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RESPONSES OF A MARL LAKE TO FERTILIZATION $\stackrel{1}{\vee}$

by

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Introduction

The addition of fertilizer to a lake or pond causes a temporary shift in chemical equilibria and thereby yields facts concerning dynamic chemical processes. The securing of information of this sort, as well as the evaluation of the benefits of the fertilizing elements upon productivity, are the principal objectives of fertilization experiments. The present study was planned with the practical aim of finding means of improving the fishing of an unproductive Michigan watershed. The West Branch of the Sturgeon River is by reputation one of the poorer trout streams of the northern section of Michigan's Lower Peninsula. A large fraction of the volume is the outflow from Hoffman Lake, a shallow unproductive marl lake. It was reasoned that the low productivity of the stream might be related to the unproductive character of the headwater lake and that enrichment of the lake might benefit the stream. The present paper deals only with the response of Hoffman Lake to three years of fertilization. Responses of the stream will be dealt with in a later report.

Marl lakes, such as Hoffman, are commonplace in the Lower Peninsula of Michigan. They are recognized by their light-colored bottom which brightens the water color to an emerald or a blue-green. Typically, they have little submerged vegetation, and the deeper basins are characterized by an abrupt slope or dropoff (Hooper, 1956). Marl lakes are unproductive of fish and in Michigan have been among the first lakes to receive the attention of fisheries management personnel for lake improvement work.

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The extensive literature dealing with pond fertilization is of limited value in predicting results of the fertilization of marl lakes. Most pond studies have been in more southern latitudes than Michigan and in areas of soft ground water. Ball and Tait (1952) and Ball and Ford (1953) point out that hard-water ponds in Michigan respond to fertilization in a different way than the soft-water ponds of the southern states. The results of many years of study of the ponds at Wielenbach (Dernoll, 1925; Wunder, 1949) cannot be applied to Michigan waters since these Bavarian ponds had small reserves of alkali and required frequent liming with chalk or quicklime. In contrast, Michigan ponds and lakes often have heavy concentrations of lime. Logs, debris, and rooted plants in the water develop thick encrustations of marl, and suspended marl particles are nearly always visible in the waters.

Nelson and Edmondson (1955) produced a 2. 5- to 7-fold increase in photosynthetic rate by fertilizing an Alaskan lake. Smith (1952) reported an improved growth and survival of brook trout following fertilization of Crecy Lake, New Brunswick. The soluble phosphate from a single application of calcium superphosphate to a Scottish loch made by Brook and Holden (1957) persisted for 105 days and an increased crop of phytoplankton was maintained for 2 years following this treatment. These lakes are poor in lime compared to most Michigan waters. Barrett (1952) and Ball and Tanner (1951) have reported on the fertilization of Michigan lakes. Barrett determined the fate of phosphorus added to a series of stratified lakes which ranged between 138 and 192 parts per million in alkalinity.

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He concluded that fertilization was impractical because the added phosphorus sank to the hypolimnion and was adsorbed by the bottom sediments. He suggested, however, that fertilization might be effective in an unstratified lake having water of alkalinity near the lower limit of alkalitrophy (120 ppm.) and having soils with a high capacity for phosphorus regeneration. Hepher (1958) discusses the fate of phosphorus added to Israel fish ponds having a high calcium content. Loss of phosphorus from the water after fertilization was believed to be the result of precipitation by calcium as calcium phosphate and fixation by calcareous muds. Hayes et al., (1952) proposed a theory of dynamic chemical exchange to account for the observed translocation of radioactive phosphorus added to a Nova Scotian lake. The studies of Hutchinson {1941). Hutchinson and Bowen (1947), and Mortimer (1941-1942) have emphasized the dynamic aspect of the nutrient substances in natural lakes. Marl lakes, such as Hoffman, present a radically different physical and chemical environment than acid and circumneutral lakes. Here the organic colloid layer of the mud surface is replaced by marl and periphyton algae. The excess of calcium in mud and water unquestionably influences the movement of phosphorus and other nutrients. The dynamics of phosphorus exchange in this system have not been investigated.

Study area

Hoffman Lake, Charlevoix County (T. 32 N., R. 4 W.). has a surface area of 120 acres, a maximum depth of 22 feet, and a mean depth of 8 feet. The lake is fed by springs and seepage along the south and west

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shores. Studies made on the ground water, feeding a similar marl lake of the same general region, have indicated that, as it comes from the ground, the ground water contains considerable free carbon dioxide so that it is neutral or slightly acid even though highly buffered with bicarbonate. When the ground water reaches equilibrium with the atmosphere, loss of carbon dioxide raises the pH and brings about precipitation of marl. The numerous springs about the lake probably add marl to the lake by this process.

Fertilization program

In 1954 fertilizer, having an analysis of 10 percent P_2O_5 , 10 percent nitrogen, and 10 percent potash, was applied at a rate of approximately 50 pounds per acre (Table 1). This rate was doubled in 1955 when it became apparent that the 1954 rate had produced little if any response in the phytoplankton. In 1956 the 1954 rate was used again. The formulation of fertilizer used in 1955 and 1956 had an analysis of 12 percent P_205 , 12 percent nitrogen, and 12 percent potash.

Applications were made in midsummer (July 31-August 9); thus the summer could be divided into an early pre-fertilization period and a late fertilized period. Application was made from a moving boat. Only the shallow water of the lake was treated. In 1954 and 1955 all the fertilizer was spread over the half of the lake farthest from the lake outlet. This was to permit thorough mixing of fertilizer with the lake water before it entered the stream outflow. In 1956 the procedure was

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Table 1. --Applications of fertilizer to boffman Lake

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reversed and the half of the lake nearest the outlet was treated and the half most distant from the outlet was not treated. This increased the concentration of fertilizer in the outflow and delayed the appearance of fertilizer in the untreated half. The yearly quota of fertilizer was applied in two applications spaced from 4 to 10 days apart (Table 1).

Sampling stations

Sampling stations 1 and 2 were used for plankton sampling. They were located in water 3 and 5 feet deep respectively. The three sites selected for collecting chemical samples were widely spaced so that horizontal variations in chemical concentration could be detected. Station A was at the southwest corner of the lake near the point of maximum depth, Station B was near the geometric center of the lake, and Station C was nea. the lake outlet (Figure 1).

Methods

Chemical procedures in most cases followed those given in the tenth edition of Standard Methods for the Examination of Water, Sewage, and Industrial Wastes (American Public Health Association, 1955). Ammonia nitrogen was determined by direct nesslerization, total phosphorus by the molybdate method after acid digestion (Ellis, Westfall and Ellis, 1946). Water transparency was estimated by using an underwater photometer and with a Secchi disk. In 1954 and 1955, one gallon of surface water was collected each week for analysis of nannoplankton. Samples were centrifuged through a Foerst electric centrifuge. Phytoplankton

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Figure 1. --Hydrographic map showing

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location of collecting stations.

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Figure 1

could not be identified from the solids removed from the water by this method. Further analysis of the solids recovered by the centrifuge was made in the following manner: One aliquot of the solids was oven dried, weighed, ashed in a muffle furnace and re-weighed. This procedure was repeated on a second aliquot that had been first treated with dilute hydrochloric acid to remove carbonate. Loss on ignition after acid treatment estimates only the carbon dioxide derived from organic matter. Subtracting this quantity from the total loss on ignition gives an estimate of the carbon dioxide from carbonate.

Our failure to find identifiable phytoplankton in the 1954 and 1955 samples led to a change in procedure in 1956. One quart of water was collected each week and filtered through a membrane filter. Solids collected by the filter were divided into three aliquots. The first two aliquots were processed in exactly the same manner as the aliquots of the centrifuged samples. The third aliquot was preserved for identification of phytoplankton.

Quantitative measurements of the periphyton growth in the lake were made in the following manner: artificial substrates (cedar shingles and concrete bricks) of uniform surface area were suspended in the lake water for varying periods of time. At the end of a test period, substrates were removed from the lake. The attached material was scraped off and the chlorophyll extracted from the periphyton with 95 percent ethyl alcohol. The optical density of the extracted pigment was then measured in a photoelectric colorimeter. Optical density was converted to Harvey plant pigment units to make comparisons with previous studies possible.

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In 1954 and 1955, substrates used for collecting periphyton were placed only at Station C. Some of the substrates were placed in the standing water of the lake near the outlet and others were introduced into the stream channel itself. Hence in 1954 and 1955 these substrates were located at the opposite end of the lake from which the fertilizer was applied. Under these conditions we believed that a response to fertilization at this point was a good indication that a response had occurred over the entire lake. Since the periphyton growth at this station may have been influenced by the outflowing current, in 1956 we collected periphyton at a second station (Station F) located at the west end of the lake. At this station, the water was 15 feet deep. At Station C shingles were attached to logs lying in shallow water and brick substrates were suspended by wires from submerged logs and branches. At Station F only shingle substrates were used. At this station, shingles were nailed to a circular wooden float which was anchored $2 \text{ et below the water's surface.}$

Physical conditions

Variations in surface temperatures were large during the three years fertilization experiments were in progress (Figure 2). In 1954, surface temperatures averaged 2° F. lower than in 1955, and in 1956 the average was 3. 8° F. below 1955. Windy and unsettled weather brought about large fluctuations in 1954 and 1956. In the summer of 1955, the weather was hot and calm, and there was little variation in surface temperature except during the early part of the pre-fertilization period.

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Figure 2. --Temperature, transparency and suspended solids before and after fertilization.

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SURFACE TEMPERATURE

Figure 2

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Fertilizer applications brought about an immediate decrease in transparency (Figure 2). In 1954 and 1956 this decrease was short-lived and persisted for less than a week after each treatment. In 1955, however, the reduced transparency, which first appeared in late July after the first application, continued until late August (Figure 2). The 1955 treatment also brought about a greater reduction in transparencies than in 1954 or 1956.

Periods of reduced transparency immediately after fertilization coincide with increases in suspended solids (Figure 2). An increase of 16 ppm. in suspended solids occurred within 72 hours after the first application in 1954. Similar but smaller increases in solids were apparent in 1955 and 1956. In all three years, increases in solids were of such short duration and occurred so soon after fertilization that it seemed improbable that they could represent phytoplankton responses. Analyses of the suspended solid fractions verified this belief by showing that the solide which appeared immediately after fertilization were chiefly carbonate particles.

Separation of suspended solids with a membrane filter in 1956 rather than with the Foerst centrifuge seemed to alter the character and amount of the material collected. Notable was a seasonal trend in the organic fraction that was not evident in 1954 and 1955 (Figure 2). Organic matter decreased from a high in early July to a minimum in late July. One week after fertilization, organic suspensoids increased considerably and remained high throughout the post-fertilization period. Algae were identified from the filtered samples but not from the samples that were

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centrifuged. The large carbonate fraction which appeared in 1956 during the pre-fertilization period indicated that the membrane filter also removed a greater quantity of suspended marl than the centrifuge (Figure 2).

The weight of suspended carbonate that appeared in the water after the first application of fertilizer in 1954 was approximately 12 times greater than the total weight of fertilizer applied to the lake. In 1955 the solids were approximately four times the weight of fertilizer and in 1956 three times the weight of fertilizer. In all three years, the solids increase that followed the second application of fertilizer was small or insignificant. Since the weight of fertilizer applied was of a smaller order of magnitude than the increase in suspended carbonate, it would appear that these solids were not formed by a stoichiometric chemical reaction. The greater amount of carbonate removed by filtering in 1956 as compared to centrifugation in 1954 and 1955 suggests that there were colloidal particles present which were not removed by the centrifuge. If large amounts of m aterial of this small size existed prior to fertilization, the post-fertilization increase in suspensoids probably represented a coalescence of carbonate particles brought about by the change in the ionic balance of the water rather than by the formation of a precipitate. Support for this belief lies in an indication that there was a change in the optical properties of the suspended matter at fertilization. Although the peak concentration of the carbonate solids in 1954 and 1955 corresponded to a decrease in transparency as measured by a photometer and Secchi disk, this change was accompanied by a slight decrease rather than an

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expected increase in turbidity, as measured with a Hellige turbidimeter. This rather anomalous situation can be explained by a change in character of suspended solids that would alter the relationship between light transmission characteristics as compared to light scattering properties. The relationship between transparency and scattering is by no means constant judging from the variability encountered in natural waters (Hutchinson, 1957).

Chemical conditions

Total phosphorus

The maximum concentration of phosphorus recorded after fertilization was approximately the same value in all three years (45 to 47 ppm.) (Figure 3). This concentration represents 52 percent of the phosphorus added in 1954; 52 percent of the 1955 addition (after first application). and 51 percent of the 1956 applications. Clearly there was a large and immediate loss of phosphorus from the water phase. The average total phosphorus content of water samples collected for 27 days after fertilization was 27 ppb. in 1954, 31 ppb. in 1955 and 22 ppb. in 1956. This is to be contrasted with the pre-fertilization level that remained below 10 ppb. The difference between the 1954 and 1955 postfertilization average is not statistically significant. This is surprising since the quantity of phosphorus added in 1955 was twice the amount added in 1954. The average concentration in 1956 was, however, significantly smaller than that in 1954. This was perhaps due to a greater loss of fertilizer to the stream in 1956 when the fertilizer was spread over the

Figure 3. --Conductivity, methyl-orange alkalinity, nitrogen and phosphorus before and after fertilization.

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half of the lake adjacent to the outlet. Phosphorus persisted in the lake at a level greater than before fertilization for at least 25 days each year. It persisted somewhat longer in 1955 than in 1954 or 1956.

Soluble phosphorus

The added phosphorus remained in the lake as a soluble compound for a short time. The pre-fertilization level of soluble phosphorus, however, was soon re-established, within four days after each addition of fertilizer in 1954. In 1955 some soluble phosphorus remained somewhat longer. The soluble phosphorus fraction disappeared from the water rapidly compared to lakes with a low or moderate calcium content that have been fertilized (cf. Brook and Holden, 1957; Nelson and Edmondson, 1955; Hayes et al.. 1952).

Phosphorus of suspended solids

In 1954 analyses were made of the phosphorus associated with the suspended solids. The phosphorus of suspended solids which can be dissolved by 0.05 N HCl must represent either sestonic phosphorus in the form of calcium phosphate or phosphate adsorbed on solids. $After$ each addition of fertilizer this phosphorus fraction increased and then decreased to about the pre-fertilization level (Table 2) much in the same way as the carbonate fraction of suspended solids increased and fell (Figure 2). Since this decrease in suspended carbonate and phosphorus coincided with an increase in transparency, it appears that the phosphorus associated with solids settled from the water along with considerable marl.

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Table 2. --Phosphorus of suspended solids and lake water in 1954

* Less than 1 part per billion.

** Phosphorus was absent in fractions insoluble in dilute HCl.

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Whether the phosphorus of suspended solids existed as phosphorus adsorbed on colloidal marl particles or as a calcium phosphate precipitate cannot be decided from the data at hand. However, conditions of pH and calcium concentration existing at fertilization suggest adsorption rather than precipitation (Hepher, 1958). Acid soluble phosphorus associated with suspended solids appears to have made up a large fraction of the phosphorus in the water after each treatment in 1954. On August 2-3 after the first application, approximately one-third of the total phosphorus was in this form (Table 2).

Non-centrifugable phosphorus

If the phosphorus of the suspended solids is subtracted from the total phosphorus on various dates between August 2 and 27. it appears that from 10 to 20 parts per billion of non-centrifugable phosphorus remained in the water. The exception was on August 12 when a concentration of 33 parts per billion was indicated. This exceptionally high concentration of phosphorus results from a high and possible erroneous value encountered at one of the three collecting stations.

Since only a small fraction of the non-centrifugable phosphorus existed in the inorganic state, it appears that much or all of this fraction existed as dissolved organic matter, non-centrifugable bacteria or nannoplankton. This fraction appeared in the water soon after the first addition of fertilizer. Thereafter there appears to have been little change in noncentrifugable phosphorus, indicating either that there had been little additional uptake or that uptake was balanced by losses to the lake bottom.

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Nitrogen

In 1954 the maximum concentration of nitrogen after fertilization was 65 percent of the amount added to the water. In 1955 a maximum of only 37 percent of the added nitrogen appeared in samples. Ammonium nitrogen fell to a pre-fertilization level more rapidly than did total phosphorus but persisted about the same length of time as the soluble phosphorus.

Alkalinity and conductivity

.Although alkalinity and conductivity changes were of small magnitude, there are clear indications that both decreased at the time of fertilization. The decrease in 1954 and 1955 indicated that about 10 ppm. of calcium carbonate had been lost from the lake water. This loss was of the same order of magnitude as the increase in the amount of suspended carbonate removed by the centrifuge from samples collected immediately after fertilization. In 1956 alkalinity and conductivity changes associated with fertilization were not well rnarked because fertilizer was applied only in the vicinity of the outlet.

pH

The pH of the lake water varied between 8. 1 and 8. 5 during the summers of study. Fluctuations during and after fertilization were minor and could not be attributed to the chemicals that were added.

Phytoplankton

The only recognizable plankton material in the centrifuged samples {1954 and 1955) were broken diatom fragments. Filtered samples (1953), however, contained a sparse algal flora. In most samples the number of cells present was too small to permit a meaningful quantitative treatment. Blue-green algae and diatoms were the predominant types. A greater nuniber of genera were identified from post-treatment samples collected between August 14 and 26 when the organic content of the solids was highest, than frorn pre-treatment samples. Although both the trend of the organic content of the solids and the qualitative nature of the plankton in 1956 suggest a slightly greater and more varied phytoplankton population after fertilization, the response was poor compared to other waters that have been fertilized. When the solids had their highest organic content and when the greatest number of phytoplankton species were present (August 14-26), transparency was as great or greater than before fertilization.

Periphyton

.An increased growth of periphyton in the lake after fertilization was more apparent than the phytoplankton response. Each year after fertilization conspicuous bright green strands of Spirogyra appeared on shoal areas where little or no algae had been noted previously. Similar increases in benthic algae after fertilization have been noted by Brook and Holden (1957).

The accumulation of periphyton chlorophyll on brick and shingle substrates placed near the lake outlet (Station C) during a 30-day prefertilization period can be compared with the accumulation d ring the 30-day post-treatment period (Table 3). Significantly greater chlorophyll production is indicated on both brick and shingles after treatment with the possible exception of the shingles in 1955. In this instance, two standard errors about the pre-treatment and post-treatment means overlap slightly. However, an analysis of these data by pairing pre-treatment and post-treatment shingles has indicated a significant difference at a 95 percent confidence level. The response of periphyton during the posttreatment period seems to have been greatest in 1954 and least in 1955.

In 1956 we removed shingles from the lake at weekly intervals. These data indicate more clearly the time of increased periphyton growth in relation to fertilization (Figure 4). In the case of shingles located in standing waters near the lake outlet, a 10-fold increase in the weekly accumulation of periphyton was noted a week after fertilization. These shingles continued to accumulate periphyton at a rate greater than before treatment until the experiment was concluded on September 5 (Figure 4). Periphyton growth at the deep-water station (Station F) was much lower than at the outlet station and the post-fertilization response did not occur at this station until the second week following the application. Since all of the fertilizer was applied to the outlet half of the lake in 1956 and none in the vicinity of Station F, a delayed and reduced response of periphyton at the deep-water station compared to the outlet might be expected.

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Table 3. -- Chlorophyll extracted from bricks and shingles placed at Station C for 30-day periods before and after fertilization date

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Figure 4. --Chlorophyll production on cedar shingles placed near the lake outlet (Station C) and opposite the outlet (Station F) before and after fertilization in 1956. Shingles at Station C were anchored just below the water surface. Shingles at Station F were located 2 feet below the water surface. A logarithmic transformation has been used in analysis of data. Scales shown for standard errors are appropriate for logarithmic means.

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Figure 4

Proximity to the lake bottom may also have influenced the accumulation of periphyton. Shingles at the outlet were close to the lake bottom and could receive nutrient regenerated from the bottom and carried into the open water. Such an exchange was less likely the case of the shingle float which was anchored in water 15 feet deep. Although the total production of accumulation at Station F was small as compared to the outlet, the percentage increase in periphyton growth following fertilization at the two stations appears to be of similar order of magnitude (Figure 4).

Discussion

Three years of fertilization of Hoffman Lake tends to confirm the hypothesis of Barrett (1954) that fertilization of marl lakes is inefficient because of the loss of phosphorus to the bottom muds and because fertilizer added to the water is relatively ineffective in stimulating plankton production. This inability of the phytoplankton of marl ecosystems to effectively utilize such a source of nutrients is of interest. This may be due to the adsorption of nutrients by the particulate lime in the water and to the lack of dissolved organic substrates (e.g., chelating agents) which can hold nutrients in a form which is available to plankton algae (Schelske, Hooper, and Haertl, 1962).

A conspicuous feature of Hoffman and other marl lakes is the periphyton which encrusts the bottom and other substrates. The favorable response of benthic algae to fertilization noted above indicates that these plants are able to effectively use the added nutrients even though the

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nutrients were used very little by the plankton. The precipitated or adsorbed phosphorus which settled to the bottom may have been the source of nutrient utilized by the bottom algae after it had been made available by pelometabolic processes. A major share of the primary production of marl lakes may take place at this site rather than in the open water.

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