8-1-1978

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Publication No. 61

1978

PROJECT COMPLETION REPORT

Project No.: A-041-ARK

Starting Date: 9/1/74 Completion Date: 8/31/77

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ACKNOWLEDGEMENTS

The work upon this publication was supported with funds provided by the Office of Water Research and Technology, U. S. Department of the Interior, through the Water Resources Research Center of the University of Arkansas under grant A-041-ARK as authorized under Water Resource Research Act of 1964, P.L. 88-379 as amended by P.L. 89-404 and P.L. 92-175.

The many thoughtful and important contributions of Dr. Ramona G. Rice, her numerous suggestions and dedication were invaluable to the successful completion of the research. I am also grateful to Dr. Joe Nix, Ouachita Baptist University, for his technical expertise concerning extraction procedures. Special thanks is given to Mr. Evert Baker, Manager of Lake Fayetteville, for his assistance in sample acquisition.

ABSTRACT

The present investigation examines seasonal variations of algal assemblages in a south-central reservoir, Lake Fayetteville, Arkansas, in an attempt to evaluate the role of various trace metals in relation to these seasonal variations. Iron, manganese, cobalt, copper, lead and zinc concentrations were evaluated for the period of one year from March, 1976 to March, 1977 with concomitant examination of algal assemblages. In addition to collection of this material, correlations between specific taxa and metals in the water fraction have been evaluated.

A detailed literature review dealing with the role of micronutrients in various algal groups has been discussed by Rice (1978) with further evaluation and amplification of the data contained in this report and additional physicochemical parameters.

Seasonal variations of phytoplankton assemblages were observed in a mesotrophic lake in northwestern Arkansas for a period of one year. Simultaneous determinations of iron, manganese, cobalt, lead, copper and zinc were made using atomic absorption spectroscopy. All algae were identified to species where possible. Relations between variations of seasonal phytoplankton assemblage succession and micronutrient variations were examined. Distinct patterns of all metal concentrations are described to occur in a cyclic pattern as a result of biological, physical and chemical factors.

Four major assemblages were observed: a spring Coelosphaerium nagelianum-Aphanizomenon flos-aquae dominated assemblage, a

summer serially dominated assemblage consisting of Oscillatoria spp., Merismopedia trolleri and Microcystis aeruginosa, an autumnal cyanophycean assemblage dominated by Anabaena circinalis and a winter bacillariophycean-chrysophyte assemblage characterized by Melosira granulata, Navicula spp., Fragillaria crotonensis, Asterionella formosa and Uroglena sp.

Particulate manganese concentrations were highly correlated with distributions of cyanophytes in the spring (r=0.66), summer (r=0.96) and autumn (r=0.79). Particulate cobalt also was related to cyanophycean distributions during the spring and fall blooms with correlation coefficients of 0.5 and 0.65, respectively. Differences in levels of correlations for the spring and autumn blooms were attributed to species composition and possibly related to the nitrogen fixation ability of the species present.

Cobalt is believed to be secreted by Navicula with subsequent incorporation by A. formosa and F. crotonensis as confirmed by a correlation of 0.67 with cobalt. A suggested successional relationship exists between Navicula and A. formosa and F. crotonensis.

Particulate lead was highly correlated with populations of Navicula and Stephanodiscus nigarae; correlation coefficients of 0.57 and 0.61, respectively, were recorded. Uroglena sp. also were observed to interact with the element (r=0.64). Possible lethal effects of lead on the bacillariophytes were noted while no such events were found in the case of the chrysophytes.

Micronutrients at no time were observed to be limiting. Two metals, copper and zinc, could not be correlated with any obvious algal succession. Iron may be associated with distributions

of certain euglenoid species but this was not confirmed conclusively.

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INTRODUCTION

Roles of micro-nutrients in natural ecosystems have been primarily evaluated from physico-chemical and in vitro nutritional algal investigations. Few studies have attempted to associate micro-nutrients with certain algal blooms. No one has compared the seasonal distribution of micro-nutrients with annual phytoplankton succession. This study demonstrates the association between the annual cycle of planktonic algae and micro-nutrients.

Mortimer (1971) has described physical distributions of nutrients to be dependent upon wind and wave action and thermal characteristics in the Great Lakes. Nix (1970, 1974) observed similar parameters to affect the micro-nutrient distributions in four south-central reservoirs. Definite stratification exists during the summer with development of an anoxic region and metal accumulation in the hypolimnion (Delfino and Lee, 1972, Rice, 1978). The thermocline overlying the anoxic region is then thought to act as a membrane restricting movement of nutrients from the nutrient-rich hypolimnion to the nutrient-poor euphotic zone (Delfino and Lee, 1972, and Dugdale, 1967, Rice, 1978).

Chemical input into the lake occurs at the soil-water interface with mobilization of manganese and iron occurring from the sediment into the hypolimnion under anoxic conditions. These nutrients become available to other waters during lake destratification or "turnover". Several mechanisms of chemical exchange at the soil-water interface have been proposed by Mortimer (1971). Limited trace metal movement has been explained due to metal interaction in an adsorptive manner with copepod movement by Martin (1970).

Trace metals have been long recognized as essential to the growth of algae. A complete literature review relating metal requirements of various alga taxa on a physiological and limnological basis has been provided by Rice (1978). Two criteria for requirements of a metal that have been determined from in vitro investigations are the death of a non-replaceable role of the element in a fundamental cellular process of the alga. The first evidence concerning micro-requirements for iron, manganese, cobalt, zinc and copper was presented by Chu (1942). This evidence was later confirmed by Provasoli and Pinter (1953). In detailed reviews, O'Kelly (1974), Goldman (1965), Eyster (1964), and Wiessner (1962) have reported micro-nutrient requirements of these metals for the algae. However, copper and lead, at elevated concentrations, are known to be algae inhibitors.

Iron is required in chlorophyll synthesis, ferrodoxin formation in the Cyanophyceae, in hydrogenase development, and as a component of various algal enzyme systems. Chu (1942), Provasoli and Pinter (1953) and Trainor (1969) established iron requirements for the Bacillariophyceae, Chlorophyceae, and Cyanophyceae. Glover (1977) further established general iron requirements for the Chrysophyceae and additional species of the Bacillariophyceae. Iron probably is best recognized as a requirement among the Cyanophyceae. Gerloff and Skoog (1957), Trollope and Evans (1976) and Morton and Lee (1974) reported specific iron requirements by various Cyanophyceae for growth. Simpson and Neilands (1976) and Murphy, et al. (1976) determined this metal to be important

in siderochrome formation among the Cyanophyceae and further extended the hypothesis that siderochrome secretion by these algae suppresses the growth of other iron-requiring algae. Seasonal variations which may be related to algal assemblage fluctuations were reported by Elder, et al. (1976) in Lake Tahoe.

The role of manganese in algal metabolism is involved in oxygen evolution systems and in the formation of lipid and protein storage products. Requirements for this metal were determined for the Chlorophyceae. Cyanophyceae and Bacillariophyceae. Knauer and Martin (1973) and Nasr and Bekheet (1970) have reported manganese requirements for brown marine algae. Gerloff and Skoog (1957) found manganese requirements of fresh-water algae related to iron and calcium concentrations in bioassay experiments. Shapiro and Lee (1975) reported manganese to be a limiting factor to phytoplankton growth in Lake Superior, but Plumb and Lee (1975) found manganese addition to samples of near-shore Lake Superior algae to be inhibitory.

Cobalt is requisite to algal growth both in its inorganic form and as a fundamental component of Vitamin B_{12} (cyanocobalamine). In its inorganic form, cobalt is known to increase the formation of biomass in the cyanophytes. Addition of Vitamin B_{12} stimulates the formation of precoursers leading to the formation of RNA, DNA and other protein cell components. Cobalt was first recognized as a micro-nutrient by Chu (1942) and was confirmed as such by Provasoli and Pinter (1953).

Various recent investigations have emphasized the role of cobalt as a cofactor in Vitamin B_{12} synthesis. Bunt (1970) reported cobalt to comprise four percent of this vitamin. Menzel and Spaeth (1962), Guillard and Cassie (1963), Gold (1964), Aaronsen, et al. (1977), Guillard (1968), Carlucci and Silbernagel (1969), Bunt (1970), Carlucci and Bowes (1970a, b), Carlucci and Bowes (1972), Haines and Guillard (1974), Haines (1974), Swift and Taylor (1974), Blankenship and Wilbur (1975), and Nasr and Bekheet (1970), demonstrated the requirement of cobalt as Vitamin B_{12}. Benoit (1957), Gorham et al. (1974), Daisley (1969), Parker and Hasler (1969), Ohwada and Taga (1972), Parker (1977) and Gerloff and Skoog (1954) dealt with the cobalt requirements for various algae for growth, including the cyanophytes in fresh-water habitats.

Zinc is thought to be important in algal metabolism at the level of dehydrogenase enzyme formation and in photosynthesis at the level of carbon dioxide fixation. While recognized as essential, this is the least investigated of the algal micro-nutrients and the exact levels of this element that are required metabolically by phytoplankton is not clear. Bachman and Odum (1960), Gutknecht (1963, 1965) and Knauer and Martin (1973) found this metal to be required for marine algae. Walker (1953) and Trollope and Evans (1976) have reported a zinc requirement for chlorophycean and cyanophycean algal growth.

Copper is recognized both as an algal requirement at micro-quantity levels and as an algal inhibitor at elevated

concentrations. In micro-quantities, copper is involved in the formation of the prosthetic group of ascorbic acid oxidase, in the formation of plastocyanin and in the photo-reduction processes of photosystem I. It also is a constituent of many algal enzymes. As an algal inhibitor, copper has received much attention in the literature. Alexander and Corcoran (1967), Seeliger and Edwards (1977), Knauer and Martin (1973), Haug, et al. (1974), Erickson (1972), Thomas and Seibert (1977), and Schell and Nevissi (1977) deal with the effects of copper concentrations in marine algae. Marvin, et al. (1970), Walker (1953), Stokes and Hutchinson (1975), Button and Hostetter (1977), Hassal (1963), and Nielson, et al. (1969) considered copper concentrations associated with fresh-water algae.

Lead is recognized as an algal inhibitor. Hessler (1975, 1974) found this inhibition to be due to its prevention of cell wall synthesis, prevention of the later stages of cell division and prevention of daughter cell separation. Seeliger and Edwards (1977), Knauer and Martin (1973), Haug, et al. (1974), Schultz-Blades and Lewin (1976), and Overnell (1975) considered lead concentrations as related to marine algae. Lovric and Strohal (1972), Monahan (1976) and Gruendling (1973) examined lead concentrations in fresh-water algae.

A site was selected on the basis of available background information. Meyer (1971), Rice (1974), Poppe (1976), and Rice (1978) examined algal assemblage distribution as related to macro-nutrient parameters for Lake Fayetteville, Arkansas.

Hulsey (1956), Browne (1967) and Jackson (1977) also conducted zooplankton analyses in conjunction with limnological surveys of Lake Fayetteville. From these prior investigations, it was possible to anticipate that this reservoir would provide an *in situ* ecosystem where extranious factors from those under investigation would either be limited or predictable on the basis of past data. Prior research and this investigation are interrelated through evaluation of temperature and seasonal algal succession. The limited water input, regular cycling of algal assemblages, small size of the lake and available background data enhanced the desirability of Lake Fayetteville for an initial investigation of this type.

A survey of the literature (Rice, 1978) revealed general requirements of trace metals by algae *in vitro*. This led to the expectation of some demonstrable relationships among the phytoplankton assemblage distributions and the fluctuations of trace metals *in situ*. The present investigation attempts to relate seasonal fluctuations of iron, manganese, cobalt, zinc, copper and lead concentrations to an annual distribution of phytoplankton assemblages in Lake Fayetteville. This investigation will present an evaluation of probable cause and effect relationships among the various algal groups and the selected metal concentrations by way of graphic and analytical examination of the data.

MATERIALS AND METHODS

A single representative sampling site was chosen for investigation. Samples were collected weekly from March, 1976, to March, 1977, with the exception of periods during January when ice cover was present. Samples were obtained at meter intervals with a 1.2 liter polyvinylchloride Kemmerer water bottle (Wildlife Supply Company). Temperature was determined *in situ* with a YSI Model 33 temperature probe. Sample aliquots were fixed with M^3 fixative (Meyer, 1971) immediately upon collection and retained for algal species and abundance analyses. Water samples were collected in polyethylene bottles and returned to the laboratory for chemical analysis.

In the laboratory, hydrogen-ion concentrations were determined using a Corning Model 7 pH Meter on unfiltered water samples. For trace metal analysis, the 250 ml aliquat of unfiltered water was retained in a polyethylene bottle and acidified to less than pH 2. A second 250 ml aliquot was filtered through a Whatman GF/A glass fiber filter, acidified to less than pH 2 and retained. The materials retained by the filter were dried in a dessicator and retained. These fractions were designated as raw, filtered and particulate fractions, respectively.

Trace metal analyses for iron, manganese, cobalt, zinc, copper and lead were performed on raw and filtered samples by atomic absorption spectroscopy. Aliquots of 200 ml were chelated with sodium diethyldithiocarbamate (DDC) and organic solvent extracted with methyl isobutyl ketone (MIBK) according to the procedures of Nix and Goodwin (1970). Particulate fractions

were digested with heat in 1:1 nitric acid solution and diluted with glass distilled water up to 200 ml. Samples were extracted with DDC and MIBK. Atomic absorption analyses were performed with the use of a Jarrell Ash Model 82-270 atomic absorption spectrophotometer. Sample concentrations were determined directly from the concentration mode of the spectrophotometer which was standardized with standards of known concentration of the metal analyzed. Standard curves for diluted standard series were calculated with the use of a Monroe 1860 calculator. Linear regression analyses were performed on each standard curve and the goodness of fit was greater than $r = 0.98$. Wavelengths used for the metal determinations were chosen in compliance with operational guidelines for the instrument in an attempt to avoid interference of background absorbance by secondary peaks (Jarrell Ash, 1966). Standards for the concentration curves were diluted from Fisher Certified Atomic Absorption Standards (Fisher Scientific Company, Fair Lawn, New Jersey).

All glassware and plasticware utilized in the sample analyses and storage were subjected to a stringent acid washing protocol. Glassware was first washed with a commercial detergent, tap water rinsed, distilled water rinsed, rinsed twice with 1:1 nitric acid and finally rinsed twice in glass distilled water. This treatment was found to prevent contamination from metals present in tap water and detergent.

Fixed algal samples were identified to species and enumerated from 5 ml aliquots using the inverted microscope technique (Utermohl, 1958). A complete taxonomic list and

and nomenclatural citations is given in Appendix Table 1 of Rice (1978).

The IBM 370/155 computer with a Tektronix 4015-1 terminal was employed for graphics design and preparation. A modification of the "Purejoy" graphics program (Poppe, 1975, 1978) was utilized for display of physicochemical and algal assemblage parameters. Correlation coefficients were calculated with a Monroe 1860 calculator.

Statistical Analysis

Two variable linear regression analyses were performed on selected algal divisions and trace metals showing obvious observable relationships. Regression analysis was performed using the metal in the particulate fraction as the independent variable (X) and the algal abundance of the division as the dependent variable (Y).

The correlation coefficients were calculated using the following equation:

$$r = \frac{XY - \frac{XY}{N}}{\left(X^2 - \frac{(X)^2}{N} \right) \left(Y^2 - \frac{(Y)^2}{N} \right)}$$

Where N = number of paired samples

Correlation coefficients analyzed for the Cyanophyta, Bacillariophyta and the Chrysophyceae are presented with those of total algal abundance for the interaction of algal cell numbers and the metals in Tables 1-3.

RESULTS AND DISCUSSION

The data presented in this research were derived from over 470 samples collected from Lake Fayetteville, Arkansas, between March 1976 and March 1977 and represented over 15,500 analyses. Samples were taken weekly with the exception of five weeks when weather and ice cover prevented field work.

A detailed species list with authors appears in Rice (1978) for all algae encountered in this investigation.

Algal Distribution by Division

Rice (1978) has examined in detail the algae grouped as chlorophyll-a, chlorophyll-b, and chlorophyll-c containing phytoplankton.

Cyanophyta

Algae of this division have the distinction of containing only chlorophyll-a as their principal photosynthetic pigment. Therefore, a discussion of this group will of necessity also examine the distributions of chlorophyll-a in the lake.

Lake Fayetteville is a Cyanophyta dominated lake during three seasons. Similar data has been reported by Meyer (1971), Rice (1974, 1978) and Poppe (1976) for previous studies. During the annual cycle the lake also contained a cyanophyte sub-dominant population during the winter. This was due to a large contribution by Oscillatoria tenuis and Osc. rubesens which developed during late December and continued to increase under the ice cover in January.

In early spring, the cyanophycean algae were absent below the euphotic zone (Fig. 4). Within this illuminated region, densities of up to 2.6×10^7 cells/l were enumerated. The initial cyanophycean assemblage contained Aph. flos-aquae as the most important species with a reduced contribution by C. Nagelianum and Aphanothece sp. This rather stable condition persisted until late April when the typical spring blue-green bloom began to develop. The co-dominant algae of this peak were C. nagelianum and Ana. circinalis. Peak cyanophycean abundances for the year appeared by mid-May when abundance levels ranged from 1.9×10^7 to 1.5×10^8 cells/l.

Numbers of the spring species continued to decline from the middle of May until mid-July. Cell numbers within this time period ranged from 4.1×10^6 to 6.2×10^7 cells/l. During late June Oscillatoria limosa and Osc. tenuis were added to the existing population below five meters. Mid-July cyanophycean abundance levels decreased to range of 4.2×10^6 to 4.7×10^7 cells/l. During this period, Osc. limosa and Osc. tenuis expanded throughout the water column with the concurrent development of Merismopedia trolleri in the hypolimnion. This latter population expanded into the meta- and epilimnion by the first week in August. Merismopedia trolleri virtually disappeared and was replaced by Microcystis aeruginosa during the first week in August. This was a direct replacement without a change in cell numbers.

Microcystis aeruginosa became the dominant cyanophyte alga by mid-August increasing from 4.1×10^6 to 6.0×10^7 cells/l. Oscillatoria spp. were observed to decline during this period. All species present during the summer assemblage were present

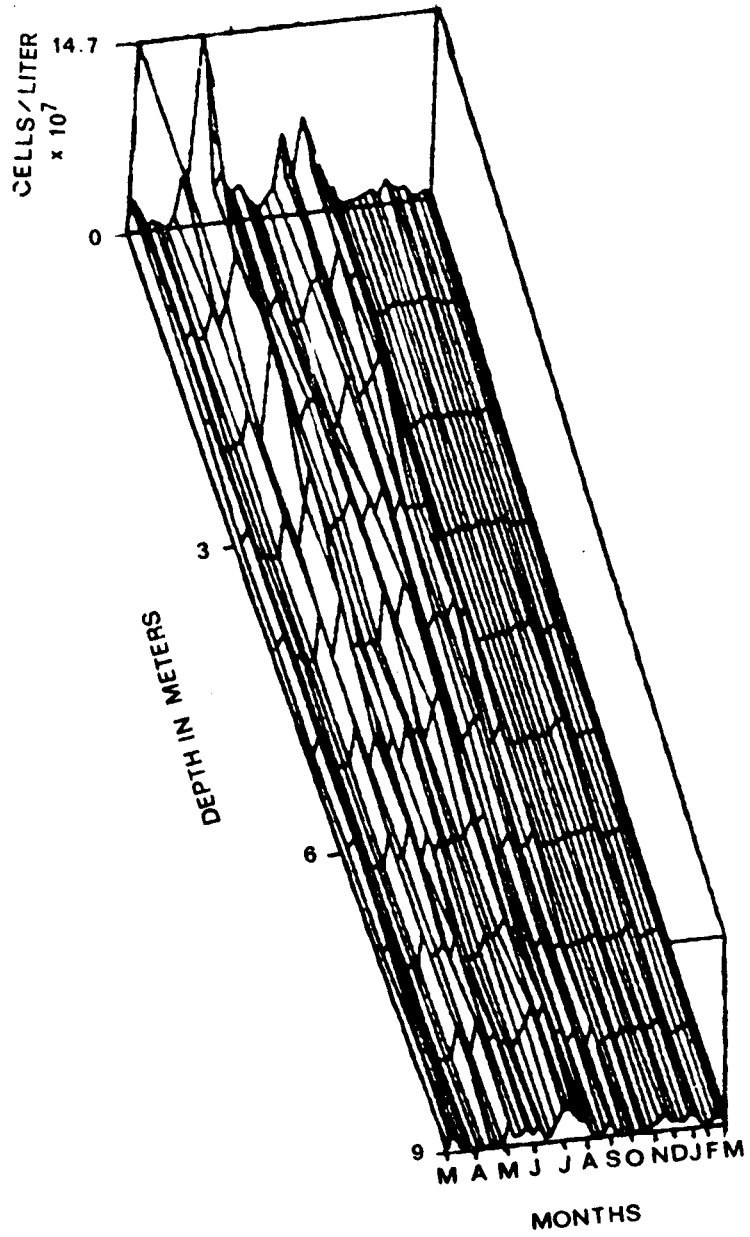

Figure 4. Distribution of the Cyanophyta (cells/l).

during the first half of September. During this period of thermal stratification, the algal abundances were similarly distributed in a range from 7.1×10^7 cells/l in the epilimnion to 2.2×10^6 cells/l in the hypolimnion. The fall cyanophycean bloom began in mid-September with Ana. circinalis emerging as the dominant alga with additional important contributions by Ana. flos-aquae and and Aph. flos-aquae. The combined abundance levels ranged from 5.9×10^7 cells/l in the euphotic zone to 1.0×10^5 cells in the hypolimnion. C. nagelianum, remaining from the spring maximum, disappeared from the entire water column during this period.

Abundance levels remained fairly stable; however, the distribution reflects a gradual settling out (Fig. 4). Late October cyanophycean abundance levels decreased to a range of 1.0×10^6 to 9.6×10^6 cells/l. Paralleling the decrease in abundance levels was a shift in species composition. The new dominants included Aph. flos-aquae and Mic. aeruginosa which persisted through the end of November.

In early December, a winter cyanophyte sub-assemblage developed with abundance levels ranging from 4.4×10^6 to 1.7×10^7 cells/l. This temporary sub-assemblage was restricted to Ana. circinalis, Osc. tenuis and Aph. flos-aquae. With the development of the ice cover, the species composition changed dramatically. Oscillatoria rubescens increased in importance and was followed by the predictable increased spring abundance of Aph. flos-aquae in the lake algal assemblage.

The pattern of the cyanophycean algal abundance levels, as mentioned above, does reflect the distribution of chlorophyll-a containing organisms. Should differences in the distribution of these algae be affected by a particular metal, the single chlorophyll

form present in these algae might prove to be important to such distribution. An important difference in the dominant algae of the spring and autumn cyanophycean assemblages was found. Coelosphaerium nagelianum with Aph. flos-aquae were co-dominants in the spring assemblage with important contributions from Ana. flos-aquae and Ana. circinalis. In the fall assemblage, Ana. circinalis was the single dominant species with important secondary contributions from Ana. flos-aquae and Aph. flos-aquae.

A further observation is the appearance of Osc. tenuis and Osc. rubsens as significant contributors to the winter algal assemblage. The growth of the Osc. tenuis population was associated with mild temperatures in December while Osc. rubesens developed in synchrony with winter ice cover. Rice (1978) found this population to cause no significant shift in elemental concentrations.

Chlorophyta

The green algae show a general distribution pattern of a spring pulse followed by an early summer surface maximum declining into a sustained summer conglomerate of volvocine and coccoid green algal species (Fig. 5). A temporary pulse of colonial coccoid species was observed in late December. Green algae were growing actively in the upper three meters with the presence of these plankters in lower waters due primarily to physical settling processes; i.e., the "plankton rain".

An early spring population of green algae ranged between 4.8×10^4 to 1.5×10^6 cells/l from early March until late April. This assemblage consisted of A. Falcatus, Gloeocystis vesiculosum Schroderia sp., with B. Braunii appearing as spring progressed. As water temperatures increased, cell numbers began to increase.

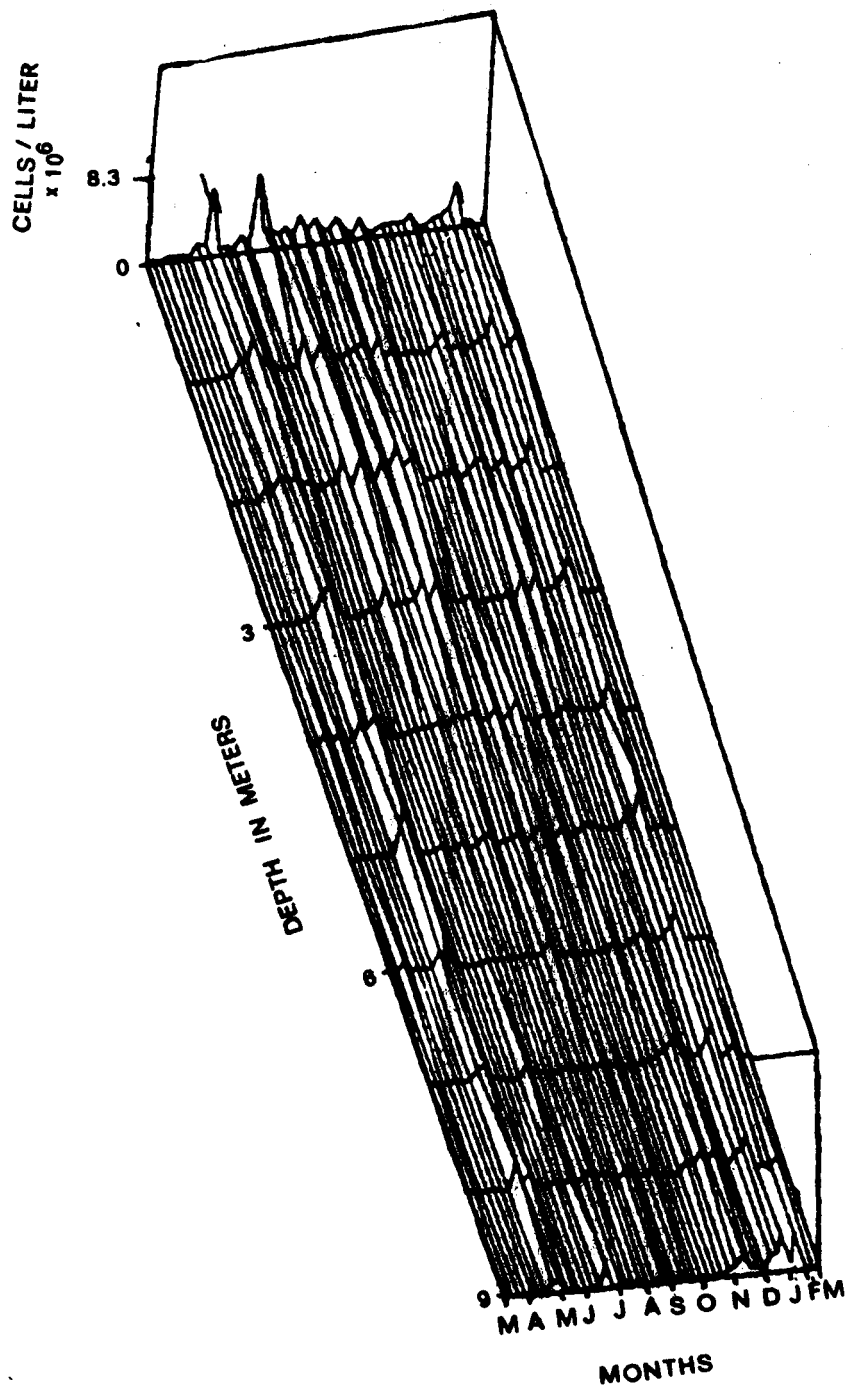

Figure 5. Distribution of the Chlorophyta (cells/l).

Abundances in late April ranged from 1.2×10^6 to 3.3×10^6 cells/l with the first minor appearances of the volvocine algae. The most important species were G. vesiculosum and D. pulchullum with small contributions by Gonium sociale and Eud. elegans.

Sphaeocystis schroteri and Eud. elgans were present as dominant green algae in the surface waters during early May. The combined maximum abundance levels were approximately 7.2×10^6 cells/l. These cell numbers decreased to 1.8×10^6 cells/l in the epilimnion with further reductions occurring in the meta and hypolimnion. No green algae were observed in the lower hypolimnion.

In late June peak annual abundance levels of 8.3×10^6 cells/l of the Chlorophyta were attained. The high abundance levels were the result of markedly increased numbers of Eud. elegans and accompanying minor increases in S. schroteri, B. braunii, and D. puchullum. As the bloom declined, there was an increased importance of the volvocine representatives, P. morum, G. pectorale and Eud. elegans. Equivalent numbers of the coccoid green species, S. schroteri, B. braunii and D. pulchullum were enumerated. Abundance levels throughout the summer ranged between $1.1. \times 10^4$ and 3.3×10^6 cells/l.

In late July the volvocine greens were Scendesemus bijuga and S. schroteri coincident with a decrease of other coccoid green algae. Indeed, in mid-August, volvocine algae disappeared from the lake while D. pulchullum and B. braunii continued to increase in importance in the euphotic zone. Abundance increased to 4.7×10^5 cells/l at seven meters in the hypolimnion and to 5.0×10^6 cells/l at two meters in the epilimnion. A similar bimodal distribution was observed in the fall.

The volvocine assemblage was terminated in early September

with a final pulse. Pandorina morum, Eud. elegans and G. sociale appeared in the assemblage, while the coccoids, B. braunii and S. bijuga also increased in importance. Numbers ranged from 2.8×10^6 cells/l at the lake surface to 1.9×10^5 cells/l at seven meters.

The autumnal profile of the chlorophyta included decreased cell abundances ranging from 1.6×10^4 to 2.6×10^6 cells/l with the higher abundances generally occurring in the euphotic zone. These concentrations persisted until late December. Botyrococcus braunii continued to be the most important chlorophyta species until late October where it was replaced by D. pulchullum and S. schroteri. These species persisted in greater abundance until late December and were distributed homogenously throughout the water column at a density of 7.0×10^6 cells/l. In late December, however, D. pulchullum was the dominant species in the euphotic zone. A period of severe weather terminated this pulse reducing the chlorophycean abundances to 1.7×10^6 to 0 cells/l throughout the remainder of the study. The most important species during this final phase of the annual cycle was B. braunii.

Conjugatophyceae

Members of this group of algae, including the Zygnematales and Desmidiales, were represented throughout the investigation by only four genera: Cosmarium spp., Closterium spp., Staurastrum chaetoceros and Mougeotia sp. Staurastrum was the most important of the desmids with fluctuations in abundance levels directly related to the presence or absence of this alga (Fig. 6).

From early May through early September the desmid abundances ranged between 8.0×10^3 and 1.9×10^5 cells/l. Staurastrum chaetocerous represented the only species present from March until

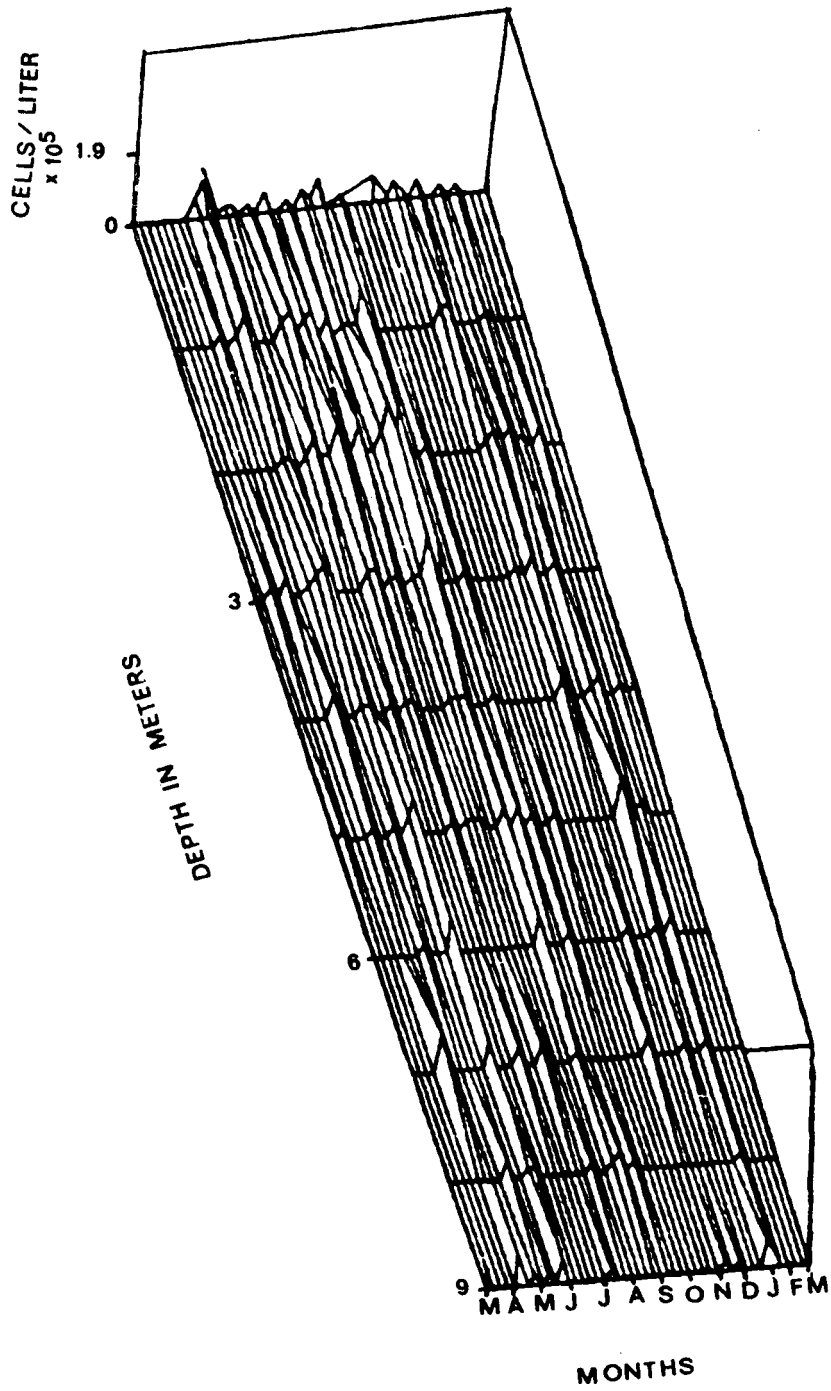

Figure 6. Distribution of the Conjugatophyceae (cells/l).

the appearance of Cosmarium spp. and Closterium spp. in mid-August. Occasional occurrences of members of the conjugatophyceae at other times during the investigation period represent isolated encounters of single individuals or the dislodgement of Mougeotia sp.

Rawson (1956) concluded that those algae present in the least abundance may be more indicative of trophic levels than those present in the highest abundance. Species of lesser importance were thought to be more sensitive to slight variations in their immediate environment. Further consideration of this suggestion would appear to be in order since the desmids comprise one of the least important groups of algae in the lake.

Euglenophyta

The Euglenophyceae were consistently present throughout the year although usually in low numbers (Fig. 7). Most noticeable in the abundance distribution patterns of this group is the major accumulation of these organisms in the hypolimnion during the anoxic period. (Rice, 1978). She further observed that following the return of oxygen to this lower region, there was an accompanying decrease in abundance of the euglenoids throughout the water column.

Abundance levels of the euglenoids ranged from 8.0×10^3 to 4.1×10^5 cells/l from March until late June. Trachelomonas volvocina and T. hispida were the only species present with T. hispida of only minute significance. In mid-May Eug. pisciformis appeared in the assemblage. This alga quickly attained equal abundance to T. volvocina.

An accumulation of euglenoids occurred in the anoxic hypolimnetic region of the lake in early July and persisted until late October (Rice,

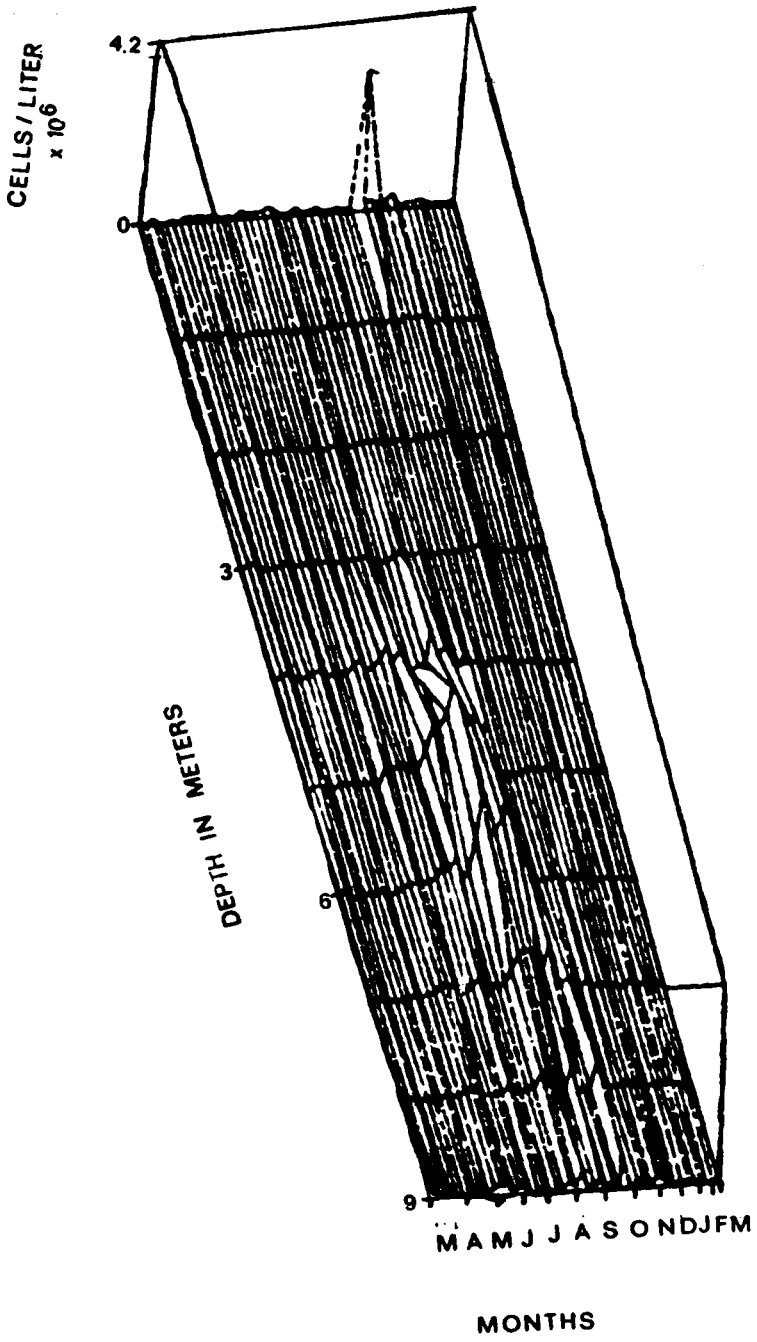

Figure 7. Distribution of the Euglenophyta (cells/l).

1978). This euglenoid population was dominated by Eug. pisciformis with a small consistent contribution of T. volvocina. Occasional contributions by T. hispida, and Lepocinclis ovum appeared in late August, persisted until the decline of the anoxic zone. Abundance levels in the epilimnion were consistent with the spring levels ranging from 8.0 x 10^3 to 2.4 x 10^5 cells/l. Cell numbers of the euglenoids in the hypolimnion pulse ranged from 3.1 x 10^5 to 4.2 x 10^6 cells/l.

After the first week of October there was a precipitous decline in the abundance levels of the Euglenophyta. The winter euglenoid sub-assemblange ranged between 0 to 2.3 x 10^5 cells/l from October through early March. This population was characterized by nearly equal contributions by Eug. pisciformis and T. volvocina. Euglena pisciformis disappeared from the lake during the January ice cover, with T. hispida returning during the final stage of the winter phase.

Of particular interest in this group of algae is the hypolimnetic development of Eug. pisciformis during summer stratification. These organisms, which are known to be both autotrophic and heterotrophic, must be able to metabolize at much reduced oxygen levels. Iron and manganese also concentrated in this region of the lake during this period. Possible interactions of these metals with this taxon will be discussed in more detail later.

Pyrrhophyta

The dinoflagellates comprised the least abundant group of algae during the investigation period. Ceratium hirundenella first appeared in the phytoplankton in late March. The subsequent appearance or disappearance of this alga was responsible primarily for the abundance

levels of the pyrrhophytes (Fig. 8). From late March until early November abundance levels ranged between 0 to 2.4 x 10^4 cells/l. After November the dinoflagellates disappeared completely from the assemblage. Some erratic contributions were made to the population at times by Gymnodinium spp. and Peridinium spp.

Once again it is interesting to note the observation of Rawson (1965) that dominate species often are those with wide tolerance ranges. Thus these dominant algae may not be as reflective of trophic conditions than the less frequent and less abundant species. The pyrrhophytes certainly qualify as the least frequent and least abundant group of algae in Lake Fayetteville.

Bacillariophyta

A general pattern with only one distinct diatom peak was noted during the investigation. In Figure 9, the single peak appears on opposite edges of the graph. These apparently are separate peaks. However, in actuality they represent a continum of a single annual succession. The decline of the winter-late spring assemblage of 1976 and the more dramatic peak in December and January corresponds to the beginning of equivalent winter pulses in 1977.

Abundance levels ranged from 4.8 x 10^4 to 5.9 x 10^6 cells/l from March until mid-May. Melosira granulata, Stephanodiscus nigarae and Asterionella formosa were the primary contributors to this bloom. Lower bacillariophycean abundances of 0 to 2.5 x 10^5 cells/l were observed throughout the summer stratification period. Melosira granualata was the primary contributor of this group from June through

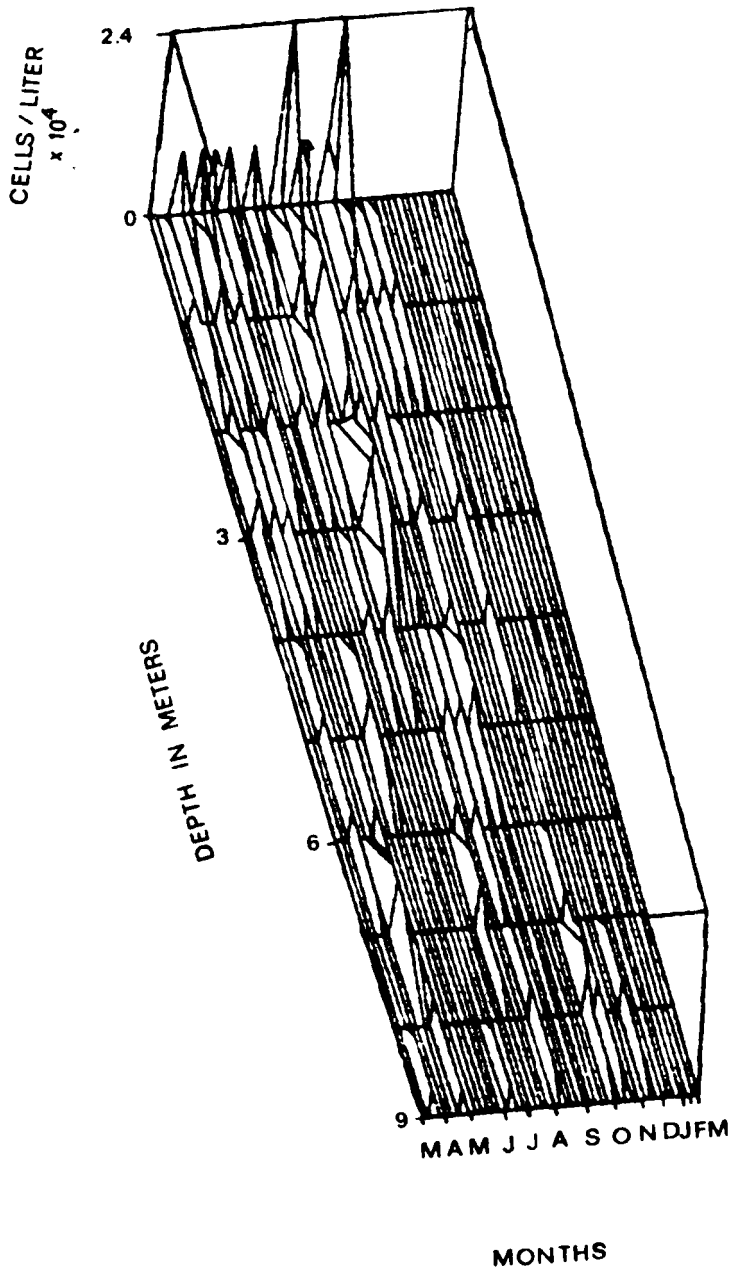

Figure 8. Distribution of the Pyrrhophyta (cells/l).

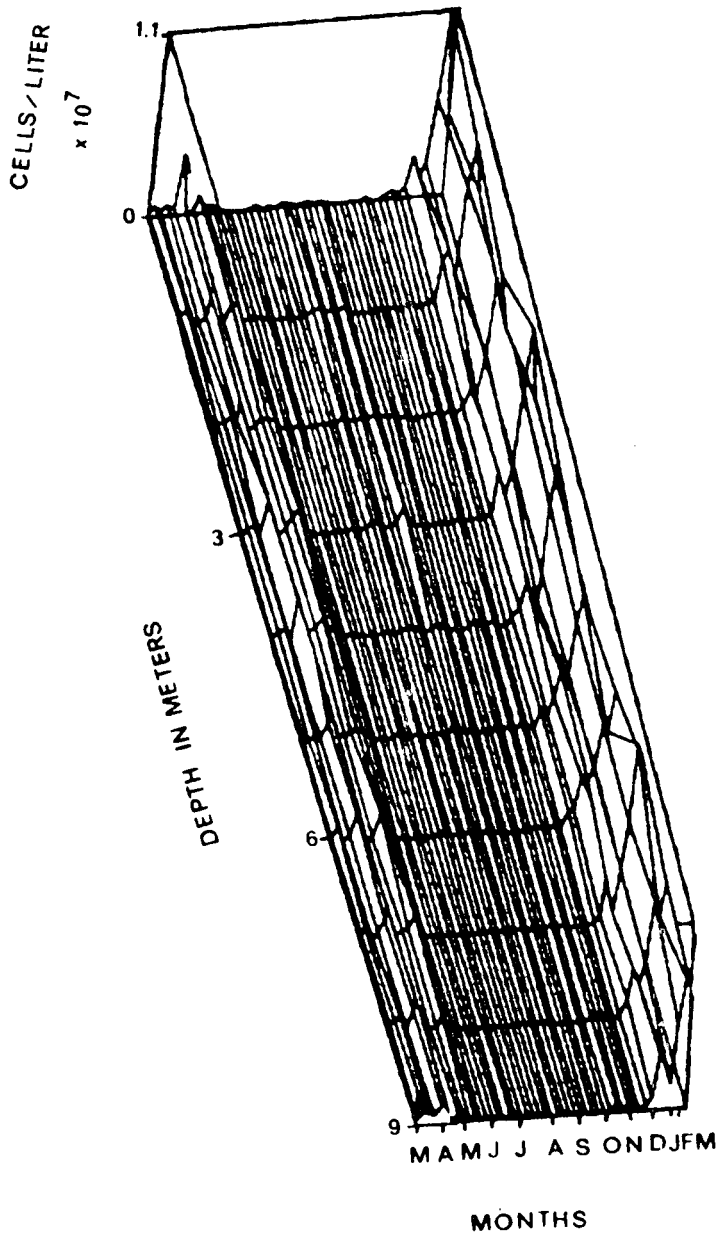

Figure 9. Distribution of the Bacillariophyta (cells/l)

the middle of August. In mid-August, Rhizosolenia sp. appeared in the assemblage. This alga persisted as an important species until mid-September when the autumnal cyanophyte bloom developed. There was an immediate disappearance of the bacillariophytes until after the autumnal cyanophyte bloom when they returned.

In late October, M. granulata once again became the dominant diatom until late November when Navicula spp. replaced this dominance. Abundances of Navicula spp. increased until mid-December when the winter bloom of A. formosa and Fragillaria crotonensis occurred with peak abundances for the sampling period ranging from 8.0×10^4 to 1.1×10^7 cells/l. This diatom assemblage persisted throughout the remainder of the year.

Chrysophyceae

The chrysophytes presented a strong, late winter-early spring peak and then were relatively insignificant for the remainder of the annual cycle (Fig. 10). Peak spring abundances ranged from 1.1×10^5 to 1.3×10^7 cells/l. Uroglena sp. was the single alga comprising this pulse from March until late April when there was a brief contribution from Synura sp. All of the chrysophyta disappeared from the phytoplankton from May until November Mallomonas tonsurata and Mallomonas caudata abundances during November ranged from 0 to 3.2×10^4 cells/l. While these lowered abundance levels clearly were of lesser importance than spring pulse, they comprised a minor fraction of the late fall phytoplankton assemblage.

Cryptophyta

Members of the cryptophyta were the second most ubiquitous phytoplanktons during all seasons (Fig. 11). A spring pulse and a fall bloom

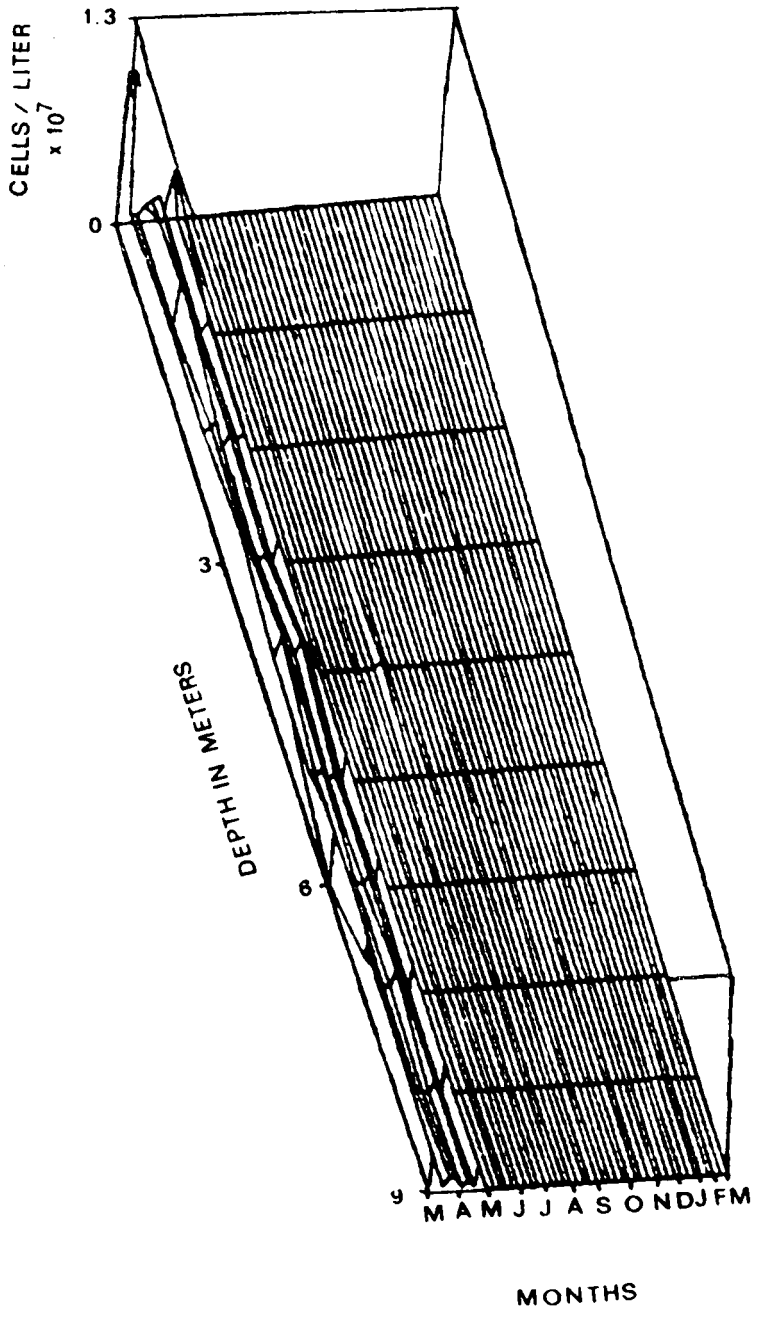

Figure 10. Distribution of the Chrysophyceae (cells/l).

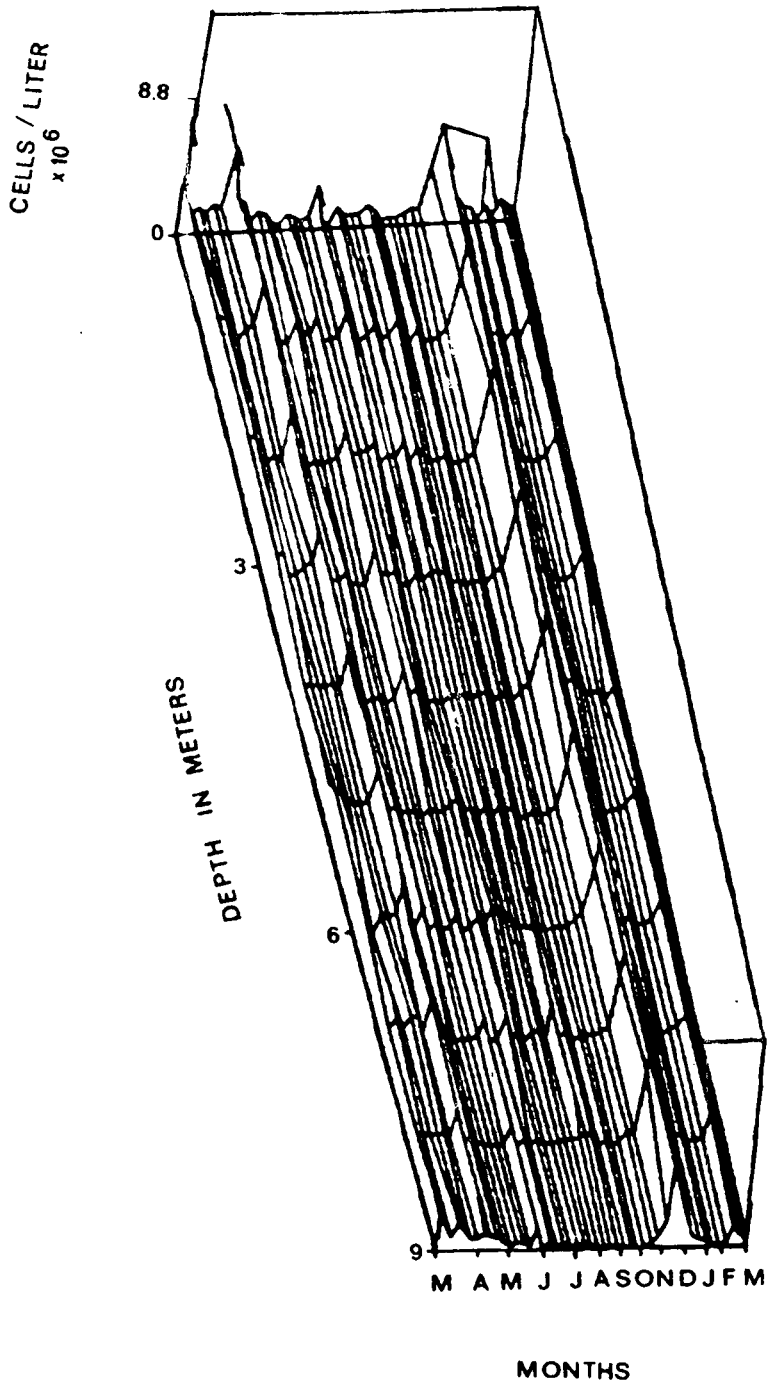

Figure 11. Distribution of the Cryptophyta (cells/l).

are separated by a stable epilimnetic population in the summer. The spring assemblage is dominated by Chroomonas acuta with sub-dominants Cryptomonas erosa and Cry. ovata, there were occasional, minimal contributions from Cry. marsonii. This spring assemblage ranged from 3.0×10^{5} to 4.4×10^{6} cells/l. This assemblage persisted throughout the summer with Chr. acuta gradually declining in abundance. Abundance levels for the cryptophytes during the summer plateau ranged from 7.4×10^{4} to 1.3×10^{6} cells/l.

The stable summer and early fall species abundance levels were truncated by a sudden increase in abundances during the first week in November. This roughly corresponded to the time of total destratification (Rice, 1978). Abundances of the cryptophyta ranged from 1.2×10^{6} to 8.8×10^{6} cells/l. This assemblage was dominated by Cryp. ovalis and Chr. acuta with the latter continuing to decrease in abundance. This pattern was continued in the stable winter assemblage with the same species present but with densities oscillating from 1.5×10^{5} to 1.3×10^{6} cells/l through March. This interim assemblage was comprised chiefly of Cry. ovalis and Chr. acuta. A trend of increasing numbers of Chr. acuta and and decreasing numbers of Cry. ovalis occurred with the onset of the second spring assemblages.

Physical Parameters

Temperature

Lake Fayetteville is a temperate, dimictic lake with stratification developing in the middle of April and becoming clearly defined by the end of May (Fig. 12). Maximum temperatures (approximately 30° C in

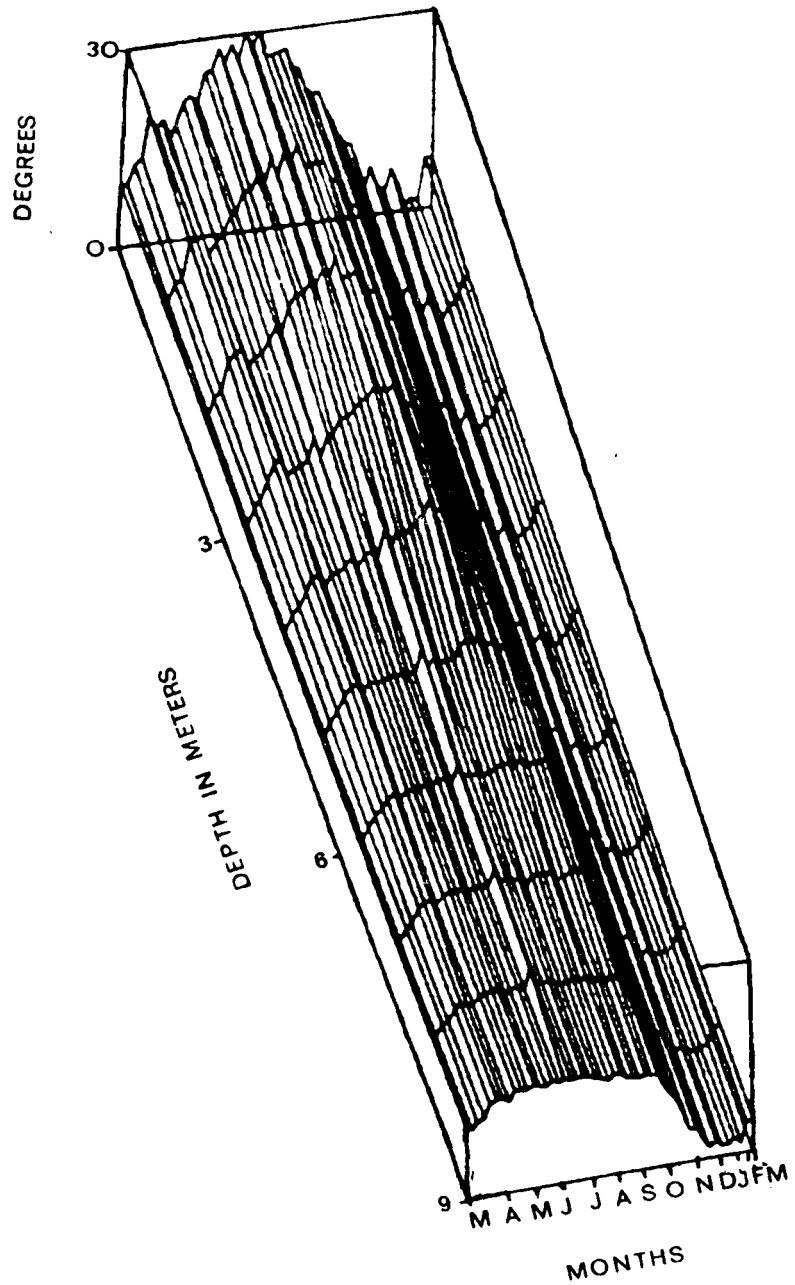

Figure 12. Distribution of Temperatures (^{O}C).

the upper three meters) were observed in late July. Stable stratification occurred during this period with temperatures varying 14 degrees from the epilimnion to the base of the hypolimnion. A well-defined thermocline developed between three and four meters throughout the stratification period. Gradual destratification started in late September and was completed by mid-October. From late October until mid-November the lake was isothermal while cooling from 13 to 11° C.

From the middle of November until the end of December, temperatures fluctuated a maximum of four degrees from week to week. A blizzard caused inverse stratification to develop in January until mid-February under the ice cover. Temperatures at the surface of the lake were two degrees cooler than those in the lower levels. Surface waters cooled to 2° C immediately below the ice with epipelic waters warming to ca. 5° at this time. These temperatures represented the coldest water temperatures during the investigation. Temperatures were characterized by a return to warmer, homogenous water temperatures ranging from 7 to 9° C by the end of February and for the remainder of the investigation.

The temperatures observed in Lake Fayetteville for the sampling program were consistent with those observed in previous investigations. This was the first time that extended inverse stratification in the lake was observed. These lowered temperatures induced conditions which are believed to have caused the presence of Oscillatoria rubesens under the ice cover.

Physio-Chemical Parameters

Dissolved oxygen concentrations during this investigation were high in the spring, stratified with reduced concentrations in the epilimnion and the development of the anoxic hypolimnion below four meters in the summer and followed by a return to increased oxygen concentrations in the fall and winter (Rice, 1978).

Rice (1978) further has observed that hydrogen ion activity showed a general pattern of increased pH in the euphotic zone in the spring and summer followed by overall decreased pH in the fall and winter. Temperature corrected specific conductance values were observed by Rice to be consistant throughout the year. Conductance ranged from 135 to 190 µMHOS throughout the year with the highest values appearing near the bottom muds during the sampling period.

Metals

Iron

All fractions of iron showed a general pattern of low concentrations throughout the water column in the early spring, late fall and winter with a noticeable hypolimnetic accumulation in all fractions during the summer.

Iron-Raw (Fe-R)

An overview of the distributional pattern of the Fe-R fraction shows a low spring concentration which continues in the epilimnion during stratification with accumulations occurring in the hypolimnion (Fig. 16). Fe-R concentrations returned to base levels during the period of destratification and continued at these reduced levels for the remainder of winter.

Fe-R ranged from 14 to 38 ug/l throughout the water column in March. Fe-R increased to approximately 94 ug/l from the lower

waters in early April with decreases to 21 ug/l occurring toward the surface euphotic zone. These conditions persisted until mid-May when nearly homogenous conditions existed throughout the water column with only a slight increase near the soil-water interface. Concentrations fell within the narrow range of 72-166 ug/l in the upper eight meters. The sample immediately above the soil-water interface contained concentrations of 424 ug/l. This suggested a possible movement from the substrate into adjacent waters.

From late May until fall destratification, concentrations in the hypolimnion increased dramatically. By mid-June hypolimnetic iron concentrations accumulated to range from 1600 to 6240 ug/l while epilimnetic concentrations ranged from 85 to 44 ug/l. However, a minor increase was observed in mid-August through mid-September when epilimnetic concentrations of Fe-R ranged from 112 to 1520 ug/l. Epilimnetic concentrations once again declined to 40 to 200 ug/l through early October while concentrations reached a maximum of 22,280 ug/l near the bottom during the first week in October.

Accompanying destratification in mid-October, Fe-R concentrations generally declined throughout the water column. Fe-R increased in the upper six meters while it decreased in the lower three meters. These upper waters contained from 220 to 400 ug/l, while waters immediately above the soil-water interface contained 14,000 ug/l. Gradual diffusion of Fe-R was observed throughout the water column until a consistent range of from 50 to 200 ug/l was noted from mid-November until the end of the investigation.

Rice (1978) has examined the epilimnetic-euphotic portion of iron distributions and found no variations in the epilimnetic concentrations that could have been suppressed by the higher hypolimnetic

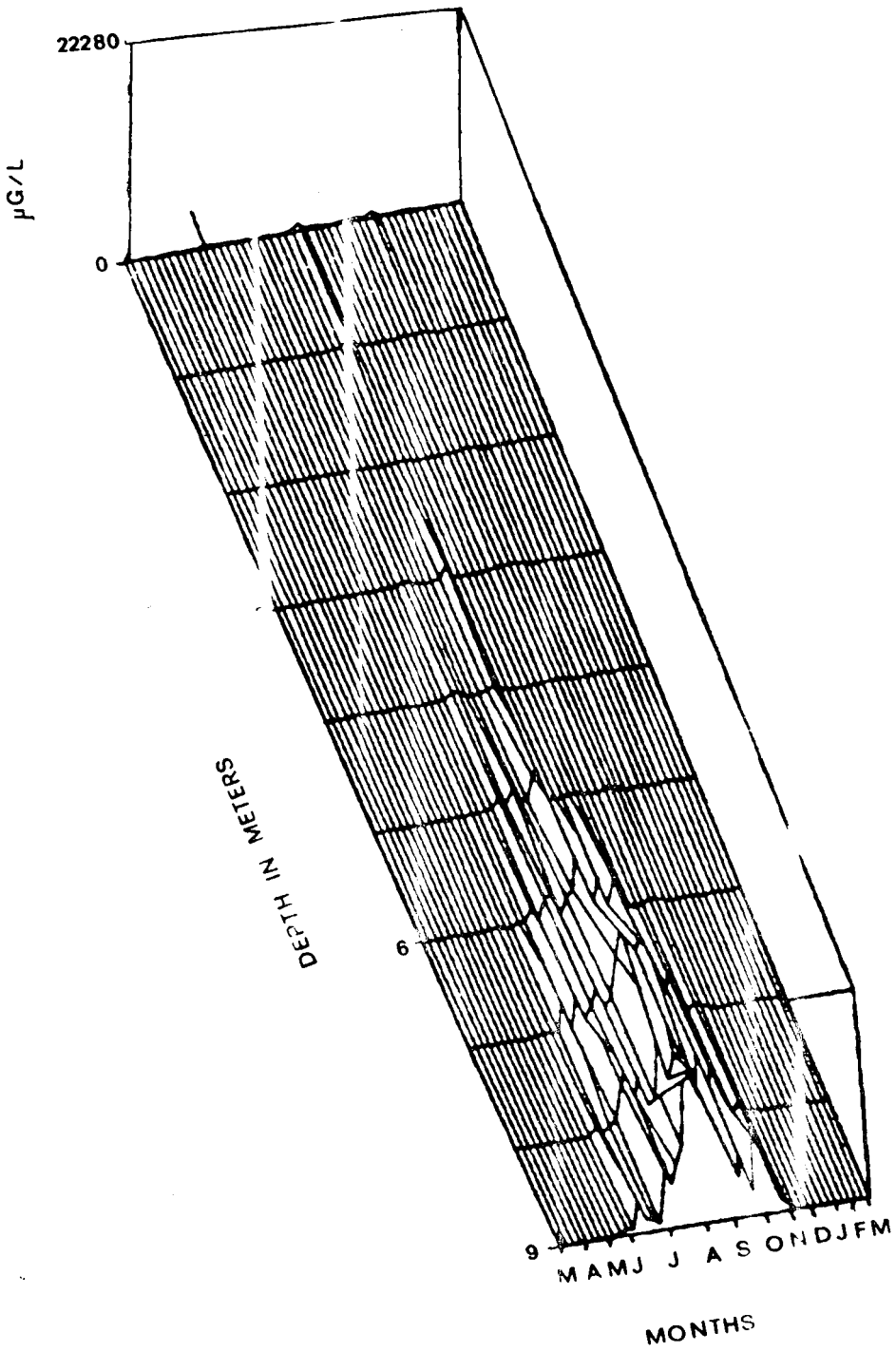

Figure 16. Distribution of Raw Iron (µg/l).

iron levels. Of interest is the accumulation of the Merismopedia-Oscillatoria-Euglena sub-assemblage in the region of iron accumulation in the lake. This might indicate iron tolerance on the part of these algae.

Iron-Filtered (Fe-F)

While general distributions of Fe-F concentrations are similar to those of the raw fraction, stratification of this fraction occurred later than for Fe-F (Fig. 17). Concentrations ranging from 5 to 76 ug/l occurred randomly throughout the water column from March through mid-May. In mid-May a gradual increase of Fe-F began in the hypolimnion with accumulations ranging from 1280 to 6200 ug/l by mid-August. Summer euphotic concentrations typically ranged from 88 to 114 ug/l during the entire season with peak Fe-F concentrations of 12,000 ug/l attained at six meters during the last week in August. The above concentrations persisted until mid-October when gradual destratification occurred resulting in concentrations from 95 to 230 ug/l. Redistribution of Fe-F throughout the waters continued until early November when concentrations ranged from 60 to 90 ug/l. Levels of Fe-F varied little from this time until the end of the sample program.

The later development of stratification of Fe-F may indicate that the differences in the raw and filtered fraction may be due to iron accumulation by algae. Generally lowered Fe-F concentrations than in Fe-R also seem to confirm this hypothesis.

Iron-Particulate (Fe-P)

Particulate iron ranged between 0 to 87 ug/l from March until the first week in April. From mid-April until the second week in May, Fe-P concentrated in the range from 12 to 1570 ug/l. A typical concentration in mid-May was approximately 200 ug/l with the values

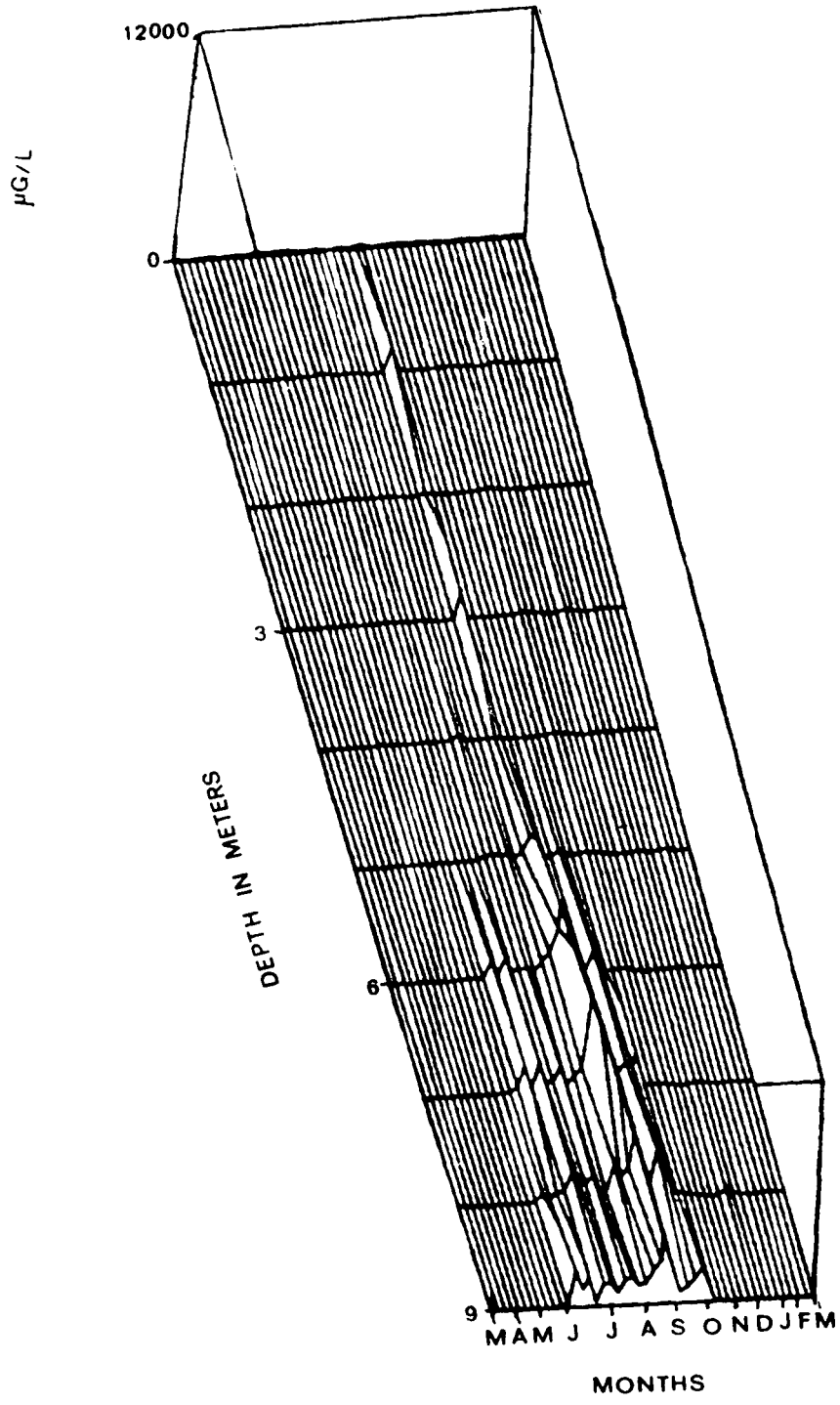

Figure 17. Distribution of Filtered Iron (µg/l).

in the higher end of the range appearing near the soil-water interface.

Corresponding to the mid-May spring cyanophycean peak, Fe-P ranged from 0 to 24 ug/l in the epilimnetic waters. Waters below this zone contained 56 to 256 ug/l. Concentrations remained within this range until after the first week of June.

Fe-P concentrations increased to a range of 170 to 7760 ug/l by the second week of June and continued at this level through the end of the month. In early July reduced euphotic-epilimnetic Fe-P concentrations were observed ranging from 0 to 236 ug/l, with increased hypolimnetic concentrations present from five meters to the lake bottom. These hypolimnetic concentrations ranged from 300 to 4470 ug/l and persisted until the end of September.

In early October, average particulate iron concentrations declined throughout the water column. Concentrations ranged from 260 to 1020 ug/l by the end of October. Concentrations continued in this range until early December when Fe-P decreased to the range of 220 to 620 ug/l throughout the water. Concentrations then immediately declined to a range of 9 to 170 ug/l until the end of January. Fe-P increased from 94 to 200 ug/l in early February where it remained until the end of the sampling period.

These fluctuations in the epilimnetic concentrations occur at times that may be associated with changing algal assemblages. This association is obvious particularly during the summer regimes. The hypolimnetic development may be due to detritus and/or insoluble forms of the metal retained by the filters. Of specific interest is the appearance of iron in the particulate form during the winter diatom assemblage. Further evaluations of these observations are necessary.

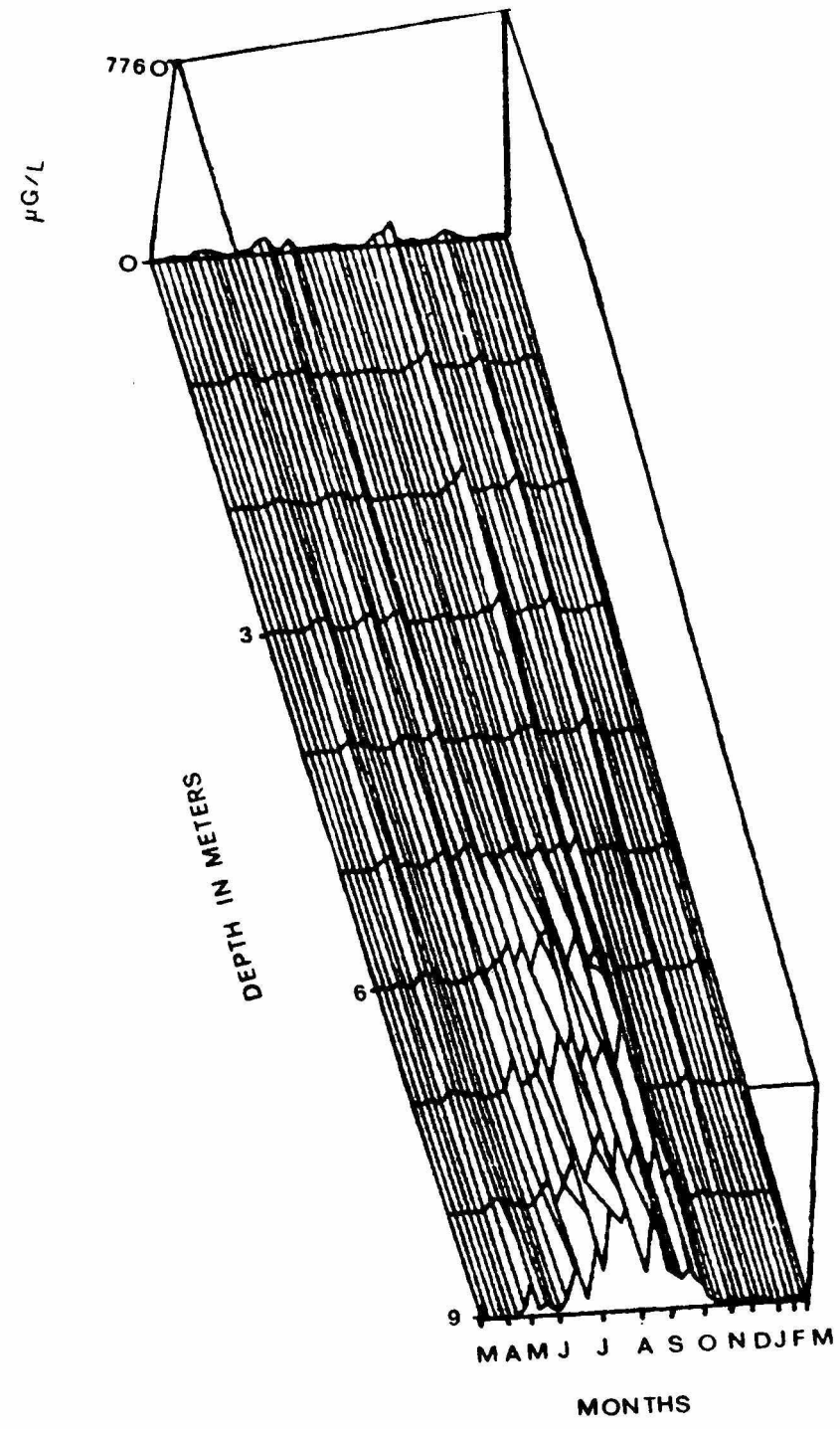

Figure 18. Distribution of Particulate Iron (µg/l).

Manganese

Manganese concentrations in the raw and filtered water fractions are very similar in profile to iron. These relations may be expected due to the equivalent chemical properties of these two metals. In the particulate fraction, large differences will be noted.

Manganese-Raw (Mn-R)

Low concentrations were observed during the spring only to be isolated in the epilimnion during summer stratification with accumulations of manganese occurring in the hypolimnion. A return to lower concentrations occurred throughout the water column following destratification. Concentrations ranged from 6 to 62 ug/l from surface to one meter off bottom from March through mid-April. The exception to this range was the sample above the soil-water interface which was from 100 to 200 ug/l during this period. In mid-April these increased concentrations began to migrate upward and by early May concentrations increased to between 61 and 240 ug/l throughout the water column.

A pattern of decreased epilimnetic concentrations and increased hypolimnetic levels developed in mid-May. Epilimnetic concentrations ranged from 18 to 28 ug/l while hypolimnetic concentrations were from 80 to 800 ug/l. This pattern and accompanying increasing concentrations continued from mid-May to mid-October. In mid-August when peak Mn-R concentrations of 10,560 ug/l were reached in the hypolimnion, epilimnetic concentrations ranged only from 64 to 200 ug/l.

Total manganese (Mn-R) in late October ranged consistently from 530 to 910 ug/l with the exception of a peak of 2000 ug/l near the bottom. Manganese declined slowly to a range of 284 to 360 ug/l by mid-November. A precipitous decline occurred with the onset of

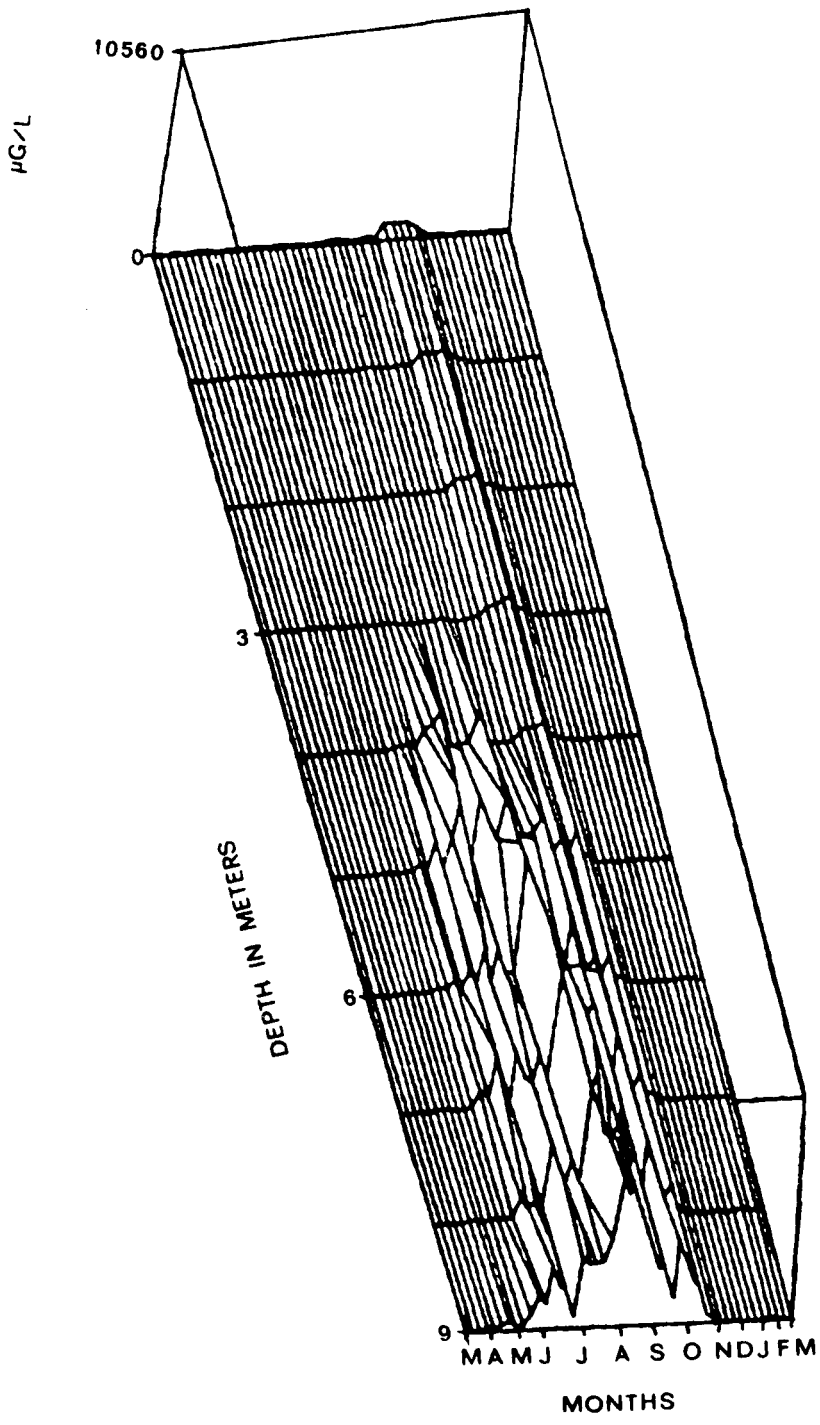

Figure 19. Distribution of Raw Manganese (µg/l).

winter, ranging typically from 31 to 175 ug/l throughout the remainder of the sampling period.

Of importance is the characteristically low epilimnetic concentration pattern with increased hypolimnetic concentrations that were recorded for both iron and manganese. While the elevated hypolimnetic concentrations may be due to redox chemical reactions (Rice, 1978), it is notable that while iron increased during various periods in the epilimnion, manganese did not, with the exception of the period corresponding to destratification. Further investigations may be necessary.

Manganese-Filtered (Mn-F)

A distribution pattern similar to that previously described for iron and Mn-R was also evident for soluble manganese (Mn-F) during the investigation period. From March until early April, manganese in the soluble fraction ranged from 3 to 73 ug/l (Fig. 20). Slight accumulations from 100 to 114 ug/l appeared in the lower depths of the lake between seven meters and the bottom. These concentrations persisted until mid-May when concentrations above seven meters ranged between 10 and 48 ug/l and soluble manganese below this depth ranged from 190 to 2000 ug/l. Higher hypolimnetic concentrations gradually extended upward in the water column with a range from 1000 to 4000 ug/l by the end of June. Epilimnetic concentrations ranged from 16 to 24 ug/l during this period and for the entire summer. Soluble manganese accumulated at five meters and below while increased concentrations occurred at three to four meters in the raw fraction. This may be of interest for further examination.

The pattern of lowered epilimnetic levels with increased hypolimnetic concentrations persisted until the end of October.

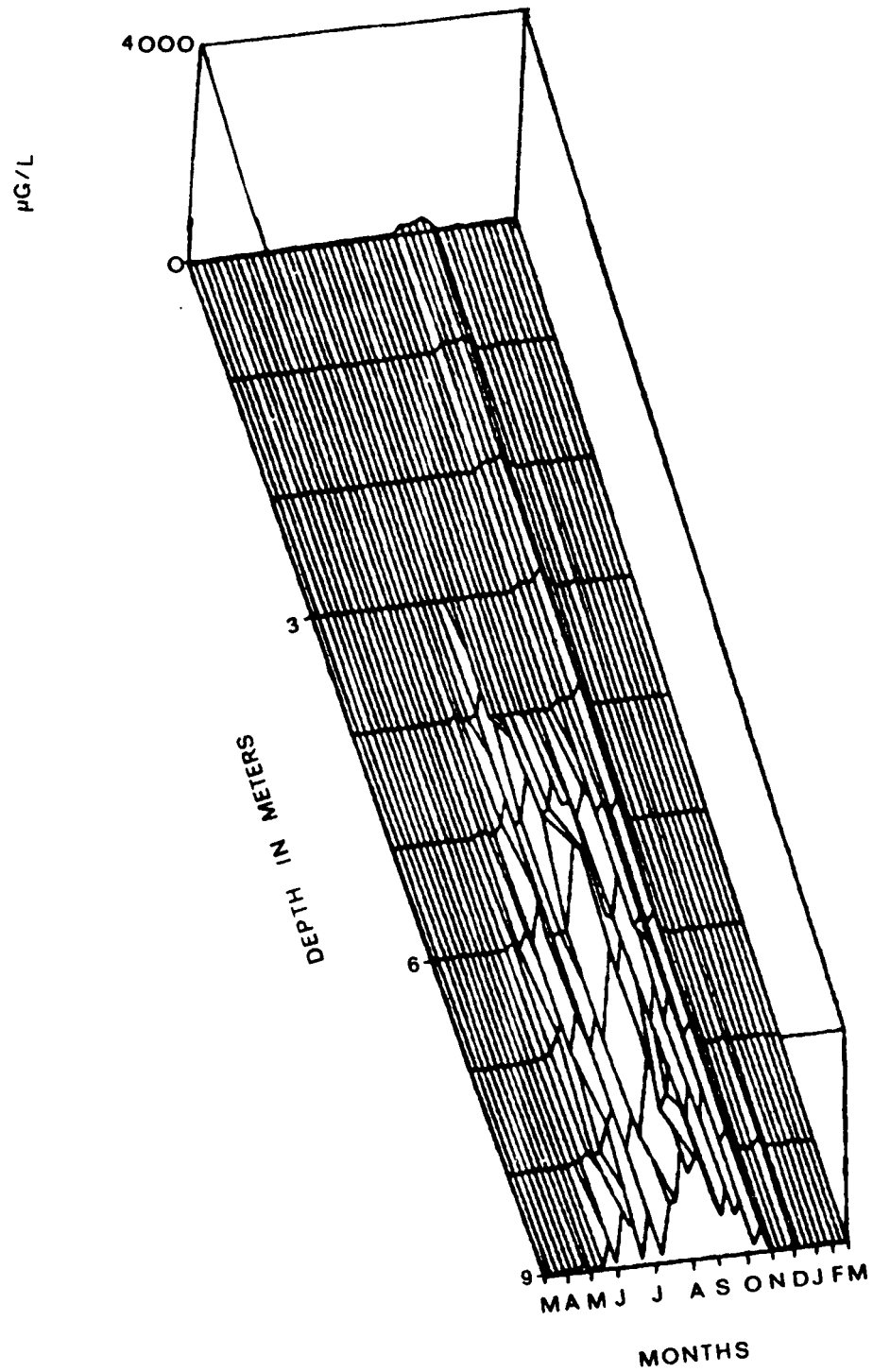

Figure 20. Distribution of Filtered Manganese (µg/l).

Early November levels decreased to near homogeneity from 400 to 570 ug/l throughout the lake. Concentrations declined precipitously to from 26 to 50 ug/l in mid-November and continued to decline the rest of the month to a range of 16 to 21 ug/l. The concentrations increased to between 166 and 660 ug/l the first week in December, followed by an immediate decline to the earlier range. Concentrations for the remainder of the winter period were from 10 to 100 ug/l. The increase in Mn-R which developed in the metalimnion at three to four meters is of particular interest. With this exception the filtered manganese concentration distributions were found to be similar to those of total, soluble and particulate iron and total manganese fractions.

Manganese-Particulate (Mn-P)

Particulate manganese concentration distributions depart noticeably from those of the fractions previously described. Concentrations generally increased through the spring and summer to peak during the autumn. Concentrations then declined to low winter and early spring minima.

Insoluble manganese (Mn-P) ranged from 6 to 137 ug/l through mid-April (Fig. 21). Accumulations to a range of 67 to 137 ug/l occurred in mid-April and continued through mid-May. This correlated with a build-up in cell numbers of the spring cyanophycean assemblage. Increased concentrations of Mn-P at the three to five meter level of the lake were observed in mid-May. Concentrations generally ranged from 196 to 480 ug/l at these depths. This range continued throughout the summer. This accumulation occurred in synchrony to a development of cyanophycean algae in this region of the thermocline. In late September increased concentrations were observed throughout the

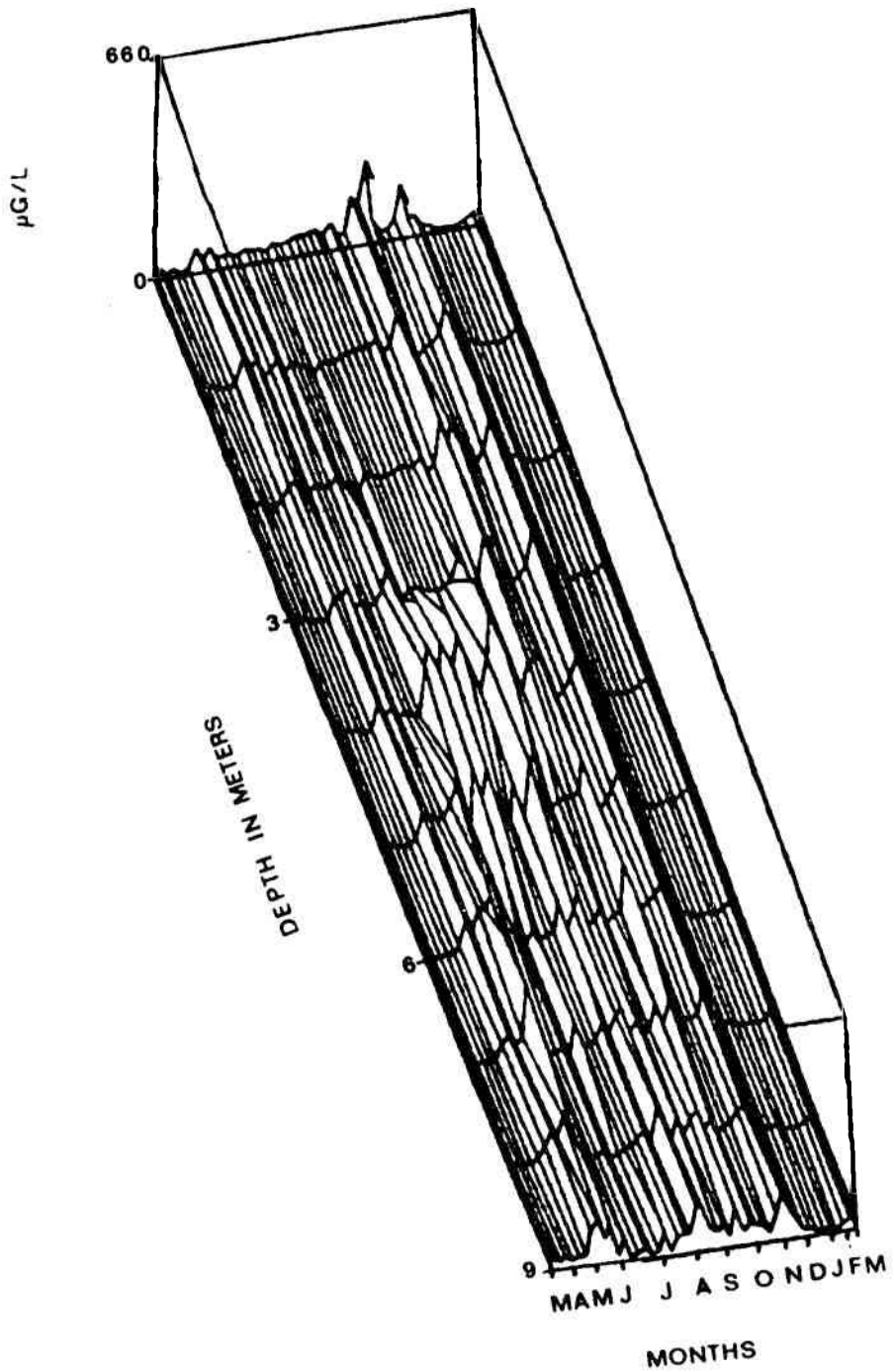

Figure 21. Distribution of Particulate Manganese (µg/l).

entire lake. Concentrations were from 67 to 398 ug/l until mid-October. This was also correlated with an increase in cyanophyte algal cell numbers. Insoluble manganese decreased in late October to a range from 34 to 92 ug/l.

Increased concentrations between 68 to 112 ug/l occurred during early November and by mid-month had gradually increased to between 116 and 210 ug/l. A decline to a range of 66 to 80 ug/l was observed by the end of November. Insoluble manganese decreased to between 8 and 51 ug/l in early December and persisted at these concentrations for the remainder of the sampling period.

The gradual increase of manganese in the particulate form in the spring corresponds to a general increase in algal cell numbers and, in this case, these cells are blue-green algae. It is important to note that peaks of manganese at three to five meters correspond to the difference in the raw and filtered manganese samples. This peak is associated with the development of a metalimnetic algal population and a rapid change in water density. The thermocline is believed to act as a membrane retarding diffusion and passage of ions and gasses across this barrier and it was observed that in Lake Fayetteville many cyanophytes fall into this zone during the higher summer temperatures and "ride" thermocline. These observations and the increased particulate manganese concentrations during the peaks of the three cyanophyte blooms seem closely related. Increased fall levels of insoluble manganese are correlated with increases in blue-green cell numbers and associated with destratification and the subsequent redistribution of detritus throughout the water column.

Cobalt

Ionic cobalt concentrations generally varied between 0 and 47 ug/l throughout the sampling period. Distributions are similar in the raw and filtered fractions. A general pattern of increasing cobalt throughout the study period was observed until the winter when a decline in total and soluble cobalt occurred. Lower average concentrations in the particulate fraction were observed during late summer and early winter periods.

Cobalt-Raw (Co-R)

Co-R ranged from 1 to 41 ug/l throughout the sampling period (Fig. 22). Concentrations in March increased throughout the lake from an initial range of 5 to 10 ug/l in early March to a final range of 13 to 26 ug/l by the end of the month. Total cobalt ranged from 10 to 22 ug/l in the lake from April through mid-May.

In the middle of May concentrations of cobalt ranged from 11 to 154 ug/l, corresponding to the peak in cyanophycean abundances. Co-R was nearly inversely proportional to the cyanophycean algal abundances. The week following the bloom peak, raw water samples contained 13 to 20 ug/l of cobalt. This range then declined dramatically to from 3 to 12 ug/l during late May. Concentrations continued within this lowered range until mid-June, after which concentrations increased to a range of from 13 to 20 ug/l.

Co-R continued to increase to from 20 to 30 ug/l until after the first week in August when concentrations once again declined to from 11 to 17 ug/l by mid-August. These decreases and reduced concentrations were observed during the onset and development of the autumnal cyanophyte maxima. Cobalt remained stable until late September when concentrations ranged from 18 to 25 ug/l. This was

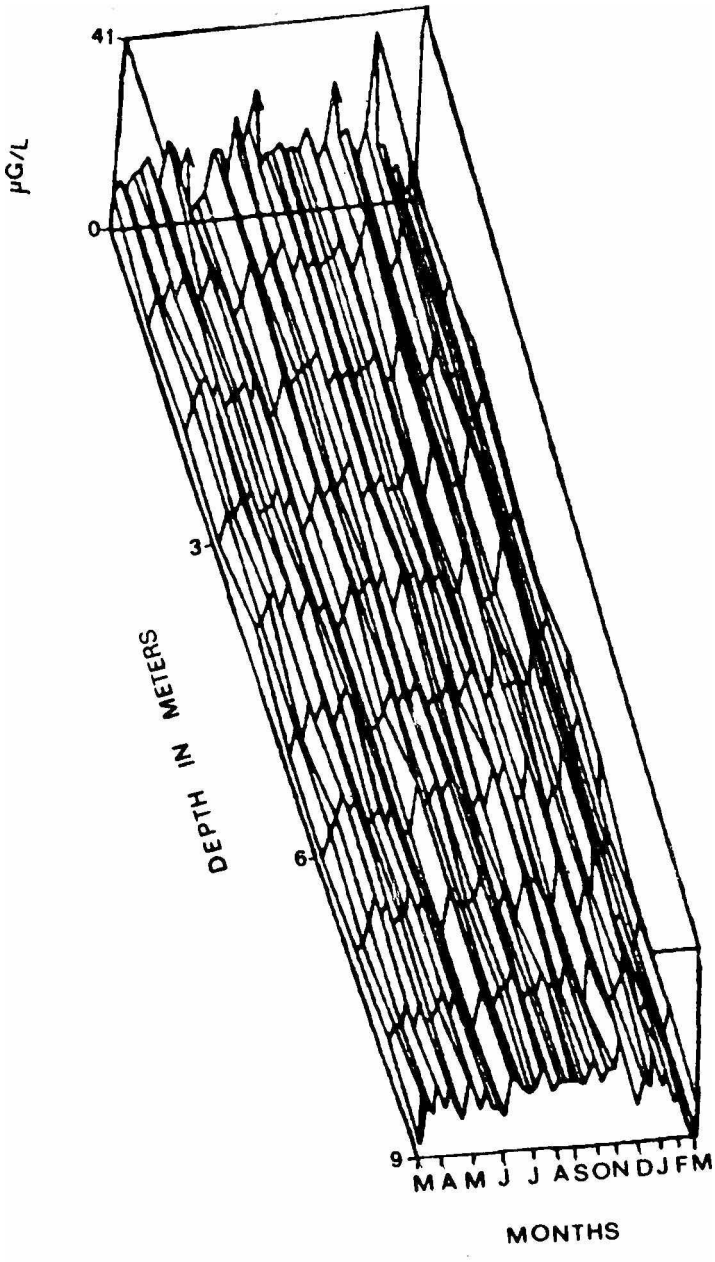

Figure 22. Distribution of Raw Cobalt (µg/l).

followed by a decline to 11 to 20 ug/l in early October with a brief increase in cobalt associated with lake destratification to increase the range to between 26 and 41 ug/l by mid-October.

Concentrations in early November immediately declined to a range of 16 to 24 ug/l, and remained constant there until the second week of December when levels of this metal increased to between 36 and 46 ug/l but by the end of December cobalt had declined to a range of 13 to 19 ug/l. These concentrations continued to decline for the remainder of the study to a range from 1 to 10 ug/l.

The mid-May decrease of cobalt corresponds to the peak of the Cyanophyta bloom. Gradual increases in the concentrations and the stable summer concentrations in this fraction may be due to a steady-state input of cobalt from dying cyanophycean algae. As noted, the fall pulse of higher concentrations appears to correspond to an addition of the metal by destratification. Of particular interest is a peak of cobalt concentrations in December, at a time which corresponds to an increased diatom population. Of further interest is that some diatoms are known to release cobalt in the form of Vitamin B_{12} to their surrounding environment. Preliminary evidence would seem to confirm this phenomenon occurring in a natural aquatic ecosystem (Rice, 1978).

Cobalt-Filtered (Co-F)

Cobalt in the filtered fraction ranged from 5 to 47 ug/l throughout the year. This indicated the presence of soluble colbalt in the environment at levels observed by most investigators to be adequate for culture maintenance. The Co-F followed concentration distribution patterns similar to those outlined for the raw fraction.

Soluble cobalt (Co-F) ranged from 50 to 20 ug/l from March until

the first week in June. Concentrations then declined to a range from 5 to 11 ug/l and remained stable until late June, gradually increased to range from 25 to 30 ug/l by the first week in August. Soluble cobalt declined sharply to range from 0 to 15 ug/l in mid-August, only to return to between 18 and 21 ug/l by the end of October. Again, corresponding to the time of destratification, concentrations increased to between 20 and 34 ug/l.

Soluble cobalt declined in November to a range of 9 to 17 ug/l and continued within this range until mid-December. In mid-December concentrations peaked for the sampling period in a range from 20 to 47 ug/l and correlated to the bacillariophycean increase. Cobalt gradually decreased in the filtered fraction to a range of 0 to 9 ug/l from early January to the end of the sampling program.

Soluble cobalt decreased during the cyanophycean bloom in the spring, remained constant during the summer, increased destratification, and increased again during the diatom assemblage. This correlation suggests secretion of a cobalt complex by the bacillariophytes and its probable utilization by the spring assemblage (Rice, 1978).

Cobalt-Particulate (Co-P)

Particulate cobalt (insoluble) distributions are approximately inverse to the raw and filtered fractions (Fig. 24). Co-P ranged from 0 to 22 ug/l throughout the sampling period. A consistent background concentration was recorded throughout the year with the exception of late summer when maximum concentrations were reported in August. This was followed by a decline in Co-P during the fall and a later increase in the late winter-early spring samples.

Spring and early summer levels of Co-P ranged from 0 to 13 ug/l where they persisted until the end of August when concentrations

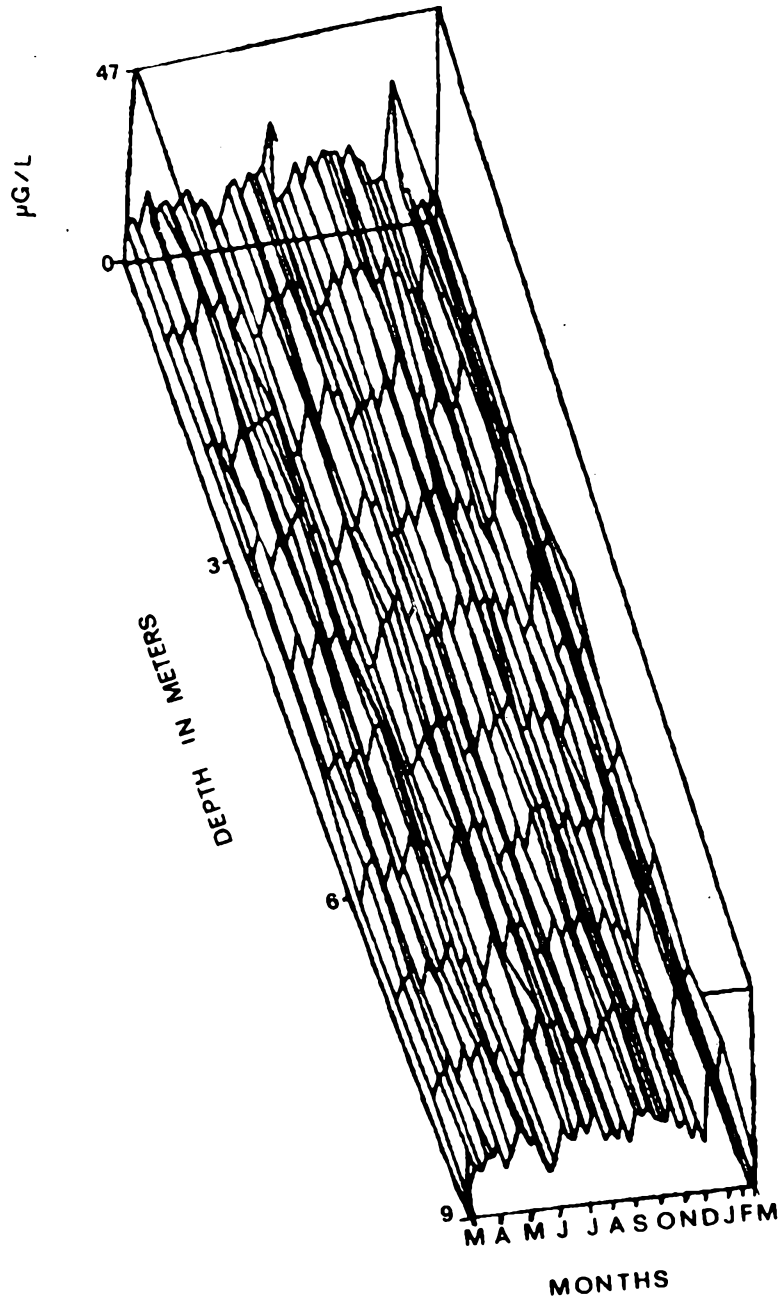

Figure 23. Distribution of Filtered Cobalt (µg/l).

increased to 6 to 22 ug/l. This increased range was evident until the middle of September and correlated with the seasonal autumn bloom of cyanophycean algae. Concentrations in late September declined drastically to 0 to 13 ug/l where they remained through the middle of November. In mid-November concentrations declined again to range from 0 to 3 ug/l through the end of December when levels increased to from 5 to 13 ug/l. The concentrations then remained at this range for the remainder of the sampling period.

Three notable events were observed in Co-P fraction: (1) steady concentrations of cobalt appeared in the insoluble fraction during the spring cyanophycean bloom; (2) an increased amount of cobalt was present during the autumn cyanophycean bloom; and (3) increased amounts of cobalt appeared in the algae of the late winter assemblage. The variations in Co-P concentrations correlate with phytoplankton dynamics. The data suggest that the autumn assemblage may actively incorporate cobalt while it is secreted by the early bacillariophycean assemblage and utilized by the succeeding winter assemblage.

Zinc

Zinc concentrations showed major difference in the raw, filtered and particulate fractions.

Zinc-Raw (Zn-R)

An overall trend toward increasing zinc concentrations was observed throughout the sampling period with zinc concentrations for the entire sampling regime ranging from 3 to 490 ug/l (Fig. 25). Concentrations in the spring generally ranged from 11 to 52 ug/l and were within this range until the end of May. Later Zn-R increased to a range of 14 to 490 ug/l in early June with the higher concentrations observed near the epipelic zone. Zn-R rapidly declined during

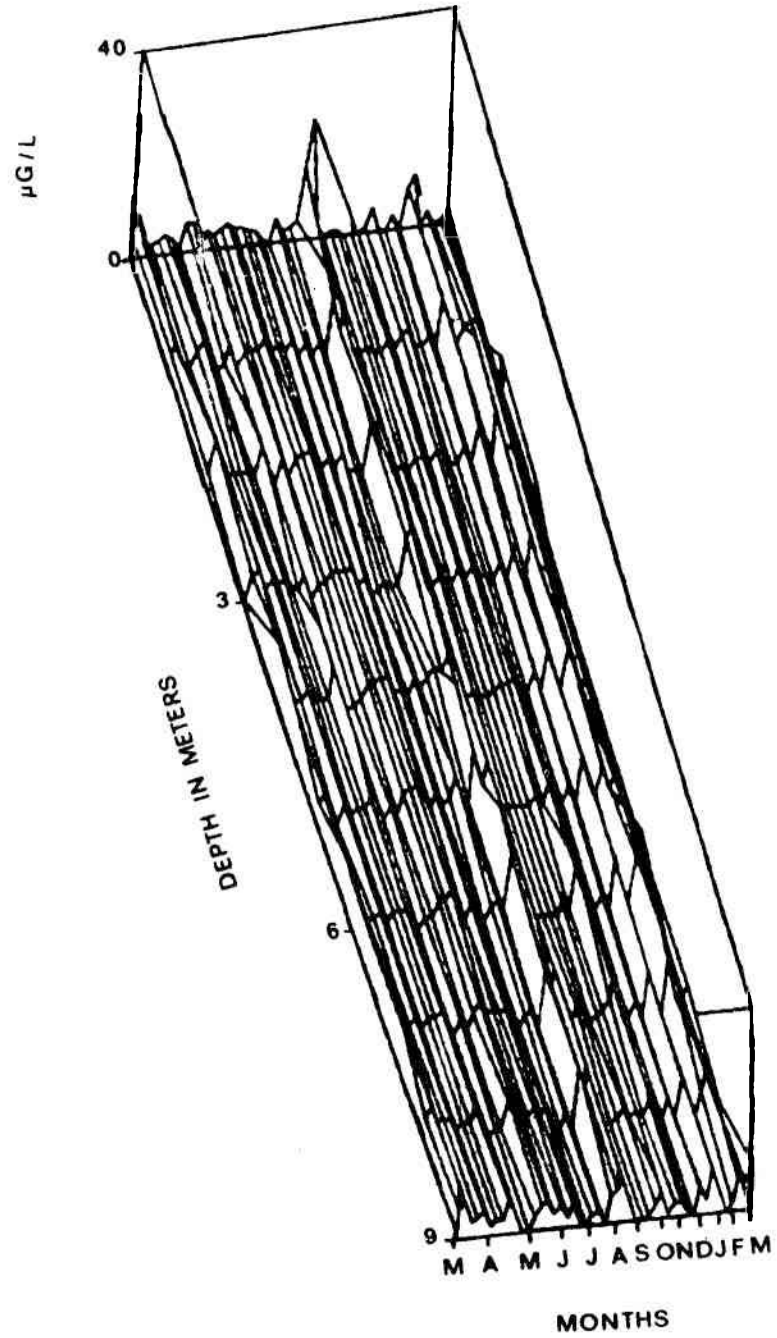

Figure 24. Distribution of Particulate Cobalt (µg/l).

the second week in June to from 3 to 11 ug/l with nominal ranges from 25 to 40 ug/l again attained by the mid-June and persisted until early December. A small increase to 33 to 100 ug/l developed during mid-December with a return to 31 to 46 ug/l during late January. These concentrations of Zn-R persisted until late February. A short-lived minor peak, within a range of 30 to 70 ug/l, occurred in late February and was followed by an immediate decline to 22 to 32 ug/l by the first week of March.

Zn-R showed no clearly defined relationships to any of the algal groups. Gradual accumulations of this metal over the year may be due to solubility or other physico-chemical interactions and must be evaluated further with respect to the entire algal community (Rice, 1978).

Zinc-Filtered (Zn-F)

Zinc in the filtered fraction (soluble zinc) proved much more erratic in distribution than that of the raw fration (Fig. 26). However, concentrations from 3 to 100 ug/l occurred and showed the same trend as the Zn-R of increasing concentrations as the season progressed.

Soluble zinc remained in the range from 10 to 38 ug/l until the end of April when concentrations increased in the upper four meters to a range of 48 to 64 ug/l and waters below the euphotic zone contained lower concentrations similar to those of early spring. There was a return to the lower zinc ranges from 13 to 40 ug/l during mid-May. These concentrations were observed throughout the water column.

Concentrations of soluble zinc from 27 to 128 ug/l declined from the first week in June to a range of 3 to 37 ug/l by the second week. Zn-F then increased to a range of 33 to 91 ug/l where the

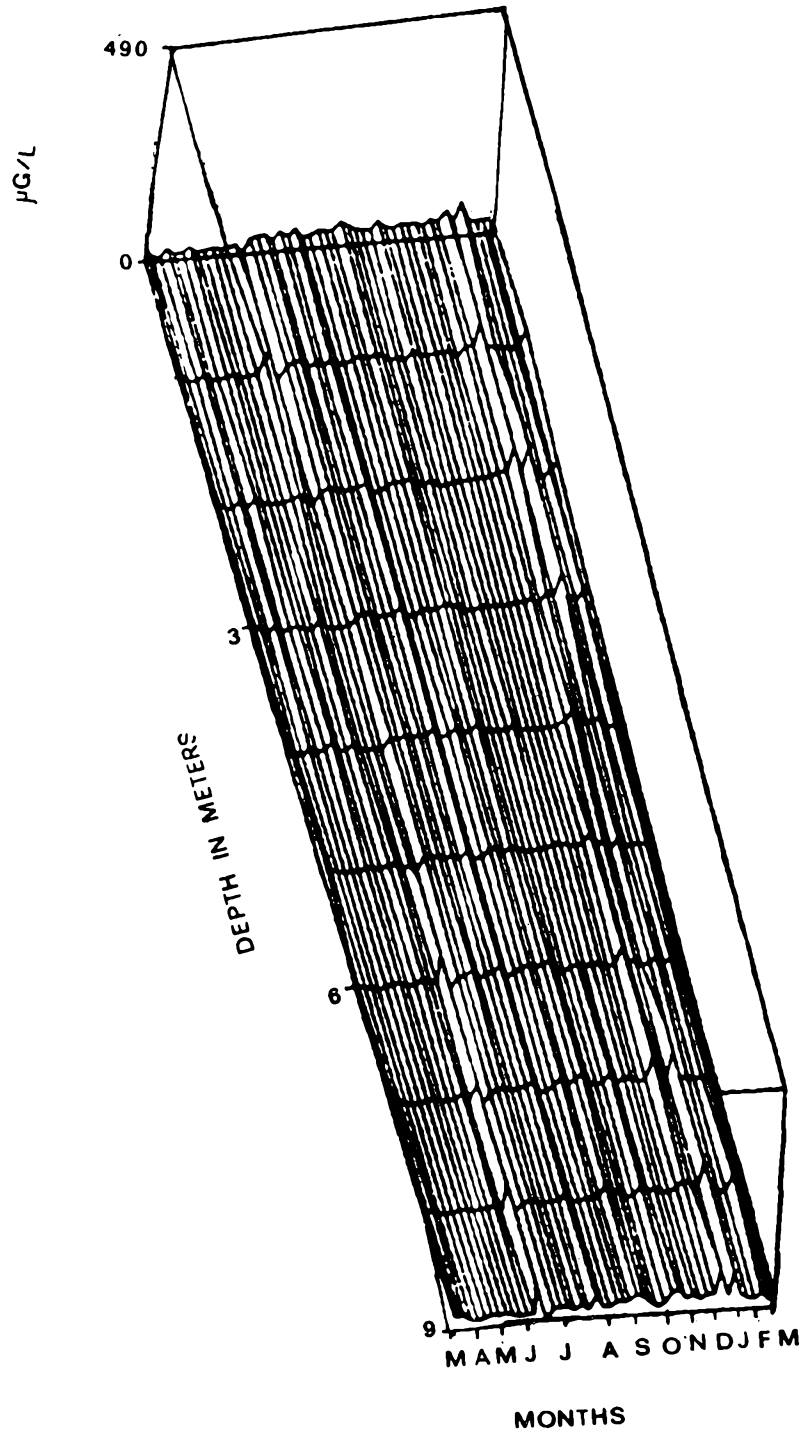

Figure 25. Distribution of Raw Zinc (µg/l).

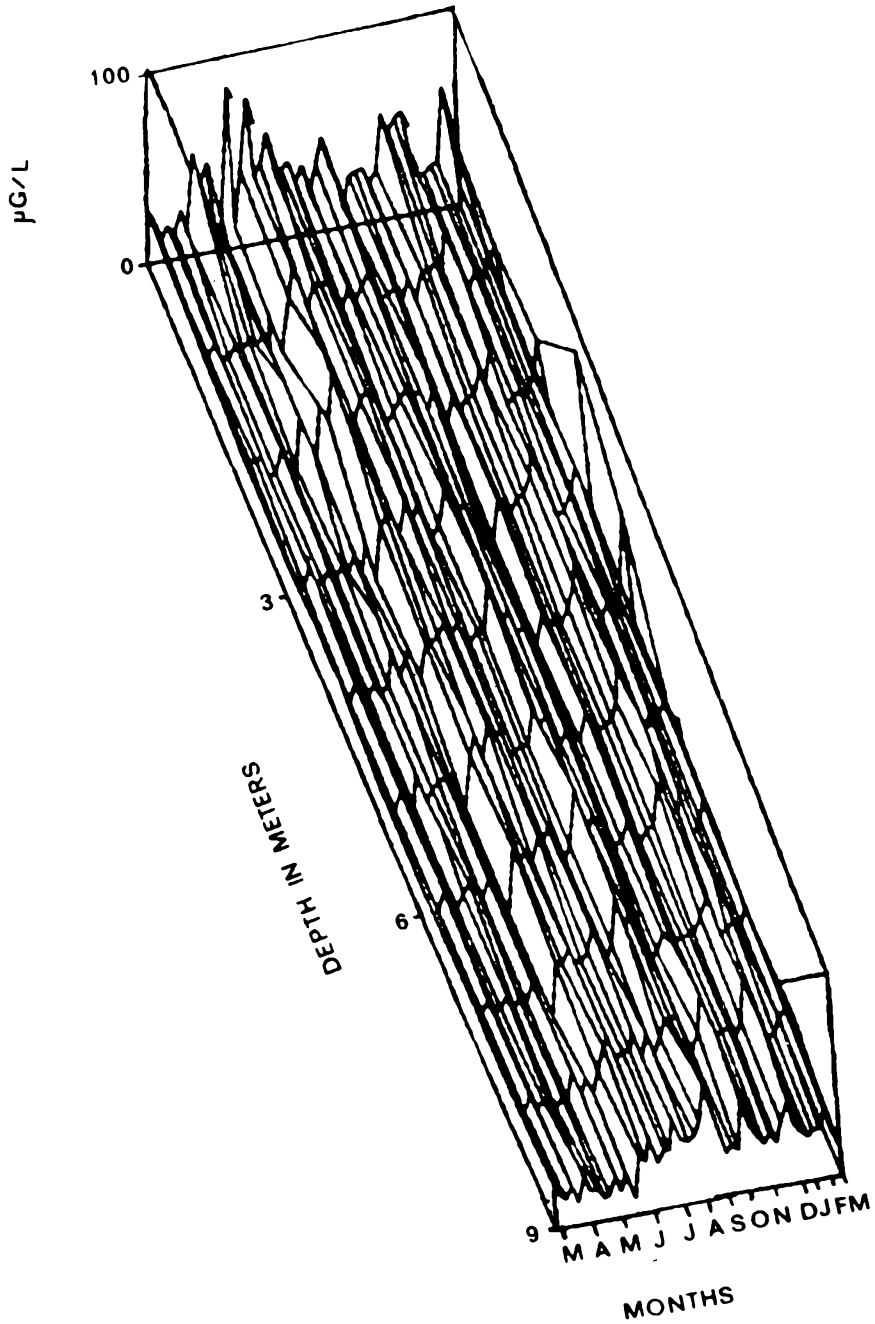

Figure 26. Distribution of Filtered Zinc (µg/l).

concentrations remained constant until early September. Zn-F declined in concentrations to between 30 and 43 ug/l in mid-September where soluble zinc concentrations remained until mid-November.

Zn-F concentrations once again increased to 31 to 56 ug/l in mid-November and continued to increase to 40 to 100 ug/l by early December. Concentrations then gradually declined throughout the water column to between 26 and 90 ug/l for the remainder of the sampling program.

Detailed examination of differences in concentration ranges between the raw and filtered fractions of zinc samples revealed no contamination from procedural sources. It is believed that differences in the sample concentrations of this metal is due to cell rupture during filtration procedures. No clearly defined patterns for the filtered fraction of zinc corresponding to algal assemblage dynamics were apparent.

Zinc-Particulate (Zn-P)

Particulate zinc, with the exception of one epilimnetic sample, ranged from 0 to 46 ug/l throughout the year (Fig. 27). Zn-P concentrations were absent until mid-April when a range from 0 to 45 ug/l was observed. These concentrations remained until the end of April when Zn-P disappeared. No increases of particulate zinc were observed until mid-June when levels ranged from 0 to 17 ug/l. Concentrations of Zn-P remained in these ranges until mid-July when detectable zinc once again disappeared from the particulate form.

In early September there was an anomalous peak of zinc in the surface sample at a concentration of 100 ug/l. Otherwise, zinc was

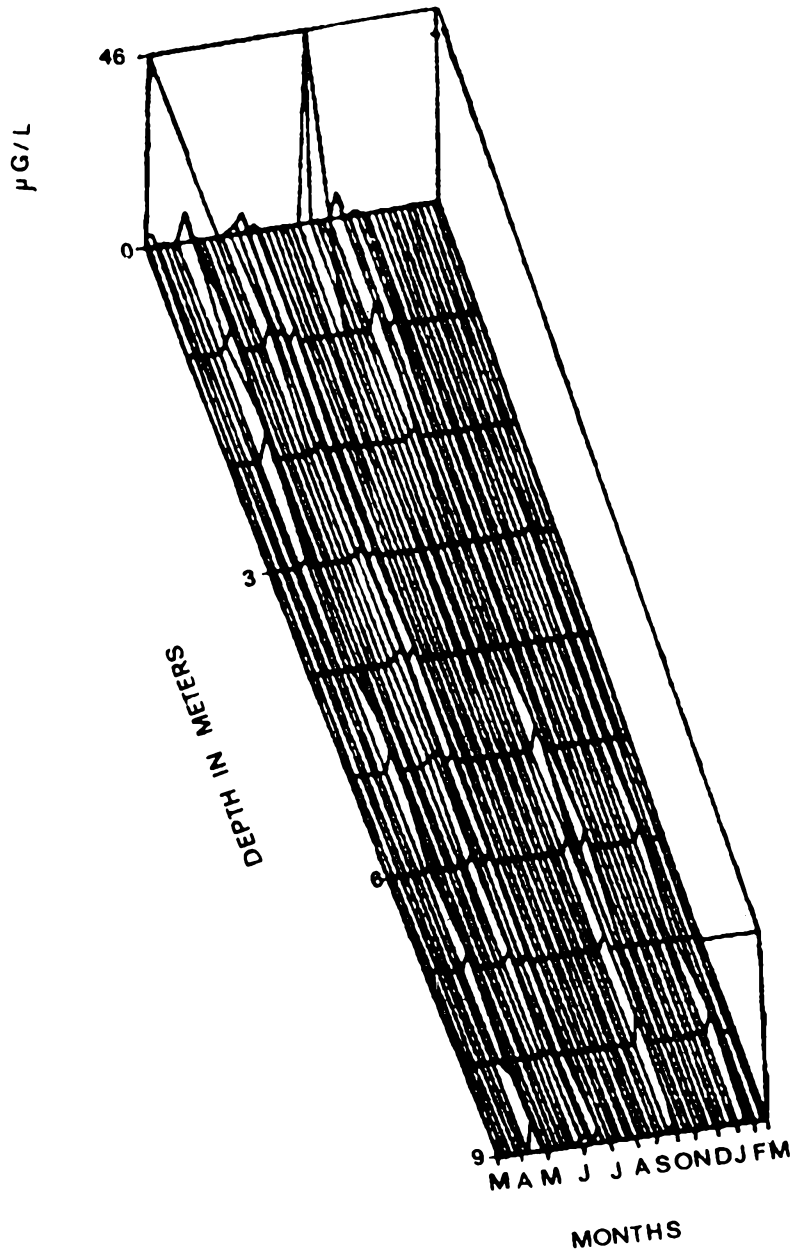

Figure 27. Distribution of Particulate Zinc (µg/l).

absent until early October when Zn-P appeared in concentrations up to 37 ug/l. Zn-P once again disappeared at the end of October and was virtually absent for the remainder of the sampling period.

Zn-P appears at the initiation of the spring and fall blue-green algal assemblages. The second, mid-summer appearances also are associated with a distinct blue-green assemblage. This suggests that there may be a specific association between zinc and the cyanophyte. Further investigations will be necessary to confirm these correlations.

Copper

Copper concentrations showed a general trend toward low spring and summer concentrations with late fall and winter concentrations observed to increase markedly. Raw and filtered copper levels were between 1 and 99 ug/l for the sampling period, while particulate copper levels presented a notably different distributional pattern and a reduced range from 0 to 20 ug/l.

Copper-Raw (Cu-R)

Cu-R concentrations ranged from 3 to 82 ug/l throughout the investigation period (Fig. 28). Cu-R in the spring and summer varied from 3 to 13 ug/l where concentrations remained relatively constant until early September. Concentrations were from 17 to 62 ug/l in mid-September with copper slowly increasing to range from 24 to 77 ug/l by the end of October. A rapid decline in copper concentrations to a range of 5 to 35 ug/l occurred to remain at these concentrations until the middle of November. Then copper again increased to range from 34 to 82 ug/l by the end of December. Copper rapidly declined under the ice cover to range from 7 to 25 ug/l and remained at these concentrations through March.

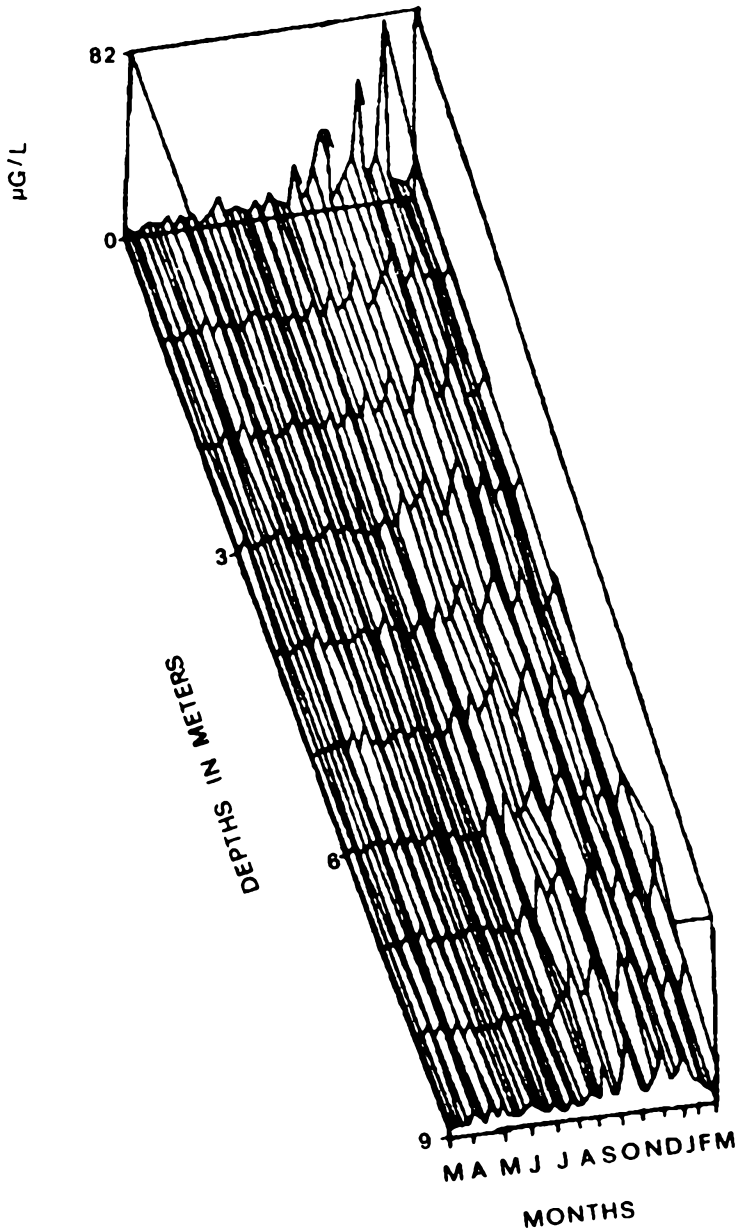

Figure 28. Distribution of Raw Copper (µg/l).

This particular cycling pattern for copper indicates a possible utilization of the metal by the spring and summer algal assemblages, but not the fall and winter phytoplankton. The high concentrations of this metal in the winter period would seem to indicate non-utilization of copper by the species of diatoms in the winter assemblage.

Copper-Filtered (Cu-F)

Soluble copper (Cu-F) showed a similar distribution to that of the raw fraction throughout the sampling period (Fig. 29). Concentrations in this fraction typically ranged from 2 to 9 ug/l and remained at these levels until late April when concentrations increased to 10 to 17 ug/l. Copper declined to a range of 1 to 10 ug/l in range and remained relatively constant through the end of June. Concentrations increased to a range of 9 to 28 ug/l and declined immediately from 4 to 10 ug/l and persisted at these levels until the end of August.

Cu-F concentrations at the end of August increased to from 5 to 45 ug/l. The concentrations declined to 4 to 8 ug/l by mid-September only to increase immediately to a range of 8 to 48 ug/l. They remained high until the last of October when levels again declined to 5 to 10 ug/l.

Copper increased to a range of 18 to 99 ug/l by early November with concentrations remaining at this level until the end of the month. Levels then declined slightly to from 10 to 28 ug/l to persist until mid-December. By late December, concentrations ranged from 34 to 90 ug/l with copper concentrations under the January ice cover observed to range between 7 and 29 ug/l. Soluble copper persisted in this range through March.

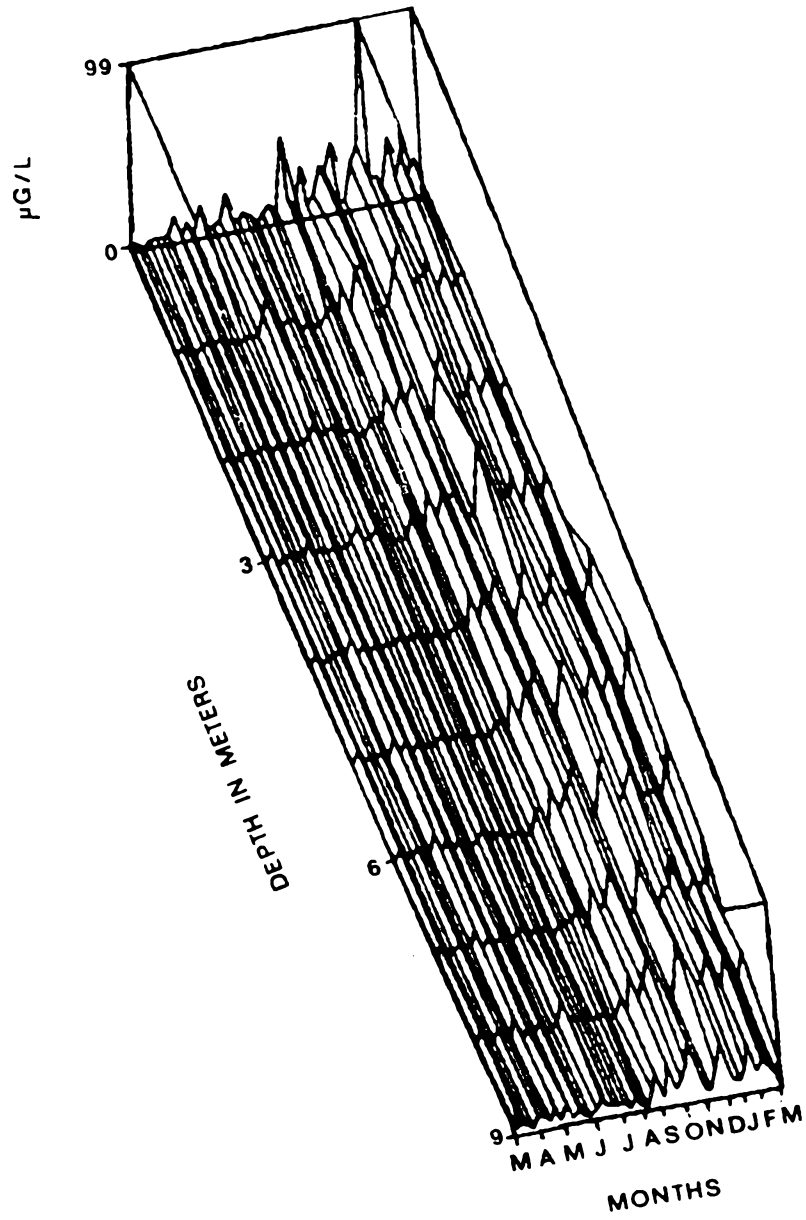

Figure 29. Distribution of Filtered Copper (µg/l).

The problem of increased concentrations in the filtered fraction over those in the raw fraction was once again encountered. Extensive analysis of controls assured no contaminants in the filters, water or chemicals. The anamolous copper source may originate from necrotic algae being disrupted during filtration. It was observed that increases of Cu-F concentrations correlated with high numbers of algae in the lake. During these periods, numerous algae were dying and disruption could occur during filtration.

Copper-Particulate (Cu-P)

Copper in the insoluble fraction (Cu-P) typically ranged from 0 to 20 ug/l throughout the investigation period (Fig. 30). Distributions of these concentrations presented three peaks, one in the early summer, and one in the fall and one in the winter with intervening levels near or at zero.

Levels of copper in early spring ranged from 0 to 4 ug/l where they remained until early June when the first increase of copper was noted in the insoluble form. A range from 1 to 6 ug/l increased from 4 to 14 ug/l by late June. By the end of June concentrations of copper were absent in measurable quantities in the lake. Cu-P concentrations remained in the 0 to 4 ug/l range until late October when concentrations increased to range from 1 to 7 ug/l. These persisted until mid-November when Cu-P again disappeared. In early December, insoluble copper once again appeared temporarily with a range up to 20 ug/l and then disappeared for the remainder of the sampling period.

Increases in this fraction occurred throughout the lake and were for the most part either present or definitely absent from the samples. In June, a definite remnant of a cyanophycean assemblage was changing

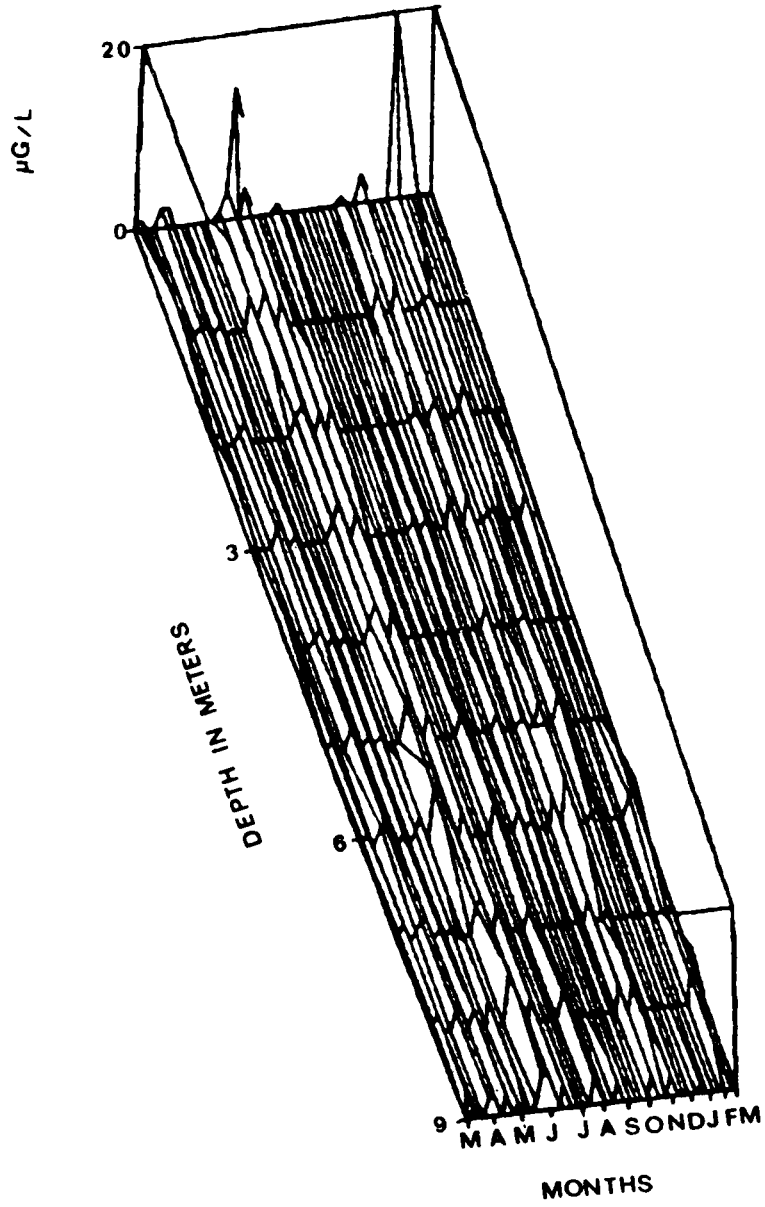

Figure 30. Distribution of Particulate Copper (µg/l).

in species composition and once again in early November a fluctuation of copper occurred in relation to the decline of the autumn cyanophycean assemblage. Copper accumulations in the insoluble fraction occurred during the diatom winter pulse. This represented a most dramatic confirmation that lysing from necrotic cells might be contributing to the filtered fraction concentrations of this meta..

Lead

Lead concentrations in the water column showed a general trend toward increasing concentrations throughout the spring, summer and fall and returned to lowered concentrations during the winter. Lead ranged from 40 to 80 ug/l throughout the investigation period in all fractions.

Lead-Raw (PB-R)

Concentration of Pb-R in the water gradually increased from 9 to 21 ug/l in early March to a narrow range of 13 to 18 ug/l by early April. Pb-R continued to accumulate to a range of 34 to 39 ug/l by the end of May with concentrations persisting in that range until mid-September. Pb-R concentrations then attained 37 to 58 ug/l after which it gradually declined to a range of 10 to 40 ug/l and remained within this range for the remainder of the sampling period. No clear-cut response to any algal assemblage was observed. A possible factor in the accumulations of this metal is increased solubility due to increased temperatures. With the declining temperatures in late fall and winter, corresponding decreases in concentrations of lead was observed.

Lead-Filtered (Pb-F)

Distribution patterns of soluble lead closely resembled that of

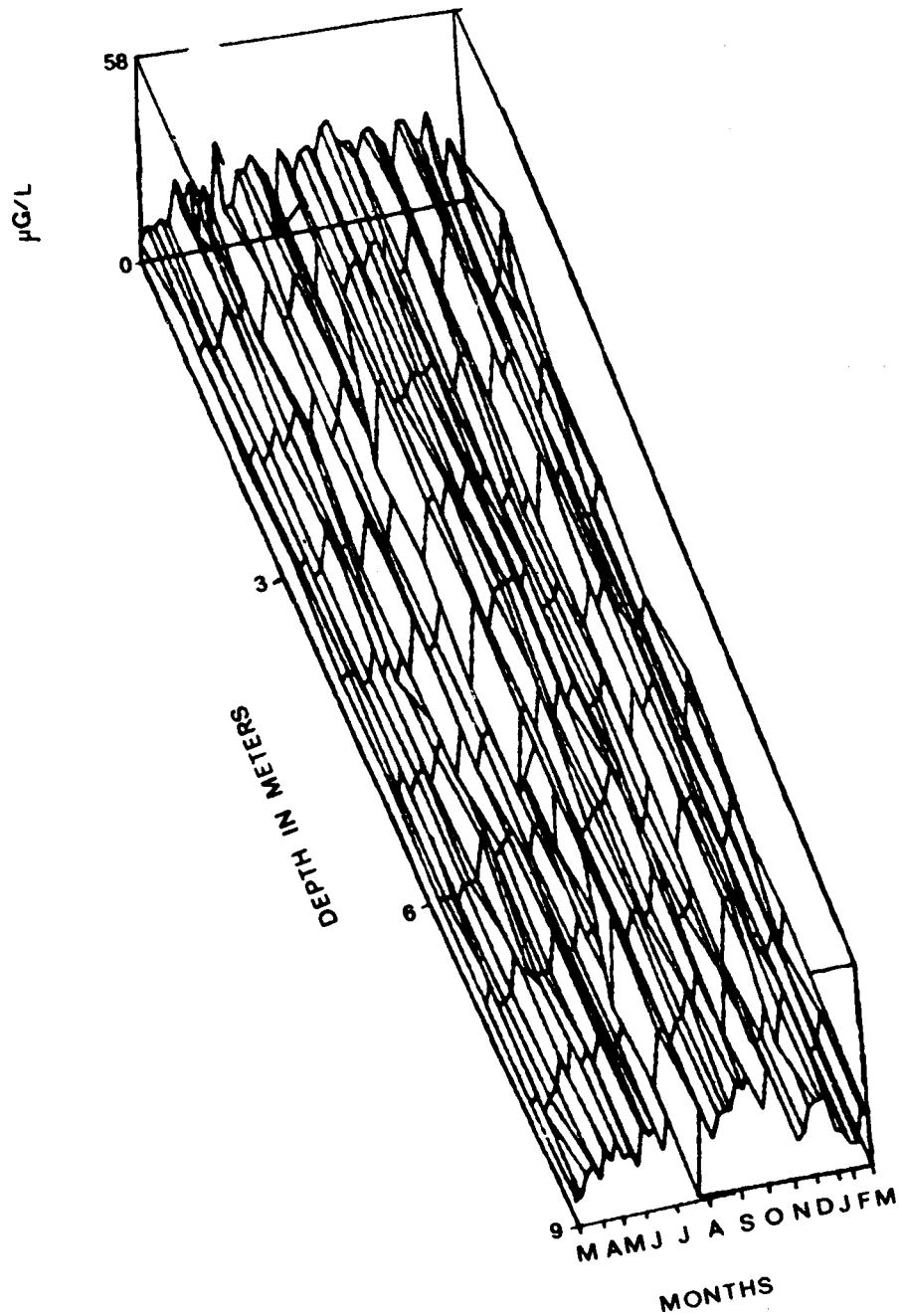

Figure 31. Distribution of Raw Lead (µ g/l).

Pb-R (Fig. 32). A trend toward increasing concentrations peaked in early autumn and declined afterward. Annual soluble lead concentrations ranged from 40 to 85 ug/1.

Soluble lead concentrations consistently ranged between 9 to 38 ug/1 from March until the end of May. Notable increase in Pb-F occurred the last week in May with soluble lead ranging between 26 and 42 ug/1 and remaining at these levels until mid-June. Pb-F concentrations then declined to a range of 18 to 31 ug/1 until the end of June. During July concentrations increased from 28 to 45 ug/1 where they remained until mid-September. Pb-F concentrations continued to increase to a peak range for the sample period of from 30 to 85 ug/1 during the last week of September.

Pb-F concentrations declined to a range of 32 to 56 ug/1 by the first week in October where they persisted until mid-December when it decreased to a range of 8 to 37 ug/1 at this time. Concentrations continued to decline throughout the remaining sample period with a range between 4 to 24 ug/1 in early March.

There was no observed stratification pattern in lead concentrations in either the soluble or raw water fraction. This was in particular contrast to the stratification distributions of iron and manganese. Chemically, copper and lead are similar in their properties. However, it is intuitively obvious that their concentration distributions in the lake are independent and not in synchrony as were iron and manganese. Copper concentrations increased most notably during the winter and spring while this was the period of concentration decrease for lead concentrations. Whether or not a specific inverse relationship exists remains for more extensive evaluation.

Pb-F in the water column might, most easily, be related to

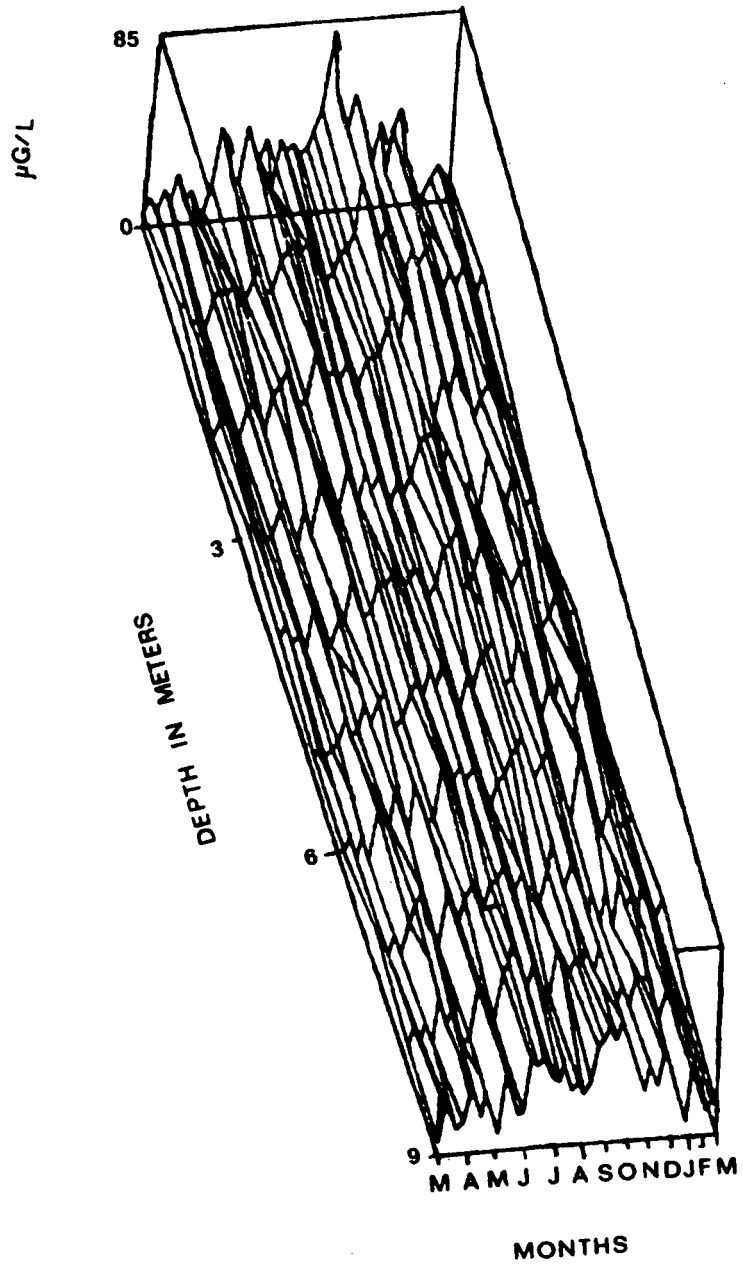

Figure 32. Distribution of Filtered Lead (µg/l).

solubility factors. Also highest lead concentrations are associated with cyanophyte assemblages. Pb-F maxima occurred after the mass die-off of cyanophycean phytoplankters.

Lead-Particulate (Pb-P)

Insoluble forms of lead (Pb-P) showed two divergent peaks of concentrations, one during the spring and one during the late fall and early winter (Fig, 33). These divergent peaks were similar to those of the bacillariophycean abundance maxima and also the single spring chrysophytes pulse. Pb-P concentrations ranged up to 27 ug/l throughout the sample period with Pb-P below the detection limit during most of the investigation period.

From early to mid-March, concentrations of lead from 1 to 8 ug/l were observed. These concentrations declined during the last half of March and increased to a range of from 6 to 21 ug/l during early April. These higher ranges continued until mid-May when Pb-P again was undetectable. Concentrations rapidly increased to a range of from 2 to 15 ug/l from the end of May until the end of June when Pb-P again was undetectable.

Pb-P was observed during early July in concentrations from 4 to 20 ug/l and remained at these concentrations until mid-August. Concentrations then were absent until late October when concentrations from 1 to 23 ug/l again were observed. These concentrations declined and were undetectable by mid-November. Pb-P ranged between 5 and 13 ug/l by the first week in December to increase to a peak range of 5 to 27 ug/l by the end of the month. Particulate lead then declined to near zero in January under the ice cover, and increased to a range from 0 to 8 ug/l for the remainder of the sampling period.

The concentration patterns of Pb-P and the bacillariophytes

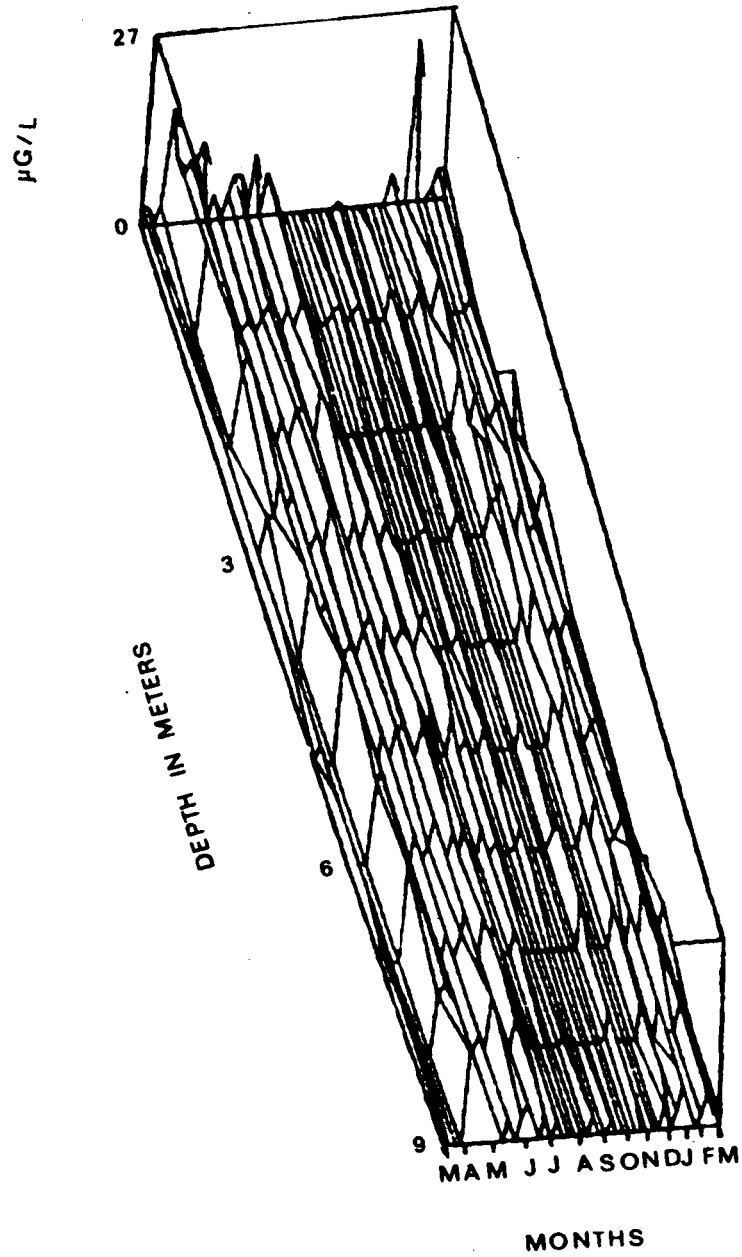

Figure 33. Distribution of Particulate Lead (µg/l).

and chrypophytes are similar. This element may be sorbed by these algae rather than being involved in a metabolic pathway or a portion of a structural component.

Statistical Analyses

Preliminary statistical analyses have been performed on the algal groups showing inspectional relationships to various metal concentration variations. This analysis is beyond the original scope of the present investigation but provides statistical support for important evaluations. Parallel power transfer and time series analyses have been applied to physico-chemical, chlorophyll concentrations and total algae by Poppe (1975, 1978). Data representing total algal fractions and the linear regression coefficients for this data in Tables I-III were provided by Rice (1978).

Four major phytoplankton assemblages contributed to the following annual cycle in Lake Fayetteville: a spring maximum, a summer plateau, an elevated autumnal cyanophycean assemblage and a winter bacillariophyte-chrysophyte assemblage. The discussion that follows evaluates the relationships between phytoplankton assemblages or sub-assemblages and the dynamics of concentrations of iron, manganese, cobalt, lead, copper and zinc. The results indicated that while the raw and filtered fractions are representative of available elemental concentrations, the particulate or insoluble fraction represents the metals incorporated into the phytoplankton. Therefore, only the particulate metal fraction will be interpreted as related to algal assemblage dynamics.

A typical mid-May cyanophycean bloom included the co-dominant algae Coelosphaerium nagelianum and Aphanizomenon flos-aquae with

maximum cell numbers observed during the investigation with 1.4×10^8 cells/l. During this bloom, increases in metal concentrations were observed suggesting incorporation of the metals. The greatest increases were noted for manganese and cobalt. During the period corresponding to peak algal abundances for two weeks in mid-May, correlation coefficients of 0.51 and 0.66, respectively, were observed, indicating a linear relationship between total algal abundances and particulate manganese. Correlation coefficients of 0.51 and 0.66 were calculated for the cyanophyceae and particulate manganese for the same time period. The identical correlations are a reflection of the assemblage composition which consists almost totally of Cyanophyta (Table 1).

Manganese has been shown to be involved in cell wall development, photosynthesis and carbon dioxide fixation. The utilization of manganese in basic cellular processes and structural components would explain uptake of this metal by the algal fraction (Wiessner, 1962; Eyster, 1964). The correlation between algal cell numbers and quantities of manganese appearing in the insoluble fraction in the present investigation confirm that uptake of manganese occurred.

During previous investigations of Lake Fayetteville (Meyer, 1971; Rice, 1974; Poppe, 1976; Poppe, 1978; Rice, 1978), Aph. flos-aquae always had been the single dominant cyanophyte, although frequently Coe. nagelianum was an important secondary species. Goldman (1965) reported that high levels of manganese inhibited the growth of Aph. flos-aquae. This observation might explain the assemblage shift to a Coe. nagelianum-Aph. flos-aquae co-dominant assemblage. Without a specific inhibition range for this cyanophycean alga, such an interpretation must remain a hypothetical.

Cobalt also had a distinct peak associated with the spring

Table 1

Correlation coefficients of the Cyanophyta and total algal abundances (cells/l) as compared with manganese and cobalt concentrations (µg/l).

Date	Cyanophyta vs.		Total algal abundance vs.	
	Mn-P	Co-P	Mn-P	Co-P
Total water column:				
4-20-76	0.57	0.37	0.69	0.36
4-27-76	0.32	0.50	0.35	0.45
5- 4-76	0.32	0.22	0.32	0.05
5-11-76	0.36	0.24	0.40	0.25
5-18-76	0.51	0.00	0.51	0.00
5-26-76	0.66	0.53	0.66	0.52
6- 4-76	0.27	0.47	0.27	0.47
Metalimnion (3-5 m)				
6-10-76	0.46		0.47	
6-16-76	0.27		0.28	
6-22-76	0.79		0.86	
6-29-76	0.96		0.98	
7- 7-76	0.75		0.55	
7-13-76	0.45		0.49	
7-21-76	0.25		0.15	
7-27-76	0.37		0.17	
8- 3-76	0.57		0.57	
8-10-76	0.92		0.93	
Total water column:				
8-19-76	0.46	0.19	0.47	0.17
8-26-76	0.49	0.11	0.02	0.09
9- 1-76	0.42	0.06	0.39	0.06
9- 8-76	0.19	0.36	0.18	0.35
9-15-76	0.10	0.51	0.09	0.52
9-28-76	0.79	0.65	0.74	0.35

cyanophycean bloom. Two weeks following the cyanophyte maximum, significant correlations (r=0.52 and r=0.47, respectively) between total abundance and insoluble cobalt were obtained. Correlation coefficients of 0.53 and 0.47 for the cyanophycean algal components and cobalt occurred during the same period. The insoluble form of cobalt disappeared during the weeks of peak spring abundances.

Cobalt was reported to be required by the cyanophytes by Wiessner (1962), Eyster (1964), Goldman (1965) and Parker (1977). Goldman observed that this requirement is related to the formation of Vitamin B_{12} and nitrate reductase. The present cyanophycean assemblage consists of members which are known to fix nitrogen. The lag in cobalt incorporation might be related to the physiological condition of the organism. Aph. flos-aquae, Ana. circinalis, Ana. flos-aquae and other cyanophytes are known to be nitrogen-fixing algae with a high cobalt requirement because of their integral roles in nitrate reductase formation (Fogg, 1974). However, Holm-Hansen, et al. (1954) observed that all cyanophytes require cobalt. However, this is easier to demonstrate in nitrogen-fixing cyanophytes because of their greater cobalt requirement.

Minor increases in iron, zinc, copper and lead in the particulate form were recorded during the spring maximum. This probably is related to increases in cell numbers and to changes in the physical factors; e.g., temperature, solubility and density. The more complex factors will require further evaluation.

The summer cyanophyte assemblage was characterized by serial replacement of cyanophycean species from the start of June until the onset of the autumnal pulse in early September. Abundance levels remained fairly stable in the range of 3.7×10^6 to 8.0×10^7 cells/l

within a succession from Oscillatoria spp. to Merismopedia trolleri which was replaced subsequently by Microcystis aeruginosa. During this assemblage shift, the aforementioned species, coupled with Coe. nagelianum, Aph. flos-aquae, Ana circinalis, Ana. flos-aquae and other incidental species, tended to accumulate along the thermocline (metalimnion). The thermocline exists at the approximate lower limit of the euphotic zone (Dugdale, 1967), and acts as a "membrane" overlying the anoxic region.

The membrane restricts nutrient, gaseous and organism movement across it (Delfino and Lee, 1972). The phenomenon of cyanophyte algae settling to this level and "riding" the thermocline was repeatedly observed by Meyer (1971), Rice (1974, 1978) and Poppe (1976) as well as during this investigation.

The most significant concentration change in the metal fraction occurred with relation to particulate manganese. Manganese disappeared from the soluble water fraction and was observed to be incorporated into the insoluble component. In late June, with the addition of Oscillatoria limosa and Oscillatoria tenuis in the metalimnion, a correlation coefficient of 0.79 was recorded between cyanophycean algal abundances and insoluble manganese. This increased to 0.96 during the peak Oscillatoria spp. abundance. The correlation declined to 0.75 with a decline in abundance of these species. As Merismopedia increased in abundance with concentrated decreases of Oscillatoria spp., a declining correlation between manganese and the cyanophytes was recorded (r=0.25). With the increase in abundance of Microcystis aeruginosa, an increased correlation between manganese and the Cyanophyta was reported (r=0.92). The variations in manganese uptake by the different sub-assemblages in the present investigation may be

related to integral differences in cell structure and efficiencies of oxygen evolution systems.

Increased correlations between total algal abundances and manganese concentrations were obvious during the Oscillatoria spp. and Microcystis aeruginosa maxima. This increase was related to detrital rain from the epilimnion into the thermocline (Table 1). These events substantiated manganese uptake by various cyanophytes also present during the spring maximum. The weaker relationship with Merismopedia may be a differential requirement for this element.

The mid-September bloom of the Cyanophyta was dominated by Ana. circinalis with important contributions by Ana. flos-aquae and Aph. flos-aquae. Abundances of the cyanophytes ranged between 1.0×10^5 to 5.9×10^7 cells/l, well below the spring maximum level. Two important variations of manganese and cobalt concentrations occurred in synchrony with the mid-September bloom. Manganese in the insoluble fraction was correlated significantly to increased cyanophycean cell numbers at the fall bloom peak (Table 1). A correlation coefficient of 0.79 suggested that with increasing photosynthetic activity there is a coupled demand for manganese. Manganese was correlated more favorably with the less dense fall cyanophycean assemblage than to the higher abundances during the spring maximum, which suggests that the species present in the autumn bloom might have a higher requirement for manganese.

The correlation between the autumnal cyanophycean assemblage and insoluble cobalt is of special interest. The week preceding the bloom, a correlation coefficient of 0.51 was calculated. The significant correlation between these two parameters occurred with cobalt appearing to be incorporated during the same period. For the

week of the actual bloom peak this correlation increased to 0.65. There appear to be two possible causes for this relationship: (1) cobalt was incorporated into the cyanophycean cells during the exponential phase of the growing population and reached its peak incorporation prior to the onset of the sustained assemblage; and (2) integral physiological differences exist during the spring and autumnal blooms. The spring bloom included the co-dominants Coe. nagelianum, a non-nitrogen fixer, and Aph. flos-aquae, a nitrogen fixer, with important contributions from two other nitrogen-fixing cyanophytes, Ana. circinalis and Ana. flos-aquae. Anabaena circinalis subsequently became the dominant algal component in the autumn bloom with less important contributions from Ana. flos-aquae and Aph. flos-aquae; all are nitrogen-fixers. Since cobalt is involved in the formation of nitrate reductase in the nitrogen-fixing system (Goldman, 1965), the increased correlation between cobalt and cyanophycean abundance may be due to this basic physiological difference, i.e., nitrogen fixation. As Holm-Hansen, et al. (1954) noted, the nitrogen fixing species exerted an easily demonstrated cobalt requirement while the non-nitrogen fixing species did not.

Recent investigations both in situ and in vitro indicated an iron requirement for the Cyanophyta, especially in the role of siderochrome formation (Simpson and Neilands, 1976; Murphy, et al., 1976). Since these siderochrome molecules are ferric specific and bind iron in the soluble form, an increase of iron might be expected in the filtered and raw water fractions along with the presence of the siderochrome complex. However, during the present investigation no strong increases in iron occurred in the soluble fraction that might be interpreted as being due to siderochrome secretion.

An extended bacillariophycean assemblage existed from October until the end of March. This assemblage also has been observed in previous investigations (Meyer, 1971; Rice, 1974, 1978; Poppe, 1976). The principal event prior to the onset of this winter algal assemblage was the destratification of temperature and oxygen (Rice, 1978). During the return to isothermal conditions and evenly distributed oxygen concentrations there was a general and gradual redistribution not unlike a rapid diffusion process throughout the water column. A similar redistribution, especially in iron and manganese concentrations, was associated with the breakdown of the hypolimnion. This redistribution resulted in increased concentrations of all metals to the particulate fraction because of detrital masses being agitated into upper level waters.

The winter bloom was initiated by an increase in Melosira granulata during late October. Navicula succeeded M. granulata in late November which was followed by Asterionella formosa and Fragillaria crotonensis. Abundances ranged from 8.4×10^4 to 1.1×10^7 cells/l throughout the winter period.

Concentrations of both cobalt and lead seemed to vary in strong correlation with the Bacillariophyceae. Cobalt is known to be excreted by cultures of certain bacillariophytes, but the physiological role of lead has not been determined. Cobalt was incorporated by the bacillariophytes of the late January and February assemblage consisting primarily of A. formosa and F. crotonensis. Incorporation of cobalt was confirmed by correlation coefficients of 0.54, 0.57, and 0.67 (Table 2). However, one week the correlation coefficient declined to 0.24 and corresponded to the time of melting and fracturing of the ice cover and wind driven mixing. The soluble fraction of cobalt increased during the earlier Navicula bloom which was thought

Table 2

Correlation coefficients of the Bacillariophyceae and total algal abundance (cells/l) as compared with cobalt and lead concentration (µg/l).

Date	Bacillariophyceae		Total algal abundance vs.	
	Co-P	Pb-P	Co-P	Pb-P
Total water column:				
3- 7-76	0.07	0.02	0.27	0.11
3-16-76	0.12	0.26	0.17	0.68
3-23-76	0.16	0.00	0.23	0.00
3-30-76	0.14	0.08	0.15	0.07
4- 6-76	0.70	0.47	0.04	0.26
4-13-76	0.20	0.27	0.36	0.35
4-20-76	0.22	0.34	0.36	0.21
4-27-76	0.37	0.11	0.45	0.30
5- 4-76	0.13	0.22	0.05	0.03
5-11-76	0.28	0.61	0.25	0.06
5-18-76	0.00	0.00	0.00	0.00
5-26-76	0.40	0.17	0.52	0.60
11- 3-76	0.01	0.22	0.16	0.05
11-10-76	0.35	0.00	0.06	0.00
11-17-76	0.27	0.00	0.01	0.00
11-23-76	0.00	0.57	0.00	0.00
12- 2-76	0.23	0.16	0.24	0.16
12- 8-76	0.15	0.16	0.43	0.34
12-15-76	0.22	0.21	0.11	0.22
12-20-76	0.43	0.24	0.56	0.34
1-20-77	0.54	0.34	0.19	0.26
1-28-77	0.57	0.23	0.64	0.07
2-16-77	0.24	0.43	0.26	0.02
2-24-77	0.67	0.28	0.31	0.32
3- 1-77	0.24	0.19	0.37	0.25

to be correlated to Vitamin B_{12} secretion. The incorporation of cobalt by the A. formosa-F. crotonensis assemblage indicated a successional relationship between these genera and Navicula (Swift and Taylor, 1974; Parker, 1977; Ohwada and Taga, 1972).

A similar correlation also was observed during the 1976 spring F. crotonensis-M. granulata and Stephanodiscus nigarae assemblage prior to the onset of the spring syanophycean accumulation. A correlation coefficient of 0.70 was found for this assemblage as related to cobalt. The only known function of cobalt in diatoms is in the formation of Vitamin B_{12} (Benoit, 1957; Bunt, 1970; Haines, 1974; Carlucci and Bowes, 1970b; Daisley, 1969; Guillard and Gassie, 1963).

Holm-Hansen, et al. (1954) stated that a discussion of a cobalt requirement is synonymous with discussing a Vitamin B_{12} requirement. Goldman (1965) and Bunt (1970) found most of the cobalt in lakes to be present in the form of Vitamin B_{12}. The present investigation does not distinguish between nacent cobalt and Vitamin B_{12}. However, it is reasonable to assume that most of the cobalt in Lake Fayetteville is in the form of Vitamin B_{12}.

Another metal associated with the Navicula populations was lead. A correlation of 0.57 existed during the peak abundances of this organism and insoluble lead. After the decline of the Navicula population the correlation coefficient decreased to 0.16 during the development of the A. formosa-F. crotonensis sub-assemblage. These data suggest an intimate association between Navicula and lead. A correlation of 0.61 existed between lead and the spring A. formosa-F. crotonensis-S. nigarae assemblage. It should be noted that the total algal abundance vs. lead yielded a minimal correlation coefficient of 0.06 (Table 2). These data suggest in turn that lead is associated

with the bacillariophycean fraction, most probably with S. nigarae.

Lead, however, has no known physiological role and has been reported to be toxic to many algae, including the Bacillariophyta. Hessler (1974, 1975) reported lead to delay and/or prevent cell division. Possibly, the accumulation of lead by Navicula may result in the termination of the population. A similar mechanism may limit the appearance, duration and size of the S. nigarae population.

Schultz-Blades and Lewin (1976) proposed that lead uptake in marine diatoms involves two stages: (1) immediate uptake at a limited number of binding sites; and (2) translocation into the cytoplasm. Schultz-Blades and Lewin's (1976) observations support the correlations between lead and the growth of the Navicula population observed in the present investigation. The high correlation at the population peak may represent the "binding" stage. Hessler (1974, 1975) reported that immediate cessation of division occurs upon incorporation or translocation. The precipitous decline of the Navicula population might have been caused by inhibitory or lethal accumulations of lead.

During the spring of 1976, a temporary strong pulse of the Chrysophyceae followed the winter assemblage. This was dominated by Uroglena sp. with cell abundances between 1.1×10^5 and 1.3×10^7 cells/l. Particulate lead (Table 3) was correlated with the Chrysophyceae during the early development of this assemblage (r=0.64). The literature does not report any effects of lead on the Chrysophyceae. No lethal effects were observed in the Chrysophyceae. The abundances confirmed the increase in cell numbers from early March through mid-April, while the correlation coefficients declined (Table 3). A less significant correlation of 0.39 occurred between Synura sp. and lead. The association between lead and the chrysophytes may be the result of adsorption of the enveloping gels.

Table 3

Correlation coefficients of the Chrysophyceae and total algal abundance (cells/l) as compared with lead concentration (µg/l).

Date	Chrysophyceae vs. Pb-P	Total abundance vs. Pb-P
3 -7-76	0.21	0.11
3-16-76	0.64	0.68
3-23-76	0.00	0.00
3-30-76	0.09	0.07
4- 6-76	0.39	0.26
4-13-76	0.10	0.35
4-20-76	0.46	0.21
4-27-76	0.18	0.30
5- 4-76	0.26	0.03

Two non-bloom producing taxa include the Chryptophyta and the Euglenophyta. The cryptomonads were the second most abundant algal division, second only to the Cyanophyta. Cryptomonads were abundant throughout the annual cycle with two pulses, one in the spring and the other in the fall. These pulses seem unrelated to trace metal incorporation. The two pulses of cryptomonads after bacillariophycean and cyanophycean blooms occurred when the assemblages were dying. During the spring, following the die-off of the winter bacillariophycean assemblage, the cryptomonads increased and then declined to a steady consistent abundance throughout the summer and early fall. Following the decline of the autumnal cyanophycean assemblage and destratification, a second temporary cryptomonad increase developed.

The cryptomonads are both autotrophic and heterotrophic. The increased spring and autumn abundances of this division were thought to be related to a change from the autotrophic to the heterotrophic mode of nutrition in response to increased organic detrital concentrations.

The Euglenophyta, while not associated with a specific bloom were, however, associated with a dramatic hypolimnetic phenomenon. Euglena pisciformis was the primary representative with cell numbers accumulating to between 3.1×10^5 to 4.2×10^6 cells/l. During summer stratification and the development of anoxic conditions (Rice, 1978), this organism attained its maximum abundance. Associated with the hypolimnetic population are similar increases in iron and manganese. Delfino and Lee (1972) suggested that the increase in iron and manganese is due to anoxic chemical reactions. Preliminary evaluation indicated that this association may be due to chance between the euglenoids and iron manganese. Insoluble iron and manganese accumulated in much

greater concentrations than can be accounted for by the Euglenophyta themselves. Poppe (1976) observed a similar euglenoid population, but it was dominated by Lepocinclis ovum. The euglenoid Trachelomonas is known to accumulate iron and manganese on the surfaces of the lorica. However, this genus did not occur in adequate numbers to explain iron and manganese accumulations. Correlations between the euglenoids and iron and manganese require further evaluation.

Minor correlations were observed among the various algal taxa and zinc or copper. A significant correlation for these metals and phytoplankton assemblages has not been established. These metals may cycle independently of the algal assemblages.

SUMMARY

An investigation into the distribution of six trace metals and four major phytoplankton assemblages has shown that there exists a spatial and temporal correlation of these parameters in Lake Fayetteville. The cycling of iron, manganese, cobalt, lead, copper and zinc were examined with respect to spring, summer and autumn cyanophycean dominated assemblages and the winter bacillariophycean-chrysophyte assemblage. Two metals, copper and zinc, are not associated with the succession of algal assemblages. Definite patterns of metal concentrations cycled annually as a result of biological interactions, fluctuations in physical factors; e.g., temperature and nutrient inflow, and chemical reactions. Nutrients at no time were limiting.

A spring cyanophycean assemblage with the co-dominants Coelosphaerium nagelianum and Aphanizomenon flos-aguae displayed distinct uptake of manganese and cobalt with subsequent incorporation into cellular materials. Correlation coefficients of 0.66 and 0.53 were found between the Cyanophyta of this bloom and manganese and cobalt, respectively. These relationships substantiated a significant co-variance of these algae and the metals. Minor increases of iron and lead during the spring maxima were attributed to physico-chemical factors rather than purely biological factors.

The summer assemblage consisted of serial dominants Oscillatoria spp., Merismopedia trolleria, and Microcystis aeruginosa. These algae accumulated in the region of the thermocline with increased manganese incorporation by Oscillatoria spp. and Microcystis aureginosa as confirmed by correlation coefficients of 0.96 and 0.92.

The fall cyanophycean assemblage was dominated by Anabaena

circinalis with important contributions by Anabaena flos-aquae and Aphanizomenon flos-aquae, all nitrogen fixing cyanophytes. An increased correlation coefficient between these algal abundances and manganese (r=0.79) and cobalt (r=0.65) indicated basic physiological differences, possibly because of nitrogen fixation, in the spring and autumnal assemblages.

Evidence emerged to confirm cobalt utilization by the cyanophytes of both the spring and fall blooms during the sustained growth phase of the assemblage. This may be related to cobalt requirements in the formation of nitrate reductase in the nitrogen fixation pathway.

The winter bacillariophyte-chrysophyte assemblage was dominated by Melosira granulata, Navicula spp., Asterionella formosa and Fragillaria crotonensis with a late spring addition of Uroglena sp. The principal event prior to the onset of this winter assemblage was destratification breaking down the hypolimnion, and with accompanying redistribution of metal concentrations and organic detritus. A strong correlation indicating lead and cobalt incorporation by the diatoms and lead uptake by the chrysophytes was observed.

Cobalt incorporated by A. formosa and F. crotonensis was indicated by a coefficient of 0.67. This cobalt appeared to be secreted by the earlier Navicula spp. bloom, which in turn indicated successional relationships between A. formosa and F. crotonensis with Navicula. A similar event was observed for Stephanodiscus nigarae.

Navicula populations and S. nigarae presented high correlations of 0.57 and 0.61, respectively, with lead. This also was observed (r=0.64) for the chrysophyte Uroglena sp. Adsorptive processes which proved lethal for the bacillariophytes but not for the chrysophytes, were responsible for this pattern. Lead appears to be a determining factor for the succession of these algae.

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