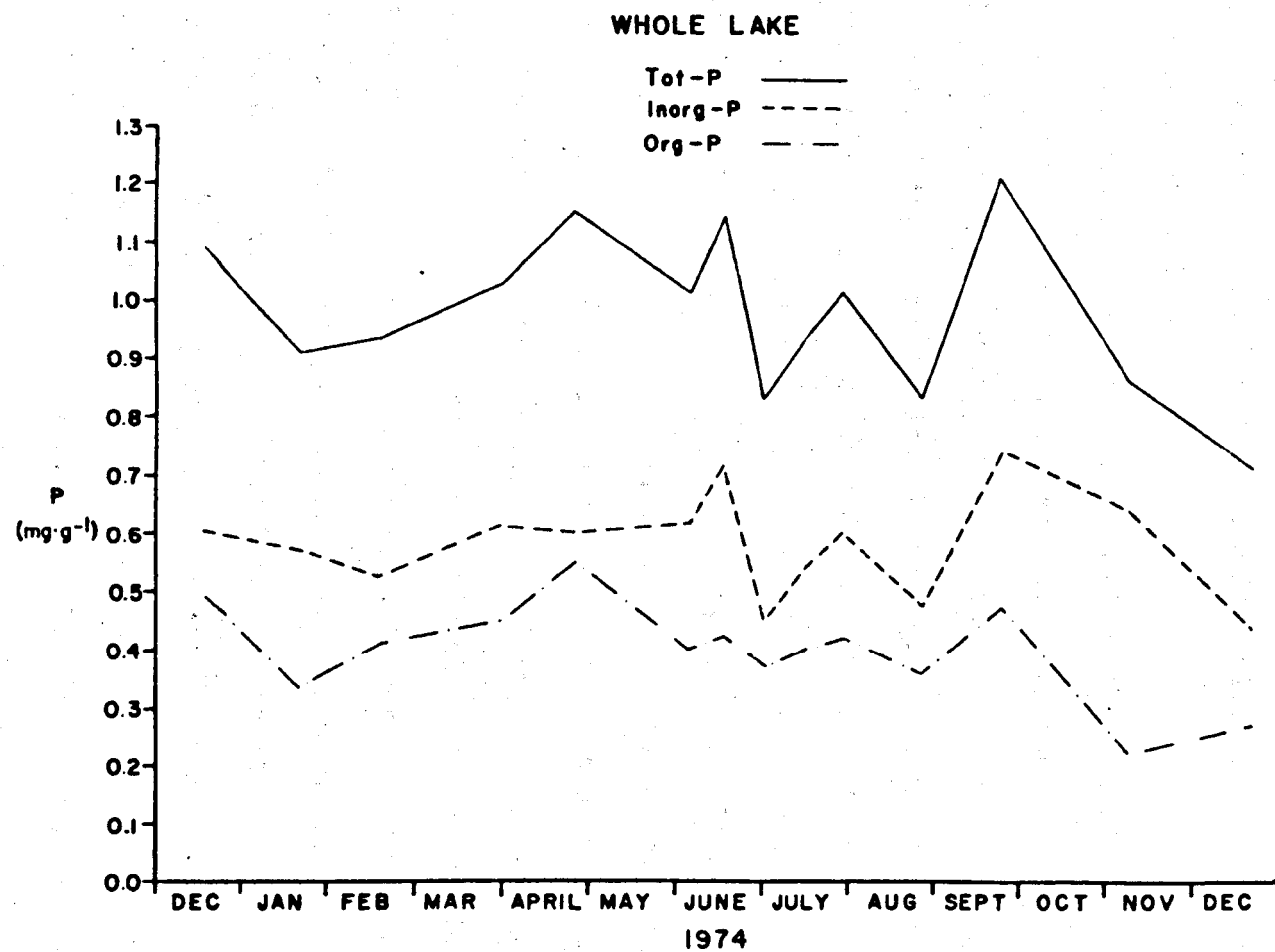


Figure 14. Seasonal trends of total phosphorus (Tot-P), inorganic phosphorus (Inorg-P), and organic phosphorus (Org-P) in the whole lake.

the water by turbulent mixing. At the end of September total P increased as less inorganic P was being utilized and the primary producers were dying.

Sediment organic P is a result of conversion of inorganic P to organic matter in the water as well as by the flora and fauna of the sediments. The organic P status of sediments is a function of the rate of input of organic P in the form of plant and animal residues and of the rate of organic P mineralization and immobilization processes. The only organic P compounds known to exist in sediments are inositol phosphates, phospholipids, nucleic acids, nucleotides, and sugar phosphates (Cosgrove, 1967). As with soils, inositol hexaphosphate is the major component of sediment organic P.

Organic phosphorus was highest at Station IV as was organic carbon. As with organic C the large macrophytic biomass was probably responsible for this. Organic P was positively correlated with organic C ($r = 0.86$) in the lake sediments. This is not surprising as Sommers, et al. (1972) found that organic P is associated with organic matter complexes. Figure 15 portrays the relationship between organic P and organic C. In the whole lake organic P was also positively correlated with organic N ($r = 0.90$) and IVS ($r = 0.86$) but no other parameters. At Station I, which was in the limnetic zone, organic P was also only correlated with organic C, organic N and IVS. However, at Station IV in addition to these parameters, organic P was also

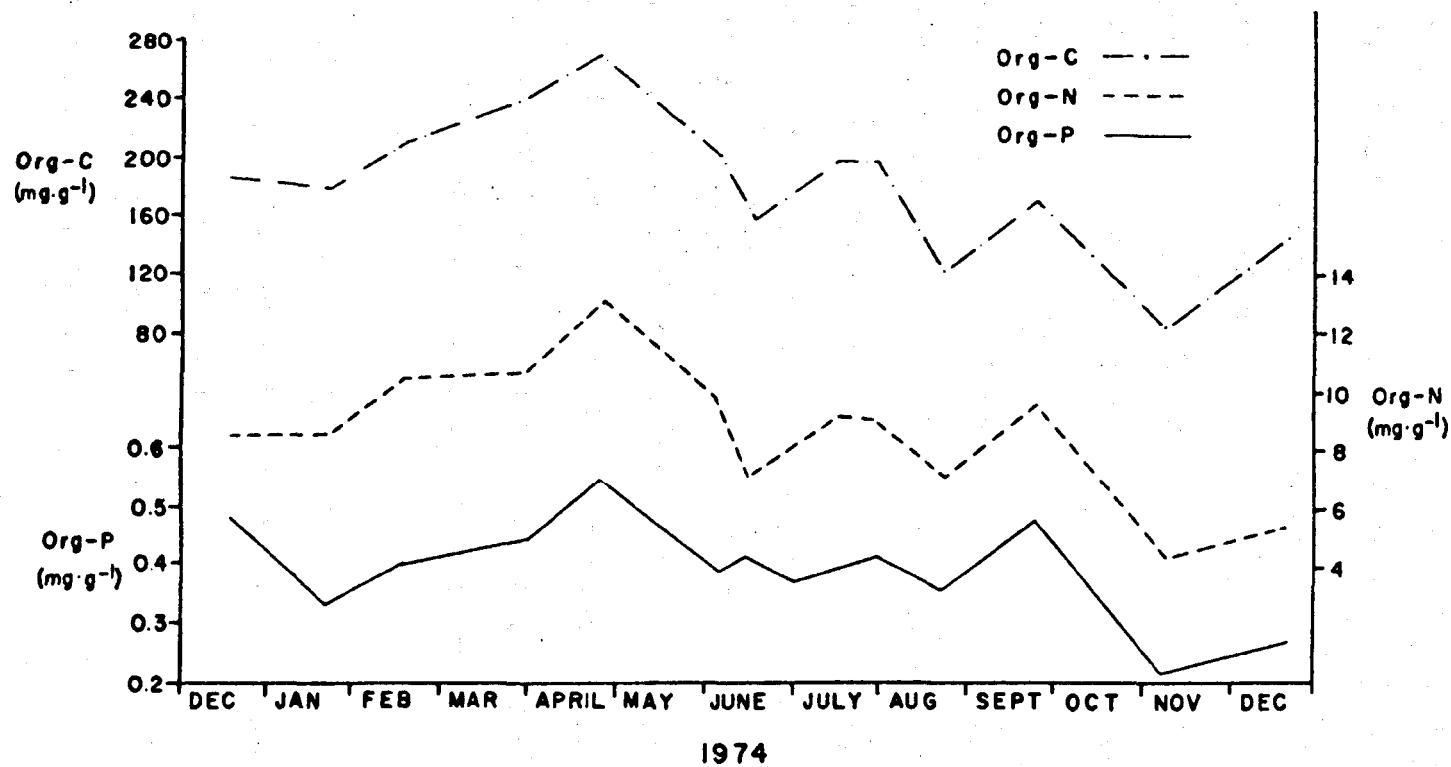


Figure 15. The relationship between organic carbon (Org-C), organic nitrogen (Org-N), and organic phosphorus (Org-P) in the whole lake.

positively correlated with iron oxides ($r = 0.76$). Since it has already been shown that iron oxides are correlated with organic C at this station, organic P may be associated with a complex of organic matter and amorphous iron. It has been hypothesized that aluminum may stabilize organic P and other organic components against decomposition in soil (Jackman, 1964). Since extractable aluminum was not correlated with organic P, it appears that extractable iron may serve the same purpose in these sediments.

Figure 14 shows the seasonal trend of organic phosphorus. During the ice cover period organic P increased to a maximum of 0.548 mg.g^{-1} on 25 April. Some of this organic P probably originated from the previous autumnal death of macrophytes. Mineralization during this period would probably have been slow due to both the low temperature and oxygen concentration in the bottom waters. During the summer, organic P generally tends to decrease as it mineralizes faster than the rate of inorganic P immobilization. Thompson and Elack (1947) showed that mineralization of organic P increased with increasing temperatures in soils.

Organic phosphorus mineralization occurs chiefly through the hydrolysis of the phosphate ester bond by the phytase activity of bacteria. The rate of hydrolysis is chiefly regulated by the factors controlling the interaction of organic P with the appropriate enzymes. Greaves and Webley (1969) showed that inositol phosphate in soil exists

as part of a complex containing carbohydrates and nitrogenous materials which inhibits phytase. Since it has been shown that organic P is closely correlated with organic matter and organic N in Georgetown Lake a similar complex may be retarding organic P mineralization. It has also been shown that inorganic P concentrations of greater than 0.5 M inhibit hydrolysis of inositol phosphate (Greaves, et al., 1967). Since the sediments of Georgetown Lake consistently have inorganic P concentrations that exceed this level, this phenomenon may also be occurring in these sediments.

Figure 16a portrays the seasonal trends of organic P at Station I. As with the sediments at the other stations, organic P was higher during the ice cover period. During the summer, organic P was lower at Station I but remained stable throughout this period. Although phytoplankton would be settling to the bottom, organic P did not increase. Apparently mineralization occurred at about the same rate as deposition. Since organic P decreased during the summer at the other stations it might be expected that the same would occur at this station. Mineralization may be retarded more at this station than other stations since it contained more clay minerals. Greaves and Webley (1969) have shown that clay minerals adsorb the enzymes necessary for phytase activity and reduce their activity.

Inorganic phosphorus was highest at Station II with a mean concentration of $0.731 \text{ mg} \cdot \text{g}^{-1}$ (Table 3). This may be due to higher phos-

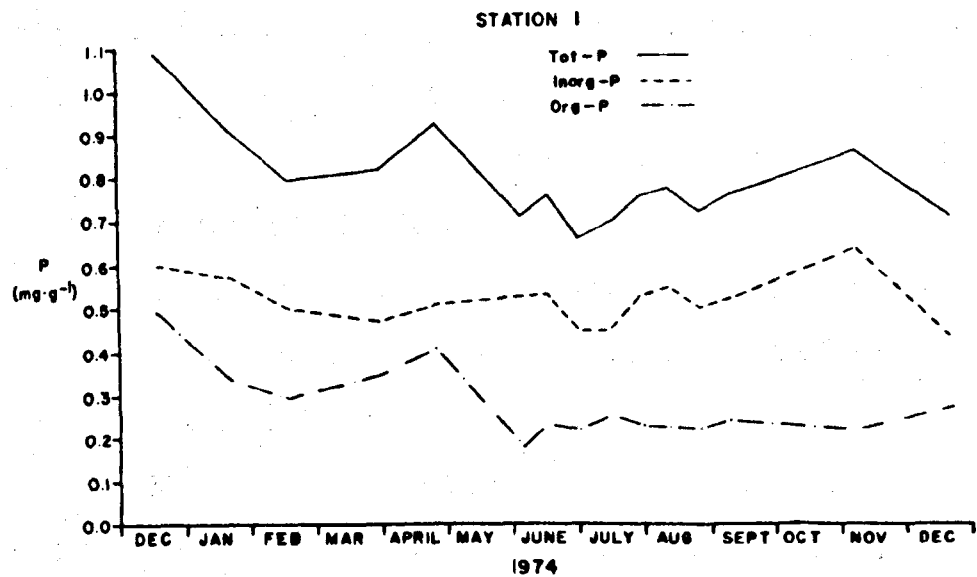


Figure 16a. Seasonal trends of total phosphorus (Tot-P), inorganic phosphorus (Inorg-P), and organic phosphorus (Org-P) at Station I.

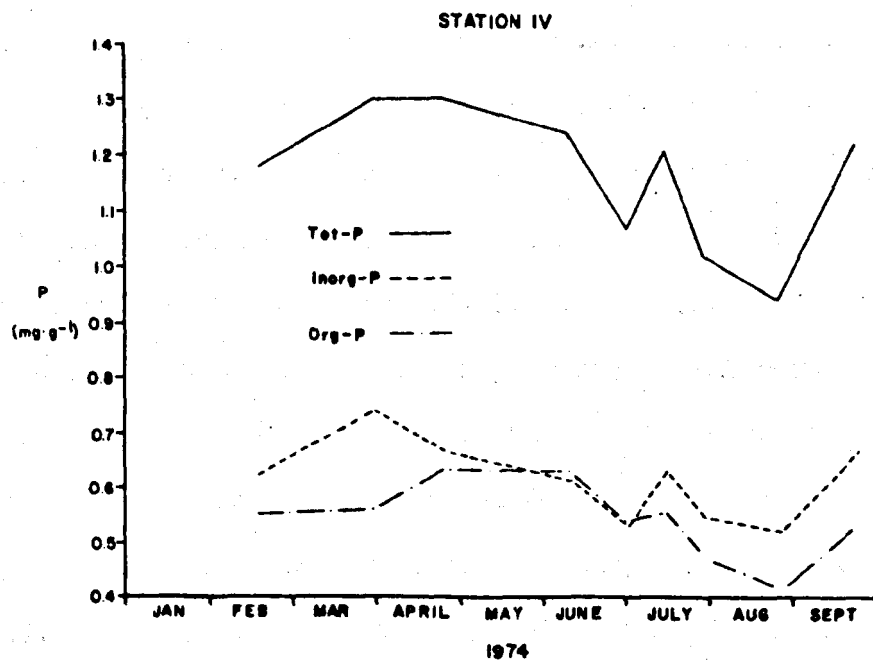


Figure 16b. Seasonal trends of total phosphorus (Tot-P), inorganic phosphorus (Inorg-P), and organic phosphorus (Org-P) at Station IV.

phorus in this area when the lake was formed, as Station IV was consistently higher in inorganic nitrogen and most other nutrient parameters. With the exception of Station V, inorganic P was lowest at Station I. This station probably has less inorganic P because of the deep-water withdrawal through the dam.

Inorganic phosphorus was not well correlated with any other sediment parameters at all stations. At Station IV, inorganic P was somewhat correlated with organic P, organic N, organic C and IVS. Williams, et al. (1971b) have shown that total inorganic P is well correlated with iron extracted by the sodium dithionite method. Since this relationship was not observed in these sediments perhaps organic matter is more important in retaining inorganic P than iron compounds. It has been suggested that calcium, manganese, and aluminum compounds may participate in phosphorus fixation in sediments. Of the forms determined, all were negatively correlated with inorganic P at all stations. Iron was positively correlated with inorganic P at Stations I and IV, $r = 0.11$ and $r = 0.45$, respectively. Thus it appears that although organic matter may be the more important determinant of inorganic P concentration, Fe_2O_3 may also participate, but exchangeable Ca, exchangeable Mn, and Al_2O_3 do not.

Inorganic phosphorus increased from January through June (Figure 14), probably as a result of the slow mineralization of organic P. Mineralization appeared to increase in June as oxygen became more

abundant and the sediment temperature increased. During the summer inorganic P fluctuated but there was a general decrease until the end of September. This decrease was probably due to inorganic P being taken up by the macrophytes as well as being released into the water by turbulent suspension of the sediment. Inorganic P was higher in the fall due to the rapid mineralization of organic P from decomposing macrophytes and algae as noted by Nickols and Keeney (1973). At Station IV a similar seasonal trend was observed (Figure 16b).

Inorganic phosphorus at Station I had a somewhat different seasonal pattern than at the other stations (Figure 16a). During ice cover inorganic P decreased until April, although mineralization was probably proceeding at a slow rate. As shown in Figure 5a, inorganic phosphorus increased in the bottom waters at this time. As discussed earlier, although some of this phosphate may have originated as phosphorus precipitated with hydrous ferric oxides, the majority came from adsorbed inorganic P. Li, et al. (1972) found that the total exchangeable phosphorus in sediments was the same under aerobic and anaerobic conditions. This supports the statement that this inorganic phosphorus was not present as an iron mineral complex because there would be a dissolution of the crystalline phase under anaerobic conditions and exchangeable P would increase. Li, et al. (1972) hypothesized that there must be a gel complex instead and that during anaerobic conditions there is an alteration of the oxidation state of

iron which changes the position of the equilibrium between adsorbed P and solution P. It is the solution P, i.e. phosphate dissolved in the interstitial water, which is released into the overlying waters.

Porcella, et al. (1970) and Harrison, et al. (1972) have shown that anaerobic and aerobic bacteria may be partially responsible for the solubilization of inorganic phosphates in sediments. Aerobic bacteria are capable of removing phosphates bound to sediment particles by the production of organic acids which sequester metallic cations. This is dependent upon the existence of a sufficient carbon source. This probably would not be a problem in Georgetown Lake as organic C is relatively high, especially in the littoral zone. During aerobic conditions these bacteria store phosphates. Under anaerobic conditions the bacteria die and the stored phosphates are released. Some phosphates may be adsorbed on the sediment particles but much is dissolved in the interstitial water and consequently released into the overlying waters. Bacteria known to mobilize phosphorus are Pseudomonas, Bacterium, and Chromobacterium (Wetzel, 1975).

Inorganic phosphorus at Station I generally increased during the summer (Figure 16a). This was probably caused by the mineralization of organic P. Even though inorganic P increased, organic P did not decrease, suggesting that the organic P in the decaying algae were being mineralized as fast as they were sedimented. Inorganic P had increased at the beginning of November although organic P was stable.

As noted by Knight, et al. (1976), phytoplankton declined drastically at the end of September. Nichols and Keeney (1973) noted that organic phosphorus may be mineralized rapidly in fresh decaying plant matter.

Inorganic phosphorus may be fractionated using different extractants to remove different forms of inorganic P. The idea was first developed for soils by Chang and Jackson (1957). Since then the method has been refined and modified for sediments. Table 4 gives the ranges and means of the various inorganic P fractions.

Phosphate extracted by NH_4Cl includes phosphate dissolved in the interstitial water as well as phosphate ions weakly adsorbed by sediment components. This phosphorus may be considered mobile as it is the principal form that is liberated into the overlying waters. Phosphate extracted with NH_4Cl was higher at Station IV. This may have been caused by sediment bacteria solubilizing inorganic phosphates faster at Station IV. The increased bacterial activity is indirectly indicated by the higher rate of organic P mineralization at Station IV. At both stations, NH_4Cl -P made up a very small part of the total inorganic P.

Phosphate extracted by NH_4F is thought to be phosphorus adsorbed by aluminum components. Harter (1968) observed that this extractant solubilized aluminum and was well correlated with the extracted phosphorus. However, Shukla, et al. (1971) and Williams, et al. (1971a) found that phosphorus extracted with NH_4F was not correlated with alu-

TABLE 4. RANGES AND MEANS OF SEDIMENT INORGANIC PHOSPHORUS FRACTIONS.

Parameter	Station I	Station IV
Inorganic - P (mg.g ⁻¹)	0.434 - 0.634 0.522	0.522 - 0.919 0.615
NH ₄ Cl - P (mg.g ⁻¹)	0.001 - 0.007 0.002	0.005 - 0.027 0.013
NH ₄ F - P (mg.g ⁻¹)	0.006 - 0.056 0.028	0.015 - 0.087 0.038
NaOH - P (mg.g ⁻¹)	0.040 - 0.153 0.103	0.014 - 0.090 0.037
Exchangeable - P (mg.g ⁻¹)	0.056 - 0.181 0.133	0.049 - 0.189 0.088
CDB - P (mg.g ⁻¹)	0.119 - 0.327 0.225	0.207 - 0.333 0.240
HCl - P (mg.g ⁻¹)	0.031 - 0.096 0.064	0.003 - 0.136 0.052
Residual - P (mg.g ⁻¹)	0.059 - 0.143 0.100	0.169 - 0.281 0.235

minum but was well correlated with iron. Williams, et al. (1971a) concluded that NH_4F could not be used to distinguish between Al and Fe bound forms of inorganic P in partially weathered soils such as sediments. Inorganic P extracted by this method appears to extract phosphorus adsorbed by short range order iron or aluminum in a gel complex. This phosphorus is in equilibrium with interstitial P and can easily be exchanged. Harter (1968) found that this fraction was the most important in exchange reactions with overlying waters. The $\text{NH}_4\text{F-P}$ was slightly higher at Station IV. This may be partially due to the fact that some inorganic sediment P is lost through the dam at Station I. At both of these stations $\text{NH}_4\text{F-P}$ made up a small part of the total inorganic P, 5.4% and 6.2%, respectively.

The phosphorus extracted by NaOH appears to originate from an iron bound form. This phosphorus is more tightly adsorbed than the NH_4F extracted fraction but it still is probably associated with a short-range order Fe-rich gel complex. This P would probably be adsorbed on the surface of the retaining complex. It appears that this form of P is not as mobile as NH_4F or NH_4Cl extracted P but it seems to be potentially mobile. Phosphorus extracted by NaOH was much higher at Station I. At Station IV, this form of P may be removed by macrophytes during the growing season. At Station I this form made up almost 20% of the total inorganic P but only 6% at Station IV.

Williams, et al. (1967 and 1971a) found that phosphorus solubil-

ized by NH_4F may be reabsorbed and reextracted by NaOH . To eliminate this bias and because the P extracted by NH_4Cl , NH_4F , and NaOH is capable of exchange with the overlying water, these three fractions have been combined into exchangeable P. This exchangeable P may be associated with amorphous Fe and Al hydrated oxides and amorphous aluminosilicates, all of which are characterized by numerous hydroxyl groups in surface positions which readily react with ortho-phosphate by exchange adsorption of hydroxyl for ortho-phosphate (Williams, et al., 1971b). This association was indicated, particularly at Station IV, where exchangeable P was correlated with Fe_2O_3 ($r = 0.58$) and organic C ($r = 0.50$). Although it appears that most of the phosphorus that readily exchanges with the overlying water is associated with this fraction, not all of this fraction may exchange. Bannerman, et al. (1975) found that the NaOH fraction was 30-60% of the total inorganic P yet using ^{32}P they found that only 13-18% of the total inorganic P was immediately exchangeable.

Exchangeable phosphate composed 25.5% and 14.3% of the total inorganic phosphorus at Station I and IV, respectively (Table 4). Although all of this P may not be immediately available for exchange, this is probably a valid classification since this fraction has the potential for exchange. Since most of the collected samples from Station IV were collected during the macrophytic growing season, the lower values at this station may reflect the fact that the plants are

extracting this form of the inorganic P.

Phosphorus extracted by citrate-dithionite-bicarbonate (CDB) is thought to be derived from inorganic P present within matrices of crystalline oxides and hydrous oxides of iron (Bauwin and Tyner, 1957). This form of P is referred to as nonoccluded P and is less readily extracted. Sediments generally contain small amounts of CDB-P because of the inhibitory effect of organic components, inorganic P, and H_4SiO_4 on the conversion of short range order oxides and hydrous oxides of Fe to crystalline forms (Shukla, et al., 1971 and Williams, et al., 1971b). In terrestrial soils, CDB-P is a more important part of the total inorganic P (Li, et al., 1972). The high amounts of CDB-P in Georgetown Lake sediments may reflect the fact that this is a relatively recent lake, being formed around 1900.

Phosphorus extracted by HCl is derived from inorganic P associated with nonincluded apatite (Williams, et al., 1967). The HCl-P is generally present in only minor amounts as it is probably of primary origin. This form is probably of detrital origin and at the prevailing conditions of pH and Ca and P in interstitial water of noncalcareous sediments the trend is probably towards dissolution rather than accumulation (Williams, et al., 1971a). In Georgetown Lake this form of phosphorus made up only about 10% of the total inorganic P.

Residual phosphorus is that included within resistant minerals such as feldspars and ilmenite (Williams and Mayer, 1972).

The seasonal trends of the inorganic phosphorus fractions at Station I are depicted in Figure 17. With the exception of CDB-P the various fractions did not change greatly during the sampling period. This agrees with the relative stability of inorganic P at this station (Figure 16a). Residual P and HCl-P should be relatively stable as they are components of sediment minerals and, thus, are resistant to change. Exchangeable-P would be expected to decrease during the ice cover period when phosphate is liberated into the overlying waters. Since it increased from February to March this may indicate that the source of liberated P is the mineralization of organic P instead of the solubilization of inorganic P. The CDB-P appeared to increase during the summer months from a low of $0.110 \text{ mg}\cdot\text{g}^{-1}$ on 30 March to a high of $0.327 \text{ mg}\cdot\text{g}^{-1}$ on 10 September. This seems surprising since inorganic P increased only slightly. Iron oxides, which were extracted by CDB, were well correlated with CDB-P during this period ($r = 0.92$) and increased during the summer (Figure 7).

Figure 18 portrays the seasonal trends of the inorganic P fractions at Station IV. Exchangeable P and HCl-P both decreased during the spring and summer although for different reasons. During the summer the macrophytes would selectively extract this fraction for their needs. Oborn (1964) showed that aquatic macrophytes may accumulate phosphate extracellularly. When the plants die in the fall some of the organic P is typically regenerated rapidly (Nichols and

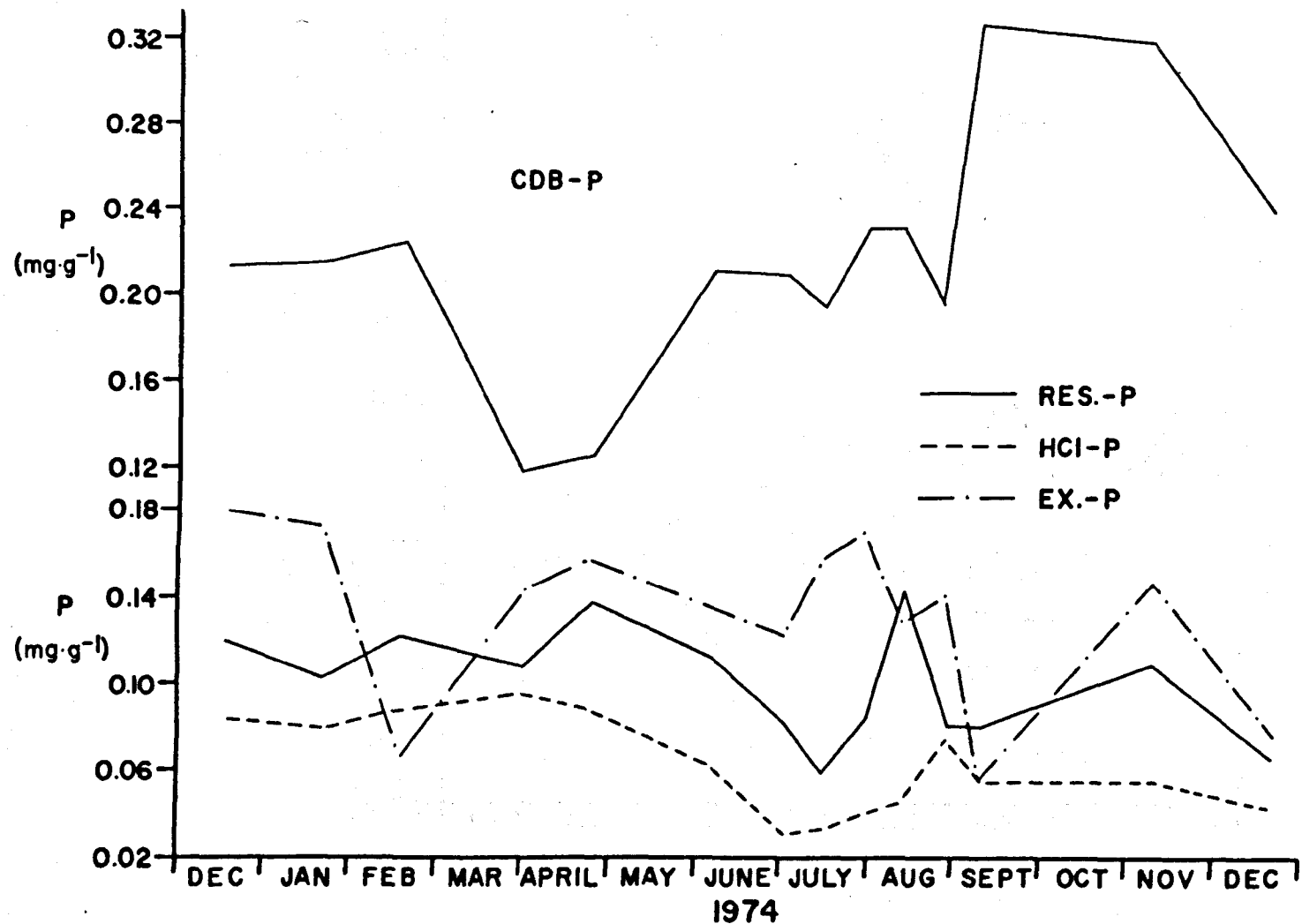


Figure 17. Seasonal trends and the relationship between citrate-dithionite-bicarbonate extracted phosphorus (CDB-P), residual phosphorus (Res-P), hydrochloric acid extracted phosphorus (HCl-P), and exchangeable phosphorus (Ex-P) at Station I.

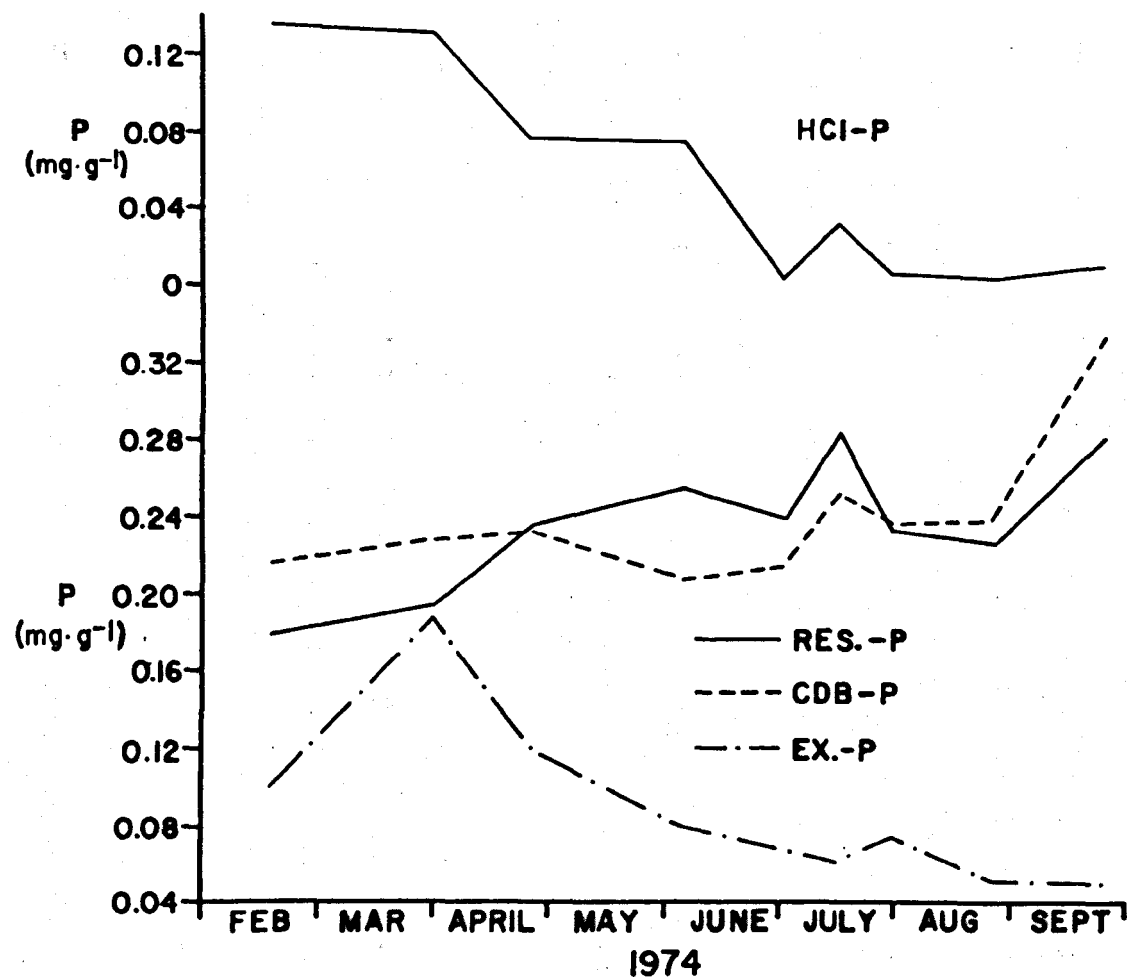


Figure 18. Seasonal trends and the relationship between citrate-dithionite-bicarbonate extracted phosphorus (CDB-P), residual phosphorus (Res-P), hydrochloric acid extracted phosphorus (HCl-P), and exchangeable phosphorus (Ex-P) at Station IV.

Keeney, 1973). During mineralization much of this P may be combined with the precipitated Ca. The HCl-P would include this phosphorus; hence, during the winter this fraction would be higher. As mentioned earlier there is probably a trend of dissolution of Ca phosphates in sediments. Since the dissolving of apatite is generally slow (Williams and Mayer, 1972), phosphorus resulting from the combination of phosphate with precipitated calcium must not be apatite but a more easily dissolved form. This dissolution results in a decrease of the HCl-P fraction during spring and summer. The increases in residual-P and CDB-P are unexpected and cannot be explained at this time.

Nitrogen

Total sediment nitrogen is composed of total inorganic nitrogen and total organic nitrogen. Inorganic nitrogen generally exists as ammonium salts which are associated with sediment particles. Part of these ammonium salts are adsorbed on humus and mineral clay particles while some may be held more tightly, such as within the crystal lattice structure of clay such as vermiculite, illite, and montmorillonite. Some nitrate and nitrite may be present but usually in small amounts. Organic nitrogen in the sediments is principally present as bound amino acids although smaller portions of combined amino sugars, and purines and pyrimidines are also present. Trace amounts of other organic nitrogen compounds (including choline, ethanolamine, creati-

nine, and allantoin) have been found in terrestrial soils (Bremner, 1967). Kemp and Mudrochova (1972) state that 20-50% of sediment organic N probably exists as complex heterocyclic nitrogen compounds.

Total nitrogen was consistently higher at Station IV than at any of the other stations (Table 3). This is also the station that was highest in organic carbon and total phosphorus. As with these two parameters the high annual macrophytic production was probably the major reason total nitrogen was higher at this station. Frink (1969b) found that total nitrogen in Bantam Lake was positively correlated with increasing water depth. This was not the case in Georgetown Lake as the deepest station, Station I, had the second lowest mean concentration. Since total nitrogen is usually well correlated with organic carbon, the higher organic matter at Station IV was more influential in determining total nitrogen concentrations than size sorting.

Throughout the sample period organic nitrogen hydrolyzed by 6N HCl comprised 62% of the total nitrogen. However, Kemp and Mudrochova (1972) suggested that the majority of the nonhydrolyzable N was also organic N associated with the humin portion of the sediments. If this fraction is included, organic N makes up 83% and inorganic N 17% of the total N. Inorganic N made up a larger percentage of the total N content than most reported studies in the literature. Keeney, et al. (1970) and Kemp and Mudrochova (1972) reported that inorganic N comprised 2-10% of the total N. The lakes these authors discussed

generally were deeper than Georgetown Lake. During the summer the bottom water temperatures are warm and oxygenated in Georgetown Lake, thus, providing a better microbial environment than in the deeper lakes.

Changes in total nitrogen were well correlated with both organic nitrogen ($r = 0.99$) and inorganic nitrogen ($r = 0.90$). The better correlation with organic N is partially attributable to the fact that it comprised a large part of the total nitrogen. The close correlation of inorganic N and organic N ($r = 0.87$) indicates that they are closely related and that inorganic N may be associated with the organic matter, possibly adsorbed on the humic colloids.

The seasonal trends of sediment nitrogen are illustrated in Figure 19. Total N generally increased during the ice cover period primarily as a result of increases in organic N. Organic N accumulated in the fall and early winter as a result of the death of macrophytes and phytoplankton. During the summer, total N decreased as organic N was mineralized to inorganic N which was taken up by the macrophytes. The lower total N concentrations in November and December are an artifact because only Station I was sampled and it consistently had lower total N concentrations.

Total nitrogen was much greater than total phosphorus throughout the lake (Table 3). The weighted mean of total N was $12.25 \text{ mg} \cdot \text{g}^{-1}$ and the weighted mean of total P was $0.918 \text{ mg} \cdot \text{g}^{-1}$. The total N to total P

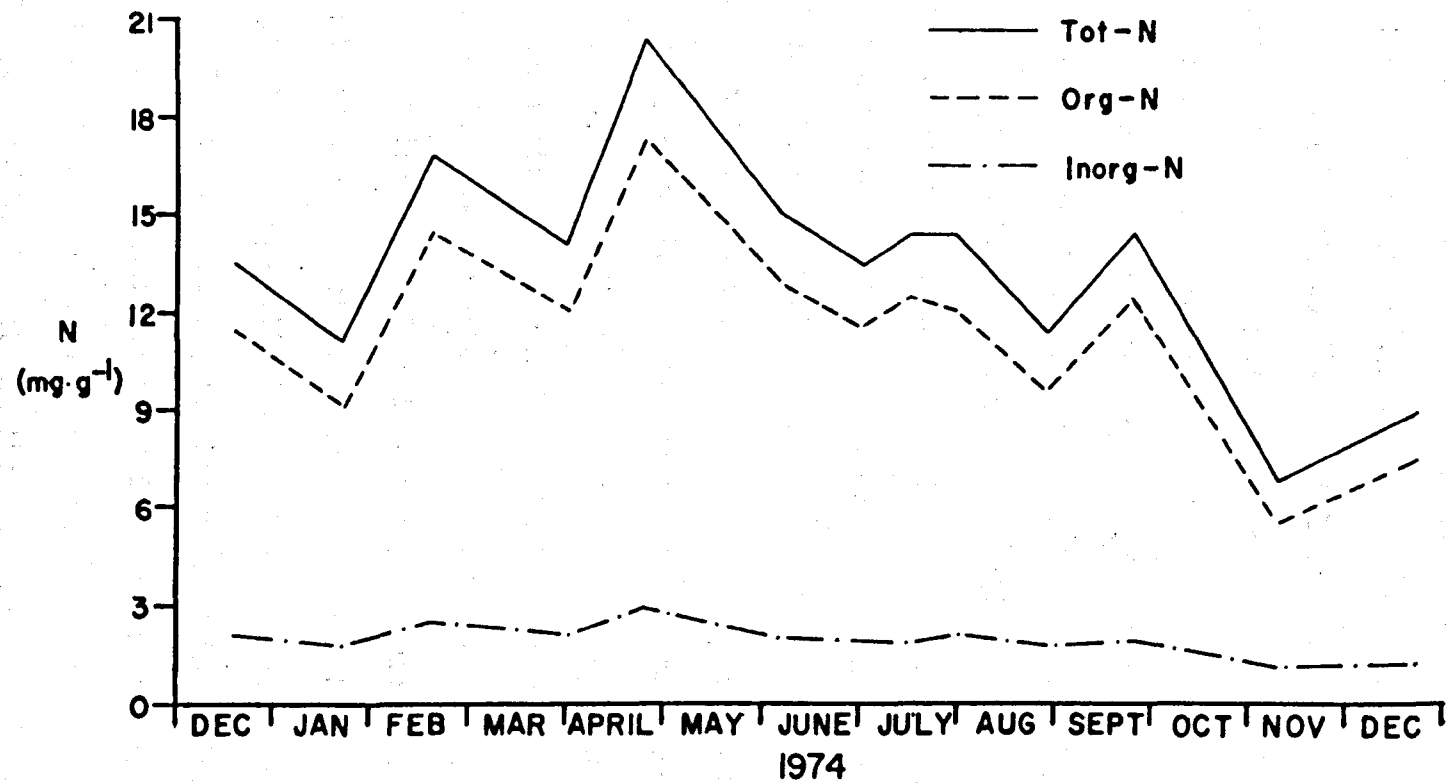


Figure 19. Seasonal trends of total nitrogen (Tot-N), organic nitrogen (Org-N), and inorganic nitrogen (Inorg-N) in the whole lake.

ratio for the whole lake averaged 31:1. This ratio is much higher than N:P ratios usually associated with phytoplankton or macrophytes which is 21:1 (Wetzel, 1975). As will be discussed in the next section, nitrogen and phosphorus are being lost from the lake sediments. It appears that phosphorus is being lost more rapidly than nitrogen. This may be due to utilization by the macrophytes. This is also indicated by the fact that the inorganic N to inorganic P ratio was higher at Stations III and IV than at Station I (Table 5).

The average C:N ratio for the lake was 15:1. This ratio is larger than for many lake sediments reported in the literature (Kemp, 1971; Isirimah, 1972; Neel, et al., 1973; and Wildung and Schmidt, 1973). Even Lake Sallie, which is a shallow eutrophic lake with abundant macrophytes similar to Georgetown Lake, had a lower ratio, 12:1 (Neel, et al., 1973). Although nitrogen may be regenerated faster than carbon another factor seems to be important. Because of the deep-water withdrawal organic C was accumulating in the sediments but total N was being lost. This is especially evident by the fact that Station I had the highest C:N ratio. Isirimah (1972) noted that a C:N ratio of 20:1 was critical in estimating net mineralization or net immobilization of nitrogen. Ratios less than 20:1, as observed in Georgetown Lake, indicate there is an abundance of N residues; therefore, net mineralization was probably occurring.

The average C:N:P ratio in the sediments was 469:31:1 (Table 5).

TABLE 5. MEAN ATOMIC RATIOS FOR THE SEDIMENTS OF GEORGETOWN LAKE.

	N:P ¹	N _I :P _I ²	C:N ³	C:N:P ⁴
Station I	26.1	6.8	16.2	424:26:1
Station II	26.8	6.5	14.4	385:27:1
Station III	29.5	7.5	14.4	425:30:1
Station IV	40.7	10.8	15.2	620:41:1
Station V	25.2	6.4	14.2	357:25:1
Weighted Mean of Whole Lake	30.5	7.5	14.9	469:31:1

1. Total N: Total P

2. Inorganic N: Inorganic P

3. Organic C: Total N

4. Organic C: Total N: Total P

This ratio is much higher than those reported in the literature. Neel, et al. (1973) reported C:N:P ratios of 286:24:1 and Wildung and Schmidt (1973) reported ratios of 236:30:1 in the sediments. The C:N:P ratio for algal protoplasm is usually quoted as 105:15:1 (Strickland, 1960). Garrett (unpublished data), using some preliminary data observed a ratio of 442:29:1, which is similar to the sediment ratio. This seems plausible as most of the primary producers are macrophytes. The C:N:P ratio at Station I is also unusually high (Table 5). This again is evidence that because of the deep-water withdrawal organic C is being accumulated while nitrogen and phosphorus are being lost from the lacustrine system.

The seasonal trend of nitrogen for Stations I and IV is portrayed in Figures 20a and 20b. At both stations inorganic N was relatively constant throughout the sampling period. On the other hand organic N fluctuated much more. Much of the inorganic N is the result of mineralization, i.e. ammonification of organic N compounds. Ammonification takes place principally by the deamination of amino acids resulting from the decomposition of proteins and polypeptides. Inorganic N concentrations are also influenced by assimilation or immobilization by microorganisms.

During the period 17 December to 30 March 1974, organic N decreased at Station I (Figure 20a). Inorganic N did not increase but instead decreased slightly. As shown in Figure 5b, ammonia was being

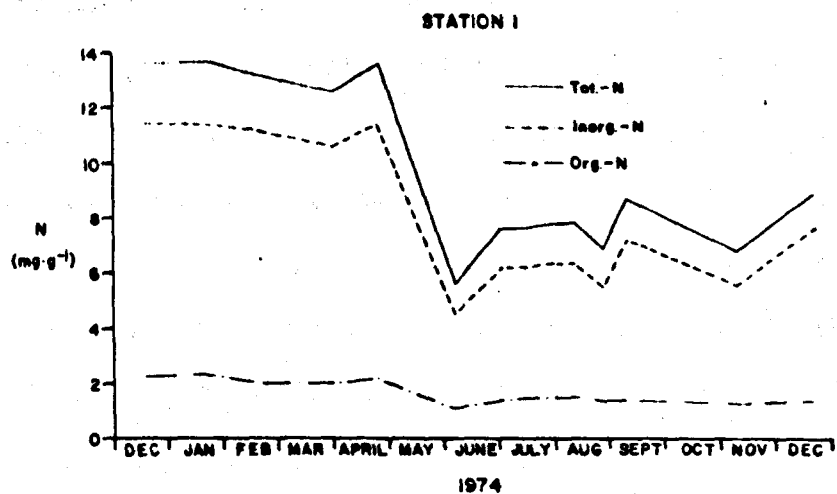


Figure 20a. Seasonal trends of total nitrogen (Tot-N), inorganic nitrogen (Inorg-N), and organic nitrogen (Org-N) at Station I.

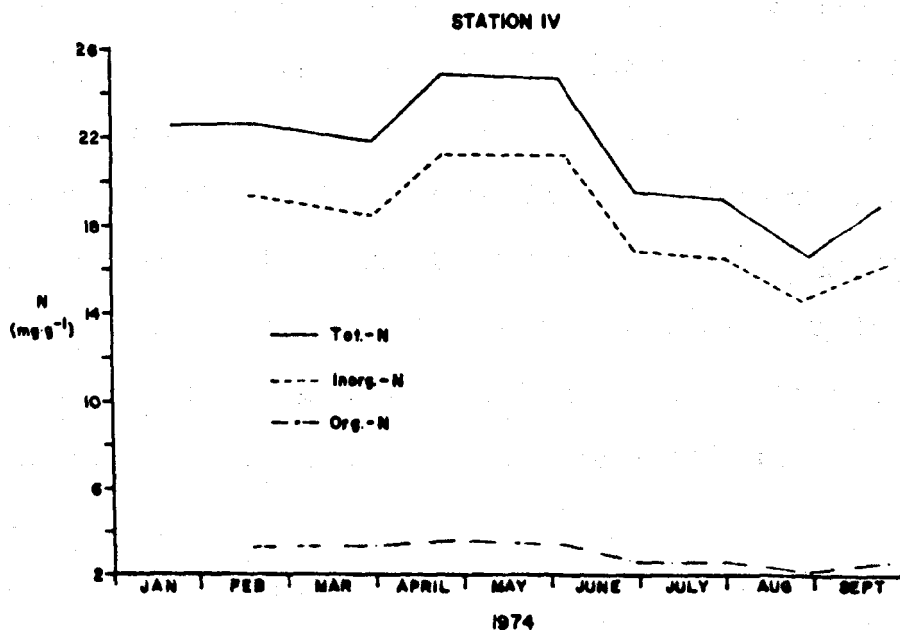


Figure 20b. Seasonal trends of total nitrogen (Tot-N), inorganic nitrogen (Inorg-N), and organic nitrogen (Org-N) at Station IV.

released into the overlying water at this time. It seems that at this time all of the organic N was being mineralized and some of the existing inorganic N was being released. Keeney (1973) noted that net mineralization may occur under anaerobic conditions and low temperatures due to the lower efficiency of conversion of organic C to all inorganic C by heterotrophic anaerobes. The sudden decrease in organic N on 5 June was probably caused by a slight movement in the sampling site. This was also observed for organic carbon and phosphorus. This shows the heterogeneity of the sediments as the distance moved was small.

During the summer the phytoplankton population was higher at Station I than during the winter (Figure 21). The phytoplankton data was obtained from Knight, et al. (1976). The general increase of organic N at this station during the summer was probably a result of phytoplankton detritus. The increase in organic N in the first part of September was probably a result of the deposition of Anabaena flos-aquae, a known nitrogen fixer. During June and July inorganic N also increased but during August and September it decreased. Isirimah (1972) noted increased immobilization at about this time in Lake Wingra.

At Station IV, organic N and inorganic N were higher during late winter than during the summer (Figure 20b). This nitrogen was probably a result of the deposition of macrophytes during the previous autumn.

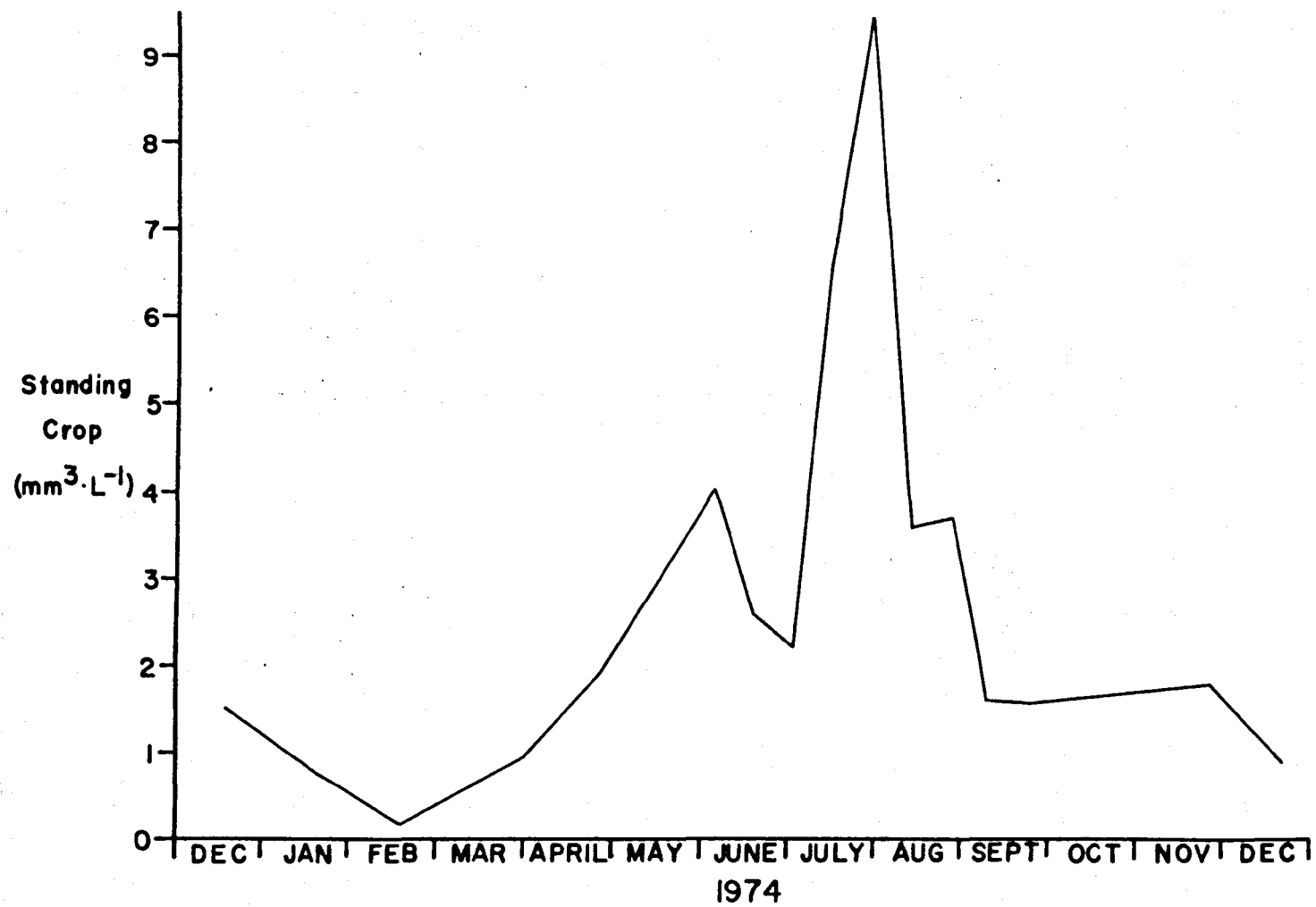


Figure 21. Seasonal trends of the phytoplankton standing crop at Station I.

During the summer both organic N and inorganic N declined until the end of August as a result of the uptake of inorganic N by the macrophytes. Since organic N as well as inorganic N was decreasing it appears that more inorganic N was being assimilated by the macrophytes than was being formed by mineralization. From Figure 20b it seems that in the sediments net mineralization was occurring as opposed to immobilization by microbial and benthic processes. This was supported by the fact that C:N ratio was less than 20:1, therefore net mineralization should be occurring.

Inorganic N was fractionated into exchangeable ammonium-N, nitrate-N, and nonexchangeable ammonium-N. Exchangeable ammonium-N is ammonia adsorbed on surfaces of sediment particles such as clay and humic colloids. This fraction also includes ammonia which is dissolved in the interstitial water. Although the nitrate determined is technically exchangeable nitrate because it is extracted by the same extracting procedure as exchangeable $\text{NH}_4\text{-N}$, it is the only form of nitrate that has been detected in soils (Bremner, 1965). Several samples were analyzed for nitrite-N but none was found. Nonexchangeable ammonium-N includes ammonium ions that are fixed within the lattices of expansible clay minerals. Some ammonium in soils is fixed by organic matter such that it is not exchangeable (Brady, 1974). This form would also be included in nonexchangeable $\text{NH}_4\text{-N}$. Not all clay-fixed ammonium is extracted by hot acid in terrestrial soils (Bremner,

1967), but Kemp and Mudrochova (1972) found that in sediments the fixed ammonium is included in the hot acid extraction. Since most of the sediment in Georgetown Lake is autochthonous the clay fraction is probably low. Therefore, it seems probable that the nonexchangeable ammonium-N includes all of the fixed ammonium-N. Nonexchangeable ammonium probably also includes a small portion of ammonium formed by the hydrolysis of amino acids of proteins and peptides and deamination of hydroxyamino acids and amino sugars (Keeney, et al., 1970).

Nonexchangeable $\text{NH}_4\text{-N}$ was the predominate form of inorganic N in the sediments (Table 6). It made up a larger percentage of the total inorganic N at Station IV than Station I (89% and 78%, respectively). Since Station IV had a higher content of organic matter the ammonium-N may be more readily fixed.

During the period December to February at Station I, exchangeable ammonium-N decreased in response to the release of ammonium-N into the overlying waters (Figure 22a). The released ammonium-N directly comes from the interstitial water which is included in exchangeable $\text{NH}_4\text{-N}$. This $\text{NH}_4\text{-N}$ is in equilibrium with exchangeable $\text{NH}_4\text{-N}$. Since net mineralization was occurring during this period exchangeable $\text{NH}_4\text{-N}$ increased in March. The bottom waters at Station IV were not as reduced as at Station I so exchangeable $\text{NH}_4\text{-N}$ at Station IV did not decrease appreciably during ice cover (Figure 22b). Exchangeable

TABLE 6. RANGES AND MEANS OF SEDIMENT NITROGEN FRACTIONS.

Parameter	Station I	Station IV
Inorganic - N (mg.g ⁻¹)	0.98 - 2.34 1.55	2.19 - 3.63 3.04
Exchangeable NH ₄ -N (mg.g ⁻¹)	0.131 - 0.494 0.327	0.165 - 0.489 0.309
Nonexchangeable NH ₄ -N (mg.g ⁻¹)	0.776 - 1.958 1.208	1.953 - 3.366 2.714
Nitrate - N (mg.g ⁻¹)	0.00 - 0.034 0.020	0.00 - 0.030 0.010
Organic - N (mg.g ⁻¹)	3.709 - 11.396 7.571	14.652-21.212 18.397
Hexamine - N (mg.g ⁻¹)	0.288 - 1.084 0.737	0.932 - 1.973 1.319
Amino Acid - N (mg.g ⁻¹)	1.973 - 4.395 2.964	5.571 - 9.515 7.686
Unidentified Hydrol. - N (mg.g ⁻¹)	0.702 - 3.546 1.995	3.028 - 5.773 4.483
Nonhydrolyzable - N (mg.g ⁻¹)	0.72 - 3.22 1.88	3.29 - 5.68 4.89

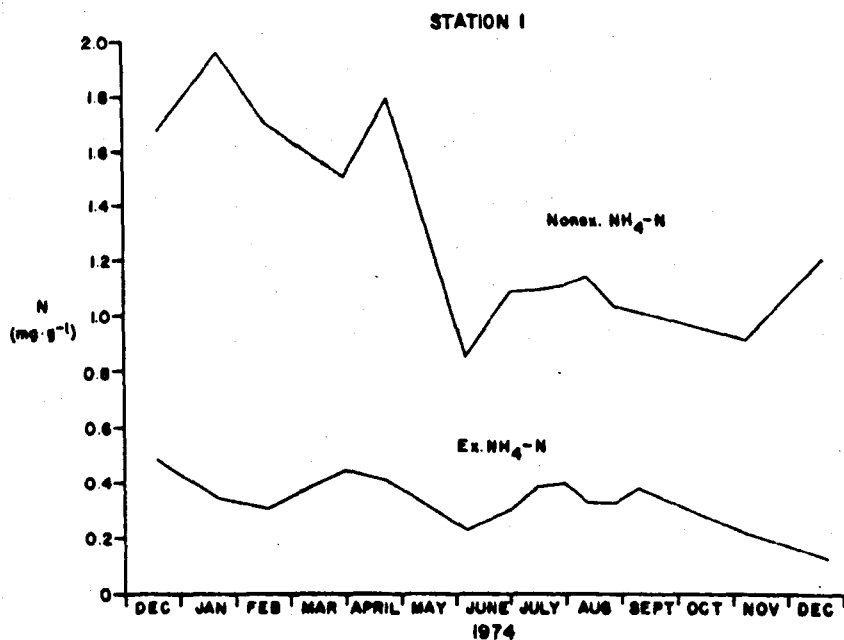


Figure 22a. Seasonal trends of nonexchangeable ammonium-N (Nonex. $\text{NH}_4\text{-N}$) and exchangeable ammonium-N (Ex. $\text{NH}_4\text{-N}$) at Station I.

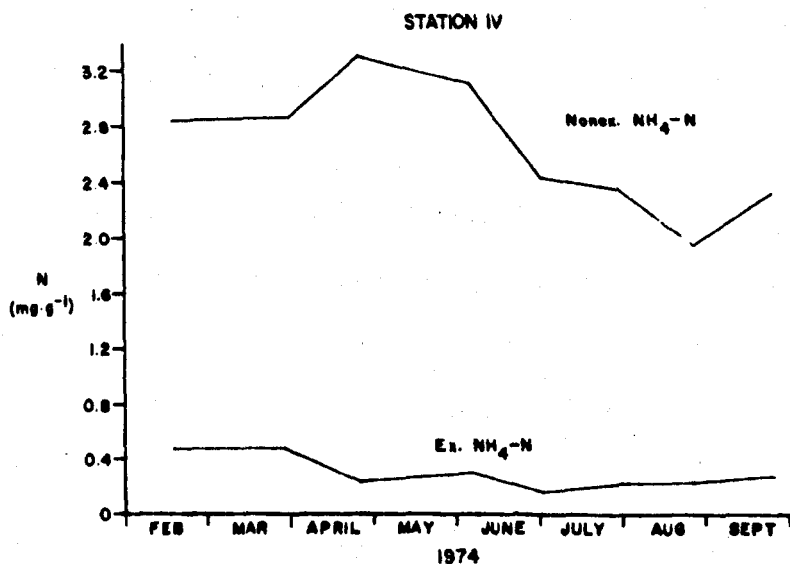


Figure 22b. Seasonal trends of nonexchangeable ammonium-N (Nonex. $\text{NH}_4\text{-N}$) and exchangeable ammonium-N (Ex. $\text{NH}_4\text{-N}$) at Station IV.

$\text{NH}_4\text{-N}$ did not increase in June as Fe_2O_3 and exchangeable Mn did because most of the ammonium was assimilated by algae. During much of the summer exchangeable $\text{NH}_4\text{-N}$ and nonexchangeable $\text{NH}_4\text{-N}$ at Station I increased in response to mineralization of organic N. Isirimah (1972) observed increased immobilization in the fall after deposition of detritus. This may also be happening at Station I in the fall as exchangeable $\text{NH}_4\text{-N}$ decreased.

During the summer, it would be expected that exchangeable $\text{NH}_4\text{-N}$ would decrease in response to uptake of ammonium by macrophytes. Except for June, exchangeable $\text{NH}_4\text{-N}$ appeared to increase during the summer at Station IV (Figure 22b). Instead, nonexchangeable $\text{NH}_4\text{-N}$, which is not available to macrophytes, steadily declined during the growing season. This failure of exchangeable $\text{NH}_4\text{-N}$ to decrease during the growing season was also observed in Lake Wingra (Isirimah, 1972).

Nitrate-N was only present in small amounts when it was present at all (Table 6). The presence of nitrate-N is a result of the process of nitrification, the biological conversion of ammonium to nitrate. This is largely dependent upon two genera of microbes, Nitromonas and Nitrobacter, which are facultative aerobes. Therefore, nitrification only takes place on the surface sediments during oxygenated conditions. Two processes remove nitrate from the sediments: immobilization and denitrification, as well as diffusion into the overlying waters. Denitrification is the biochemical reduction of $\text{NO}_3\text{-N}$ to molecular

nitrogen. Denitrification is an anaerobic process; thus, it can occur in the deeper sediments all year. Isirimah (1972) found that 60% of added $\text{NO}_3\text{-N}$ was denitrified and 30% was immobilized. Because of the small amounts of sediment nitrate it appears that net nitrification is only proceeding slowly.

On all the sampling dates but one nitrate was present at Station I (Figure 23). Since nitrate was present during the winter, even though all the sediments were anaerobic, it appears that denitrification and immobilization must have been proceeding at a slow rate. Nitrate concentrations did decline to some extent in March and April. During the summer, nitrate was higher indicating nitrification must have been proceeding faster than denitrification or immobilization.

At Station IV, nitrate was only present during the winter (Figure 23). Its presence again probably indicates that denitrification and immobilization were only proceeding slowly if at all. The complete disappearance of nitrate during the summer may have been a result of macrophytic uptake. Terrestrial plants are known to take up nitrate from the soil and, since rooted submerged macrophytes are relatives of terrestrial plants, it is probably a safe assumption that macrophytes will extract nitrate from the sediments.

As with organic phosphorus and organic carbon, organic nitrogen was highest at Station IV. This again is related to the heavy macrophytic growth in this area. The relationship between organic N,

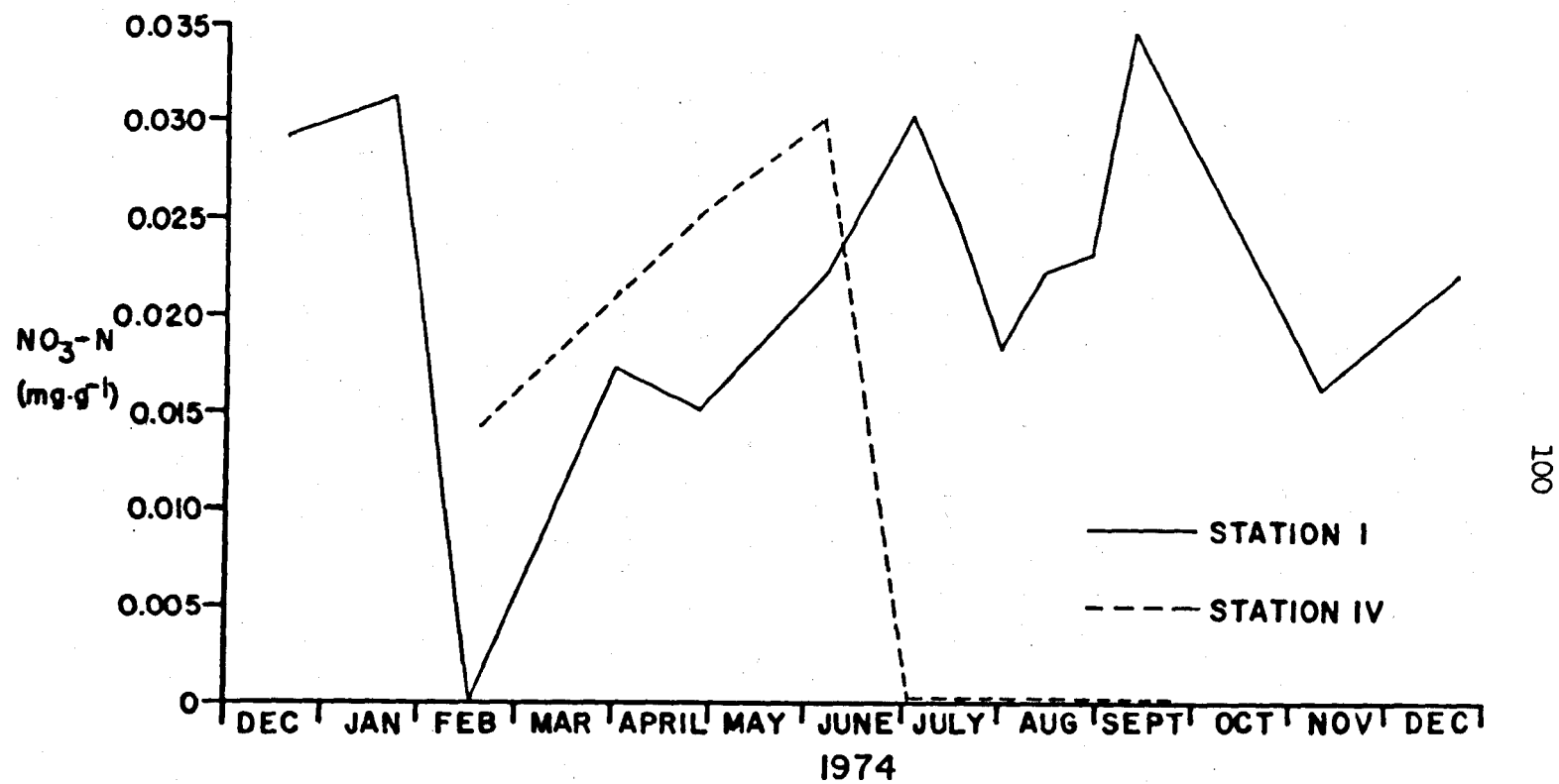


Figure 23. Seasonal trends of nitrate-N (NO₃-N) at Station I and Station IV.

organic P, and organic C in the whole lake sediments is portrayed in Figure 15. Organic N was well correlated with organic C ($r = 0.94$), much more closely than was organic P. This indicates that organic N was a more important constituent of organic matter than organic P.

Organic nitrogen was fractionated into 6N HCl hydrolyzed and non-hydrolyzed organic N. The hydrolyzed fraction was further divided into hexosamine-N, amino acid-N, and unidentified-N portions.

The amino acids released by hot acid probably come from bound amino acids instead of free amino acids (Kemp and Mudrochova, 1972). This amino acid-N probably existed in the form of peptides, proteins, and humoproteins. Some of these combined amino acids probably come from mucopeptides and teichoic acids (Bremner, 1967) since these substances are components of bacterial cell walls.

As with amino acids, hexosamine probably existed as bound material and not free hexosamine. Hexosamine comes from proteins, peptides and chitin (Bremner, 1967). The only two types of amine sugars that have been identified in either soils or sediments are glucosamine and galactosamine. Hexosamines form a large percentage of bacterial cell walls. Hexosamine-N comprised 10% of the total organic N at Station I and 7% at Station IV. The relatively large percentage of hexosamine N found in sediments has been attributed to the large-scale turnover of organic matter by microorganisms (Keeney, et al., 1970). The large hexosamine-N may also be due to chitin from zooplankton

carapaces since chitin is more resistant to decomposition than the hexosamine linkages in bacterial cell walls.

Amino acid-N made up the largest percentage of total organic N: 39% at Station I and 42% at Station IV. These percentages are higher than those obtained by Keeney, et al. (1970) or Kemp and Mudrochova (1972). This may indicate that the high amino acid-N content of Georgetown Lake sediments are due to the high protein content of plankton and macrophytes together with a low microbial turnover of sediment organic matter. This low turnover may be a result of the long periods of low oxygen tension and low temperatures since amino acid N content declines more rapidly under aerobic than anaerobic conditions in soils (Keeney and Bremner, 1966).

A small part of the unidentified hydrolyzable-N was probably in the form of purine and pyrimidine bases but little is actually known of this organic N component (Bremner, 1967).

Since all the fixed ammonium-N was probably extracted by hot acid the nonhydrolyzable-N must be organic in nature. This fraction has not been identified but is thought to be part of the soil humin (Bremner, 1967). Kemp and Mudrochova (1972) speculated that part of this fraction contained some amino acids.

Unidentified hydrolyzable-N and nonhydrolyzable-N together composed about 50% of the total organic N. The higher content of nonhydrolyzable-N may indicate that increased humification occurred in

the sediments.

The seasonal trends of the organic nitrogen fractions for Stations I and IV are presented in Figures 24a and 24b. During the ice cover period amino acid-N fluctuated but during the summer it closely resembled the trend of total organic N at Station I (Figure 20a). During the period 5 June to 12 August, amino acid-N appeared to increase. This corresponded to the time of highest algal population in the overlying waters (Figure 21). As the algal population declined, the sedimentation of plankton detritus declined and amino acid-N decreased as it was mineralized. Unidentified hydrolyzable-N decreased during the winter but nonhydrolyzable-N increased. This indicates that humification may have been occurring during this period. During the summer these two fractions fluctuated. Changes in nonhydrolyzable-N seemed to be in the same direction as unidentified hydrolyzable-N but there was a lag period. This may indicate a cause and effect relationship. This trend was not as pronounced at Station IV. The fluctuation of unidentified hydrolyzable-N at Station I may indicate that sedimenting detritus as well as benthic organisms may vary in organic matter composition with the exception of the proportion of amino acid-N.

At Station IV amino acid-N steadily declined during the summer until September (Figure 24b). Since the predominant producer at this station, macrophytes, do not generally die and decompose until the

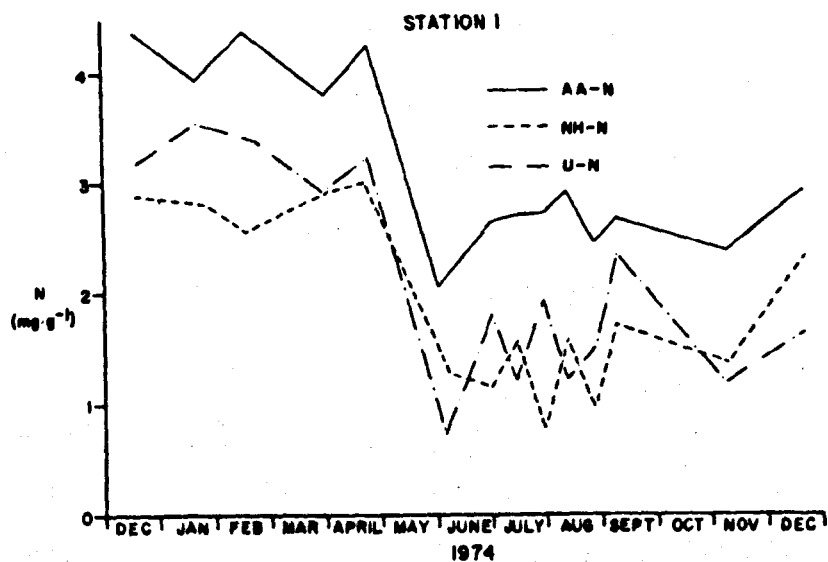


Figure 24a. Seasonal trends and the relationship between amino acid nitrogen (AA-N), nonhydrolyzed organic nitrogen (NH-N), and unidentified nitrogen (U-N) at Station I.

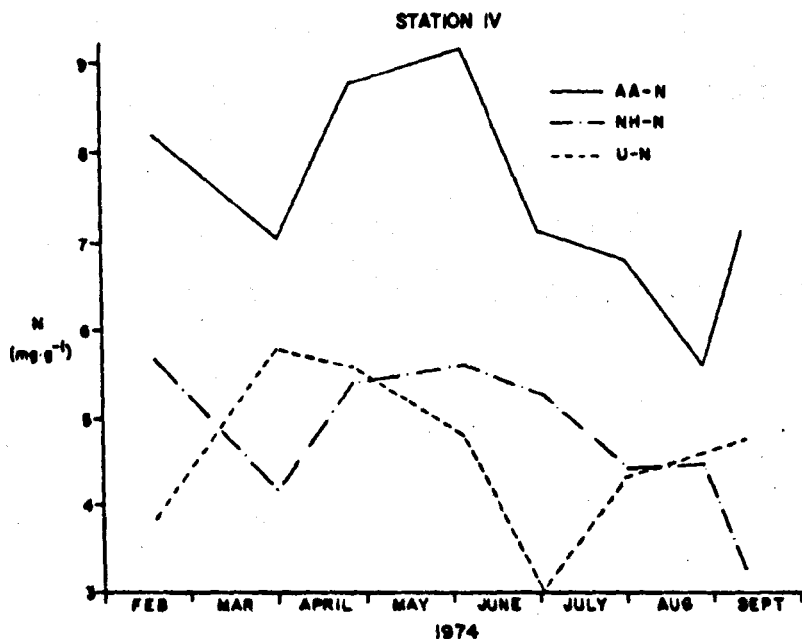


Figure 24b. Seasonal trends and the relationship between amino acid nitrogen (AA-N), nonhydrolyzed organic nitrogen (NH-N), and unidentified nitrogen (U-N) at Station IV.

fall, net mineralization may be more important here than at Station I. Apparently during the summer much of the mineralization was the deamination of amino acids. During June the unidentified hydrolyzable-N also declined but during the rest of the sampling period it increased. It is possible that only part of the mineralized amino acid-N was immobilized into the unidentified hydrolyzable-N fraction. During the summer, part of the nonhydrolyzable-N may have been mineralized as it decreased during this period.

At both Station I and IV the seasonal trends of hexosamine-N closely resemble those of amino acid-N (Figure 25). This is verification that these fractions are found in similar compounds, i.e. proteins and peptides. This relationship may indicate that much of the hexosamine-N in sediments was a result of deposition of chitin of zooplankton and benthic fauna instead of being derived from bacterial cell walls. In the surface sediment, bacterial hexosamine-N may be more important since they normally have a higher bacterial population (Hayes, 1953 and Pomroy, et al., 1965) but my samples included deeper sediment layers.

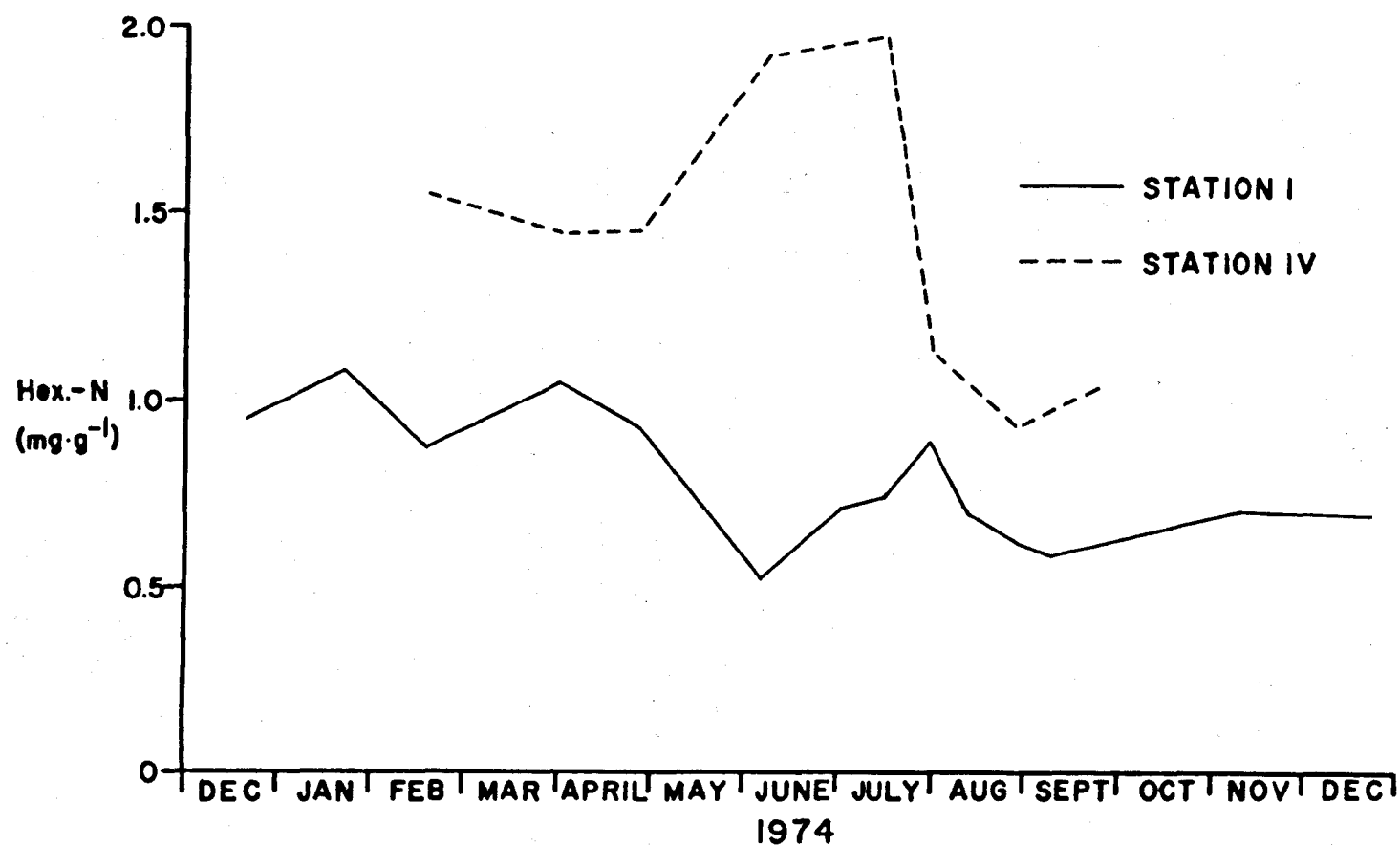


Figure 25. Seasonal trends of hexamine nitrogen (Hex-N) at Station I and Station IV.

SEDIMENT TRENDS

To estimate the annual trends of the sediment parameters, their net gain or loss from the sediments was computed. To obtain these trends, the changes for each parameter between consecutive sampling dates were determined. The differences were then summed for the year 17 December 1973 to 21 December 1974 to obtain an annual trend. Trends for specific periods of time within the year were also determined in this way. This method will only give gross quantitative and qualitative changes in the lake sediments.

All the cations did not exhibit a uniform trend during the year (Table 7). Iron oxides, Al_2O_3 , Ex-Mg, and Ex-Mn increased in the total sediments. Exchangeable Al and exchangeable Zn decreased. At Station I, with the exception of exchangeable Mn, the annual trends were not as great as for the whole lake. Only aluminum oxides and Ex-Mn increased. Oborn (1964) showed that macrophytes can concentrate iron, manganese, and calcium both intracellularly and extracellularly. Therefore, the macrophytes may be extracting these parameters from the deeper sediments and depositing them on the surface sediments when they die at shallower stations.

Organic carbon and IVS are both accumulating in the sediments of the entire lake. This is the result of the natural aging process of a lake. On an annual basis, more biomass is synthesized and deposited in a lake than is mineralized. This conclusion is substantiated by Knight, et al. (1976), who found that photosynthesis

TABLE 7. TRENDS OF SOME CHEMICAL PARAMETERS OF THE SEDIMENTS FROM 17 DECEMBER 1973 - 21 DECEMBER 1974; + INDICATES AN ANNUAL GAIN WHILE - INDICATES AN ANNUAL LOSS IN mg.g^{-1} .

Parameter	Station I	Whole Lake
Fe_2O_3	0.000	+ 8.719
Al_2O_3	+ 0.011	+ 0.056
Ex-Ca	- 0.200	+ 6.250
Ex-Mg	- 0.187	+ 6.250
Ex-Mn	+ 0.101	+ 0.056
Ex-Al	- 0.014	- 0.025
Ex-Zn	- 0.045	- 0.116
Organic - C	- 44.20	+ 27.20
IVS	- 64.25	+ 26.86
Total - P	- 0.382	- 0.020
Inorganic - P	- 0.163	- 0.001
Organic - P	- 0.219	- 0.019
Total - N	- 4.620	- 0.630
Inorganic - N	- 0.800	- 0.310
Organic - N	- 3.821	- 0.440

exceeded respiration in Georgetown Lake. Over a long period of time this surplus organic matter builds up on the bottom of the lake and eventually fills the lake. The greatest increases in organic matter in the sediments of Georgetown Lake occurred from 12 September to 21 December 1974. This is not surprising as this was the time when the majority of the macrophytes died. Organic matter appeared to decrease at Station I. This was caused by the decrease in organic matter from 25 April to 5 June as a result of a location change of this station. Ignoring this decrease, organic matter actually results in an accumulation of organic matter annually at Station I.

Total phosphorus decreased in the sediments (Table 7). This may seem unusual since Golterman, et al. (1968), Bortleson and Lee (1972), and Syers, et al. (1973) have observed that sediments act as a sink for phosphorus. This loss seems to be due to inorganic P which is released into the overlying water and then removed through the dam. It appears that with the exception of Station I, the lake sediments are accumulating total P. However, so much phosphorus is being removed from the sediments at Station I that there is a net loss of phosphorus from the lake. Inorganic phosphorus does not show an annual change in the lake as a whole but organic P does. Apparently, more organic P is mineralized to inorganic P annually than is being formed biologically. This results in a net loss of P from the lake. However, at Station I, both organic and inorganic P show an annual

loss. The amounts are larger here than in the lake as a whole which again indicates that the deep water withdrawal is causing the removal of phosphorus. Total nitrogen also shows an annual loss in the sediments. As with phosphorus, nitrogen, both inorganic and organic, show a greater loss at Station I than in the rest of the lake. In the lake as a whole, inorganic N shows an annual decrease as well as at Station I. It appears then, that organic N is being mineralized more rapidly than inorganic N is being lost through the dam. However, organic N is being lost more rapidly than inorganic N is accumulating, with the net result being a decrease in both inorganic N and organic N.

It would seem that the sediments of Georgetown Lake should be very low in phosphorus and nitrogen. The fact that this is not so is probably caused by the original substrate. As discussed earlier, this area was originally a hay meadow. As such, it was probably high in nitrogen and phosphorus. This phenomenon is probably a result of the deep water withdrawal at the dam. Wright (1967) has shown that reservoirs, with deep water discharges, liberate higher concentrations of nitrogen and phosphorus than surface water withdrawals. This is generally true because during summer stratification, higher concentrations of N and P are present in the hypolimnion than in the epilimnion. This is not true in the summer in Georgetown Lake but is true during ice cover. As discussed earlier, during the ice cover period the bottom waters become anaerobic, thus, causing certain

sediment chemicals to be released from the sediments. Among these are inorganic P and ammonium-N. Because the water withdrawal is near the lake bottom, as these chemicals are being released, they are being removed permanently from the lake. This is substantiated by the high concentrations in the outflow during most of the period of ice cover.

CONCLUSIONS

1. Georgetown Lake did not exhibit chemical stratification during the ice free period but did during most of the ice cover period. This stratification coincides with the period of anaerobic conditions in the bottom waters.

2. During the anaerobic conditions substances such as ortho-phosphorus, ammonia, iron, and silica, among others, were released from the sediments into the bottom waters. With the reintroduction of oxygen at ice out many of these substances greatly decreased in the water column.

3. During the summer months turbulent mixing appeared to suspend the surface sediments, thus making phosphorus available to the phytoplankton.

4. At the deep water station iron oxides and aluminum oxides were associated with the same particles. At the shallow water station they were associated with different particles because of iron uptake by the macrophytes.

5. The proportion of initial volatile solids attributable to organic carbon varied with the season because of the rate of benthic decomposition.

6. Inorganic phosphorus made up the largest percentage of the sediment total phosphorus. During the ice cover period total phosphorus trends were dictated by organic phosphorus because of the previous autumnal macrophytic die-off. During the summer inorganic

phosphorus regulated the total phosphorus trend because of macrophytic uptake of inorganic phosphorus.

7. Citrate-dithionite-bicarbonate extractable phosphorus made up the majority of the inorganic phosphorus. Exchangeable phosphorus composed 14 to 25% of the inorganic phosphorus, indicating much phosphorus is available to be released into the overlying waters if the right conditions exist.

8. Although organic nitrogen makes up the majority of total nitrogen, it was less important than reported in the literature. This was a result of the shallow depth of Georgetown Lake which makes the bottom environment more conducive to macrobial mineralization. This is supported by the C:N which was 31:1.

9. Nonexchangeable ammonium-N composed the largest percentage of inorganic nitrogen. Exchangeable ammonium-N made up 10-20% of the inorganic nitrogen, thus there is much nitrogen available to be released into the overlying waters.

10. Organic nitrogen was a more important constituent of organic matter than organic phosphorus.

11. The most important constituent of organic nitrogen was amino acid nitrogen.

12. Because of the deep-water withdrawal of the dam, much nitrogen and phosphorus was discharged during anaerobic conditions in the bottom waters. This was indicated by the C:N:P of 469:31:1.

This results in phosphorus from the lacustrine ecosystem.

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