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November 1976

Ecological Research Series

STUDIES ON THE RECLAMATION OF STONE LAKE, MICHIGAN

Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
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STUDIES ON THE RECLAMATION OF STONE LAKE, MICHIGAN

by

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Grant No. R-801245

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FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its fifteen major field installations, one of which is the Corvallis Environmental Research Laboratory (CERL).

The primary mission of the Corvallis laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects, and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report describes the effects of controlling domestic pollution on a eutrophic seepage lake in Michigan and the control of nutrients in water by using particulate materials which retard nutrient release from sediments.

A.F. Bartsch
Director, CERL

ABSTRACT

This report contains information relating to two factors: (1) the effects of domestic pollution abatement on a eutrophic lake, and (2) investigations into methods of reclaiming such lakes especially through the use of particulate materials which retard pollutant release from sediments.

The study lake, Stone Lake, has been monitored for approximately ten years from the time of pollution abatement. Results indicate that the sediments are major pollutant sources during stratified periods and that for such lakes to achieve meaningful improvements in water quality in a reasonable length of time, a series of external manipulations is often needed.

Monitoring data indicated a cyclic pattern of phytoplankton succession within the lake during growing season. This pattern included a steady base of green algae with alternated dominance with different kinds of blue-greens (nitrogen-fixing or non-nitrogen-fixing) - the available forms of nitrogen regulating the cycle.

Certain types of fly ash, a particulate waste product of coal combustion, was shown, in laboratory studies, to possess properties capable of precipitating orthophosphate from overlying waters and subsequently "sealing" the phosphorus within the sediments for long periods of time. A lake such as Stone Lake could thus be made permanently, or semi-permanently, phosphorus limited thereby altering the successional pattern previously indicated and significantly reducing the overall standing algal crop.

This report was submitted in fulfillment of Grant Number R-801245, by the Department of Civil Engineering of the University of Notre Dame under the sponsorship of the Environmental Protection Agency. Work was completed as of May, 1974.

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ACKNOWLEDGMENTS

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To those individuals who performed the main portion of the research obtained herein, Dr. Mark W. Tenney, Dr. Wayne F. Echelberger, Jr., Dr. Stephen M. Yaksich, Dr. Victor J. Bierman, Dr. Cajetan F. Cordiero, Mr. Timothy J. Hampton, Mr. Scott T. Girman, and Mr. Robert J. Palla, sincere appreciation is given.

SECTION I

CONCLUSIONS

In Stone Lake, Michigan, the lake sediments tend to act as nutrient sinks. During periods of dissolved oxygen depletion in the hypolimnion large amounts of phosphorus and nitrogen are released in the overlying water. Insofar as Stone Lake is typical of many natural seepage lakes with accelerated eutrophic conditions, the application of this finding to other similar systems appears warranted.

A cyclic pattern of phytoplankton succession was observed in Stone Lake during summer stratification. The pattern consisted of green algae followed by nitrogen - fixing blue-green algae followed again by green algae with available forms of nitrogen regulating the cycle.

Particulate materials, especially certain clays and fly ash, were shown to be potentially effective lake restoration tools for controlling biogeochemical cycling of pollutants from eutrophic sediments. In most cases a 2 to 5 cm layer of material was needed to control phosphate release. Supplemental chemical addition, such as lime or alum, enhances initial phosphate removal from the overlying water.

Sandy shoreline sediments low in water and organic matter have a low pollutional potential and should not require covering with a particulate layer in most instances.

Available data indicates potentially harmful effects from other water soluble extracts of fly ash, particularly sulfur (as SO_3^{-2}) and various heavy metals. Short term extremes of pH may also affect biota unfavorably.

SECTION II

RECOMMENDATIONS

Particulate materials should be field tested on a large scale to determine their effectiveness as lake restoration tools. As part of this effort further information on the costs and harmful effects (if any) should be obtained.

A more intensive field investigation of phosphorus and nitrogen cycling in eutrophic lakes should be undertaken. Such a study should focus on an evaluation of aerobic vs. anaerobic regeneration of these nutrients.

A mathematical model of a lake ecosystem should be developed which will combine nutrient regeneration with other important aspects of lake systems such as sediment-water interchange and algal and bacterial growth and decay.

Investigations into other methods of lake reclamation, such as side-stream treatment, should continue.

SECTION III

INTRODUCTION

GENERAL

This report contains information relating to two factors: (1) the effects of domestic pollution abatement on a eutrophic lake, and (2) investigations into methods of reclaiming such lakes especially through the use of particulate materials which retard pollutant release from sediments. The study was for a three year period supported by an Environmental Protection Agency grant (R-801245) awarded for the period April 1, 1971 to May 31, 1974. It was an extension of a previous grant from the Federal Water Quality Administration, the details of which can be found in a previous report (Tenney *et al.*[1]).

LOCATION AND DESCRIPTION OF PROJECT LAKE

The project lake was Stone Lake, located within the village limits of Cassopolis, Michigan (pop. 3000) approximately 40 km northeast of the campus of the University of Notre Dame. Between the years 1939-1966 it was used as a receiving water body for the secondary wastewater effluent from the village. In 1966 the residents of the village, concerned about Stone Lake's deteriorating water quality, constructed a new wastewater treatment facility located outside of the lake's natural drainage basin. Except for a few septic systems and some storm drainage from the village, all domestic sources of pollution were eliminated. Measurements indicated the total input of phosphorus to the lake was reduced by 95%.

Stone Lake is a seepage lake with no natural surface inlets or outlets. A hydrographic contour map is shown in Figure 1.

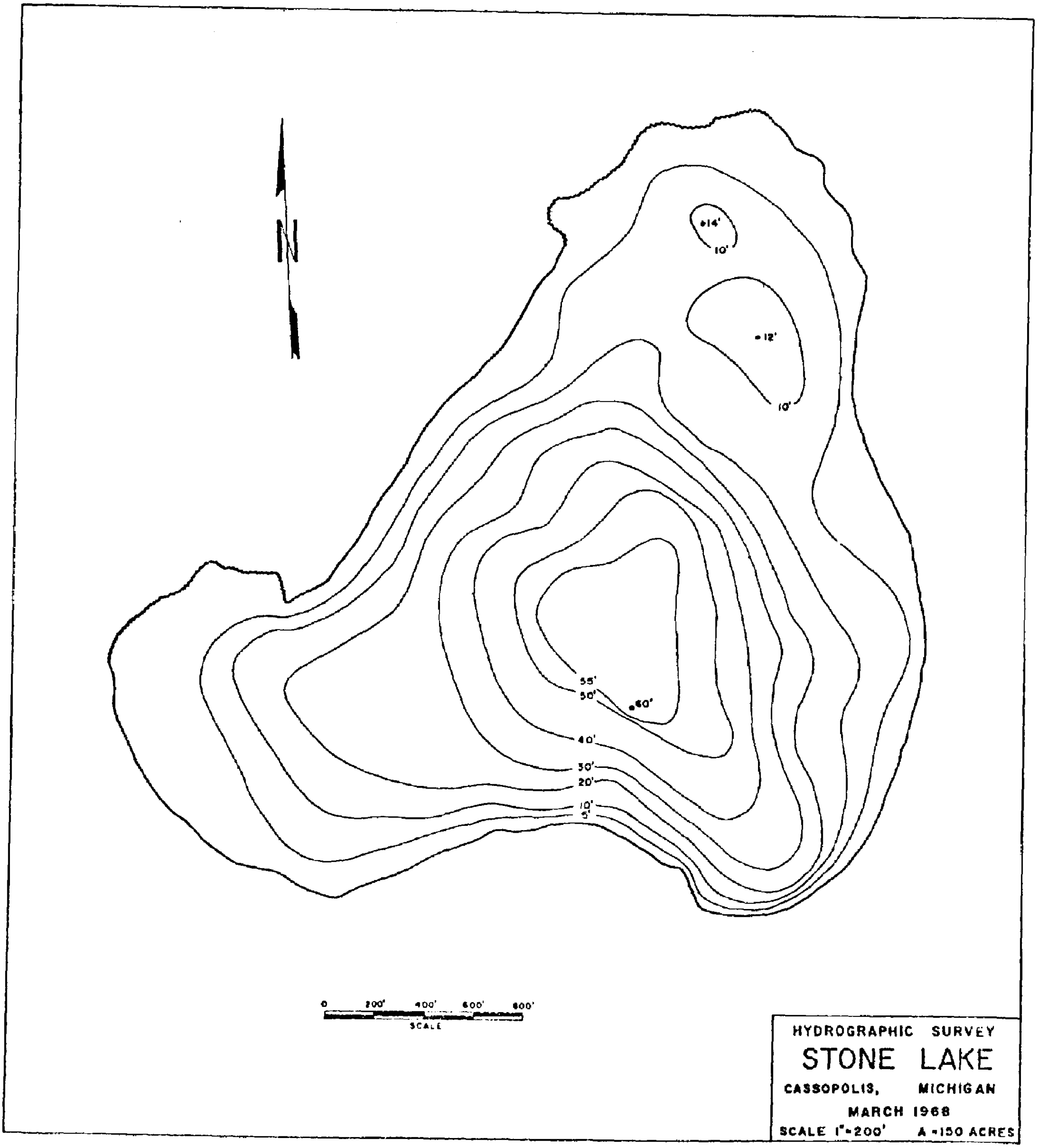

Figure 1: Hydrographic Map of Stone Lake.

Pertinent morphological data are given in Table 1.

Table 1. MORPHOLOGICAL CHARACTERISTICS OF STONE LAKE

Surface area	60 ha (150 acres)
Depth	
Maximum	18 m (60 feet)
Average	6 m (20 feet)
Volume	3.4×10^6 m^3 (2876 acre-feet)
Drainage area	176 ha (435 acres)
Urban	128 ha (319 acres)
Forest	40 ha (100 acres)
Agricultural	6.4 ha (16 acres)

The total watershed of Stone Lake is relatively small. As indicated in Table 1 the total drainage area is 176 hectares. Figure 2 illustrates the approximate boundaries of the drainage basin. Previous calculations had indicated a hydraulic retention time of approximately 11 years. However this was prior to the discovery of storm sewers from the village. The present calculated hydraulic retention time of Stone Lake is approximately 5.5 years. Further details regarding the climatological and geological characteristics of the lake can be found in Tenney *et al.*[1].

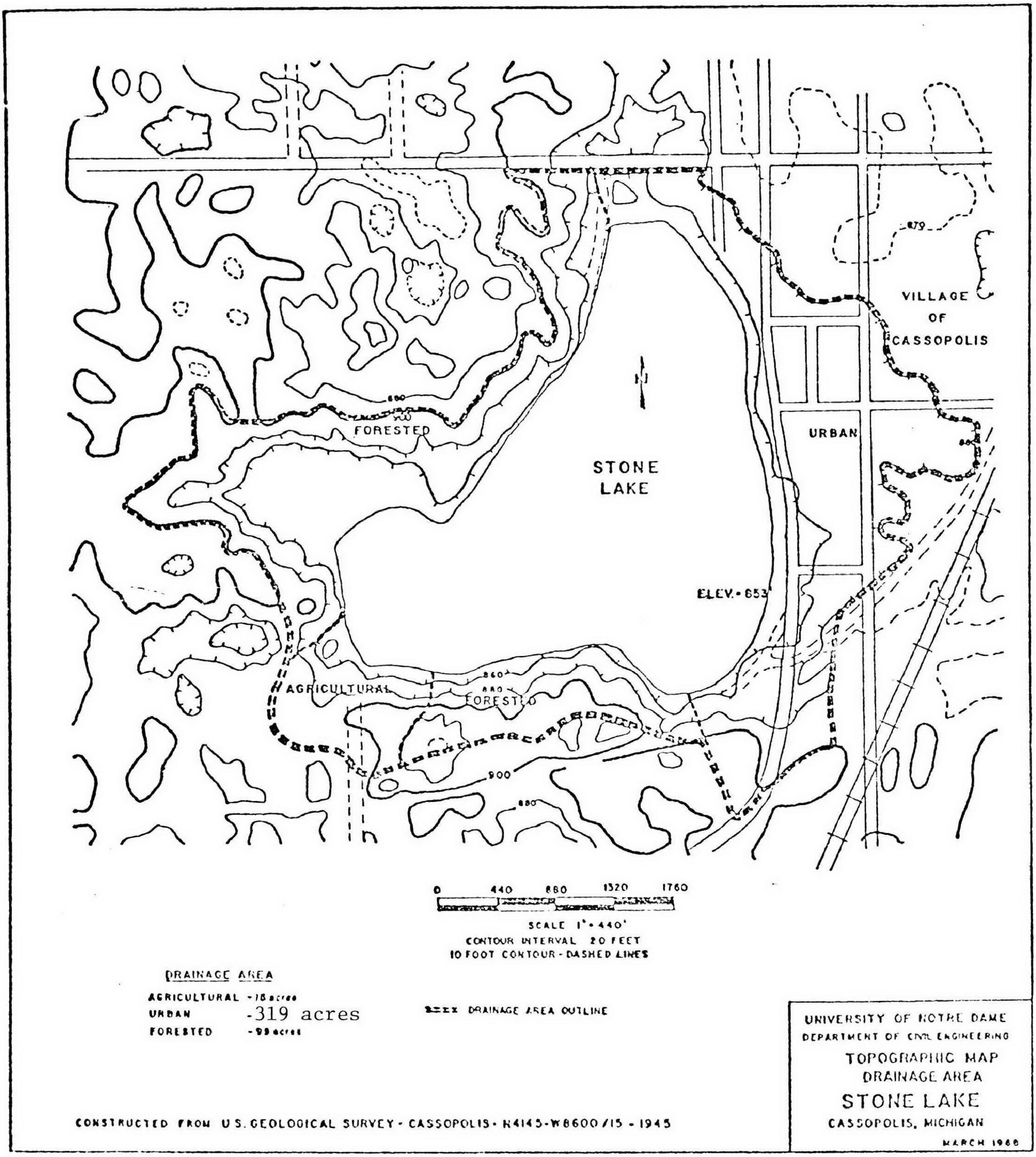

Figure 2: Topographic Map and Tributary Drainage Area of Stone Lake.

SECTION IV

WATER QUALITY OF STONE LAKE

ELEMENTAL CYCLING

Inputs of pollutants to lakes can come from many sources. Direct discharges of wastewater effluent, runoff, seepage, and rain water falling directly on the lake have been shown to be significant sources. Once the introduction of the pollutant has been made, the lake system relies upon internal biogeochemical cycling to define its fate. Of great importance in this regard is the behavior of the lake sediments. Consider a simplified steady-state model in a lake system as follows:

$$E_{in} = E_{out} + E_{sediments} \quad (1)$$

where E represents total amounts of a given element. The terms on the right hand side of the equation refer to natural flushing (including atmospheric exchange) and sediment interchange, respectively. Those mechanisms which are operative for this latter term would include chemical precipitation, sorption, ion exchange, and biological incorporation followed by sedimentation.

It is useful to compare the theoretical residence time of an element in a lake with the hydraulic residence time of the water in the lake as a means of determining the extent to which the last term influences specific lake behavior. For a given element,

$$\tau_E = \frac{[E]_{avg.}}{E_{in}} \quad (2)$$

where τ_E is the theoretical residence time of any element in the lake and $[E]_{avg.}$ is the average concentration of that element in the lake water. For the water in the lake,

$$\tau_W = \frac{\text{Average Volume}}{\Sigma \text{ Inflows}} \qquad (3)$$

where τ_W is the mean hydraulic residence time. As indicated previously by Stumm and Morgan[2], the ratio τ_E/τ_W becomes a useful parameter. If it is less than one, specific elements are being stored in the sediments. However, when this ratio is greater than one, the element is being cycled within the lake and, thus, is present at higher concentrations than would be predicted from external inputs alone. When the ratio is equal to one, there is either no exchange with the sediments or the net exchange is zero.

Because of its naturally high reactivity, phosphorus, which is the limiting nutrient for excessive algal productivity in many eutrophic lakes, has a value of τ_p/τ_W which is generally greater than one. Natural flushing with waters having low phosphorus concentrations will reduce phosphorus levels in such a system very slowly. This is illustrated in Figure 3 for Stone Lake. Orthophosphate residual predicted by simple washout ($\tau_p/\tau_W = 1$) is compared with the actual measurements made each year during circulation periods. As is evident, the two curves have basically different shapes. These differences are attributable to the influence of the sediments. That portion of influent phosphorus which is initially incorporated into the sediments is not lost entirely to the system and is available for subsequent release under proper conditions. Accordingly, lake sediments can act as sinks or sources of phosphorus at different stages within the lake's development; and for some systems can act as both a sink and a source at various times during a yearly cycle.

PHYSICAL AND CHEMICAL DATA FOR STONE LAKE

As a means of indicating the present status of Stone Lake, data for a specific year, 1973, is presented in Figures 4-11. Data for 1971-72 are found in the Appendix. Stone Lake is an example of a dimictic lake, the type most often found in the north-central United States. Figure 4 graphically illustrates the two periods of total mixing which regularly occur in a lake of this type. The spring circulation period occurred in late March (point a, Figure 4) with mixing conditions present until the middle of May. By

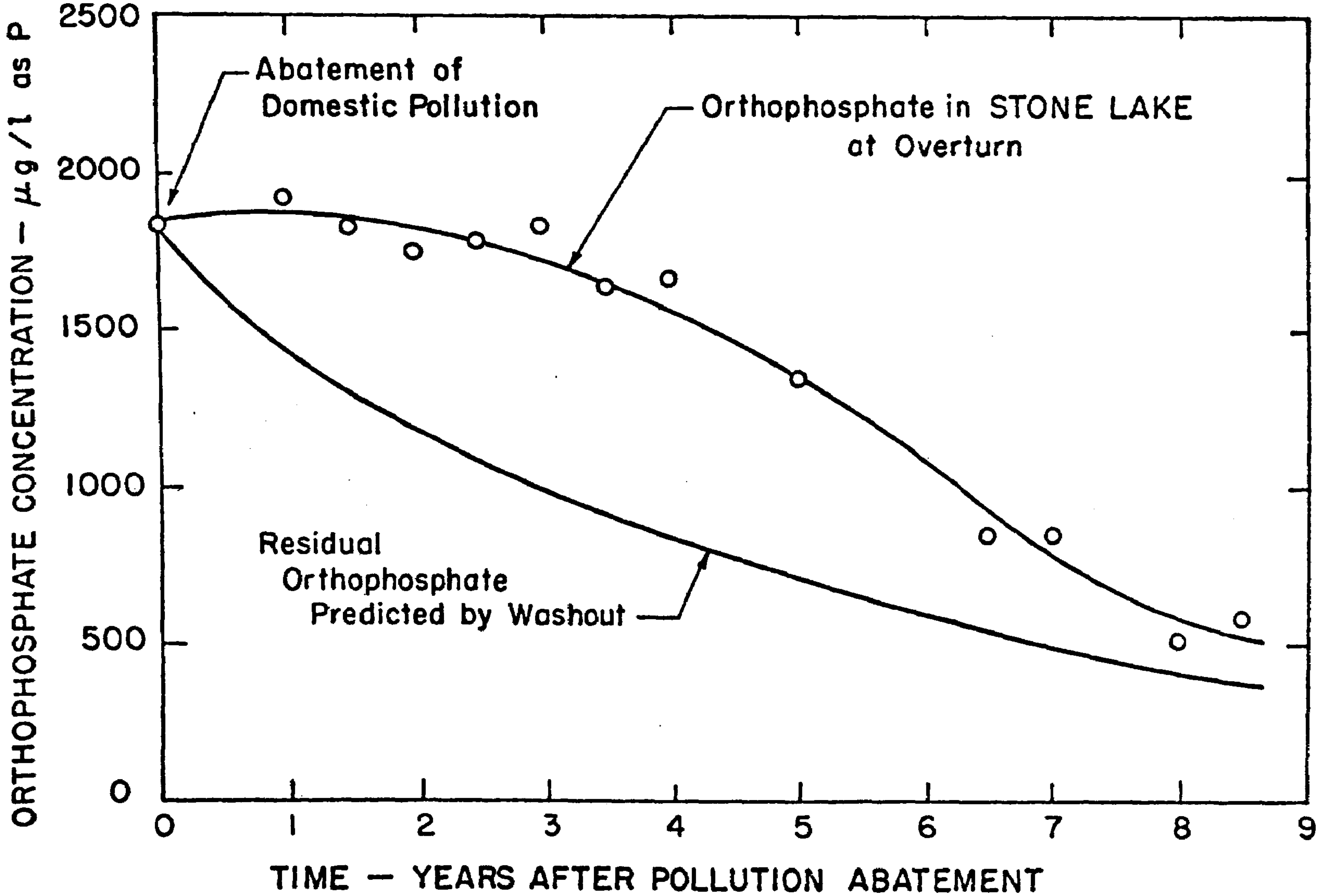

Figure 3: Washout vs. Overturn Orthophosphate in Stone Lake.

June 1 a fairly stable thermal stratification had developed which lasted until the fall circulation period at the end of October (points b through c). During the period from June through September a well-defined epilimnion existed in Stone Lake the lower boundary of which began at about 3 meters and progressively dropped to about 6 meters as the summer proceeded. The thermocline during this period can be roughly defined as that portion of the water column between 4.5 and 7.0 meters with everything below this depth being the hypolimnion. This study was concerned mainly with this period of thermal stratification when very little mixing occurs between the upper and the lower waters.

The suspended solids data for 1973 are presented graphically in Figure 5. Since Stone Lake receives very little allochthonous suspended matter, the suspended solids represent a relatively good indicator of the planktonic biomass in the lake. It should be noted, however, that this parameter does not separate living biomass from dead and decaying organisms, or other detritus. For the most part, though, the filter pads used to measure suspended solids were bright green for samples taken from the epilimnion, indicating viable phytoplankton, and brown for samples collected from below the photic zone, indicating decaying organisms. Using the suspended solids data in this manner, one can make several observations about the trends in total phytoplankton density in the lake. Although no actual algae data exist for February, it was noted that a large algal bloom occurred in this month (point a, Figure 5) beginning under the ice and persisting until spring circulation. The increase in suspended solids in March between 10 and 25 feet is possibly a reflection of the sinking of this bloom but more likely of the large Daphnia bloom which occurred at the end of March. In either case the increase is probably a reaction to the February algal bloom. No phytoplankton bloom conditions began to arise until stratification started to appear around June 1. Between mid-April and June (points b through c) the lake was dominated by macrophytes. A lake survey at the end of May showed that approximately one-third of the lake bottom (to a depth of 10-15 feet) was covered by rooted, submerged macrophytes.

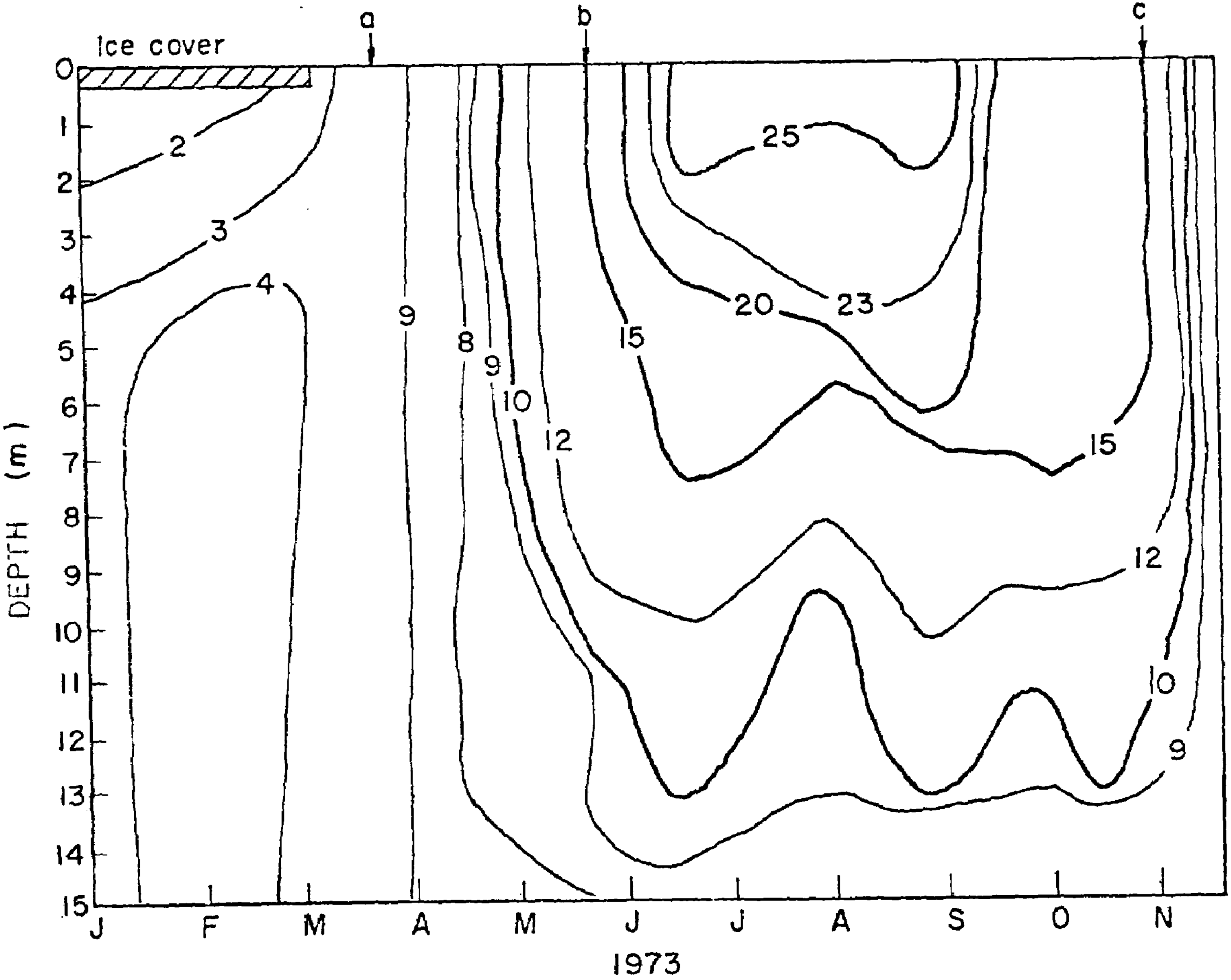

Figure 4: Temperature Profile of Stone Lake, Michigan for 1973. Contours are in Units of °C.

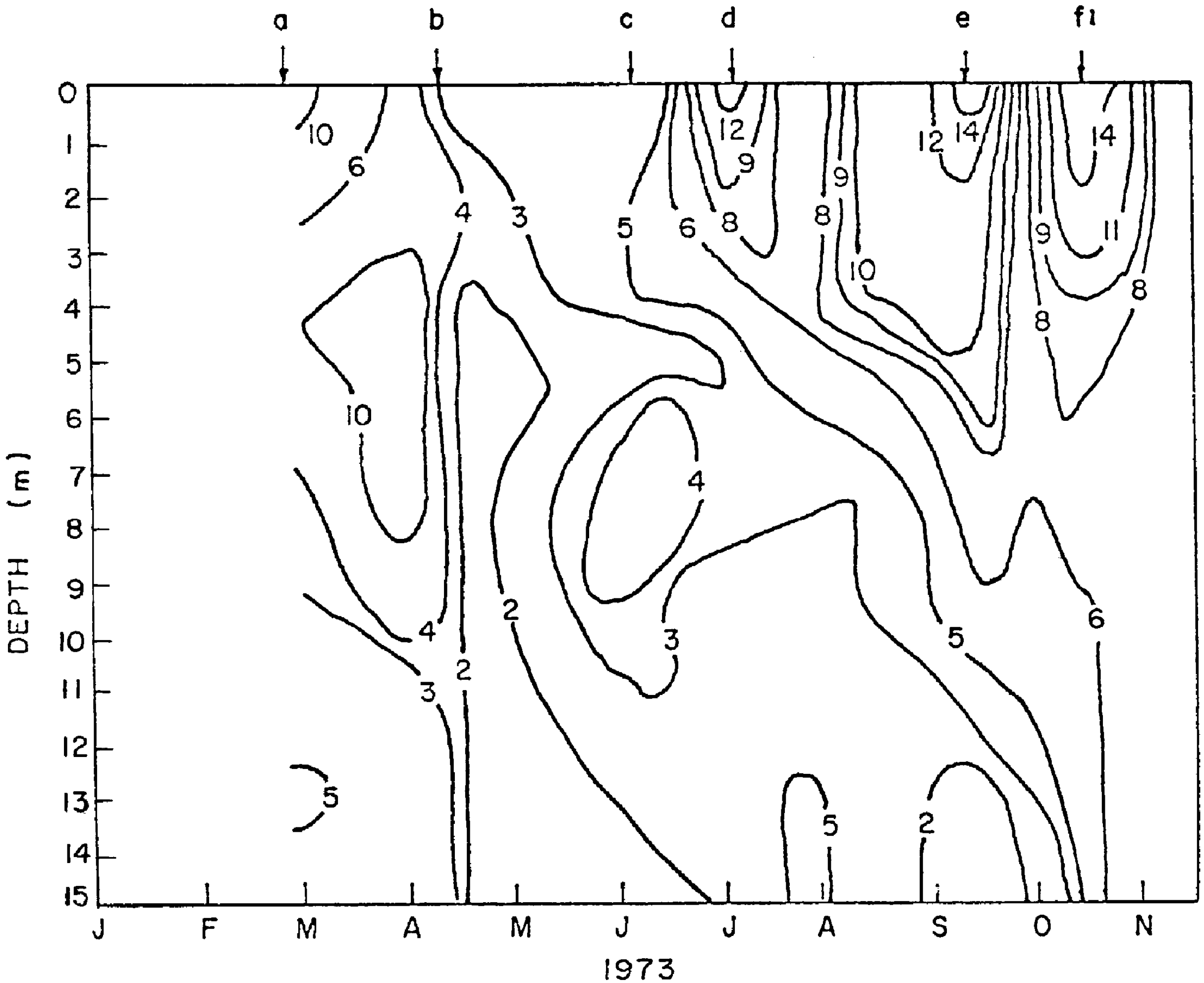

Figure 5: Suspended Solids Profile of Stone Lake, Michigan for 1973. Contours are in Units of mg/ℓ.

Coincidental with the macrophyte die-off in the first two weeks of June was the beginning of the summer phytoplankton bloom conditions. Relatively high suspended solids were attained in the surface waters by the end of June and lasted at least through the fall circulation. There were at least three individual peaks of suspended solids during this period (points d, e and f) which will be seen to coincide with individual algal species blooms. Also of interest is the gradual increase of solids in the thermocline region throughout the stratification period. The contour lines roughly follow the same deepening pattern as the thermocline, suggesting that some of this material is possibly being trapped in the thermocline region. In addition, the abrupt decrease in suspended solids with depth through this region suggests that this material is being degraded as it settles. It could also mean that the settled material has simply reached its buoyancy level, and therefore, sinks no further.

The pH and dissolved oxygen variations in Stone Lake (Figures 6 and 7, respectively) provide an indication of gross trends in photosynthesis and respiration. While Stone Lake possesses a relatively hard water (total hardness between 110-120 mg/l as $CaCO_3$) and is well buffered (total alkalinity between 120-140 mg/l as $CaCO_3$), the pH does show some variations through the year. In contrast, the dissolved oxygen changes are quite dramatic and highly significant. The interpretation of these parameters is as follows. A rise in pH and a corresponding rise in dissolved oxygen can be interpreted as an indication of high photosynthetic activity. The photosynthetic uptake of CO_2 (or CO_3^{-2}) results in an increase in pH, and the oxygen released during photosynthesis causes a rise in dissolved oxygen. Conversely, plant respiration and aerobic decomposition utilizes O_2 and releases CO_2; therefore, these processes could cause a decrease in pH and dissolved oxygen. These parameters vary diurnally; however, all Stone Lake sampling was conducted between 10 A.M. and 12 noon on each sampling date.

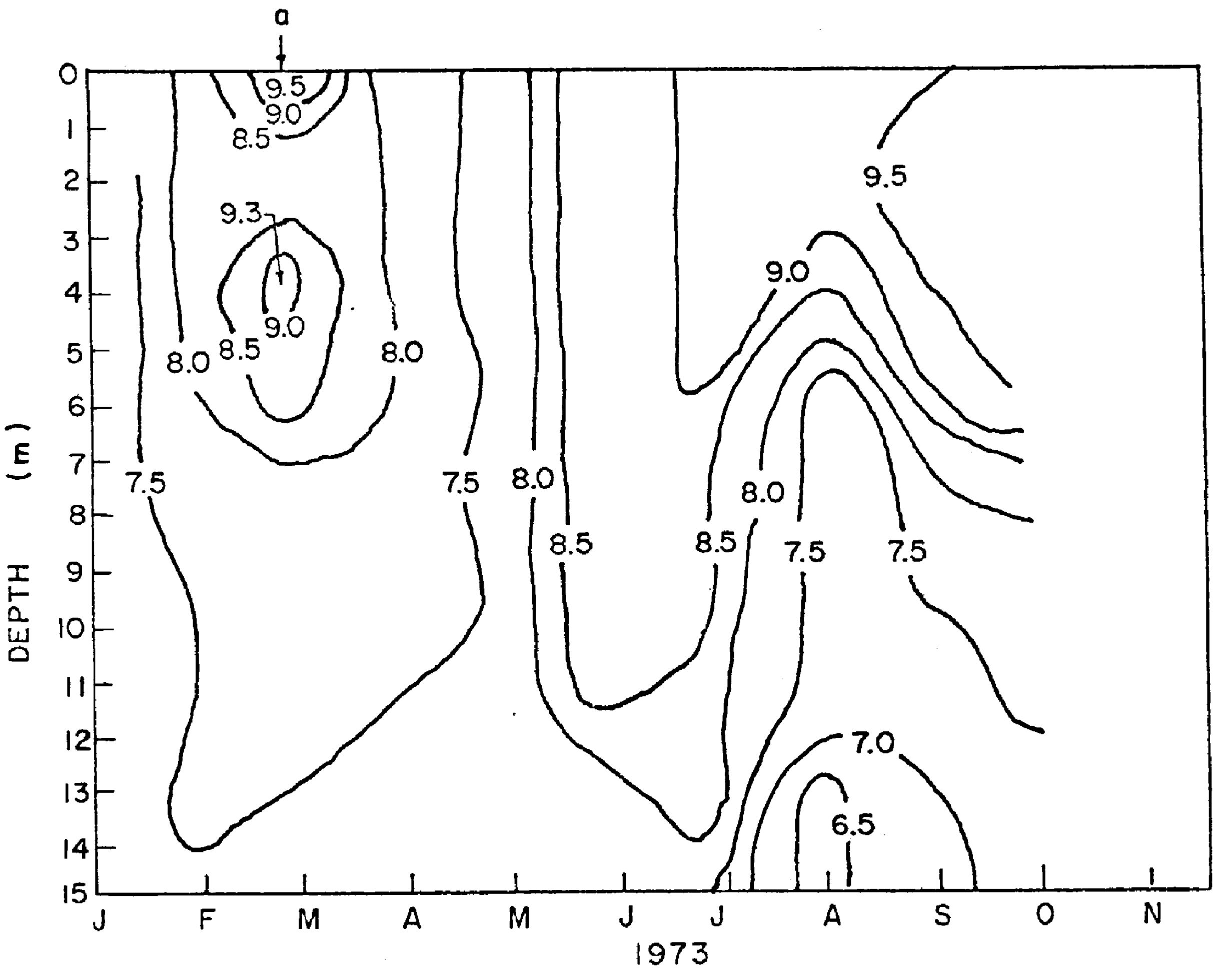

Figure 6: pH Profile of Stone Lake, Michigan for 1973. Contours are in pH Units.

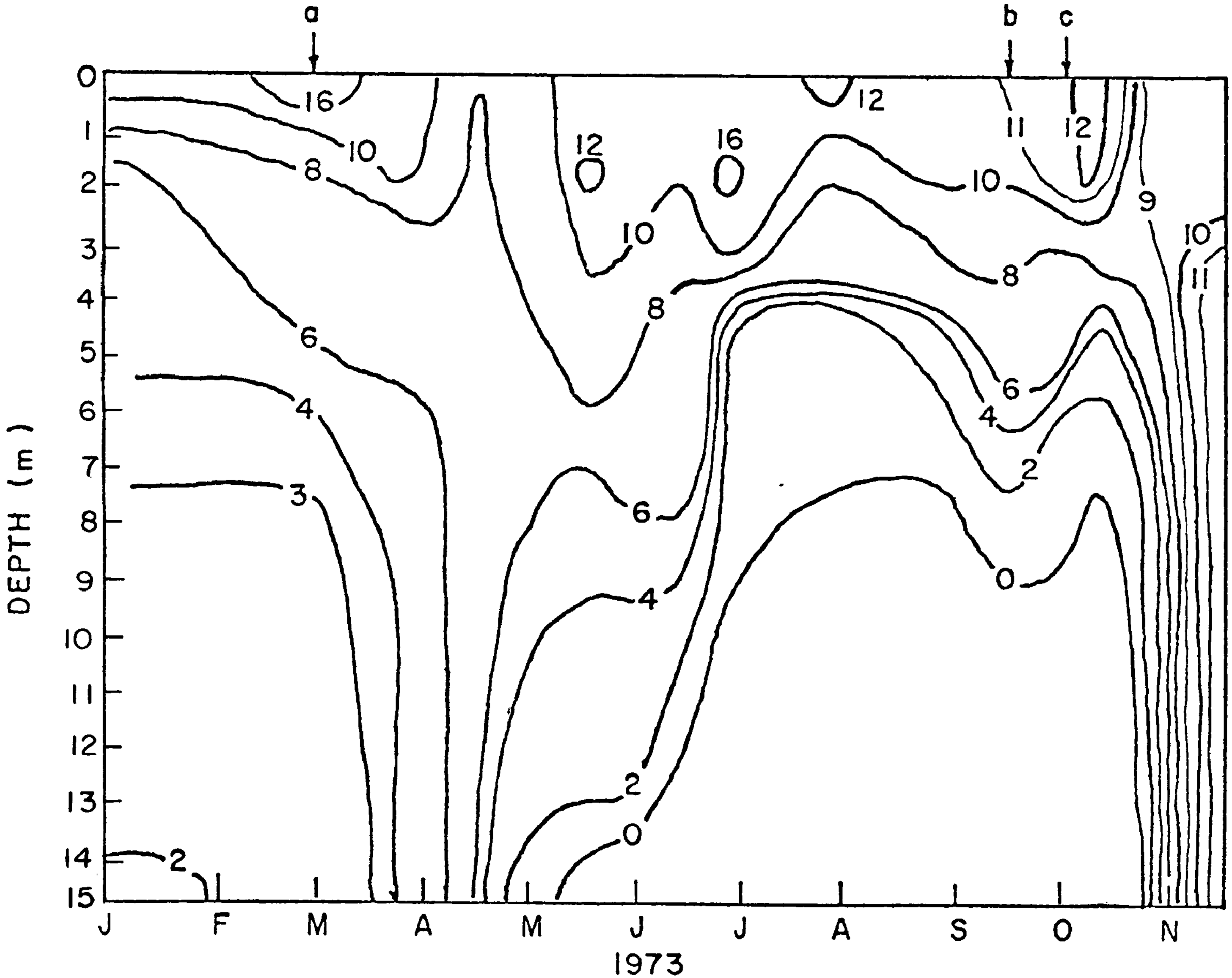

Figure 7: Dissolved Oxygen Profile of Stone Lake, Michigan for 1973. Contours are in Units of mg/ℓ.

From the pH and dissolved oxygen data for Stone Lake one can place the February algal bloom (point a) and trace the steady depletion of CO_2 and the correspondingly high dissolved oxygen in the surface water up to the onset of summer stratification. At this time the oxygen in the hypolimnion is rapidly used up, presumably by the stabilization of organic matter raining down from the epilimnion. From the middle of June to fall circulation the majority of the hypolimnion is anoxic. Also apparent from the dissolved oxygen data is the rapid decrease in this parameter through the thermocline. This seems to indicate that the oxygen in this region is being utilized as rapidly as it diffuses down from above. It is also interesting to note that the dip in the oxygen contour in mid-September (point b, Figure 7) corresponds to an algal bloom occurring at the same time (point e, Figure 5) which penetrates to deeper water as the thermocline drops. The subsequent high uptake of oxygen in the thermocline region (point c, Figure 7) corresponds to the crash and decomposition of this bloom.

Figure 8 traces the soluble orthophosphate concentration in Stone Lake through 1973. The concentrations are given in mg/l as PO_4 and are therefore approximately three times the concentrations as mg P/ℓ. The data reveal that the phosphorus concentration in Stone Lake is extremely high, even in comparison with other eutrophic lakes. It is therefore highly unlikely that phosphorus is limiting at any time in Stone Lake. This is especially true in view of reports that a phosphorus concentration as low as 0.01 mg/l at spring overturn might result in nuisance algal conditions during the summer (Sawyer[3]). It is possible, however, that changes in phosphate, even at these levels, could favor one algal species over another. In any event, it is likely that phytoplankton blooms and declines can be reflected in the phosphate concentration in terms of nutrient regeneration from algal decomposition.

In light of the above discussion, the phosphate data show some very interesting fluctuations. It should be noted that any substantial increases in phosphate in the surface waters are not likely to be the result of

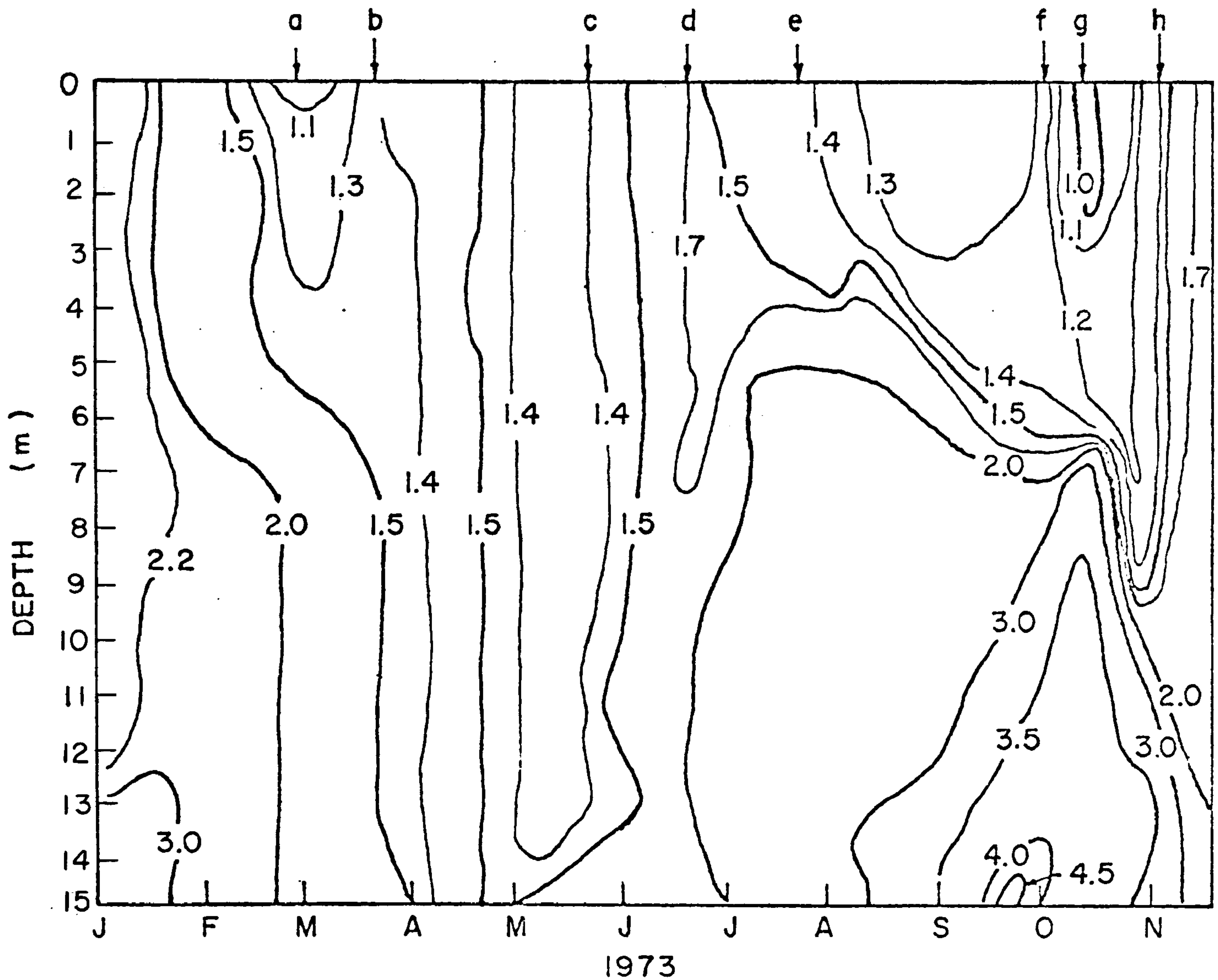

Figure 8: Soluble Orthophosphate Profile of Stone Lake, Michigan for 1973. Contours are in Units of mg/ℓ as PO_4.

allochthonous inputs. The only significant nutrient input to Stone Lake at the time of this study was surface runoff. Based on rainfall data and estimates of total phosphorus concentrations in the runoff, it was estimated that the increase in total phosphorus in the epilimnion over the six month period from mid-April to mid-October would be approximately 0.05 mg/l as PO_4. It would seem then, that the phosphorus time-variations in the epilimnion of Stone Lake can safely be attributed to biological and thermal cycling. Looking at the upper waters, several features stand out. First, the February algal bloom causes a rather dramatic decrease in phosphate (point a, Figure 8) only to be followed by what appears to be a phosphorus regeneration after the bloom (point b). Since no large algal population appears in April and May, this recycled nutrient remains as soluble orthophosphate. The macrophyte growth which took place at this time apparently did not require phosphate from the open waters of the lake; however, it appears that their die-back had a significant effect on the epilimnetic phosphate concentration. During the macrophyte withdrawal (points c and d), the orthophosphate concentration in the epilimnion and the thermocline rose 0.30 mg/l as PO_4.

The phosphorus dynamics through the summer stratification period are difficult to interpret. It is clear that the three sequential algal blooms during the period (points d to g) continually reduced the phosphate concentration in the epilimnion from 1.7 mg/l as PO_4 to 1.0 mg/l as PO_4. Any regeneration which might have taken place in this region is masked by phytoplankton uptake. It is interesting to note that the second bloom (points e to f) reduced the phosphate concentration by only 0.10 mg/l as PO_4. This fact leads one to postulate that there was an additional phosphate source during this bloom. The source may very well have been phosphate regeneration from aerobic algal decomposition in the lower epilimnion and thermocline region.

Also of note is the steady increase in soluble orthophosphate in the hypolimnion which begins with the onset of rapid phytoplankton growth at the surface (point d) and continues to the fall circulation (point h).

This build-up of phosphate also coincides with the rapid decrease of oxygen in the hypolimnion and the continued anoxic conditions until circulation. Because of the lack of additional necessary information, it is impossible to pinpoint the cause or causes for this increase. Based on the available data, this phenomenon is probably the result of aerobic and anaerobic decomposition of organic matter settling from the upper waters as well as bacterially mediated release of phosphorus from the bottom sediments with the latter most likely making the largest contribution.

The 1973 nitrogen data for Stone Lake are presented in Figures 9 (soluble organic nitrogen), 10 (soluble ammonia-nitrogen) and 11 (combined soluble nitrate plus nitrite). The soluble organic nitrogen did not appear to show too much variation through the year. For this particular year there seemed to be a progressive decrease in concentration from January through August, although this type of trend has not been consistent from year to year. Beginning in September, this parameter appeared to stratify somewhat because of an increase in the upper water concentration.

The ammonia variations in the lake suggest some very interesting possibilities. The rapid increase in ammonia at the end of February (point a, Figure 10) coincides with the crash of the February algal bloom. The increase showed up through the entire water column because of the complete mixing conditions prevailing at the time. Hutchinson[4] noted that in most lakes, maximal ammonia concentrations appear in the trophogenic zone at periods of full circulation. This increase, however, is definitely not brought on by mixing with deep water, since no ammonia is present in the entire water column prior to the increase. From this peak there was a steady decline of ammonia until the end of May when there was no ammonia left in the upper waters (point b, Figure 11). The decrease of these nutrients from March through May was most likely due either to uptake by macrophytes and green algae, or nitrification (perhaps biologically mediated) of soluble ammonia.

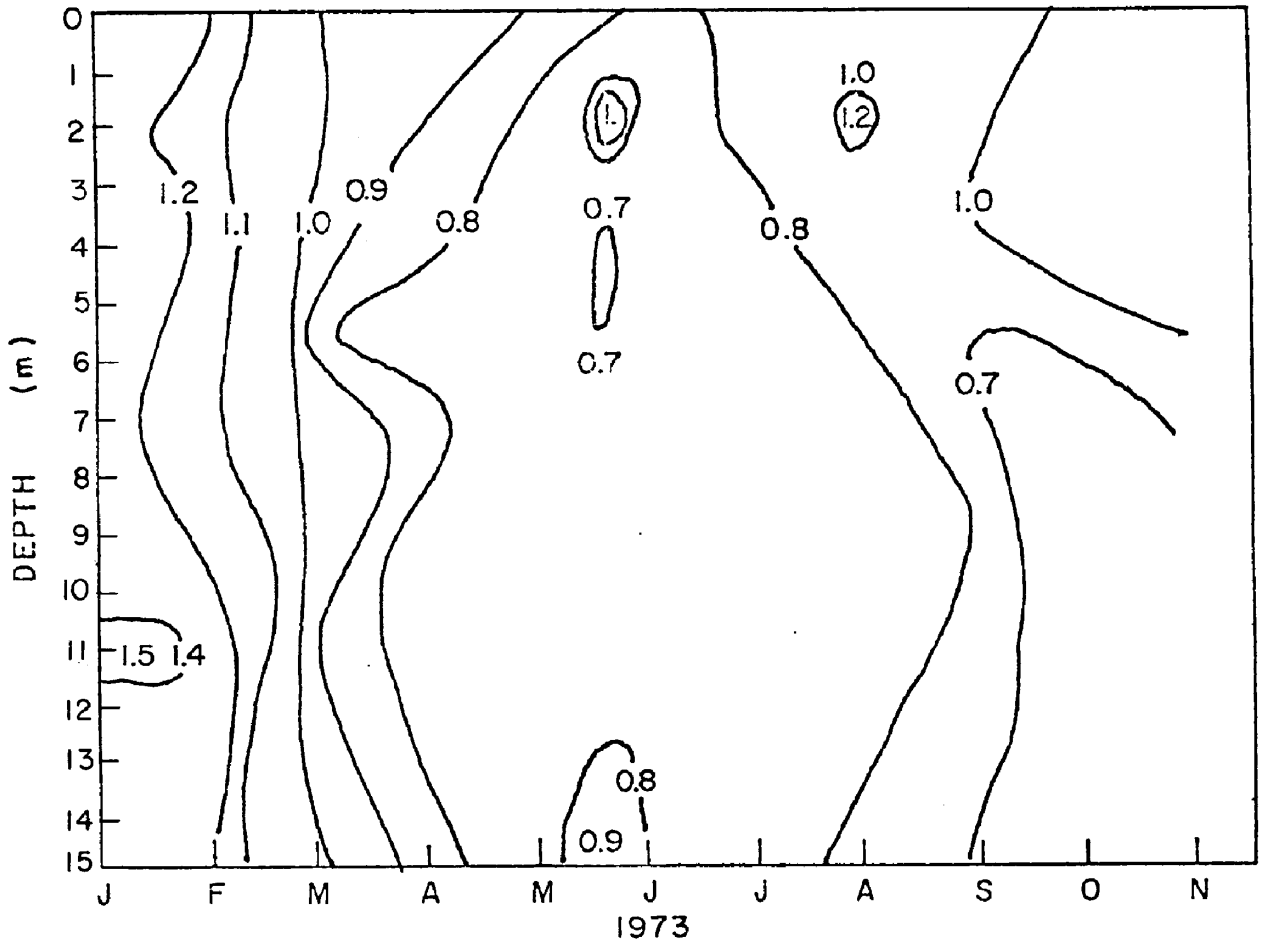

Figure 9: Soluble Organic Nitrogen Profile of Stone Lake, Michigan for 1973. Contours are in Units of mg/ℓ.

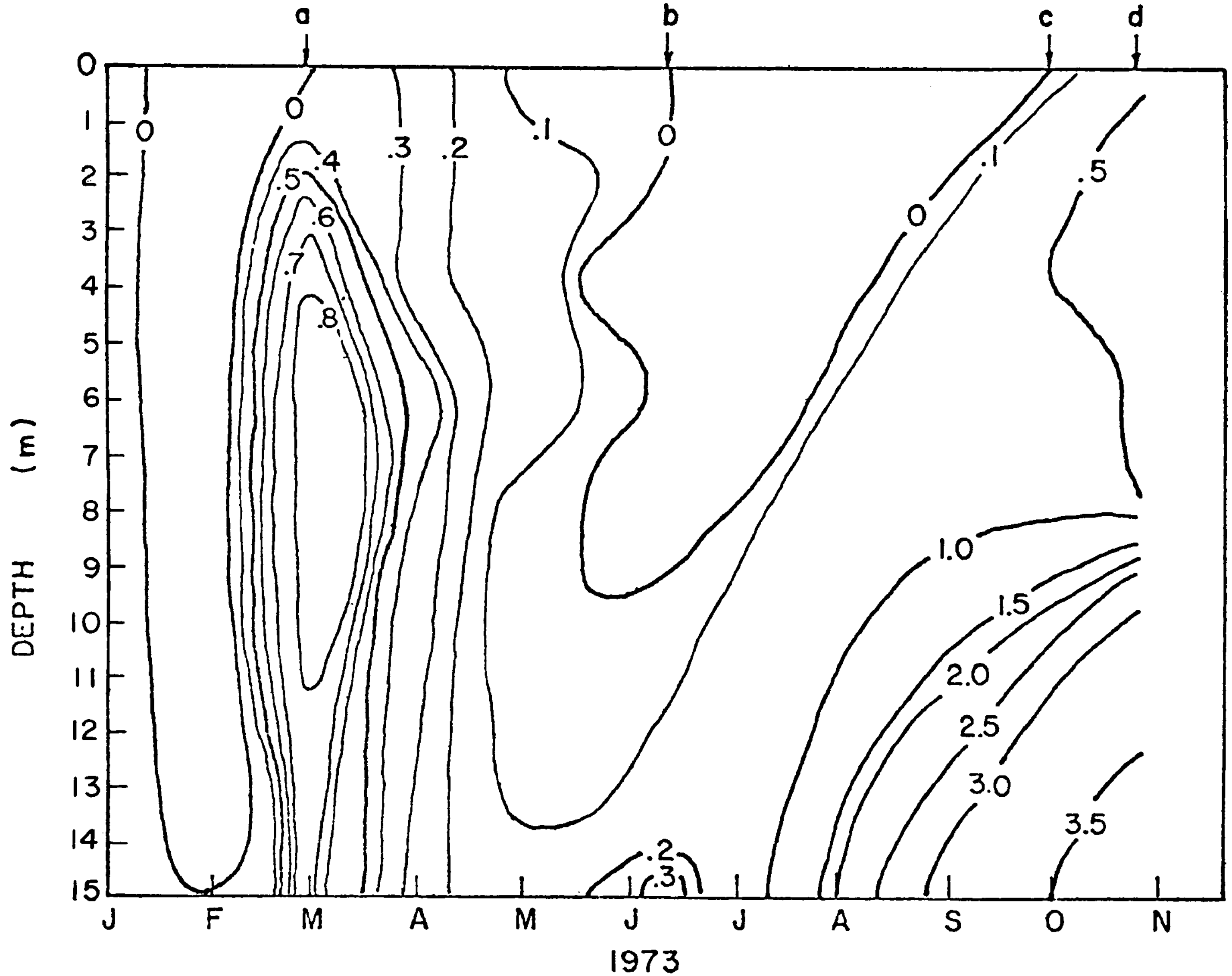

Figure 10: Soluble Ammonia Profile of Stone Lake, Michigan for 1973. Contours are in Units of mg N/ℓ.

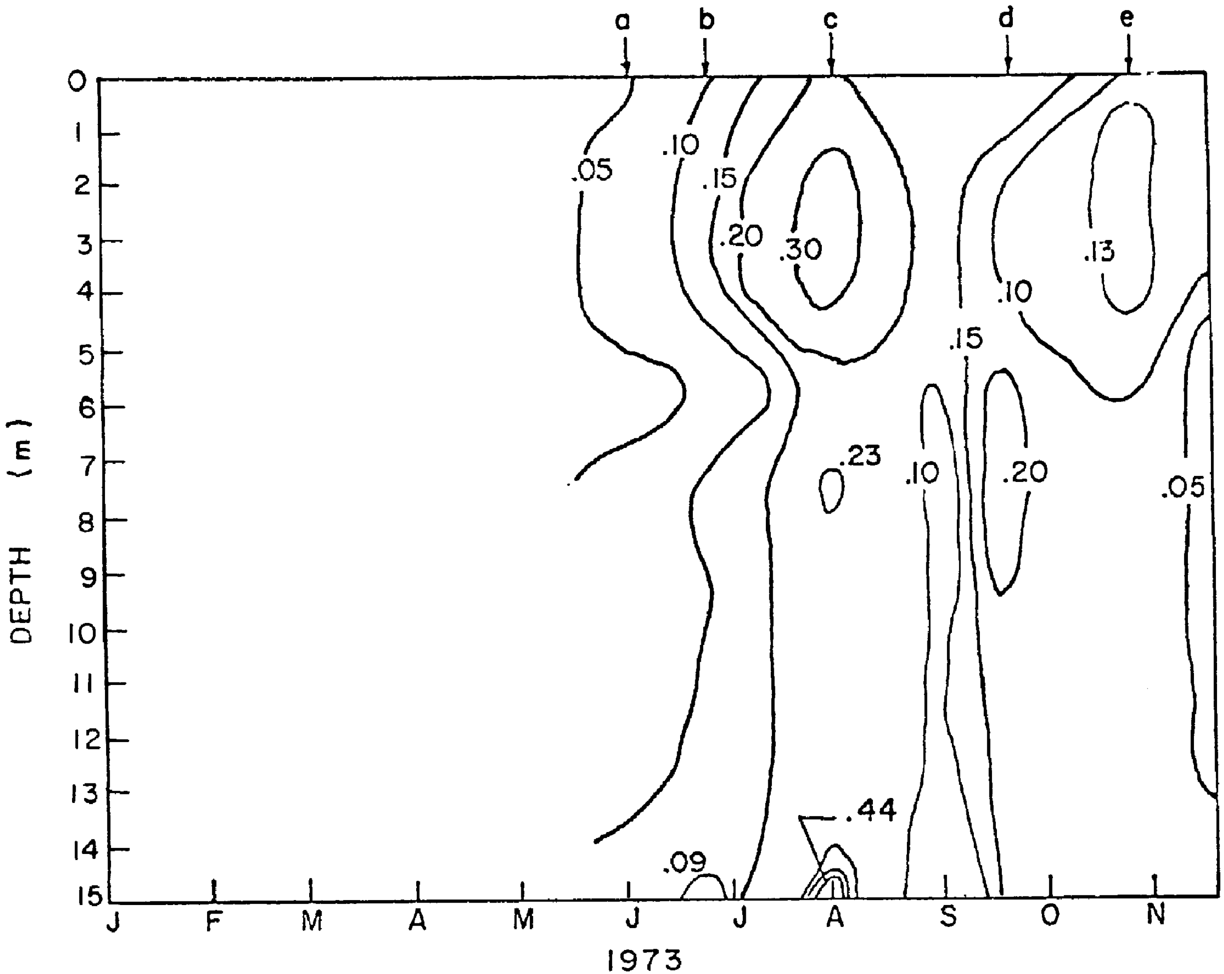

Figure 11: Soluble Nitrate + Nitrite Profile of Stone Lake, Michigan for 1973. Contours are in Units of mg N/ℓ.

In the beginning of June it would appear that nitrogen is limiting in Stone Lake yet, at this same time, a large algal bloom begins to develop. The apparent anomaly is explained by the theory that nitrogen-deficient conditions provide a definite competitive advantage to nitrogen-fixing blue-green algae[5,6]. As will be seen in the next section, the June algal bloom (point d, Figure 5) was in fact a nitrogen fixing bloom. Of further interest is the increase of nitrate in the surface waters (points b to c, Figure 11), which coincides with the wane of this algal bloom. The activity and decay of the nitrogen-fixing algae replenished the supply of inorganic nitrogen in the lake. Although ammonia is an end-product of organic nitrogen breakdown, the nitrogen regeneration appeared only as nitrate. This suggests that a rapid nitrification of the released ammonia was taking place in the surface water. There was a rapid build-up of ammonia in the hypolimnion, however, and this regenerated inorganic nitrogen remained as ammonia because of the anoxic conditions in those waters. As Hutchinson suggests, the rise of hypolimnetic ammonia is caused by decomposition of falling plankton as well as deamination of organic nitrogen compounds in the sediments.

From August 1 to fall circulation the inorganic nitrogen fluctuations become difficult to interpret. There was a gradual decrease in nitrate from August 1 through the middle of September (point c to d), which corresponds to a gradual increase in suspended solids. During this time period there was little change in the epilimnetic ammonia concentrations, except perhaps some invasion of ammonia from the hypolimnion due to vertical entrainment. About the middle of September both the epilimnetic nitrate (point d to e, Figure 11) and ammonia (point c to d, Figure 10) showed an increase again. This increase corresponds quite closely with the wane of the second summer bloom (point e, Figure 5), but it is masked somewhat by the nitrogen uptake associated with the third bloom (point f, Figure 5). As the fall mixing did not occur until about November 1, these variations are not likely to be explained by this event. These variations may be explained in terms of biological nutrient cycling with the aid of the phytoplankton data.

PHYTOPLANKTON DATA

In collecting the phytoplankton data an attempt was made to classify the dominant algae encountered down to the genus level. Although a taxonomic classification may be desirable in some instances, it was felt that the important task in studying lake nutrient dynamics was merely to separate the algae into broad functional groups. For the purposes of investigating successional patterns, the phytoplankton were categorized into five functional groups: (1) diatoms, (2) non-motile green algae, (3) motile green algae, (4) non-nitrogen-fixing blue-green algae, and (5) nitrogen-fixing blue-green algae. Each of these five groups have general differences in their nutritional requirements, optimum environmental needs, susceptibility to predation, competition, degradation, and sinking rates. A realization of what these differences are can often be used to explain why one group succeeds another.

Table 2 contains a list of the dominant phytoplankton found in Stone Lake between May and November of 1973. This list contains representatives of four of the five groups discussed above. No dominant diatom genera were encountered during this time span; however, the large February bloom may have contained a significant diatom population. In the temperature zone, eutrophic lake diatom blooms generally occur in the early spring while the water is cold and before the silicon is depleted[7].

By grouping the phytoplankton into the four functional groups previously mentioned, the successional pattern in Stone Lake becomes quite obvious. Figure 12 presents a plot of the phytoplankton densities (on a log scale) occurring in the lake through the sampling period. The values used are an average of four depths counted. For the most part the non-motile green algae were evenly distributed throughout the first twelve feet. On the other hand, the blue-green and flagellates exhibited a slight decline in numbers with depth. This is consistent with the fact that blue-greens tend to float to the surface and flagellates are capable of diurnal migrations to seek more light.

Table 2. DOMINANT PHYTOPLANKTON IN STONE LAKE (1973)

1. Diatoms

   Present, but not found to be dominant

2. Non-motile green algae

   Chlorphyta
   - _Staurastrum_
   - _Cosmarium_
   - _Volvox_
   - _Scenedesmus_
   - _Pediastrum_
   - _Apatococcus_
   - _Quadrigula_
   - _Microspora_
   - Unidentified coccoid

3. Motile green algae

   Euglenophyta
   - Unidentified

   Pyrrhophyta
   - _Ceratium_

   Crytophyta
   - Unidentified

4. Non-nitrogen-fixing blue-green algae

   Cyanophyta
   - _Microcystis_

5. Nitrogen-fixing blue-green algae

   Cyanophyta
   - _Anabaena_
   - _Aphanizomenon_

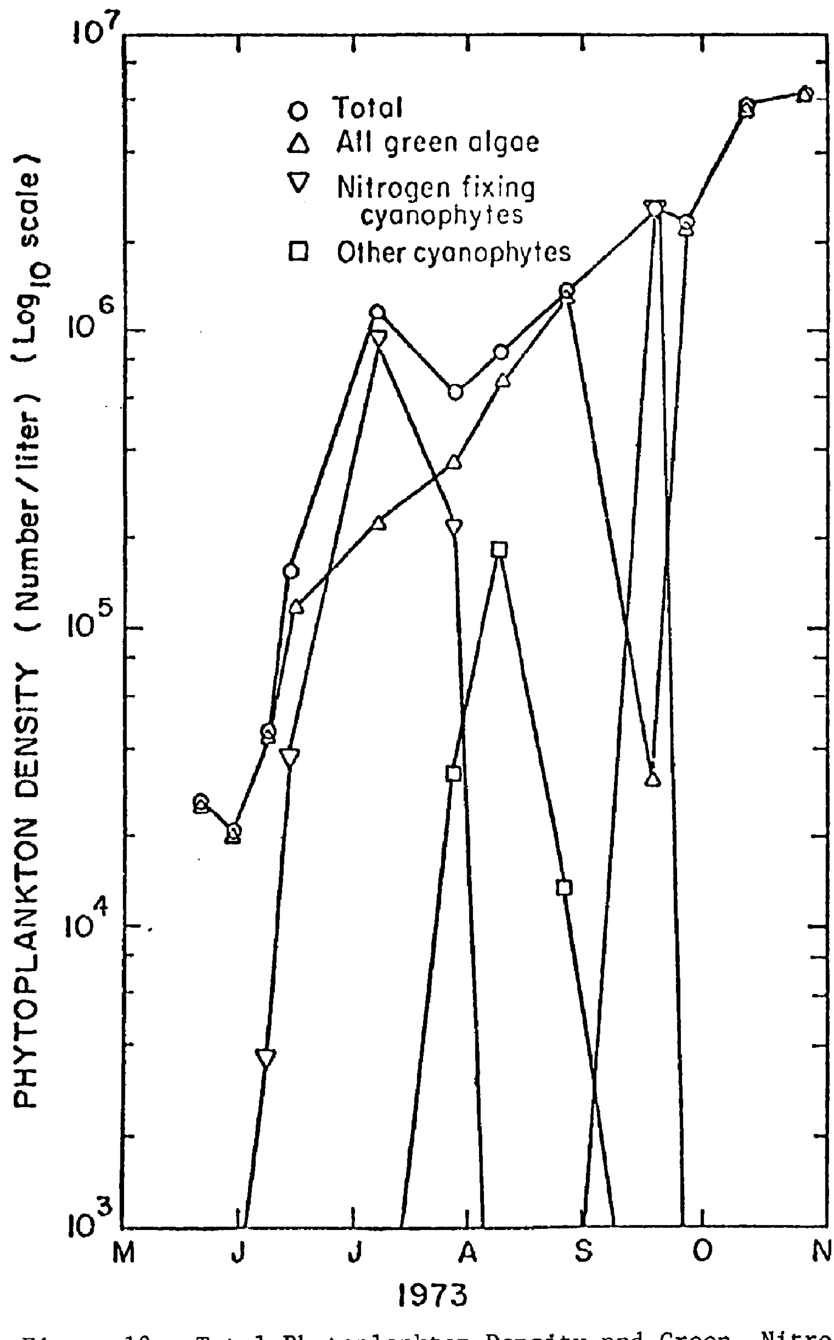

Figure 12: Total Phytoplankton Density and Green, Nitrogen-fixing Blue-green, and Non-nitrogen-fixing Blue-green Phytoplankton Groups Densities in Stone Lake, Michigan for May through October, 1973. Values Represent a Composite of Upper 12 feet of Depth.

Three peaks in the total phytoplankton are evident in this graph. The first peak occurred in the first week of July, and was followed by maxima in the middle of September and the middle of October. The population peaks correlate exactly with the suspended solids maxima in the surface waters of the lake (Figure 5). A further observation from this graph is that Stone Lake appears to be dominated by green algae. While the blue-green groups come and go, the green algae seem to be always present (though different genera within the group may dominate) and continually increasing (except for a drop in September). Several authors (Bierman[8], Payne[9], Morton,[10] et al.) have stated that green algae in general have higher maximum growth rates than blue-green algae. On the other hand, the minimum phosphorus requirement for green algae is considerably higher than that for blue-greens (Soeder[11], et al., Uhlmann[12], Shapiro[13]). The fact that green algae generally dominate in a eutrophic lake where phosphorus is never limiting is consistent with these findings.

The successional pattern of the phytoplankton groups is more easily visualized in Figure 13, which presents a bar graph of the percent composition of each algal group at each sampling date normalized to 100 percent. In mid-May the phytoplankton in Stone Lake were largely non-motile green species. Throughout June the nitrogen-fixing blue-green algae (*Anabaena* and *Aphanizomenon*) began to occupy a larger and larger percent of the population. During July the nitrogen-fixers disappeared and once again the green algae returned to dominance, although a small, short-lived bloom of *Microcystis* (the only non-nitrogen-fixing blue-green alga found in Stone Lake) occurred in early August.

In contrast to the earlier green algae dominance, the August green algae consisted roughly of equal parts of the motile and non-motile groups. In mid-September the second summer maximum was caused by another nitrogen-fixing blue-green bloom (*Anabaena*). In this case *Anabaena* completely dominated the total phytoplankton population (99 percent). Again, however, the greens recovered fairly rapidly and again the motile green algae lagged somewhat

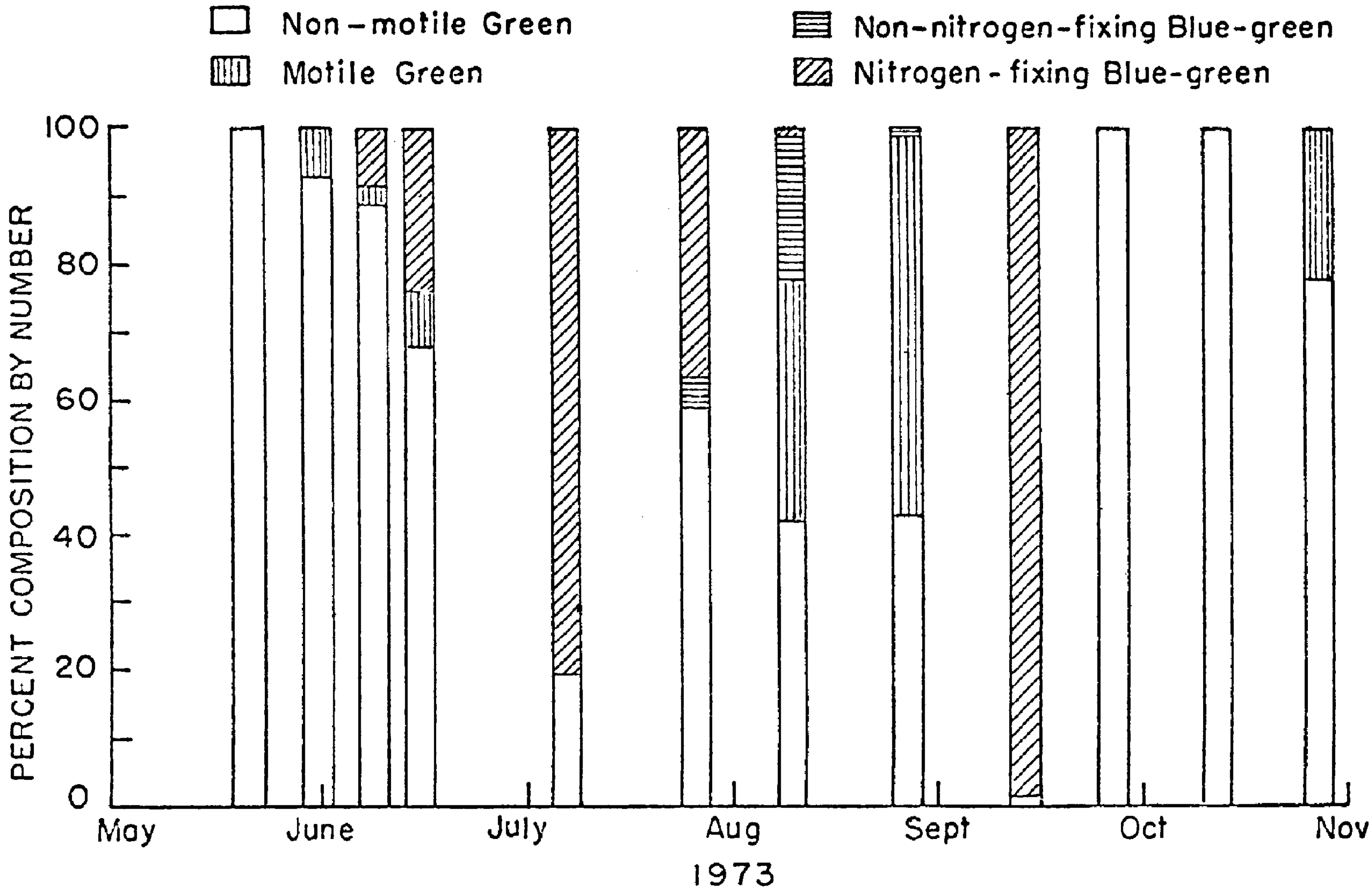

Figure 13: Composition of Phytoplankton in Stone Lake, Michigan from May through October, 1973. Relative Numbers of Each of the Four Major Groups are Normalized to 100 percent.

behind the non-motile green algae. The third and final summer peak was caused by this green algae resurgence, with *Microspora* being the dominant genus in the bloom. A final algal sample taken on November 12 (during circulation) revealed qualitatively that this final green algal bloom had been distributed through the entire water column. Also, a great deal of detritus was observed at all depths - and much more in the upper waters than before complete mixing conditions had existed.

SEASONAL SUCCESSION AND NUTRIENT REGENERATION

By comparing the time variation of nutrients in the upper waters of Stone Lake with the phytoplankton succession, one can postulate several causal relationships to explain the lake dynamics. These relationships are important to the concept of lake management and/or restoration. It is desirable to be able to predict *a priori* if a given set of environmental conditions will tend to favor a stable (non-blooming) or an unstable (frequent blooms) system. Based on the common definition of an algal bloom being about 5-20 mg/l (dry wt.) (Azad and Borchardt[14]), it can be stated that Stone Lake supports a continuous bloom throughout the summer stratification period. Often, however, the only objectionable blooms are those of blue-green algae. Knowledge of nutrient dynamics and how they affect algal dominance can perhaps lead to the prevention of these nuisance conditions.

It was noted earlier that the phytoplankton in Stone Lake began to bloom with the onset of thermal stratification. Prior to this the macrophytes in the lake were by far the dominant biomass. There are two probable explanations for the macrophyte dominance during the months of April and May. First, the complete mixing conditions in the lake at this time correspond to one of the "stress points" suggested by Round[15]. It is possible that the average residence time of the algae in the illuminated zone was not long enough to effectively compete with the macrophytes for light. Mortimer[16] has stated that a high ratio of stirred depth to illuminated depth can impose a condition of "morphometric oligotrophy". The second disadvantage which the phytoplankton faced at this time of the year was the appearance of filter-feeding zooplankton. The fact that the only green algae which were present at this time were too large to be grazed by most zooplankton suggests that the zooplankton had an impact on the rest of the algal community.

Concurrently with the phytoplankton biomass increase, the macrophytes began to die off. The decrease in weeds may have been due to shading from algae, but, in any event, the macrophyte decline brought a simultaneous increase in epilimnetic soluble phosphate. This event was not studied closely enough to determine if the phosphorus regeneration was mainly due to nutrient pumping, as suggested by Schults and Malueg[17], or to decay of the plants themselves.

As mentioned earlier, the green algae were the first to dominate the phytoplankton community. This dominance is probably due to their more rapid growth and to the excess availability of all nutrients in the spring. At the beginning of June the nitrate concentrations had become quite low (points a, Figure 11) and ammonia was already zero in the surface water (Figure 10). The low combined inorganic nitrogen provided a competitive advantage to the nitrogen-fixing blue-green algae, which began to rise at the expense of the green algal growth rate (Figures 12 and 13). The dominance and decline of Anabaena and Aphanizomenon in late June and July brought a regeneration of nitrogen in the epilimnion. The nitrogen which they fixed appeared as soluble nitrate due to their continual decomposition and the subsequent nitrification of the ammonia released. The rapid decline of the nitrogen-fixers could have been due to a number of reasons. Two plausible explanations, however, are bacterial attachment -- blue-green algae are closely associated with bacterial activity (Kuentzel[18], Lange[19]) -- and the return of the competitive advantage to the green algae because of the increased nitrogen levels. Huang et al.[20] have used nutrient enrichment tests to show that green algae, especially Chlorella, can more effectively compete with blue-greens when phosphorus and nitrogen are added to a nutrient poor environment.

Green algae dominated again through August and again depleted the nitrate in the water. This time blooms of Microcystis and a motile green alga shared the productivity. A rise in these groups could possibly have been due to the depletion of an essential nutrient other than phosphorus. Bierman[8], Shapiro[13] and Bush and Welch[21] have reported that blue-green algae, especially Microcystis, can out-compete other species for phosphorus when external concentrations are low. Warmer water has been given as a possible explanation for the development of blue-green algae (Hutchinson[22], Vinyard[23]) and this may, in fact, be a contributing factor. It has been reported that the optimum temperature for growth of most blue-green algae is about $35^{o}C$ (Fogg[24]); however Stone Lake did not exceed $26^{o}C$ during 1973 and most green algae achieve maximum growth rates at about $25^{o}C$ (Marre[25]).

The motile green algal bloom could also have been a nutrient-depletion phenomenon. Being motile, these algae may be able to more efficiently obtain an essential nutrient which is in low supply. Although it was not investigated, they may have migrated into the lower epilimnion or thermocline at night and thereby replenished their supply of a nutrient which is exhausted at the surface. Also, this particular motile-green bloom consisted of Euglenophytes. It happened to coincide with an increase in soluble organic nitrogen in the surface water (Figure 9). Hutchinson[22] has stated that Euglenophytes dominate in water rich in nitrogenous organic compounds.

Depletion of combined inorganic nitrogen signaled the onset of a nitrogen-fixing blue-green bloom (Anabaena, Figure 13) in late August and early September. This time the domination was complete and the green algae suffered a setback. The large decline in the green population (Figure 12) in this case could be due to an inhibitory substance excreted by the Anabaena. Hutchinson reported a number of studies on the effect of water collected from lakes and ponds at the time of a large Anabaena bloom on the growth of test organisms. The filtrate of this water was always algistatic to all species studies. Again the blue-green bloom crashed as quickly as it came about, with the corresponding nitrogen regeneration - this time as ammonia. It is interesting to note this type of cyclic succession of green to nitrogen-fixing blue-green and back to green which occurs during summer stratification in Stone Lake. This successional pattern will probably be common in most stratified lakes with excess phosphates and a tendency toward nitrogen limitation.

The nitrate regeneration associated with the second nitrogen-fixer bloom was somewhat masked by the rapid nitrate uptake as the green algae regained their previous status. In contrast to previous green dominations, this late September - early October bloom was dominated by one species (Microspora). Apparently Microspora is an opportunistic variety, which outgrew other greens when conditions were favorable. Subsequent to the Microspora peak, a planktonic Cryptomonad emerged. Practically all Cryptophyta require vitamin B_{12} or thiamin, usually both, for optimal growth. The Cryptomonad appearance may possibly have been the result of a vitamin excretion by Microspora or stimulated bacterial activity. Organic growth factors can be an important reason for the decline of alloauxotrophic phytoplankton. As noted earlier, this fall bloom terminated rather abruptly with the fall circulation. Fall circulation represents another of Round's "stress points".

SECTION V

STUDIES ON THE RECLAMATION OF STONE LAKE

INTRODUCTION

There is little doubt among most water resources experts that many of the nation's freshwater inland lakes have deteriorated to a point where the simple curbing of nutrient inputs is no longer enough to restore multiple water uses. Numerous restoration techniques for these lakes have been proposed and/or are being evaluated. Among them are the following: (1) dredging, (2) harvesting, (3) nutrient inactivation/precipitation, (4) total or hypolimnetic aeration, (5) bottom sealing, (6) sediment exposure, (7) ecological manipulations, (8) application of selected biocides, and (9) artificial dilution or flushing. Each of these techniques has advantages and disadvantages depending upon the particular system to which they are applied. In this section, the potential use of particulate materials to precipitate and seal phosphate in sediments will be presented.

PARTICULATE MATERIALS AS SEDIMENT SEALANTS

Several types of materials were investigated for their sealing properties on eutrophic lake sediments including clays, sand, and fly ash (Yaksich[26]). A summary of these results is given in Table 3.

Although many of these materials showed promise in the restoration of lakes through sediment sealing, particular attention was focused on the use of fly ash, a common by-product of coal combustion. The United States produces 30×10^9 Kg of this material annually, with estimates of up to 90×10^9 Kg by the year 2000. Understandably there is a great desire on the part of those concerned with its disposal for utilization in some favorable manner.

Table 3

Summary: The Effectiveness as Lake Restoration Tools of Eleven Particulate Materials.

Material	Effect on water quality	Compatability with chemicals used to improve water quality	Settling properties, time for 99 percent to settle 20 feet	Ability to control phosphate release from sediments under anaerobic conditions	Ability to resist resuspension velocity needed to disrupt barrier	Comments: effectiveness in a lake restoration project
Kaolinite Clay	Adsorbed phosphate but additional chemicals may be needed	Alum could be used to precipitate phos-	Good 40 hours	5.0 cm layer effective	Very Good 40 cm/sec	Could be used if alum was added first to precipitate phosphate and later added to reduce turbidity caused by the clay
Bentonite Clay	Very poor phosphate adsorption	Alum could be used to precipitate phosphate and reduce turbidity	Very Poor >40 days	Ineffective, it increased rate of phosphate release	Very Good 40 cm/sec	Should not be used, it would increase rate of phosphate release
Georgia Clay	Exhibited some phosphate adsorption, additional chemicals would be needed	Alum could be used to precipitate phosphate and reduce turbidity	Fair 72 hours	5.0 cm layer	Barely Acceptable 15 cm/sed	Could be used on deep water sediments if alum was added first to precipitate phosphate and later added to reduce turbidity caused by the clay
Tennessee Clay	Adsorbed phosphate, but additional chemicals may be needed	Alum could be used to precipitate phosphate	Very Good 12 hours	5.0 cm layer effective	Good 30 cm/sec	Alum could be used first to precipitate phosphate, then clay added to cover sediments
Illinois Clay	Adsorbed phosphate, but additional chemicals may be needed	Alum could be used to precipitate phosphate and reduce turbidity	Poor 28 days	5.0 cm layer effective	Good 30 cm/sec	Could be used in shallow lakes if clay was added first to precipitate phosphate and later added to reduce turbidity caused by the clay
Silt	Adsorbed phosphate, but additional chemicals may be needed	Alum could be used to precipitate phosphate and reduce turbidity	Good 24 hours	Sank below sediments and did not retard phosphate release	Fair 20 cm/sec.	Would be an ineffective barrier on flocculant sediments
Sand	Did not absorb phosphate	Alum could be used to precipitate phosphate	Excellent 18 minutes	5.0 cm layer effective	Very Good 40 cm/sec.	Not recommended as a barrier on Stone Lake sediments because of difficulty in forming a stable barrier
Fly Ash No. 1	Precipitated phosphate, but additional chemicals may be needed	Precipitated phosphate in combination with alum or lime	Very Good 6 hours	Sank below sediments and did not retard phosphate release	Good 30 cm/sec.	Would be an ineffective barrier on flocculant sediments
Fly Ash No. 2	Effectively precipitated phosphate	Precipitated phosphate; excellent with lime, good with alum	Good 24 hours	2.0 cm layer effective	Fair 20 cm/sec.	Could be used by itself, or with alum or lime to precipitate phosphate. Effectively retarded phosphate release
Fly Ash No. 3	Precipitated phosphate, but additional chemicals needed	Precipitated phosphate; excellent with lime, good with alum	Very Good 3 hours	Ineffective	Barely Acceptable 15 cm/sec	Not recommended because of failure to stop phosphate release
Fly Ash No. 4	Very effectively precipitated phosphate	Precipitated phosphate; excellent with lime, good with alum	Good 24 hours	2.0 cm layer effective	Fair 20 cm/sec.	Most effective, particularly tested in precipitating phosphate and retarding phosphate release. Effectively precipitated phosphate and settled in in situ column study by itself and in combination with lime

Table 4 indicates the range of the macro-constituents of this substance. It is composed primarily of silica, alumina, and variable amounts of iron and calcium oxides. The lime brings about phosphate removal from the overlying water and once in place fly ash displays sealing properties which effectively retard the release of phosphorus from the underlying sediments. Due to the variability of the lime content naturally present in fly ash, some lime makeup may be required to bring about acceptable levels of phosphate precipitation.

Table 4. TYPICAL RANGES OF THE CHEMICAL COMPOSITION OF FLY ASH FROM PULVERIZED COAL FIRED PLANTS (after Minnick[27])

Constituent	Range % by weight
Silica, SiO_2	34 - 38
Alumina, Al_2O_3	17 - 31
Iron Oxide, Fe_2O_3 or Fe_3O_4	2 - 26.8
Calcium Oxide, CaO	1 - 10
Magnesium Oxide, MgO	0.5 - 2
Sulfur Trioxide, SO_3	0.2 - 4

The effectiveness of fly ash in precipitating and retarding phosphate release is illustrated in Figures 14 and 15. Depending on the fly ash, a 5-20 gram/liter dose and a 2 to 5 centimeter layer should bring about the desired effects.

To see if treated Stone Lake water was phosphorus limited, and perhaps nitrogen limited also, an algal regrowth study was conducted on Stone Lake water treated with 5 g/ℓ fly ash plus 150 mg/ℓ lime, and spiked

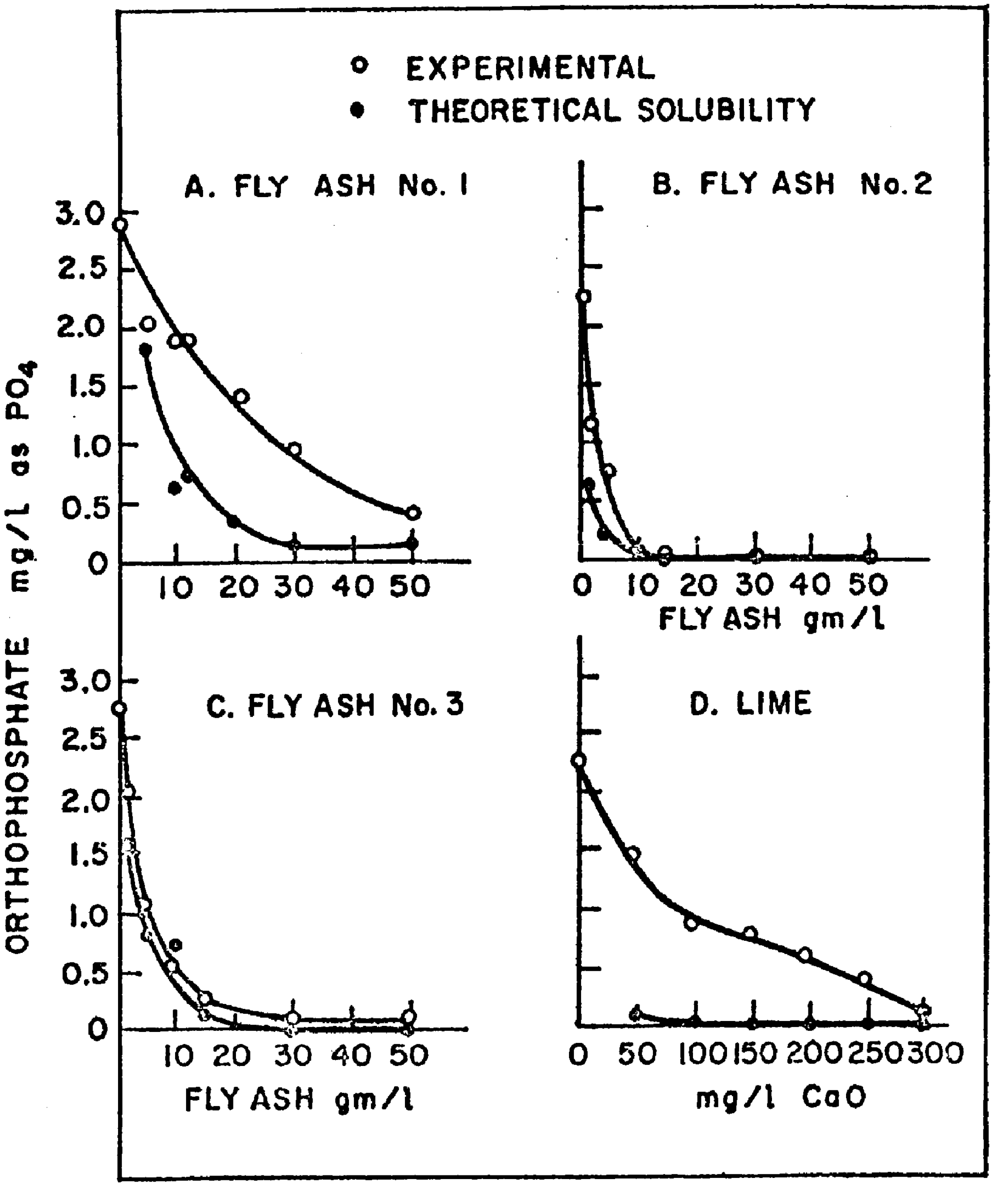

Figure 14, A-C: Effectiveness of Different Fly Ashes in Removing Orthophosphate from Solution.
D: A Similar Plot for Lime (after Yaksich[26]).

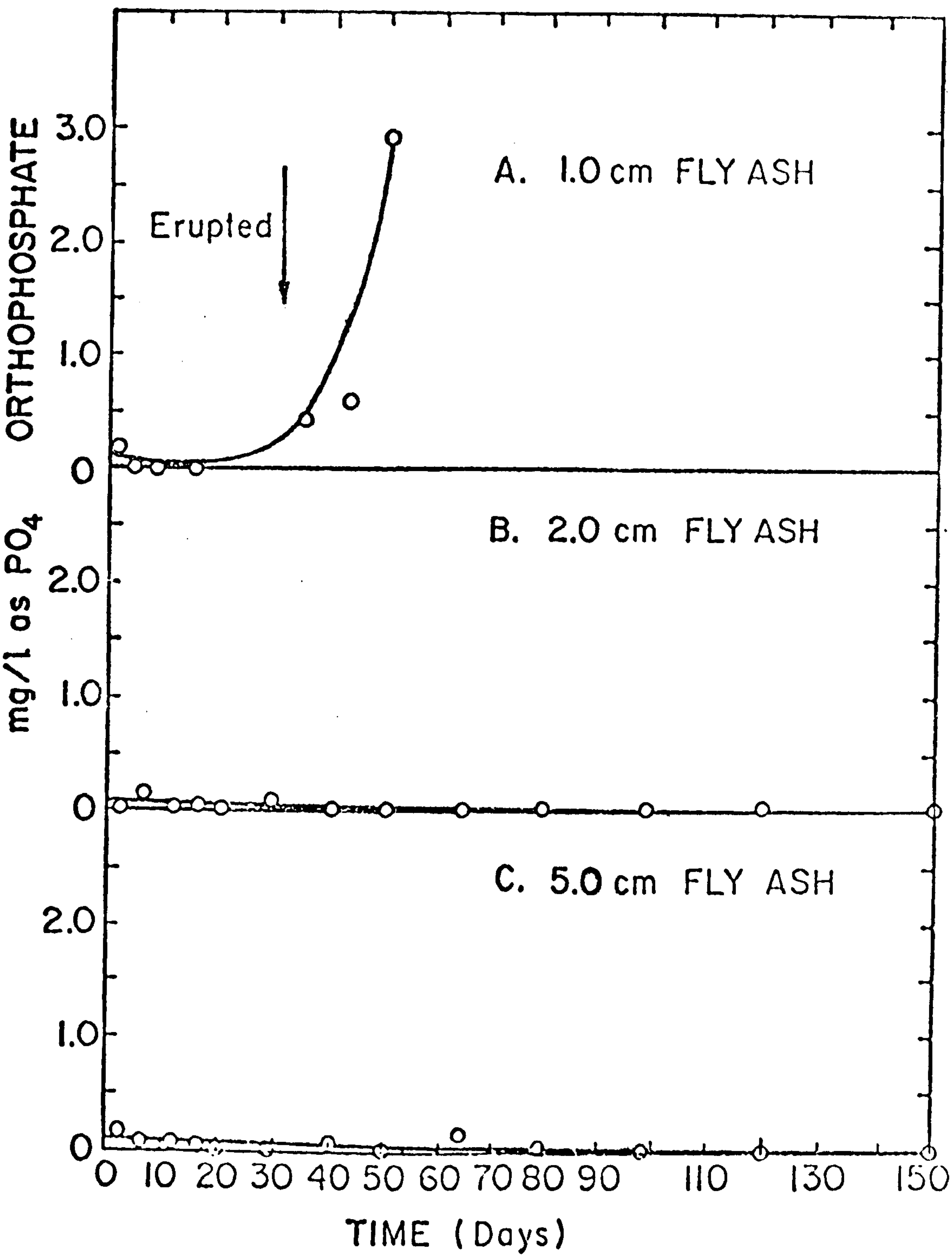

Figure 15: Effectiveness of Various Thicknesses of Fly Ash in Retarding Phosphate Release from Stone Lake Sediments. Experiments Performed in Laboratory Reactors (after Yaksich[26]).

with nitrogen and phosphorus (Higgins et al.[28]). The orthophosphate level in treated water was 7.5 μg/ℓ, while the filtered lake water had 101 μg/ℓ. Figure 16 shows almost a ten-fold cellular growth increase in filtered lake water spiked with 4 mg/ℓ of nitrogen (added by $NaNO_3$), as compared to the unspiked control. Clearly, the lake water was nitrogen deficient. Treated lake water showed the least growth, as it was deficient both in phosphorus and nitrogen. Adding 4 mg/ℓ of nitrogen to treated water did not result in any significant increase because growth was still phosphorus limited. Spiking the treated lake water with both nitrogen and phosphorus to levels equivalent to the control plus 4 mg/ℓ of nitrogen did enhance algal growth significantly, but it was much less than in the control spiked with 4 mgN/ℓ. These data suggest that the fly ash and lime treatment of polluted lake water reduces the algal regrowth potential, not only by making it phosphorus limiting, but also by either removing some additional growth factors or by adding an inhibitory substance.

Available evidence indicates that within each yearly cycle the sediments of Stone Lake act as a major pollutional source. Further research on the sediments led to a delineation of four general sediment types shown in Figure 17. These sediment types can be described as follows: (1) shoreline sediments (C1-C8 in Figure 17), which comprise 25 percent of the bottom of Stone Lake, are mostly sand, and possess little pollution potential; (2) west bay sediments (D1-D3), which occupy 15 percent of the bottom and are of an intermediate pollutional potential; (3) north bay sediments (A1-A5), 19 percent of the bottom, are of a higher pollutional potential; and (4) deepwater sediments (B1-B7), 42 percent of the bottom, and have the highest pollutional potential. The precise parameters used to define the pollutional potential are given in Table 5.

The characterization of Stone Lake sediments has led to a hypothetical differential treatment scheme in which varying amounts of fly ash and lime are added to Stone Lake reflecting the pollutional potential of the

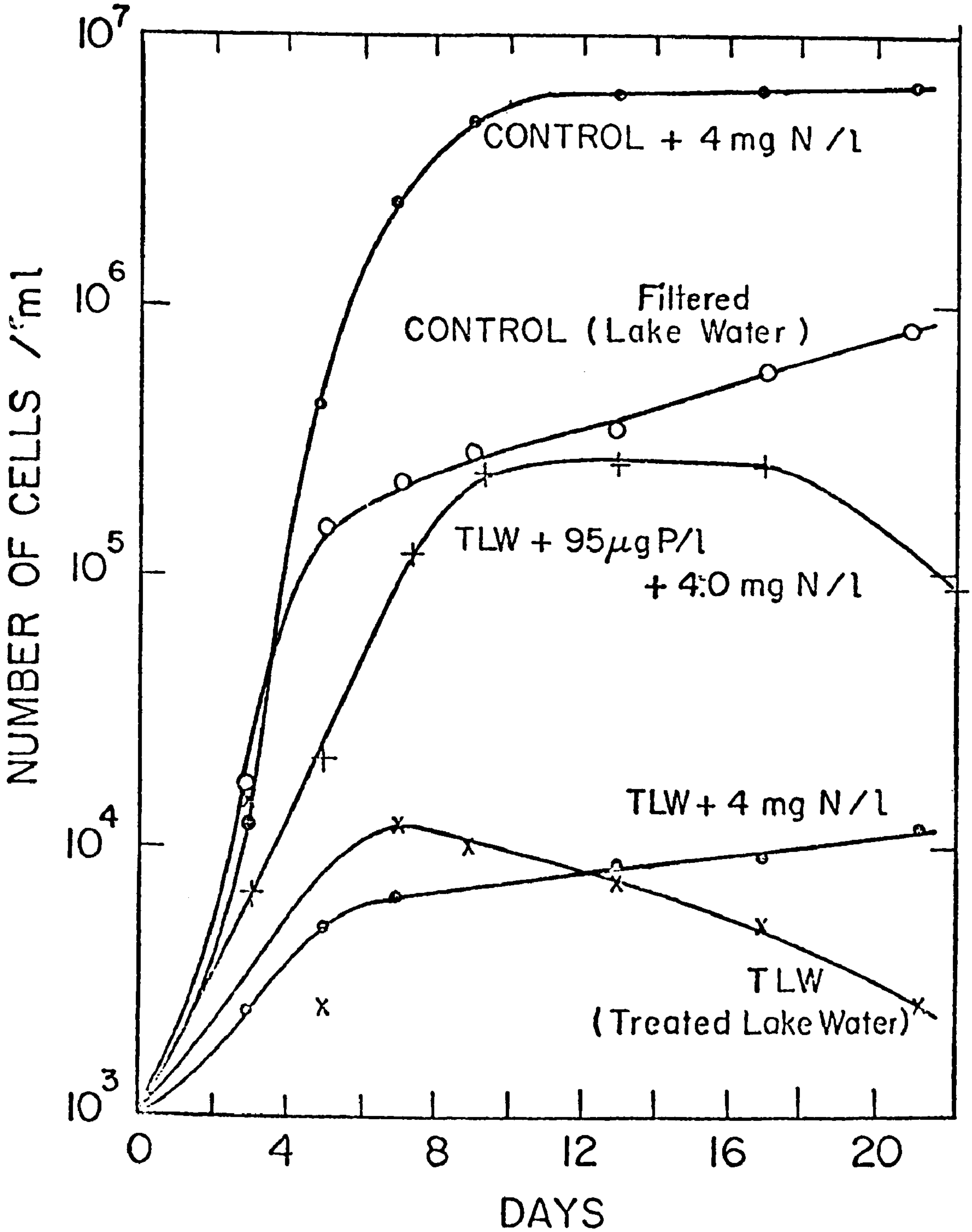

Figure 16: Algal Regrowth Study on Stone Lake Water Treated with 5 g/l Fly Ash and 150 mg/l Lime. The Top Two Curves (open and closed circles) Indicate the Lake Water is Nitrogen Limited. The Bottom Curves Show the Same Water to be Phosphorus Limited After Treatment (after Higgins et al[28]).

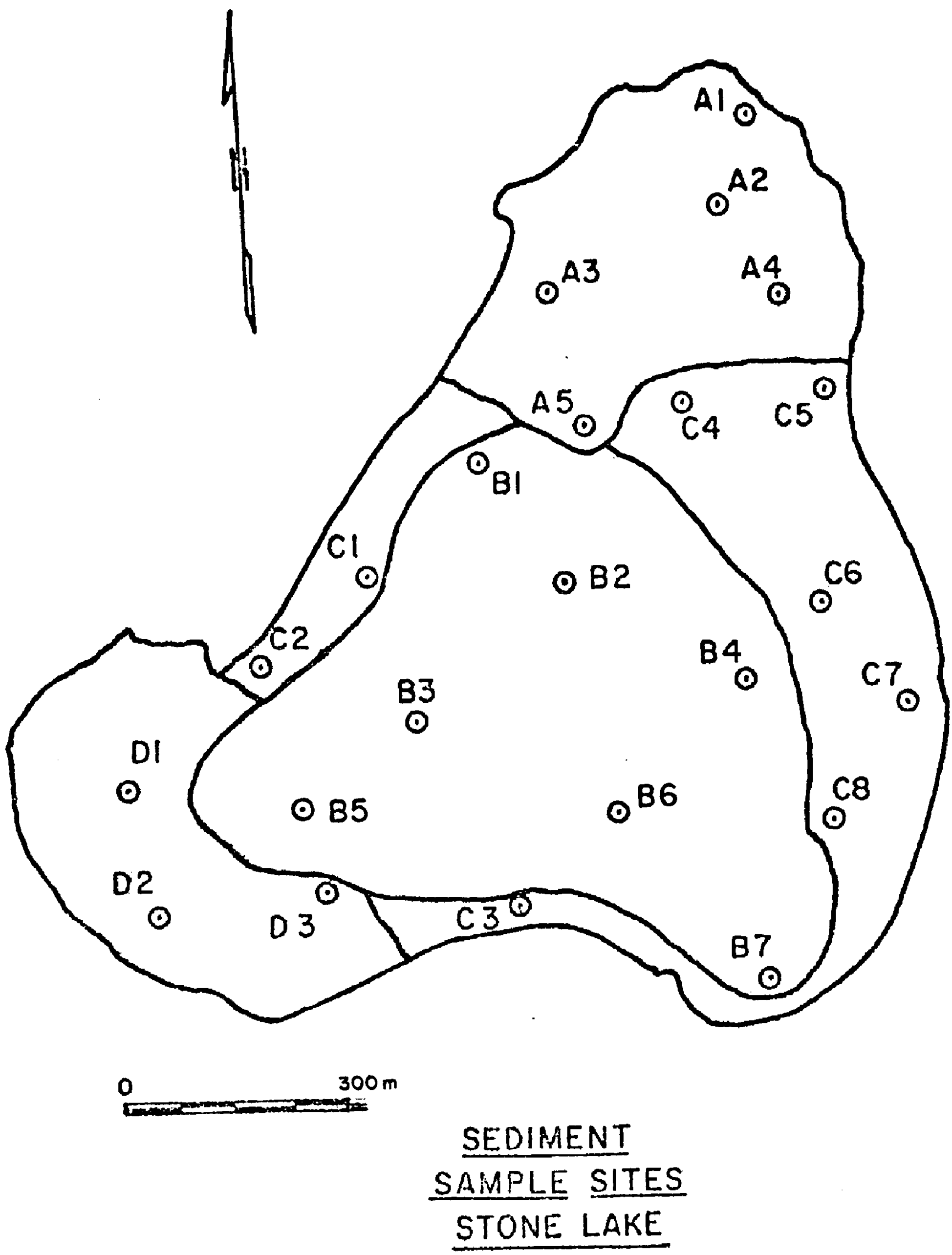

Figure 17: Sample Sites for Sediment Survey of Stone Lake (after Yaksich[26]).

Table 5

POLLUTIONAL POTENTIAL OF STONE LAKE SEDIMENTS

Location Number	Depth ft.	Soluble Orthophosphate mg/l as PO_4	Total Soluble P mg/l as PO_4	COD mg/l as O	NH_3 mg/l as N	Organic-N mg/l as N	Organic Matter % dry wt.	% Water	Retained on #200 sieve % dry wt.
A1	5	2.50	2.50	27	5.4	2.5	13.1	90.6	6.8
A2	8	7.16	8.60	36	5.6	3.1	47.0	95.3	7.4
A3	8	3.00	3.10	36	8.2	3.2	28.3	88.4	36.5
A4	8	3.75	3.95	40	5.5	3.2	44.2	93.8	8.1
A5	20	2.90	3.20	40	7.2	2.8	40.4	93.0	7.0
B1	20	5.70	5.70	48	8.5	2.2	12.3	76.1	72.3
B2	42	7.30	8.10	63	35.0	3.9	32.3	92.8	2.5
B3	44	6.10	7.10	76	39.2	3.6	22.8	93.0	3.3
B4	35	8.60	8.84	55	23.7	-	28.1	91.6	12.6
B5	27	3.40	3.80	44	28.5	3.9	37.6	92.1	1.2
B6	50	4.85	6.00	55	43.2	4.2	33.9	92.0	10.4
B7	30	6.90	6.90	55	17.0	2.8	18.2	91.5	8.1
C1	18	1.70	1.70	55	2.6	3.9	2.5	41.8	94.6
C2	5	1.25	-	72	1.6	-	1.7	27.7	99.0
C3	16	1.40	-	45	1.8	-	1.5	36.8	98.6
C4	9	1.70	-	86	2.0	-	0.7	22.2	99.5
C5	8	1.10	-	82	6.9	-	3.2	38.9	95.8
C6	7	.45	-	91	1.9	-	0.5	18.7	99.4
C7	4	.64	-	124	2.4	-	4.2	23.2	94.5
C8	12	1.32	-	107	2.4	-	0.3	23.1	98.8
D1	8	1.90	1.97	24	2.8	3.2	61.8	95.3	13.8
D2	4	3.92	4.70	34	1.5	2.2	20.2	96.2	27.5
D3	18	3.25	3.47	38	5.7	1.7	29.2	94.4	23.1

* Concentration in interstitial water.

sediments. This is shown in Figure 18. A similar approach could be used for other eutrophic lakes to which this treatment technique is applied.

FARM POND STUDY

In the summer of 1972, a one acre farm pond in Mishawaka, Indiana was treated with fly ash. The main purpose of the treatment was to evaluate fly ash application methods and to aid in the development of an application method for Stone Lake. In this respect, the treatment was a success and helped lead to the current method proposed for fly ashing eutrophic lakes.

In addition to the above studies, some monitoring of the pond was performed before and after treatment to help evaluate the effect of the treatment on water quality and biota. The pond was not an ideal test case for the long term effects of fly ash in reducing productivity because the constant enrichment from high nutrient runoff and direct input of cattle wastes could not be curtailed following treatment. In any event data were taken and visual observations made which did shed light on the technique of treating natural waters with fly ash.

The water quality data in Table 6 show that the fly ash treatment was effective in reducing the phosphate concentration in the pond. However, it can be seen from the chemical data that the pond one year later is very similar to its pretreatment state. The relatively high suspended solids can be explained by noting that the ground water well which feeds the pond is high in colloidal clay material (20 mg/l). The significant phosphate increase over the immediate post-treatment level was due to nutrient runoff from the heavily fertilized drainage area. A significant increase in the combined inorganic nitrogen concentration from July 10, 1972 to August 2, 1972 corroborates this hypothesis.

Before treatment, this pond was approximately one-half covered with a thick, filamentous algal mat, which was not skimmed off prior to treatment.

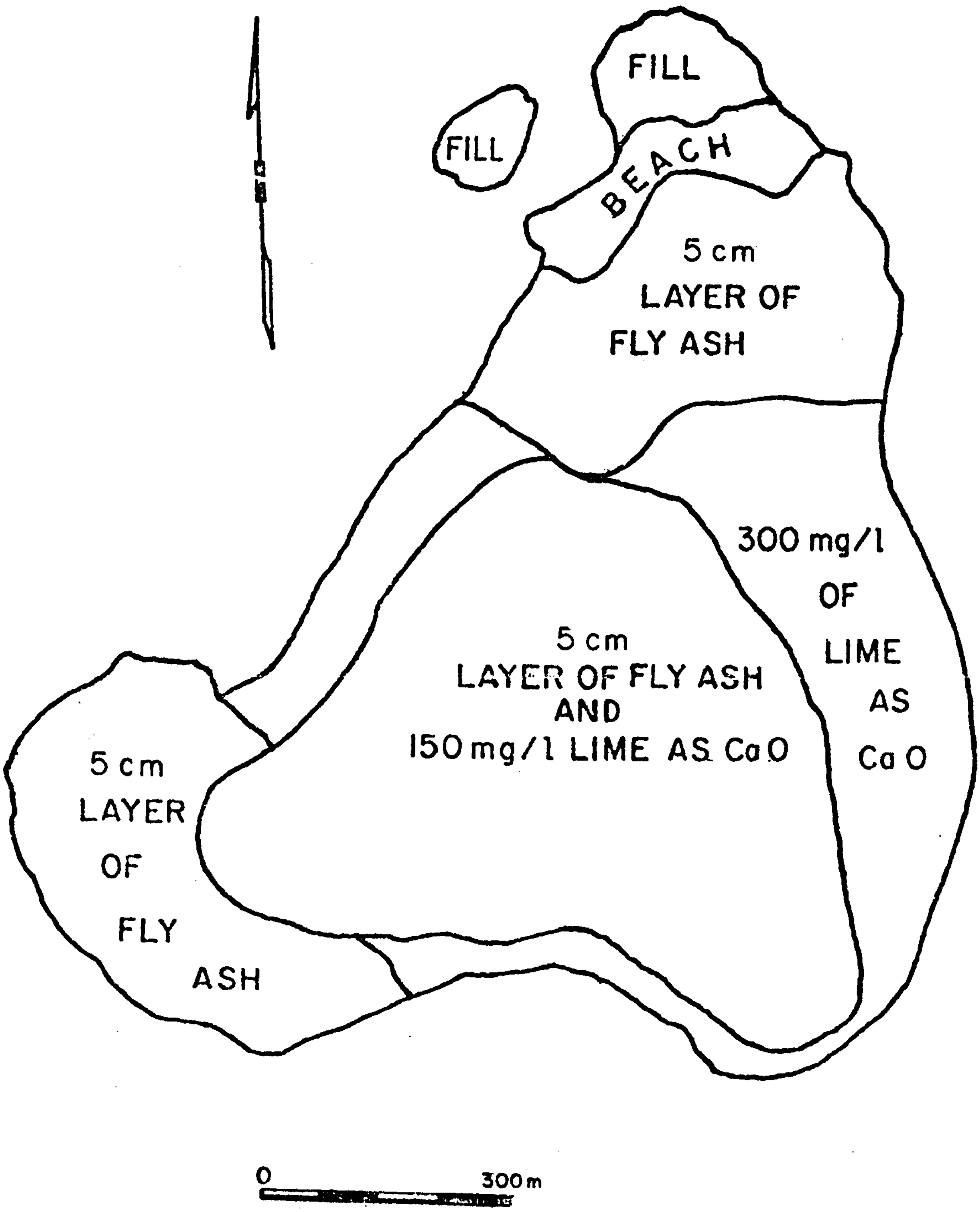

Figure 18: Restoration Plan for Stone Lake (after Yaksich[26]).

Table 6. SUMMARY OF WATER CHEMISTRY DATA FOR MISHAWAKA FARM POND

Date+ / Parameter*	Before treatment		After treatment		
	May 15, 1972	July 6, 1972	July 10, 1972	Aug. 2, 1972	July 2, 1973
pH	8.75	8.80	10.90	9.00	9.30
Suspended solids (mg/ℓ)	15.0	17.5	25.0	10.0	10.5
Alkalinity (mg/ℓ as $CaCO_3$)	84	70	181	66	45
Ca^{++} hardness (mg/ℓ as $CaCO_3$)	66	45	278	173	54
$SO_4^{=}$ (mg/ℓ as $SO_4^{=}$)	20.1	19.2	178	166	25.1
Soluble orthophosphate (mg/ℓ as PO_4)	0.086	---	0.013	0.084	0.110

* Treatment of pond took place on July 7-9, 1972.
+ Values given are an average of 4 horizontally located points in the pond.

The fly ash addition served to sink this mat, and no signs of regrowth or emergence of the mat occurred through the rest of the growing season. However, the next summer portions of the mat reappeared with a grayish tinge in color which suggests that gases produced through the winter and early spring may have buoyed the mat up to the surface. Parts of the mat were definitely green and viable indicating that the increased nutrients due to runoff allowed for the development of an algal mat similar to that present before treatment. This occurrence indicates a potential problem associated with applying fly ash over the macrophytes in Stone Lake and their subsequent decomposition. It may be necessary to harvest any macrophytes present in the lake prior to treatment. Another potential problem associated with macrophytes is their possible regrowth through the fly ash in the littoral areas of the lake after treatment.

COMPARATIVE COSTS OF RECLAMATION

One drawback to the use of fly ash, or other particulate materials, as aids to lake reclamation is the quantity of material involved. Based on previously cited studies, amounts of up to 300 tons of fly ash per acre are necessary. In spite of this, a cost analyses of various lake reclamation techniques, as applied to Stone Lake, found sediment sealing to be competitive with most other methods and considerably less expensive than some (Girman[29]). The total cost of fly ash application to Stone Lake was determined to be approximately $250,000. Table 7 indicates the relative cost effectiveness of seven reclamation techniques weighted by several factors on a scale of 1 (least effective) to 5 (most effective).

SIDE EFFECTS

Unfortunately, fly ash imparts many water soluble species to an aqueous solution. Table 8 is a partial list of these components and the probable chemical form under which each would be likely to exist.

Table 7. COST-BENEFIT TABLE (after Girman [29])

Criteria	Cost	Ease in handling & application of technique	Time of application	Fishery resources after treatment	Removal of nutrients	Potential for water-based activities	Aesthetic value	Total out of a possible 100 points
Multi-factor	5	3	1	1	4	2	4	
1) Fly ash	^{4}(20)	^{5}(15)	^{4}(4)	^{2}(2)	^{4}(16)	^{4}(8)	^{4}(16)	81
2) Fly ash & lime	^{4}(20)	^{4}(12)	^{5}(5)	^{2}(2)	^{4}(16)	^{4}(8)	^{4}(16)	79
3) Nutrient inactivation & bottom sealing (clay)	^{2}(10)	^{2}(6)	^{3}(3)	^{3}(3)	^{4}(16)	^{4}(8)	^{4}(16)	62
4) Nutrient inactivation & dredging	^{1}(5)	^{1}(3)	^{2}(2)	^{4}(4)	^{5}(20)	^{5}(10)	^{5}(20)	64
5) Nutrient inactivation & aeration	^{5}(25)	^{5}(15)	^{1}(1)	^{4}(4)	^{2}(8)	^{2}(4)	^{2}(8)	65
6) Mechanical harvesting & aeration	^{5}(25)	^{5}(15)	^{1}(1)	^{5}(5)	^{1}(4)	^{1}(2)	^{2}(8)	60
7) Replacing lake water with higher quality & a soil & plastic barrier	^{1}(5)	^{1}(3)	^{3}(3)	^{1}(1)	^{4}(16)	^{5}(10)	^{5}(20)	58

Note: Numbers in parenthesis denote the rating times the multiplication factor.

Table 8. IMPORTANT WATER SOLUBLE EXTRACTS OF FLY ASH

Specie	Major Chemical Form(s)
Ca, Mg	Ca^{+2}, Mg^{+2}
Na, K	Na^{+}, K^{+}
Fe, Al	$Fe(OH)_n^{+m}$, $Al(OH)_n^{+m}$, etc.
Co, Ni, Cu, Zn, Cd	Various hydroxylated forms
Cr	CrO_4^{-2}, $Cr_2O_7^{-2}$, $Cr(OH)_n^{+m}$
As	AsO_4^{-3}
Pb	Pb^{+2}
Hg	Hg^{o}, Hg^{+2}
S	SO_3^{-2}, SO_4^{-2}
Si	SiO_3^{-2}
Alkalinity	HCO_3^{-}, CO_3^{-2}

Not all of these aqueous extracts can be considered harmless. Several adverse effects of fly ash addition can be noted as follows: (1) high pH effects, (2) dissolved oxygen depletion, (3) biological reduction of high sulfate levels to sulfide, (4) heavy metal accumulation and toxicity, and (5) physical clogging and crushing of aquatic organisms.

In laboratory aquaria tests, 10-20 grams/liter of fly ash was found to be toxic to fish indigenous to Stone Lake (Hampton[30]). The cause of death was attributed to clogging of gills and subsequent impairment of oxygen transfer. The applicability of these conditions to an actual lake, however, is questionable since the addition of fly ash would be to local areas over an extended time period allowing fish to avoid extreme conditions of pH or turbidity.

The effects of fly ash on zooplankton and benthos are less well known and will be studied more extensively in the future.

Dissolved oxygen depletion occurs primarily due to the presence of water soluble extracts of sulfite ion, SO_3^{-2}, a well known oxygen scavenger according to the equation

$$SO_3^{-2} + \frac{1}{2} O_2 = SO_4^{-2}.$$

The effects of this reaction in an isolated lake column are shown in Figure 19. Dissolved oxygen is depleted rapidly under these conditions and reaeration takes place gradually over a four day period.

Biological reduction of high levels of sulfate ion, SO_4^{-2}, (approximately 100 mg/l) have been shown to occur under the proper conditions. However fly ash, at least initially, appears to inhibit most bacterial action such that little reduction could be measured in laboratory reactors (Palla[31]). It should be noted as well that many eutrophic lake sediments contain high levels of sulfide during stratified periods. The additional amount due to fly ash may often be considered of minor importance.

The release of toxic trace metals to natural lake systems appears to be the greatest potential drawback to the use of fly ash. Table 9 gives a range of trace metals found in several different ashes as compared with natural crustal abundances.

Of course the background metal concentrations in the specific lake sediments are a more accurate indication of potential effects; however, Table 9 gives evidence of a need for further study in this area.

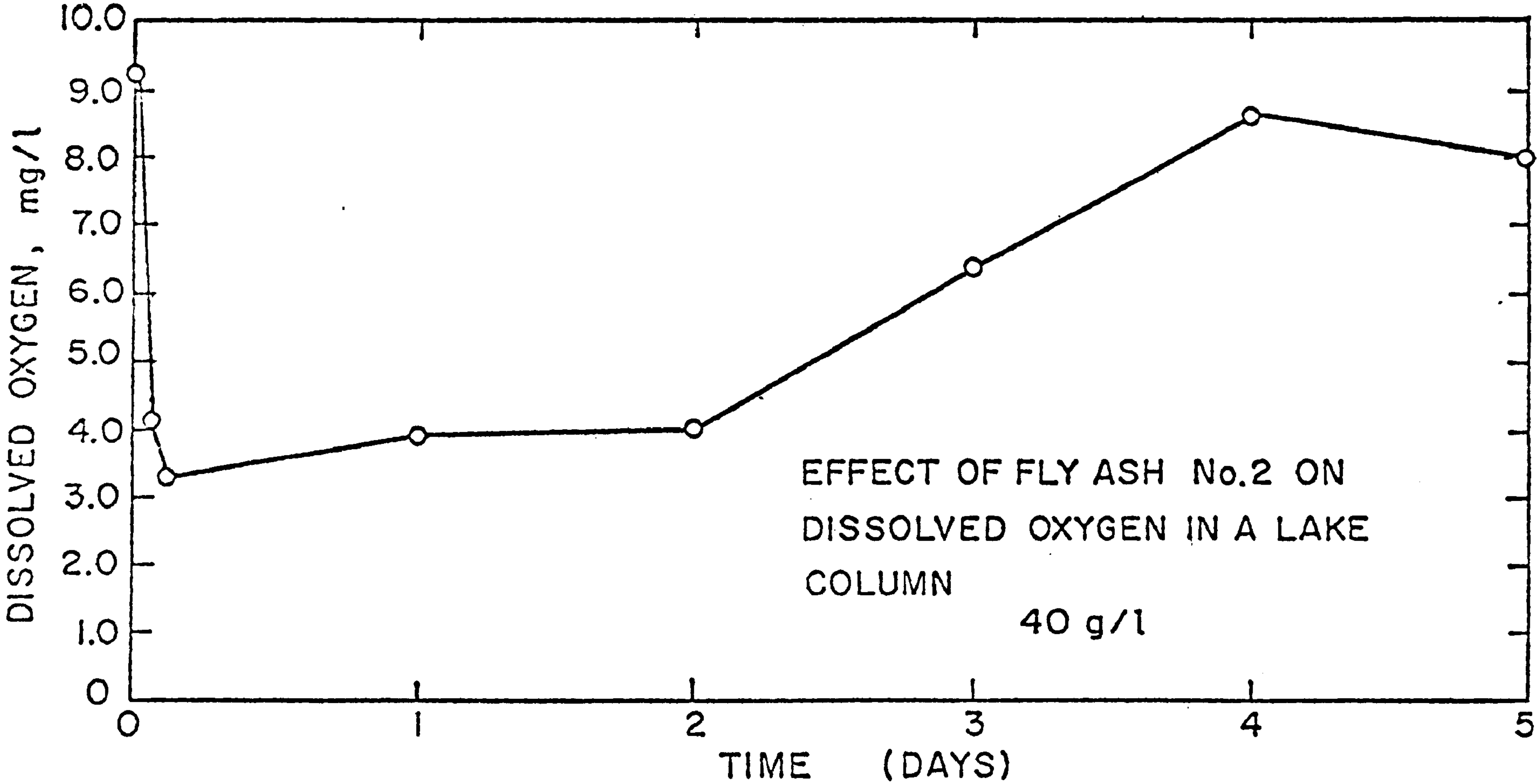

Figure 19: Dissolved Oxygen Depletion and Subsequent Reaeration in an Isolated Lake Column Following Fly Ash Addition.

Table 9. RANGES OF TRACE METALS IN FLY ASH
(after Theis[32])

Metal	Concentration Range, ppm	Avg. Crustal Abundance, ppm
As	2 - 288	1.8
Pb	9.5 - 500	13
Cu	14 - 300	40
Zn	41 - 1000	50
Cd	0.6 - 11.2	0.2
Cr	18 - 500	100
Hg	0.08 - 0.32	0.06

Several factors will affect the availability and effects of toxic trace metals on lake systems. These would include simple solubility controls, pH, the ion exchange and adsorptive characteristics of local solid phases (such as iron oxides and clays), complex formation, and biological incorporation and transportation.

Figure 20 contains standard logarithmic concentration-pH solubility diagrams for the various free metal ion and mono-hydroxo complexes of all the metals in question except arsenic (which is generally very soluble). In the normal pH range of natural waters, it is the hydroxide of these metals which controls their solubility. At very high pH's and high alkalinities, carbonate ion may control. It can be said from Figure 20 that, in general, the trace metals display drastically decreased solubilities with increasing pH. This factor would tend to keep most metals insoluble at the elevated pH levels anticipated during fly ash application.

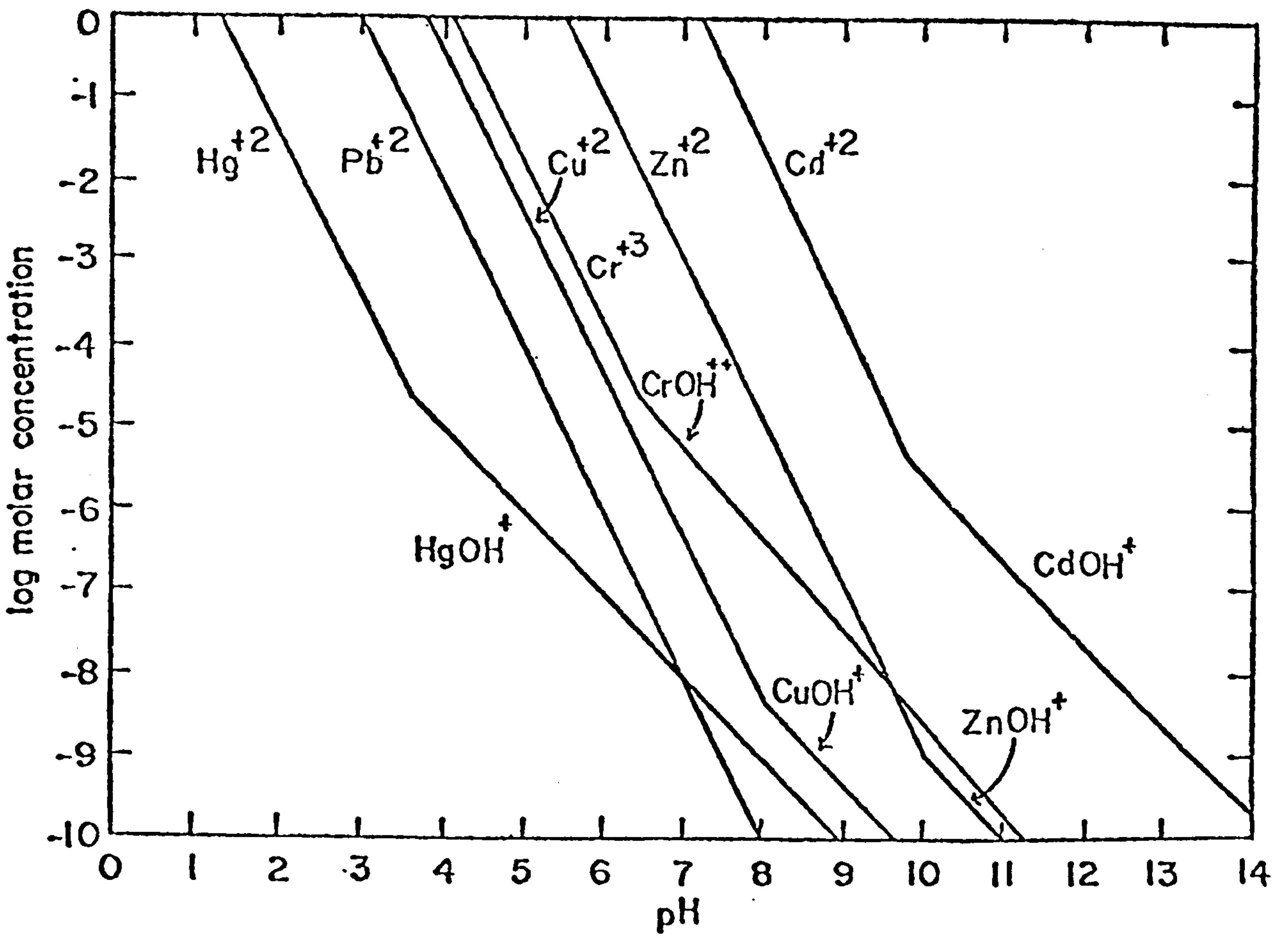

Figure 20: Solubility of Various Heavy Metals (free aqueous and mono-hydroxo species only).

Of course localized adsorption, complex formation, or biological incorportation, could functionally circumvent the relationships expressed in Figure 20. This is illustrated convincingly by the behavior of mercury from fly ash in laboratory aquaria shown in Figure 21. Two peaks of mercury release were noted, the first within a few hours of addition at an elevated pH, the second several days later at a lower pH. Although no corroborative evidence could be gathered, it is reasonable to postulate the action of a combined chemical/biological mechanism to explain the observations. The initial release, which is enhanced by the high pH, is essentially a desorption of mercury, probably in the elemental form. As conditions become more favorable for bacterial activity, it appears plausible that some of the mercury is biologically converted to an organo-mercurial, perhaps methyl mercury. The rapid disappearance of mercury is not unexpected since the reactors were at all times open to the atmosphere and many mercurial forms, particularly the two noted, are notoriously volatile.

SIDE STREAM TREATMENT

One further method of lake reclamation which was considered was the side-stream treatment of the water for selective removal of phosphorus. DePinto[34] investigated this method initially and performed laboratory bench scale studies to demonstrate its feasibility. He calculated the total cost of a 1 MGD portable treatment plant utilizing chemical precipitation to be approximately $100,000. A further analysis by Theis[35] suggested the use of activated alumina columns as selective phosphate adsorbents. A portable plant could be made significantly larger without a proportionate increase in cost. Another advantage of this method is that few, if any, undesirable constituents are added to the lake.

Of great importance in the technical evaluation of this method of treatment are the size of a plant necessary to bring about phosphorus removal in a reasonable length of time and the contribution of phosphorus from the sediments once treatment has begun. While this method itself has not been treated on a large scale, other flushing-type projects have been performed

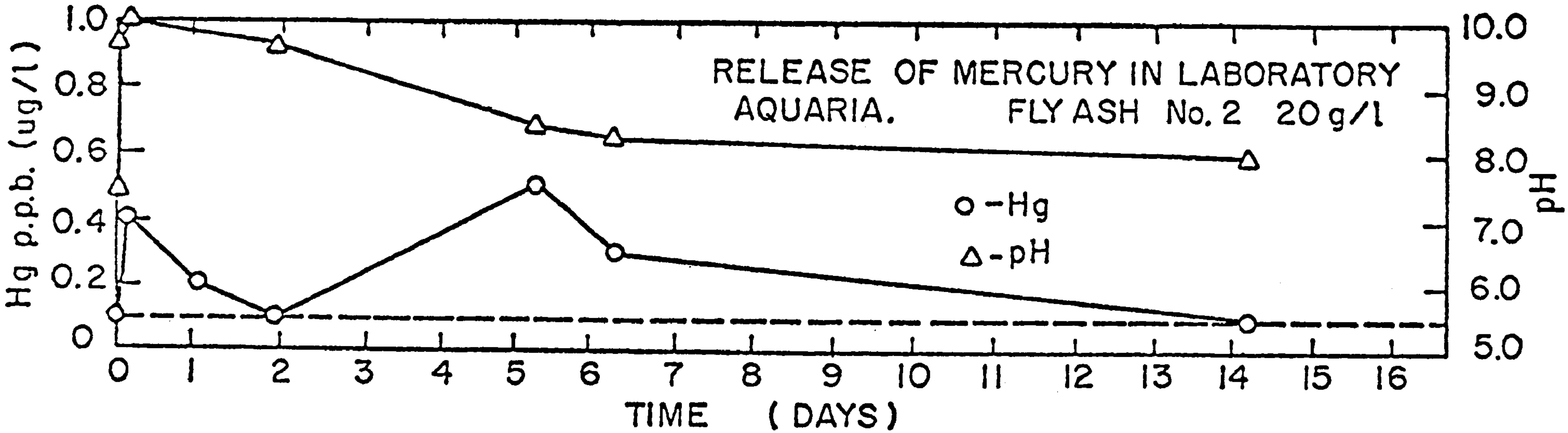

Figure 21: Mercury Release Patterns After Fly Ash Addition to Laboratory Reactors.

(Lake Washington[36], Buffalo Pound Reservoir[37], Shagawa Lake[38]) which indicate the potential of this approach as applied to lake reclamation.

MODELING EFFORTS ON STONE LAKE

The techniques of mathematical modeling can provide a systematic basis for a research approach to the complex problem of cultural eutrophication and can be extremely valuable in comparing management options for control and/or restoration. The general advantage of a mathematical model in algal growth studies is that such a model can synthesize data from many different experiments, each with its own particular scope of inquiry, and present the results in a dynamic and comprehensive manner.

A model devised by Bierman[8] focused primarily on the kinetics of algal growth in eutrophic lakes and utilized a two-step process involving separate nutrient transport and cell synthesis mechanism at the species level. This model included carrier-mediated transport of nutrients, using a reaction-diffusion mechanism, and allowed for intermediate nutrient storage in excess of a cell's immediate metabolic needs.

Applications involved one- and two-species systems where phosphorus is the regulating nutrient and two- and three-species systems where both phosphorus and nitrogen are important regulating nutrients. Effects of atmospheric nitrogen fixation as well as combined nitrogen were included. For purposes of simplicity, growth simulations were confined to aerobic surface waters and were extended only through the course of a single growing season. However, in order to make the model as realistic as possible, temperature variation, cell sinking, cell decomposition, nutrient recycle, and predation by higher animals were included.

Because of luxury phosphorus uptake, the proposed model predicts a lag between the removal of phosphorus from solution and the subsequent algal growth, and the specific growth rate predictions of the model were not compatible with the same predictions of Monod kinetics for the single-species example presented.

For the two-species case in which phosphorus is the regulating nutrient, it was shown that a slower-growing alga with a high phosphorus transport efficiency can dominate a faster-growing alga with a low phosphorus transport efficiency when the concentration of available phosphorus is low. This is shown in Figures 22 through 24 for a mixture of Chlorella, a green alga, and Microcystis, a blue-green specie. Nuisance blue-green algal blooms frequently coincide with elevated summer temperatures and low concentrations of dissolved nutrients in eutrophic lakes. In the example presented, species differences in phosphorus uptake efficiencies are sufficient to explain these correlations and it is not necessary to invoke a causal relationship between elevated temperatures and assumed higher growth rates for blue-green algae as compared to other species.

For the cases in which both phosphorus and nitrogen regulate algal growth, it was shown that the availability of nitrogen in relation to a given amount of phosphorus, especially the form of the nitrogen, can greatly affect total algal crop as well as relative species abundance. Figures 25 through 28 indicate these findings. On this basis, a need is recognized to include nitrogen dependence, especially nitrogen-fixation, as part of any algal growth model that is to be applied to field conditions.

The final set of applications considered various external inputs from diffuse and point sources such as surface runoff, direct precipitation, and nutrient loads from assumed secondary- and tertiary-treated wastewater. Use was made of the physical basin characteristics of Stone Lake. Generally, these chronic, low-level inputs significantly enhance the size and duration of the algal crops in the lake and, during the summer months when dissolved nutrient concentrations are lowest, these inputs preferentially stimulate the more efficient blue-green species. Urbanization has a very significant effect on these same parameters and, for the assumed nutrient loadings in the examples, surface runoff from the urban land in the basin was more stimulatory than if all of the wastewater produced in the basin had been tertiary-treated and directly discharged to the lake.

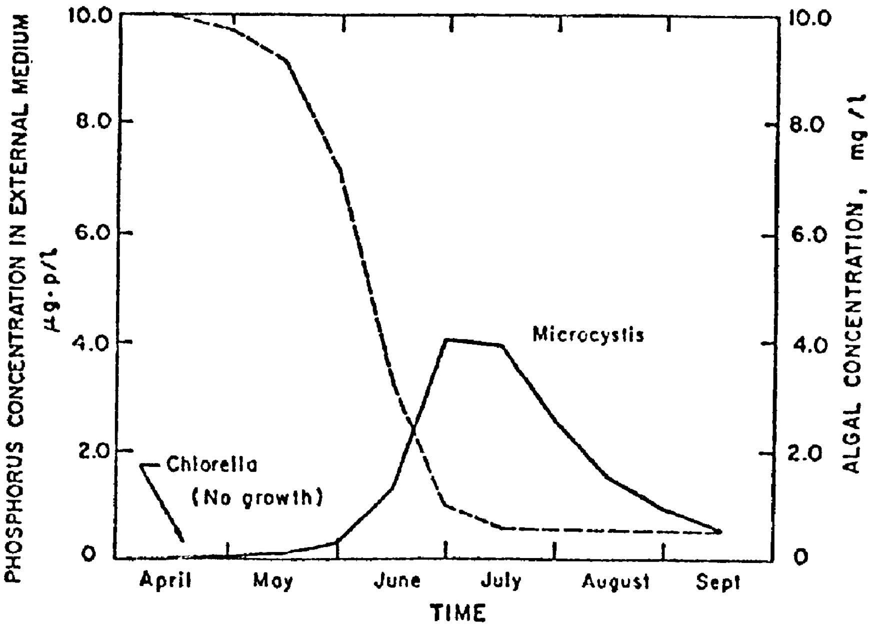

Figure 22: The slower-growing Microcystis dominates the faster growing Chlorella at low phosphorus concentrations (dotted line).

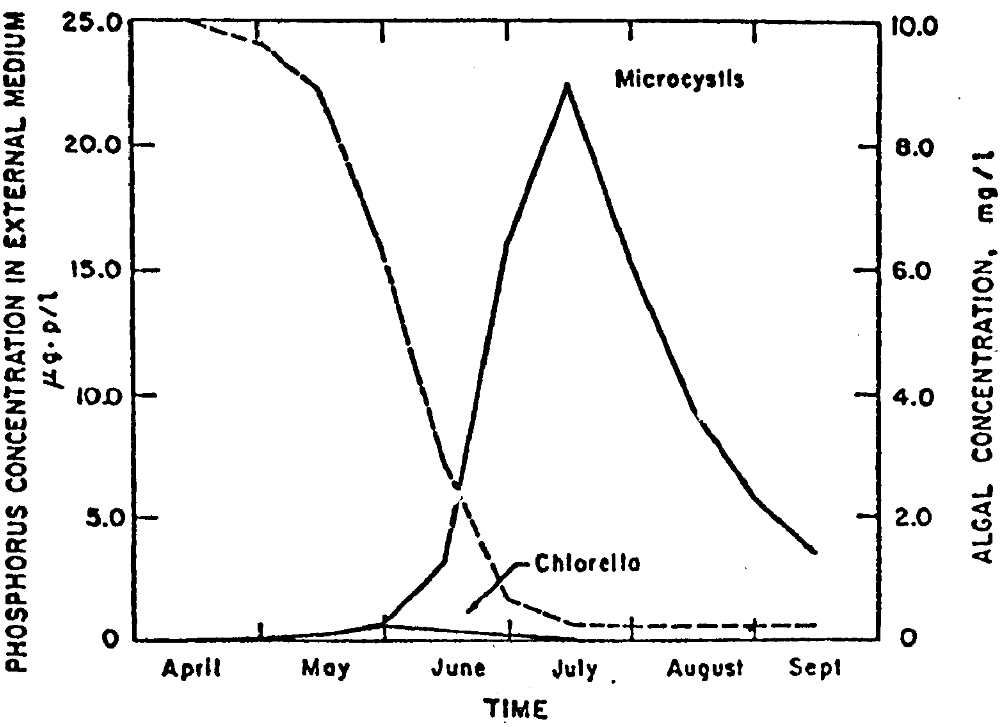

Figure 23: Microcystis increases proportionately after phosphorus concentration (dotted line) has been increased from 10 μg·P/1 to 25 μg·P/1.

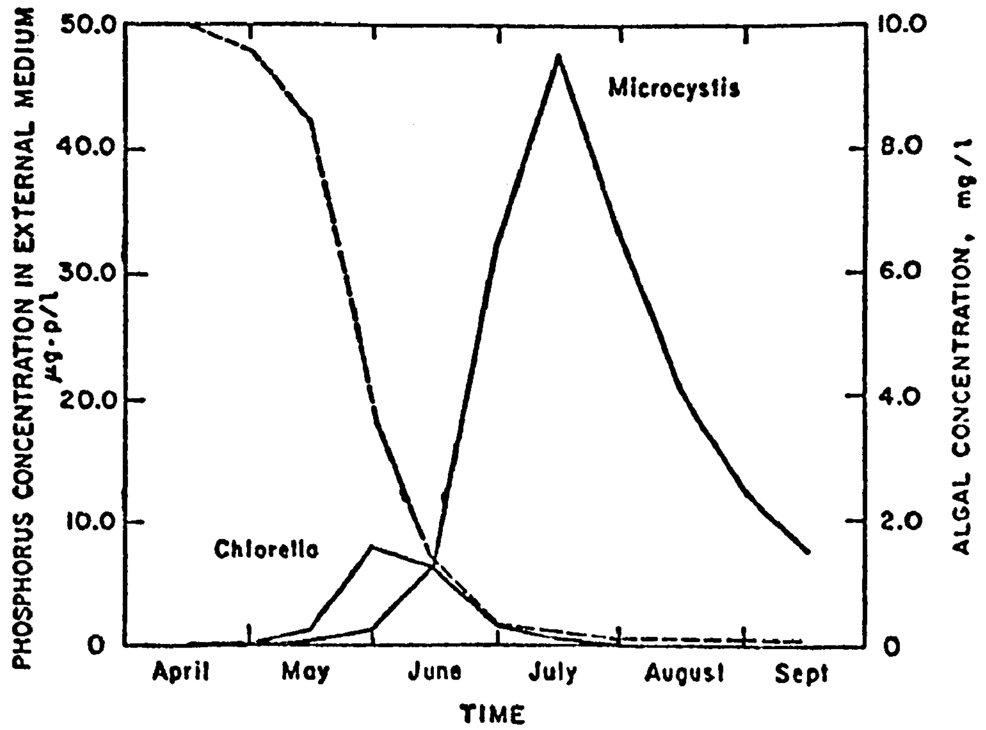

Figure 24: Microcystis does not increase proportionately after phosphorus concentration has been increased from 25 μg·P/1 to 50 μg·P/1.

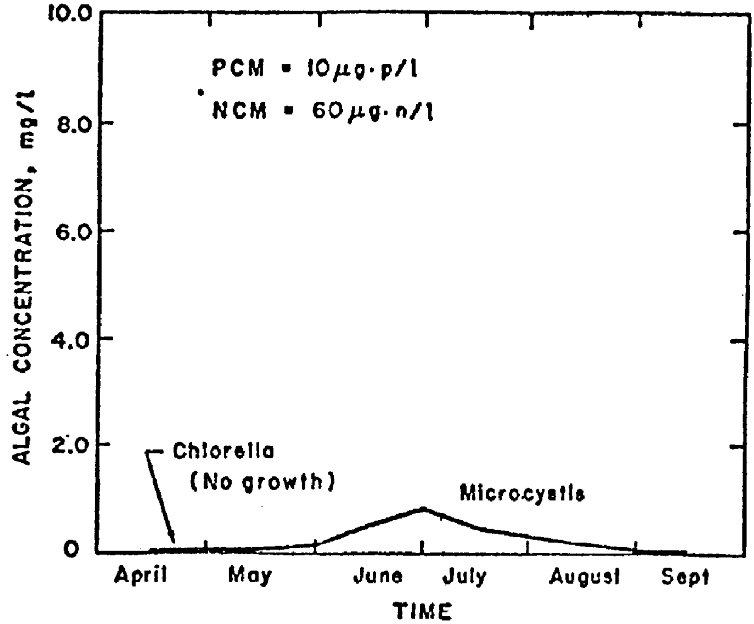

Figure 25: The development of Microcystis is limited by available nitrogen when the initial nutrient concentrations are 10 μg·P/l and 60 μg·N/l.

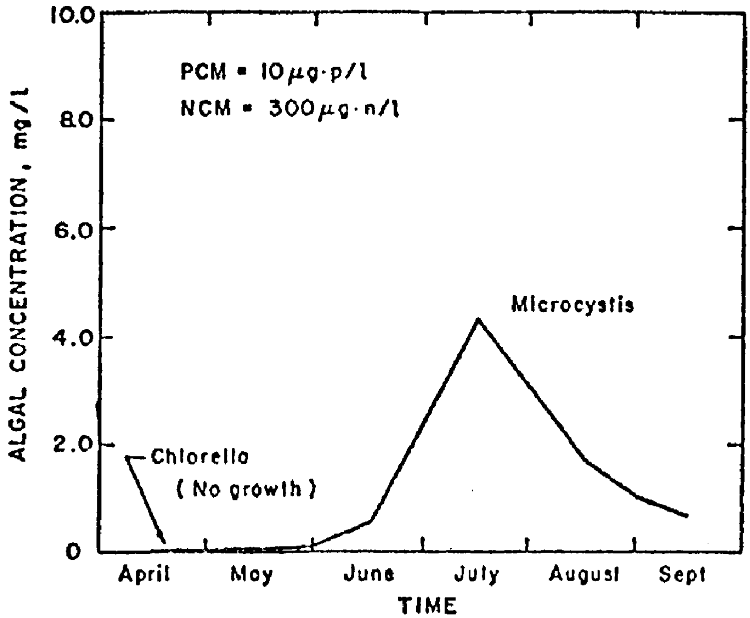

Figure 26: Microcystis uses virtually all of the available phosphorus when the initial nutrient concentrations are 10 μg·P/l and 300 μg·N/l.

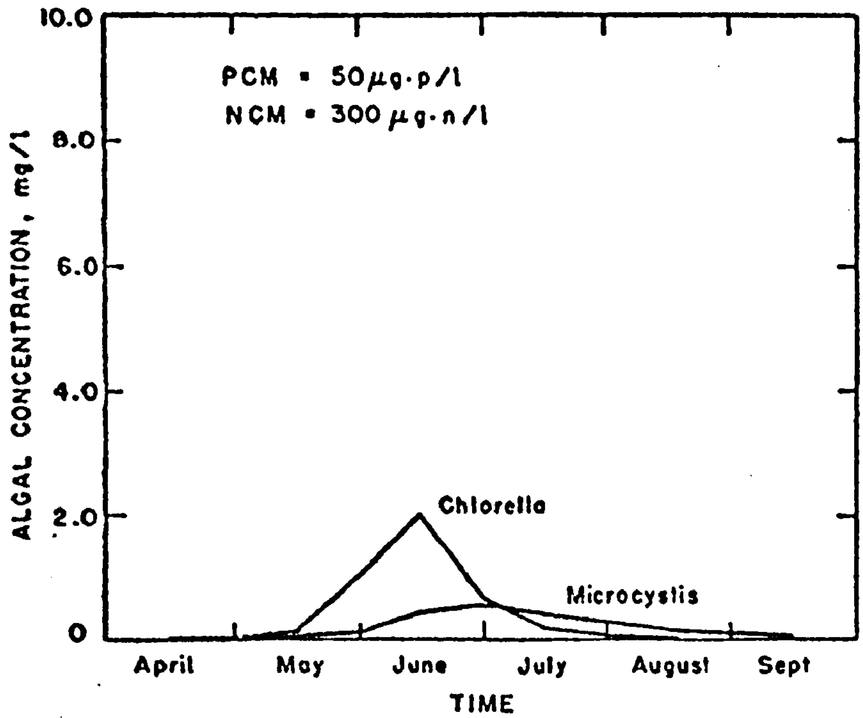

Figure 27: Chlorella can exploit its faster growth rate at a phosphorus concentration of 50 μg·P/l and it utilizes most of the limited supply of nitrogen, 300 μg·N/l, before Microcystis.

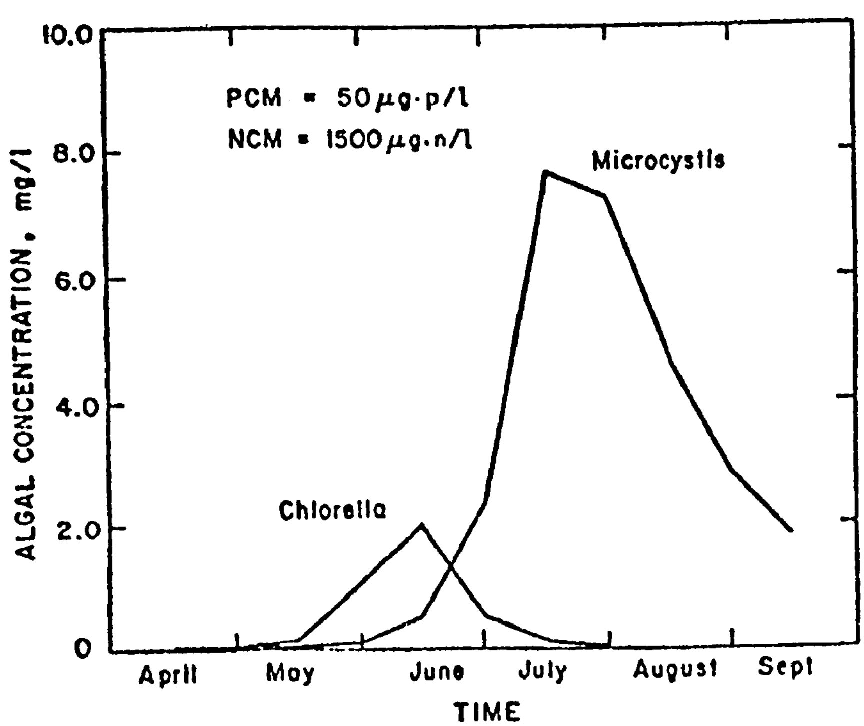

Figure 28: There is enough nitrogen in the system, 1500 μg·N/l, for both Chlorella and Microcystis to utilize the initial phosphorus concentration of 50 μg·P/l to the best of their capabilities.

A second mathematical model, devised by Cordiero[39], made use of the two step growth process mentioned previously in the dynamic modelling of a lake ecosystem. The system included both nitrogen and phosphorus limited situations and incorporated both upper (aerobic) and lower (anaerobic) waters as a means of determining the degree of cycling of these nutrients. The utility of the model was demonstrated by the simulation of lake restoration control schemes. Results for the simultaneous lowering of influent levels of phosphates, precipitation of phosphates in the lake, and the sealing of bottom sediments (such as is proposed) is shown in Figure 29 for algal populations in the overlying water.

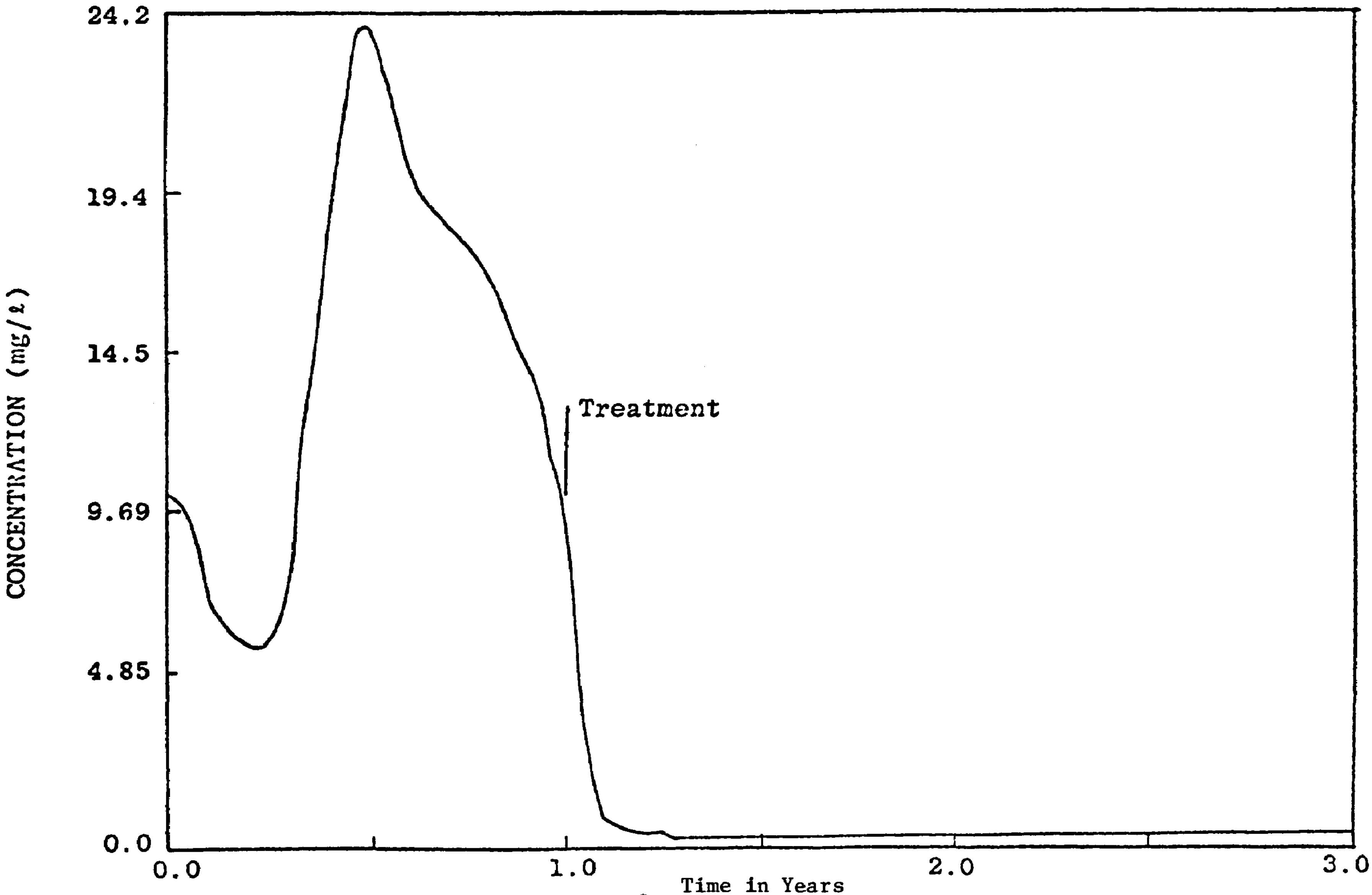

Figure 29: Effect of Reduction of $H_2PO_4^-$ in Inflow and Lake, Algal and Lower Water Precipitation at 1-year on Concentration of Algae.

SECTION VI

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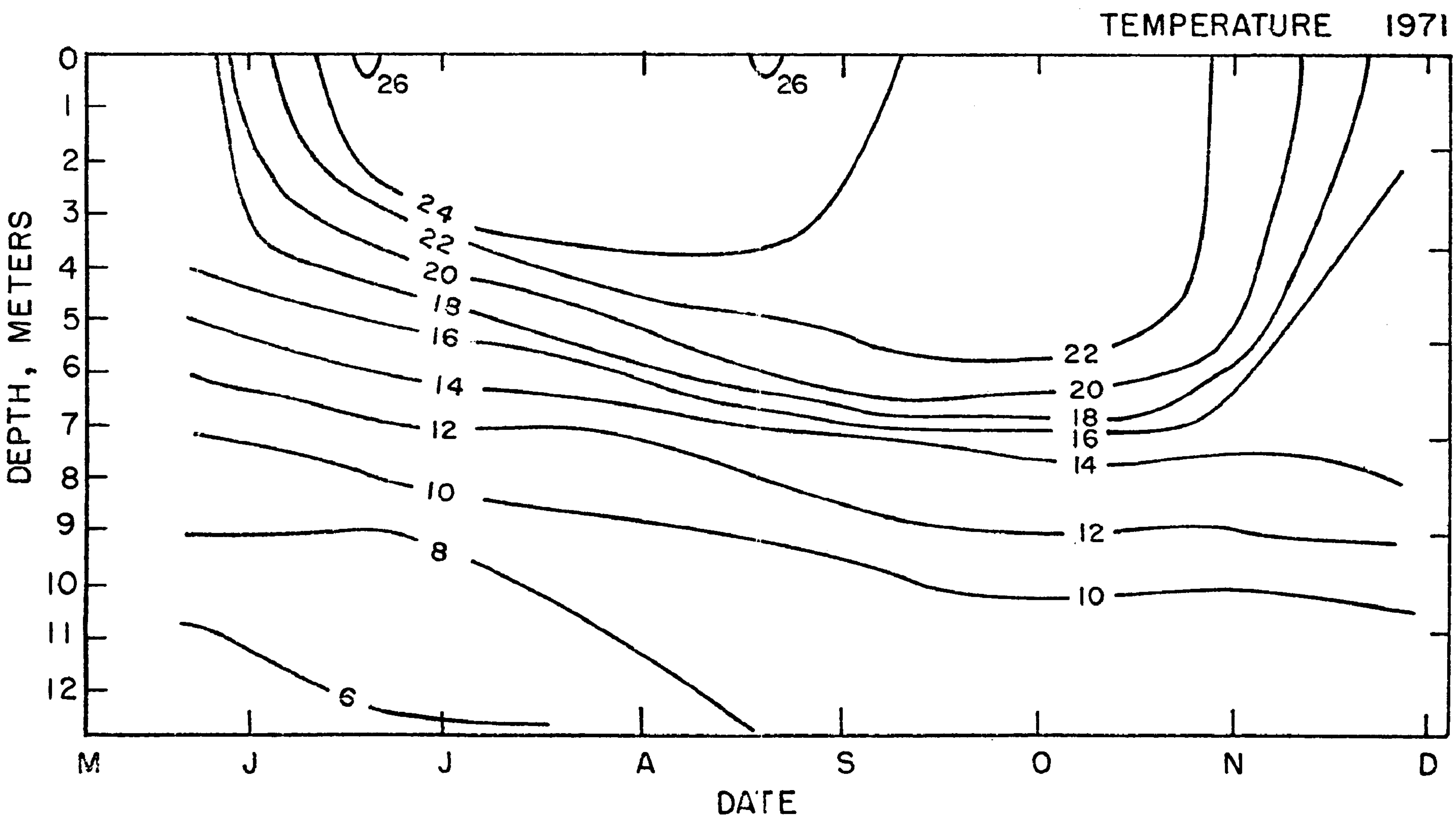
APPENDIX

WATER QUALITY DATA 1971-72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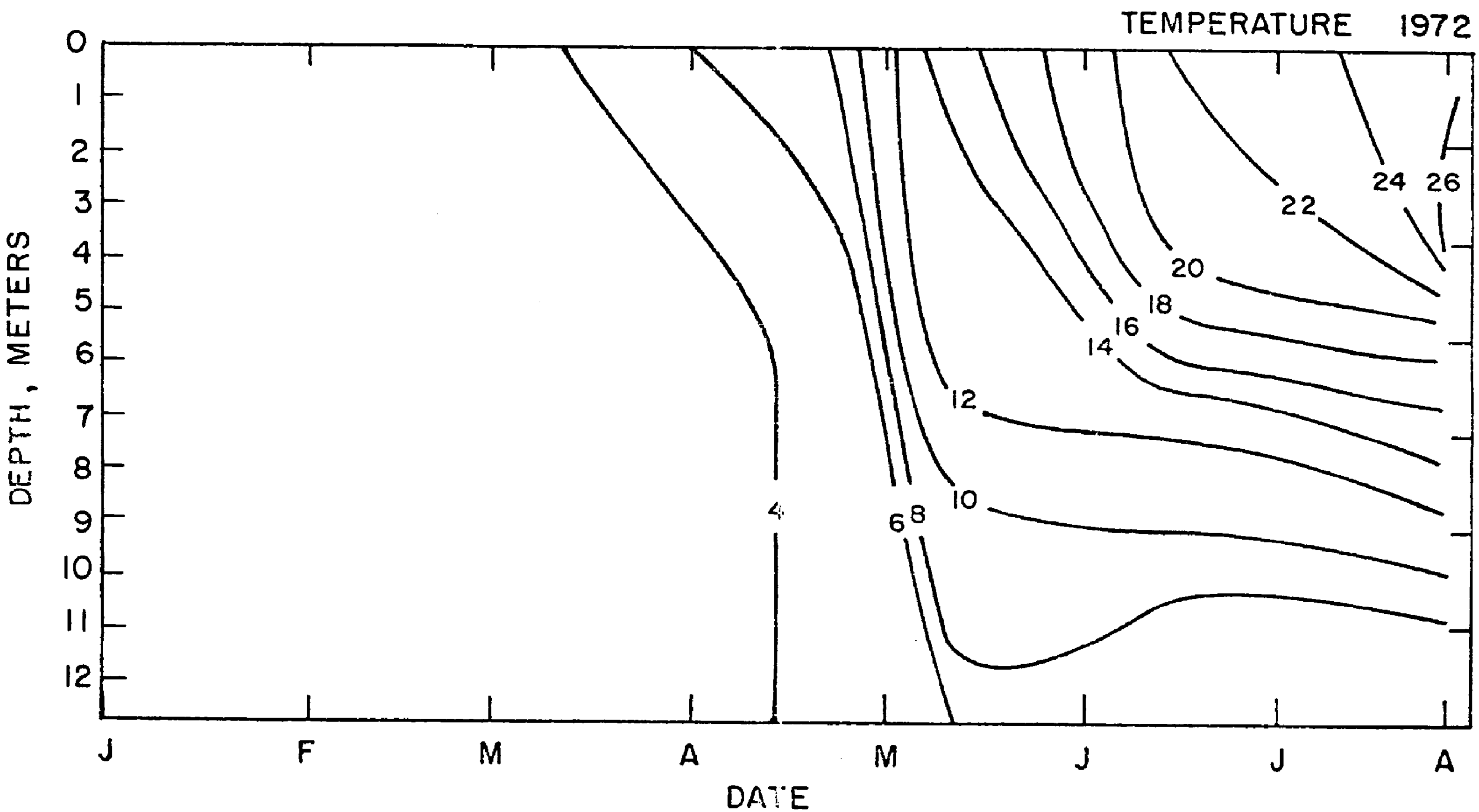
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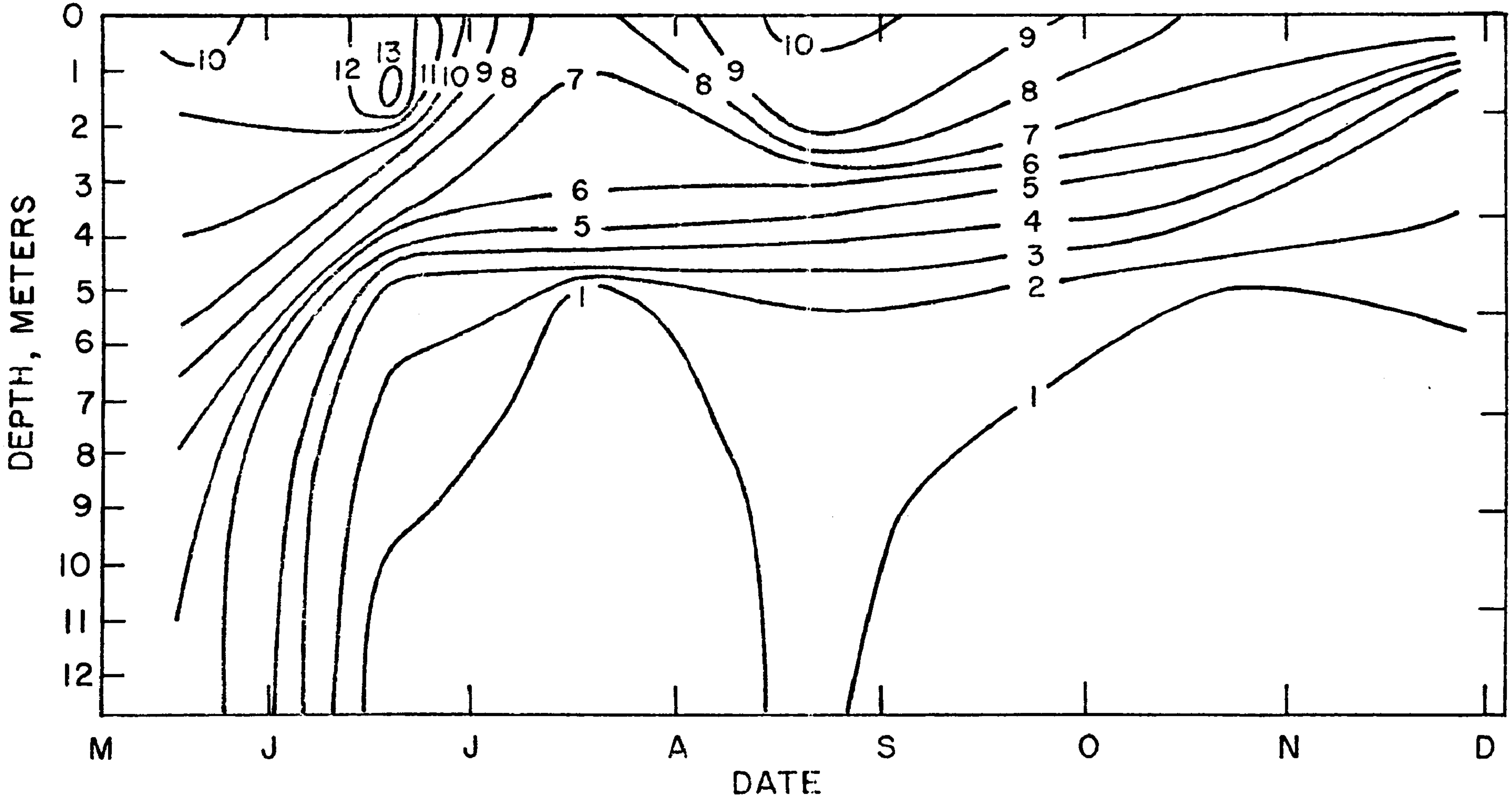

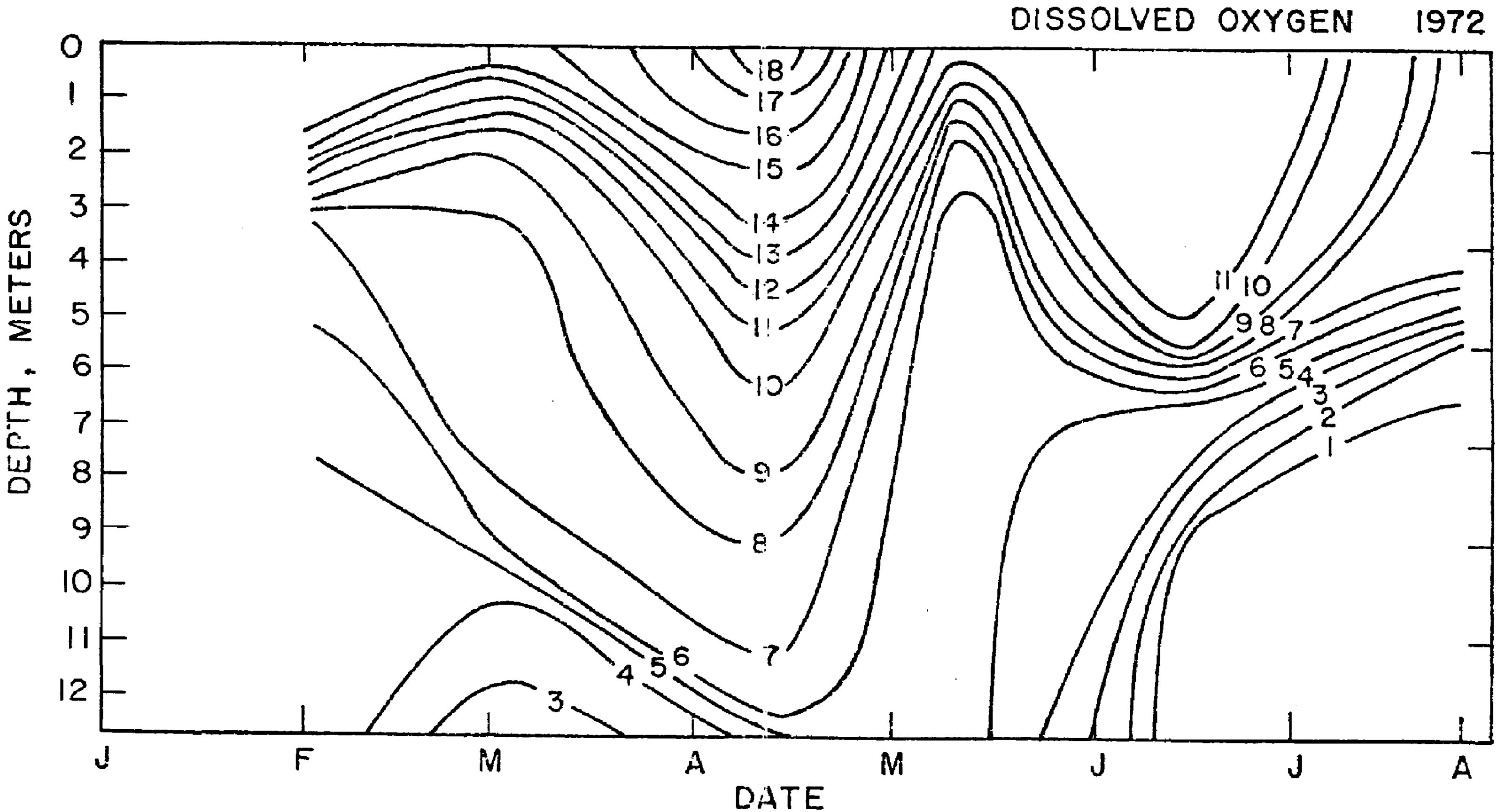
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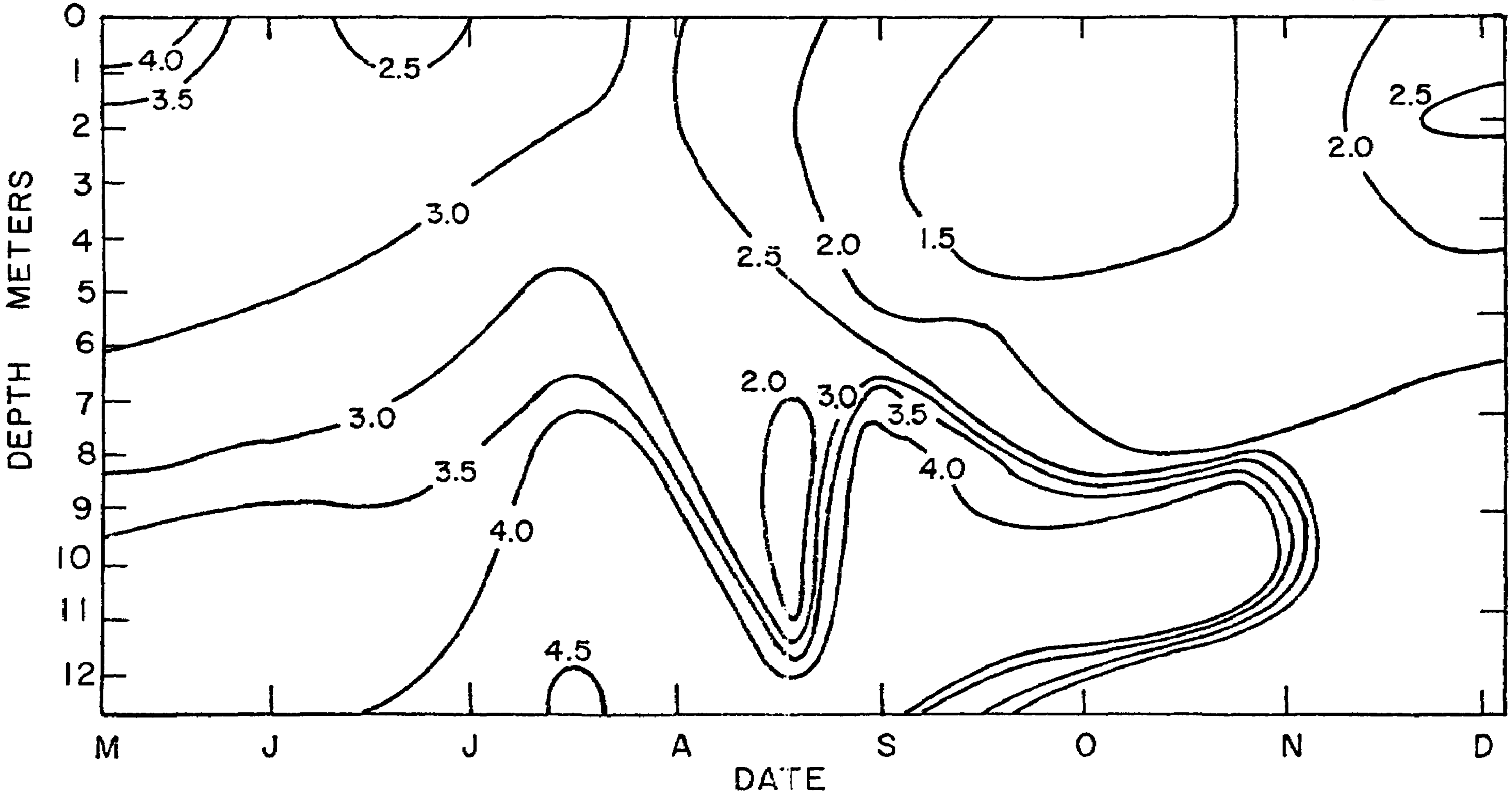

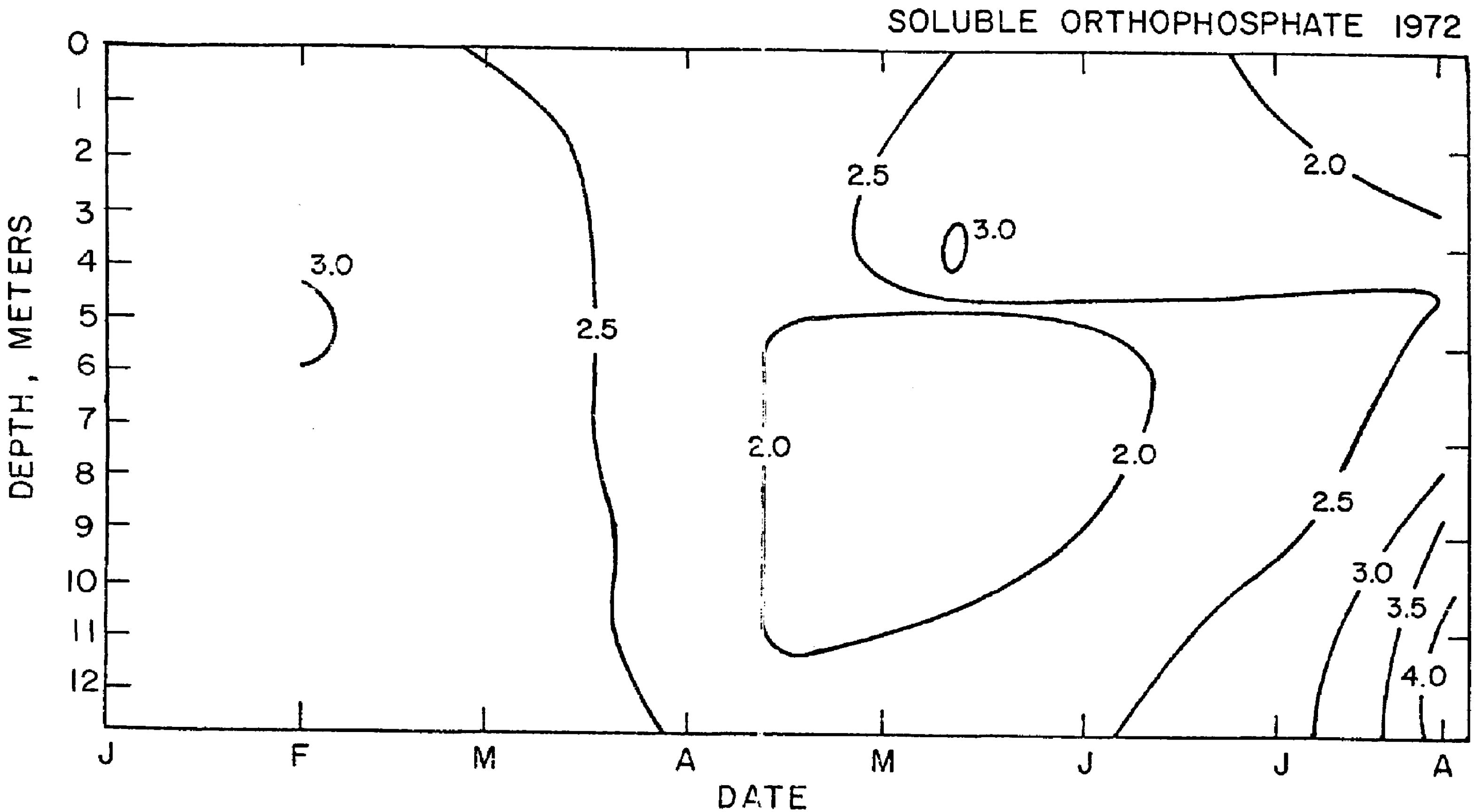
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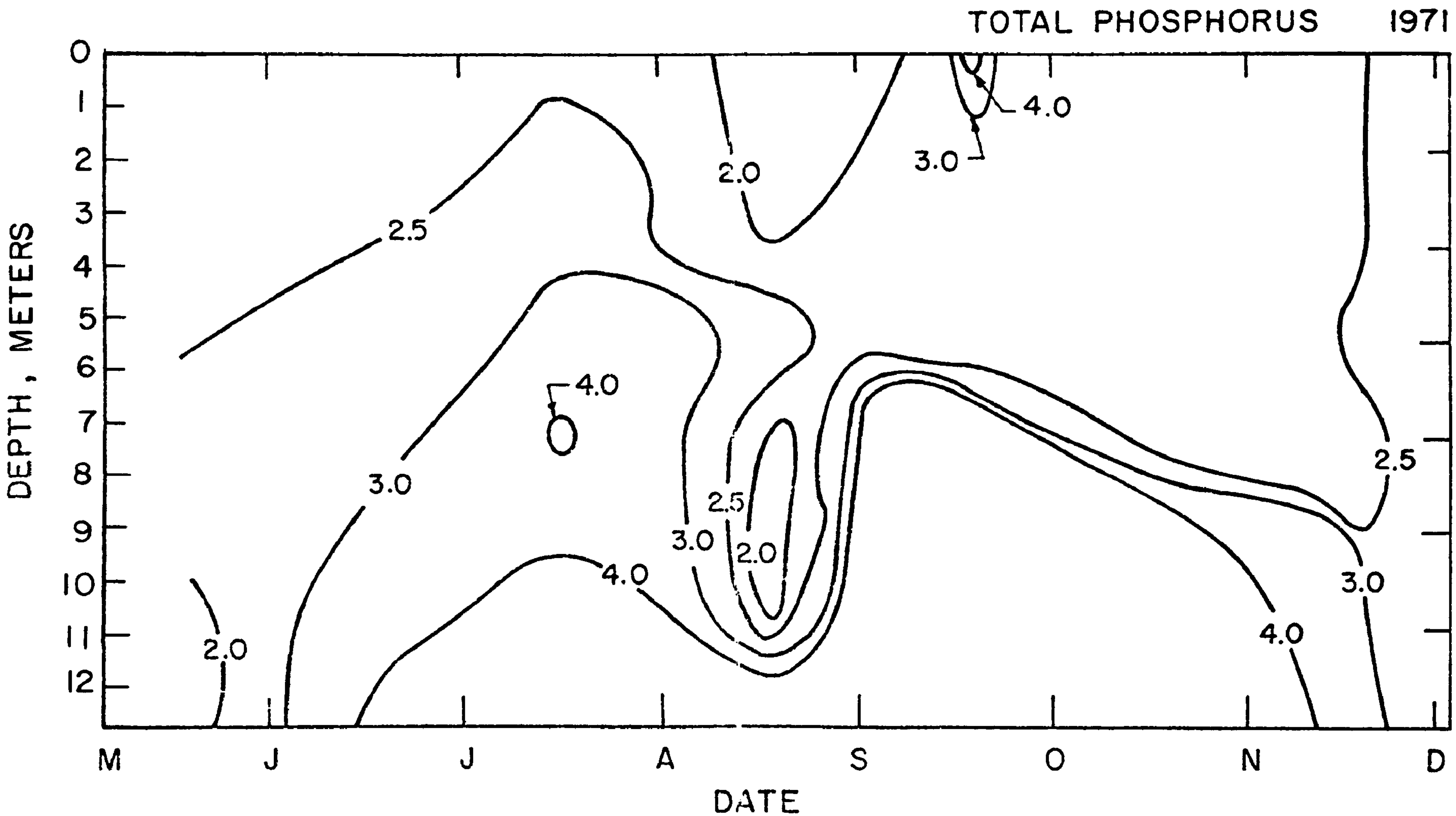

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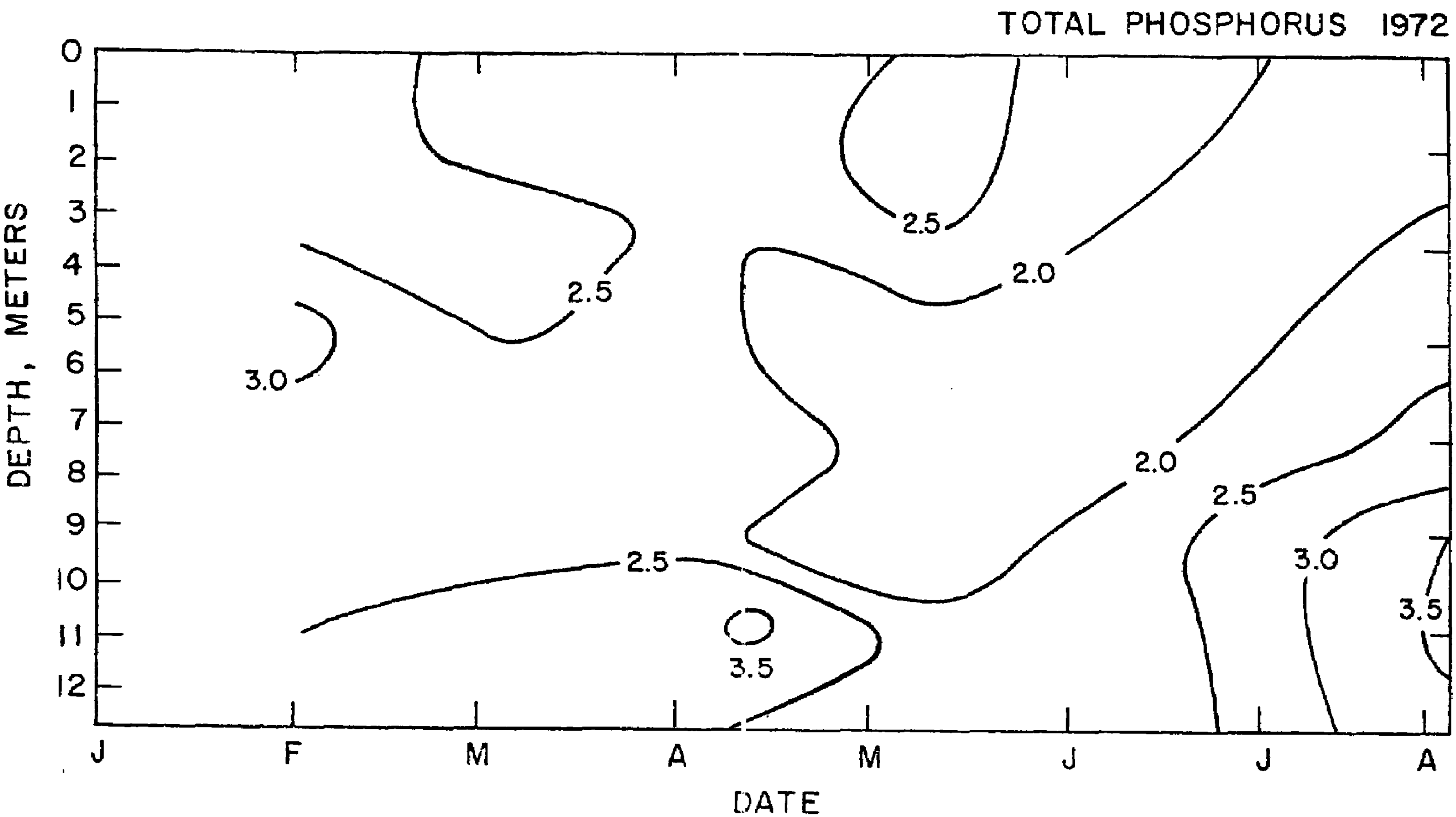
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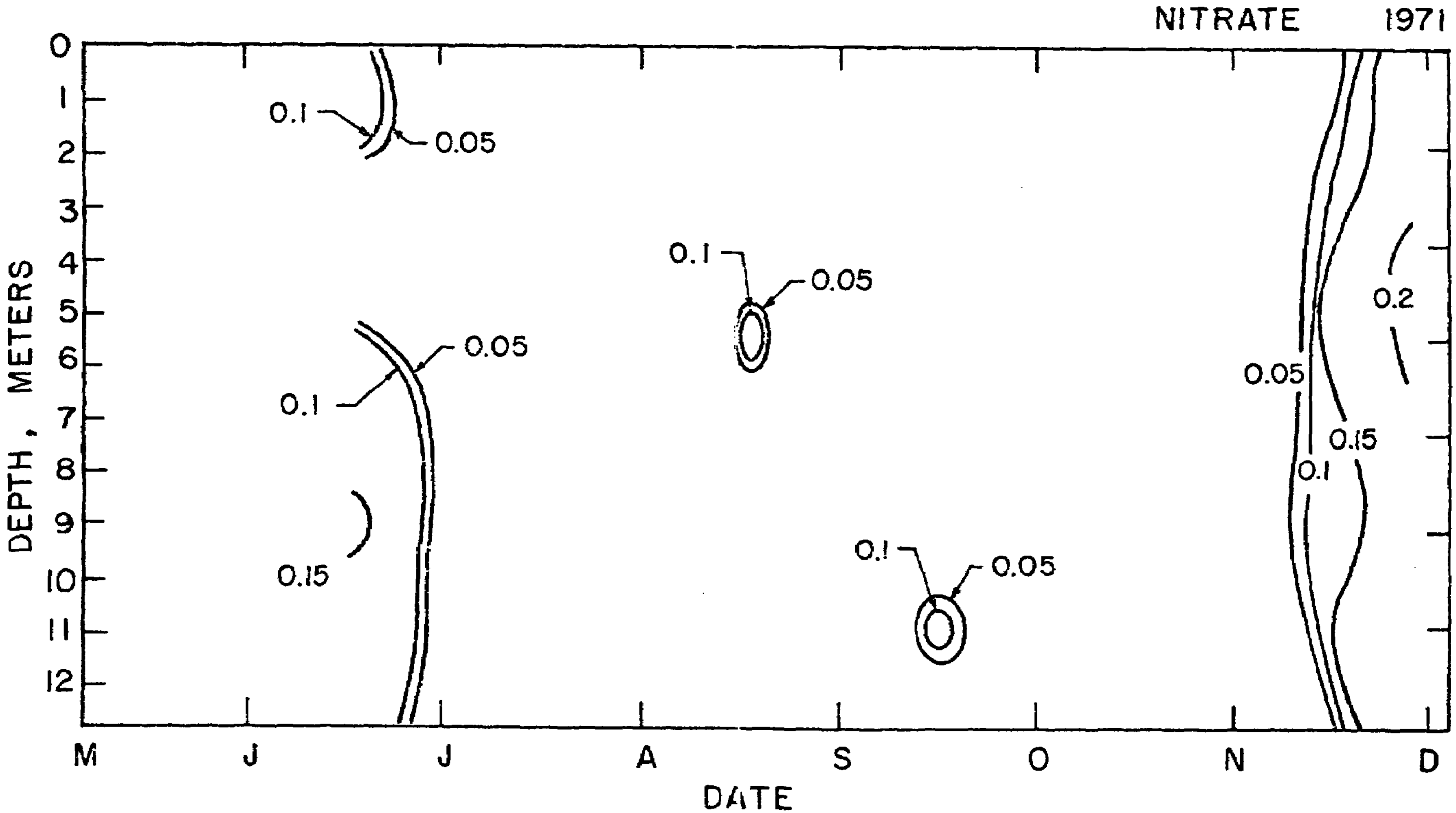
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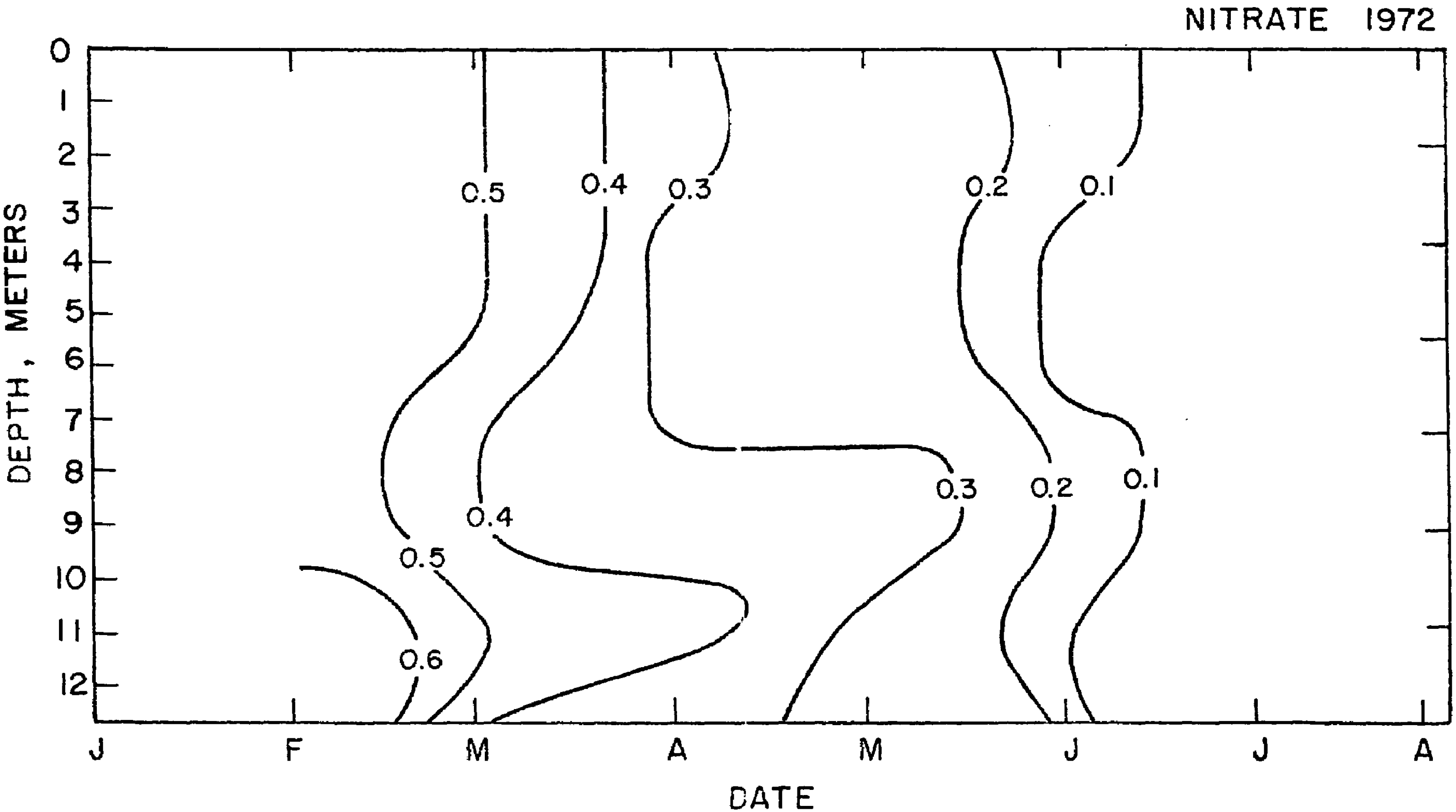
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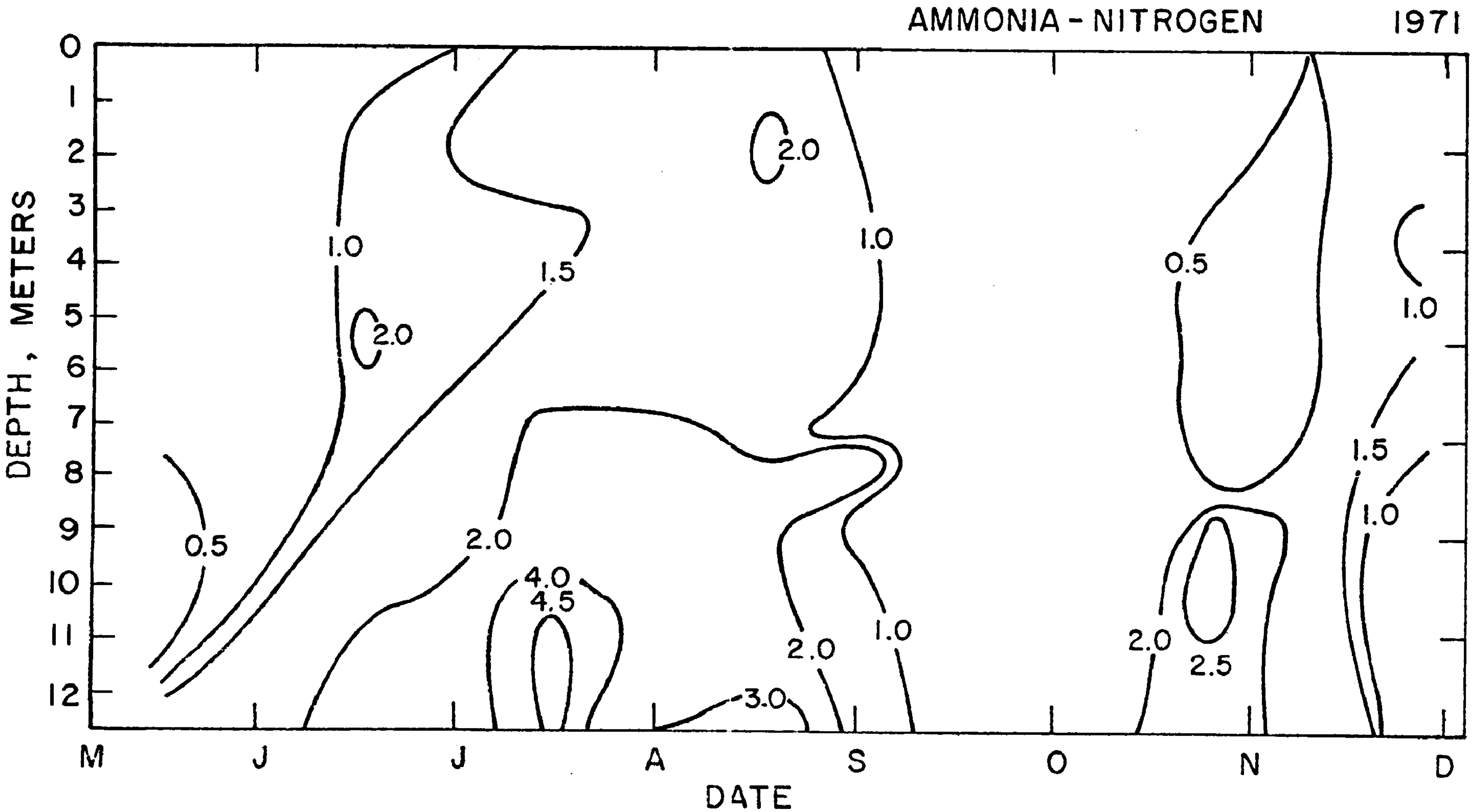
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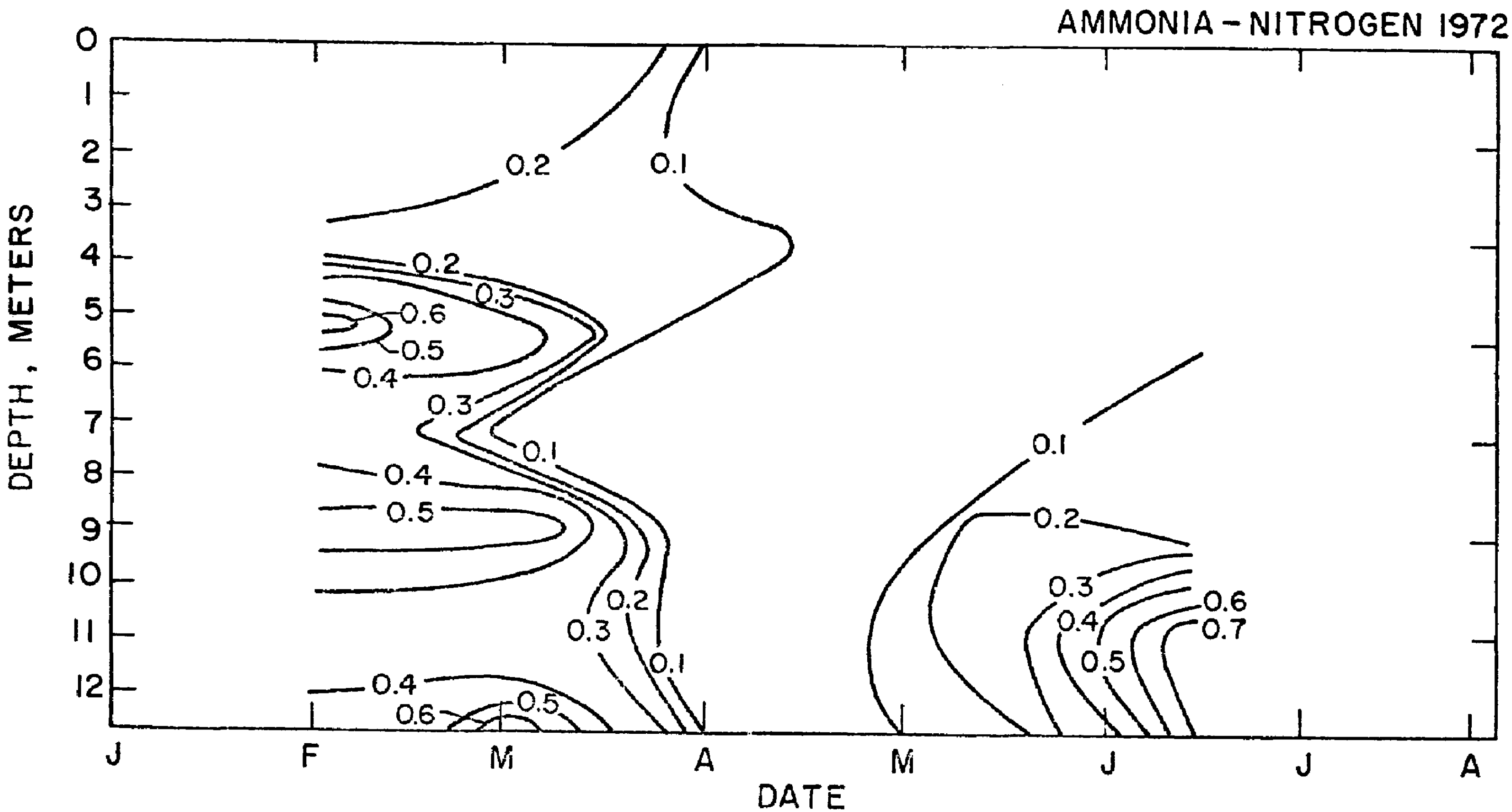
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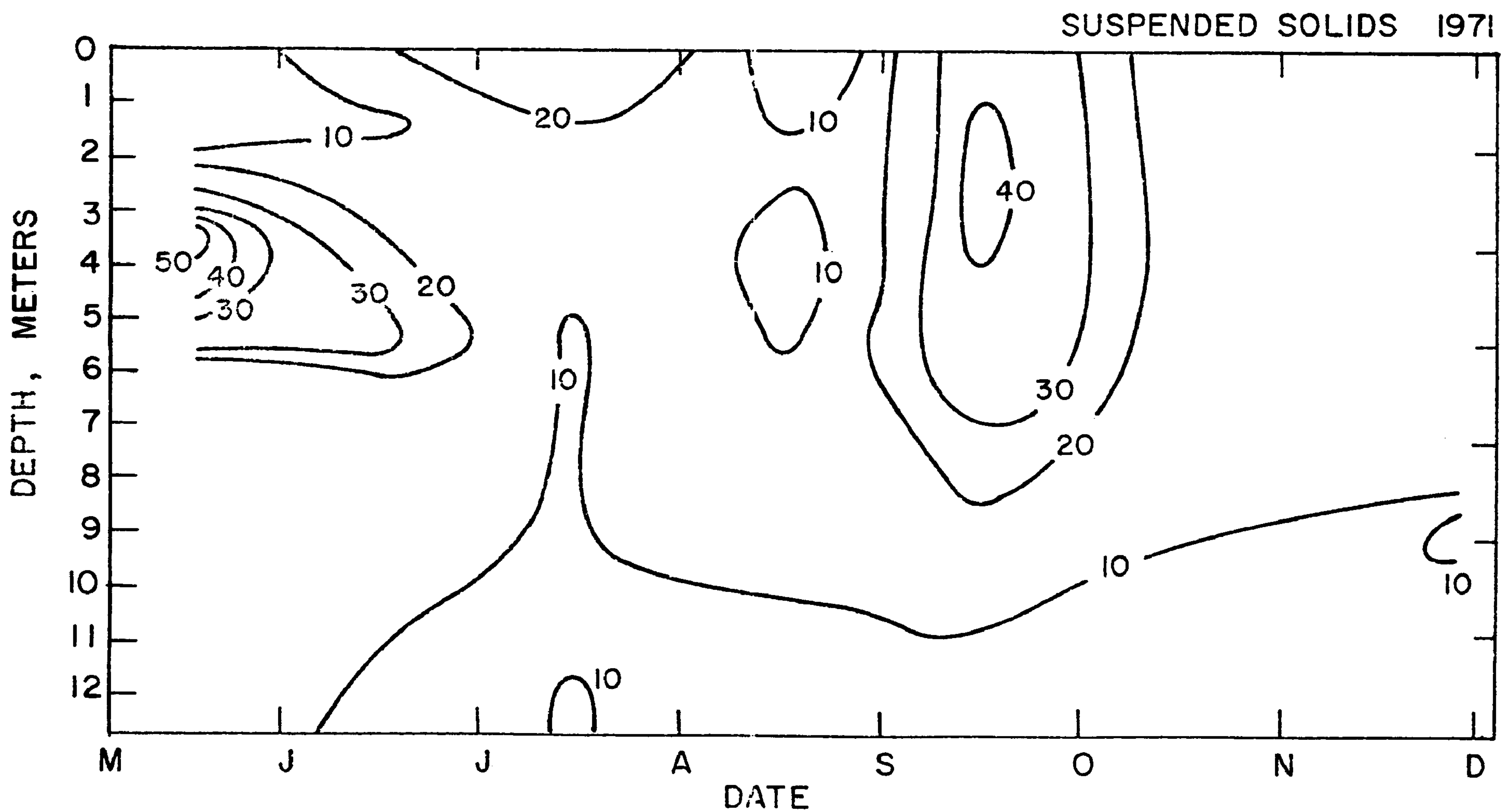
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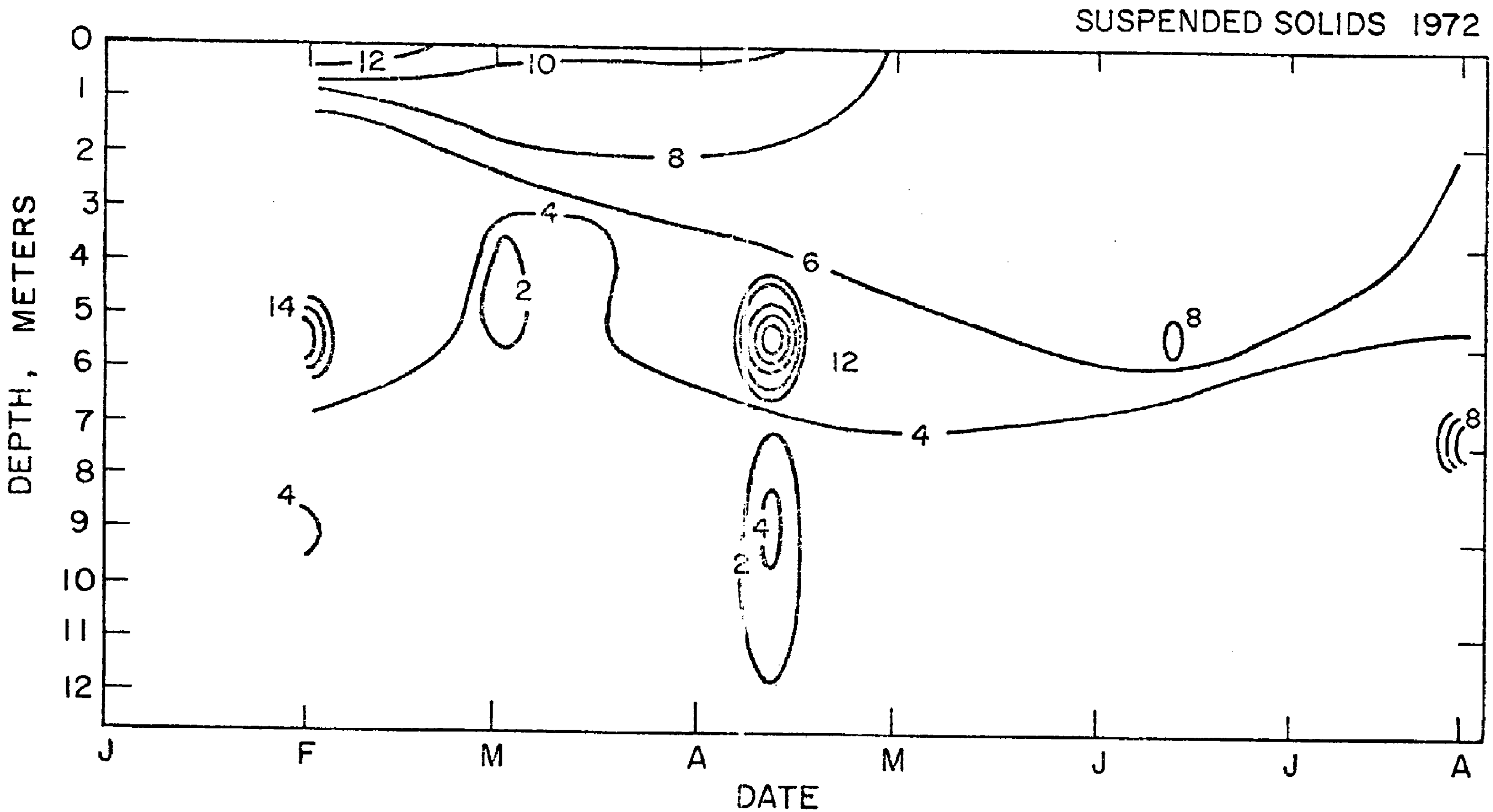
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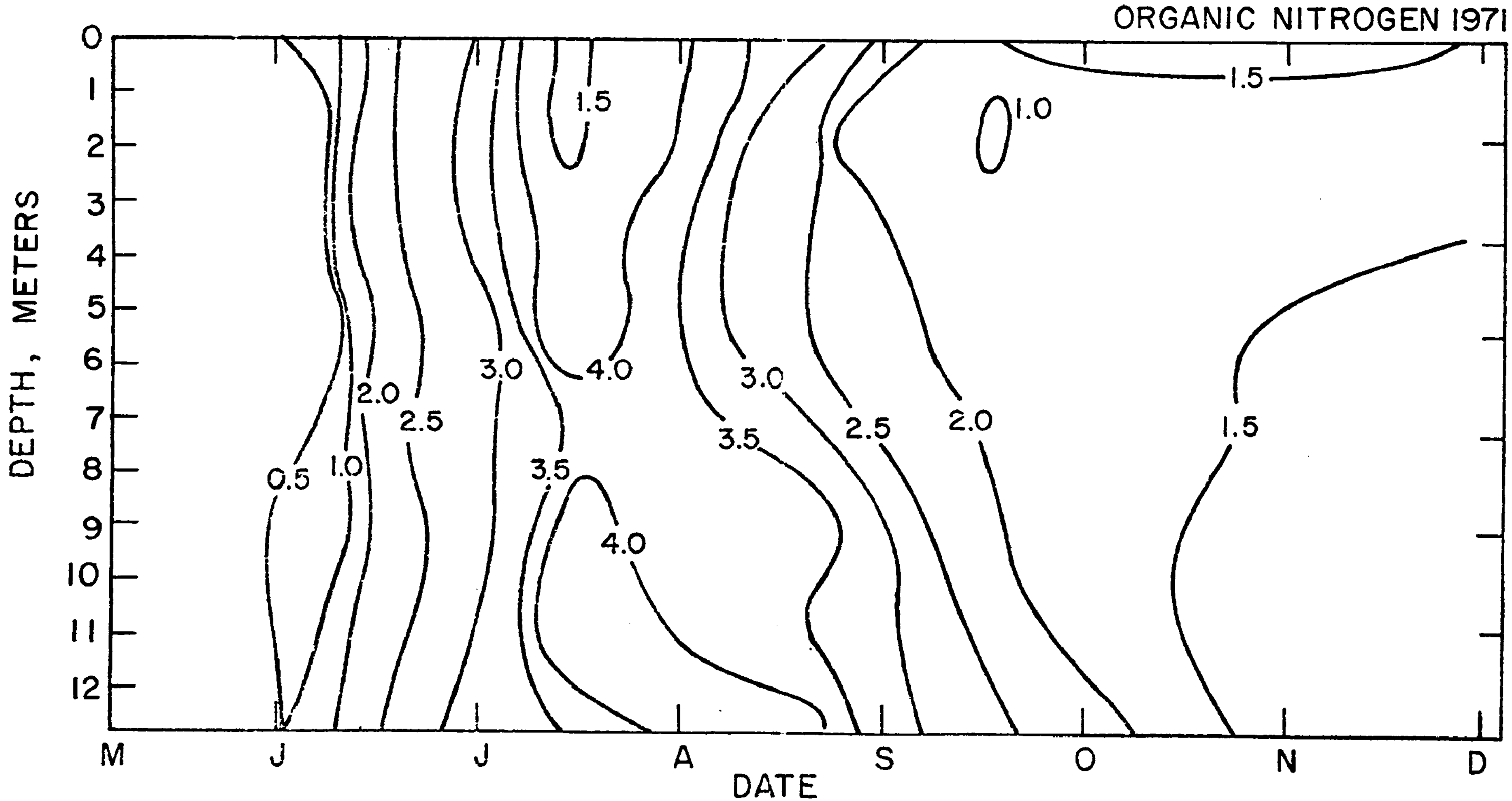
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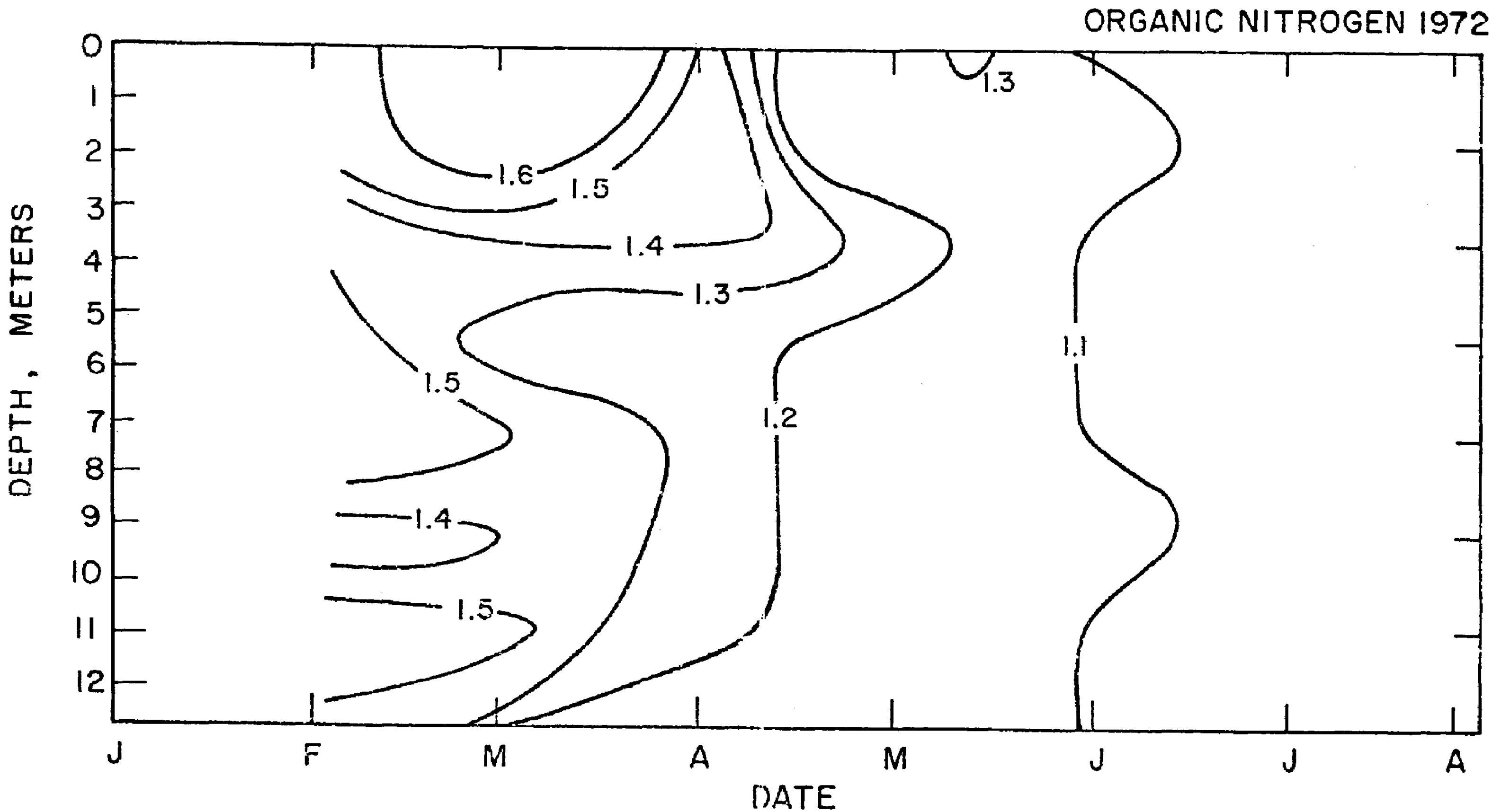
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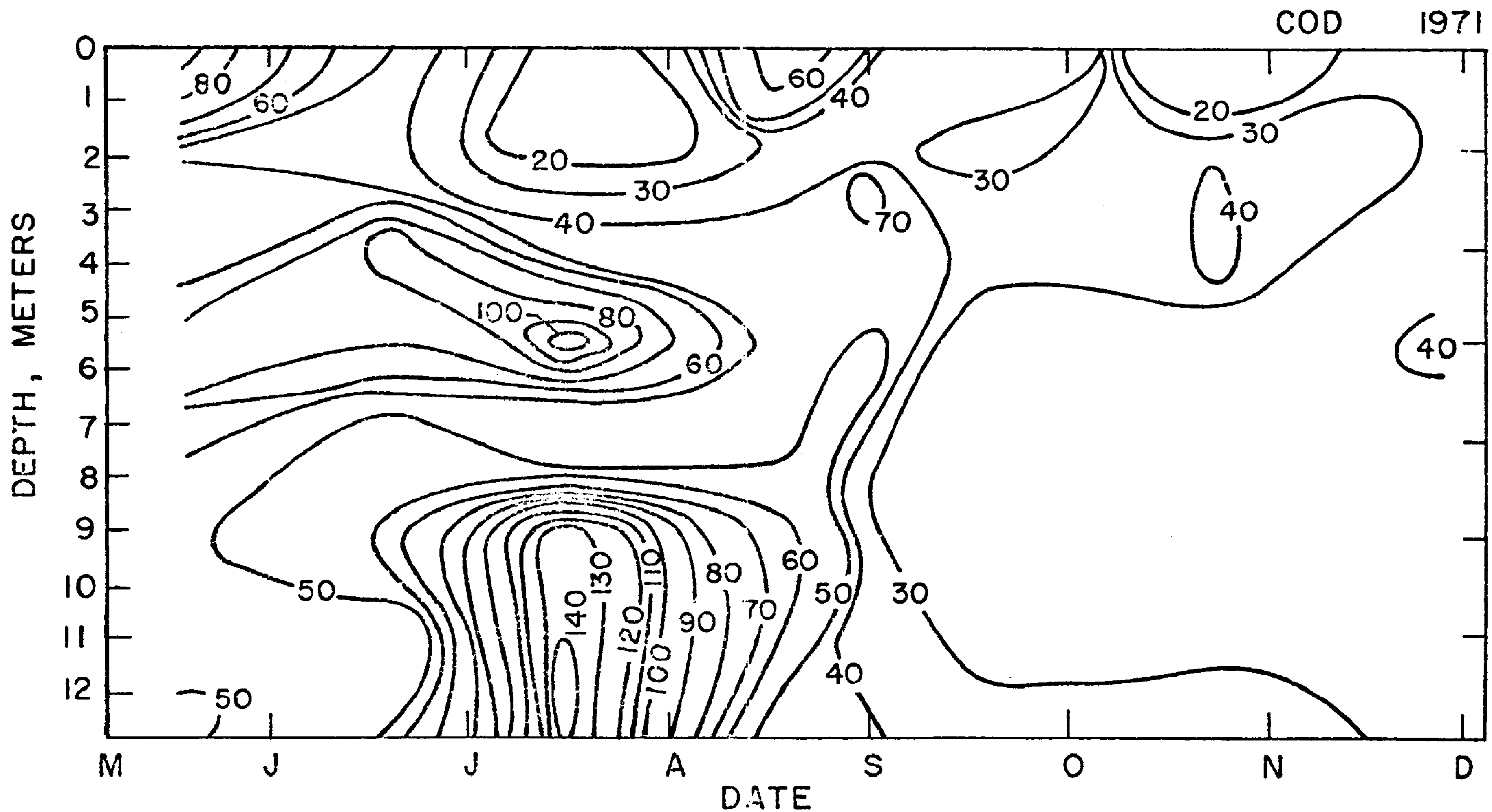
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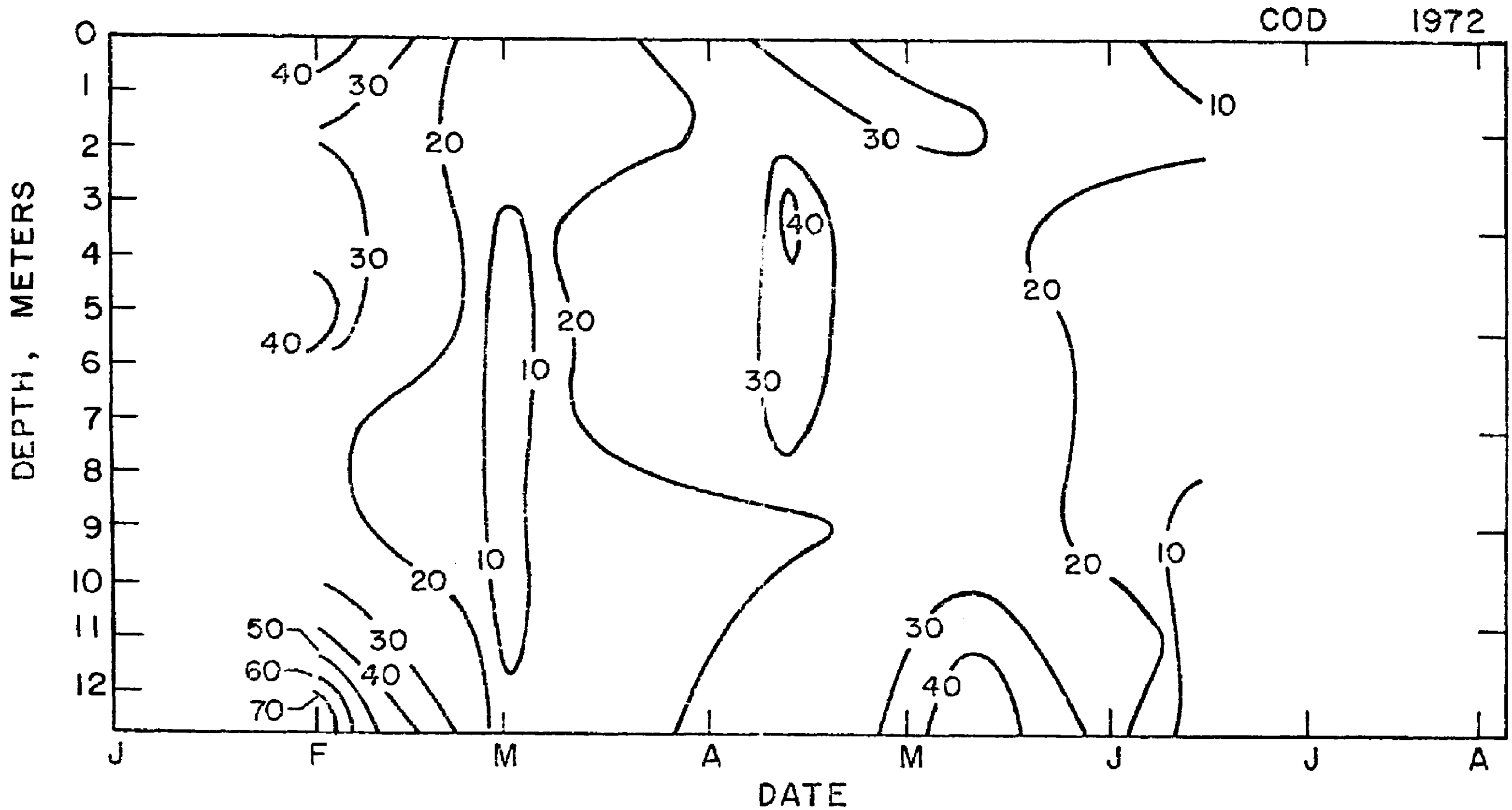
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16. ABSTRACT

This report contains information relating to two factors: (1) The effects of domestic pollution abatement on a eutrophic lake, and (2) investigations into methods of reclaiming such lakes, especially through the use of particulate materials which retard pollutant release from sediments.

The study lake, Stone Lake, has been monitored for approximately ten years from the time of pollution abatement. Results indicate that the sediments are major pollutant sources during stratified periods and that for such lakes to achieve meaningful improvements in water quality in a reasonable length of time, a series of external manipulations is often needed.

Certain types of fly ash, a particulate waste product of coal combustion, was shown, in laboratory studies, to possess properties capable of precipitating orthophosphate from overlying waters and subsequently "sealing" the phosphorus within the sediments for long periods of time. A lake such as Stone Lake could thus be made permanently or semi-permanently, phosphorus limited, thereby altering the successional pattern previously indicated and significantly reducing the overall standing algal crop.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
lakes*, limnology, phosphorus*, fly ash*, sediments*, renovating, algae, models, nitrogen, aquatic biology, bioassay *Major descriptors		08H 06F 07B

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