CHEMICAL AND BIOLOGICAL EFFECTS OF LIME APPLICATION TO BOG LAKES IN NORTHERN MICHIGAN

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Institute For Fisheries Research

by

Thomas Frank Waters

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TABLE OF CONTENTS

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LITERATURE CITED

INTRODUCTION

In the past, considerable attention has been paid by workers in many fields of research to bogs and bog lakes. The unique set of environmental conditions represented by a bog lake, with its comparative isolation from outside influences, is particularly attractive to ecologists in several biological fields. From the limnologist's viewpoint, the bog lake, with its acid and extremely soft-water conditions and its encroaching bog mat, presents an object of study which is totally different in many respects from all other bodies of water, and workers in this field have studied bog lakes in many investigational researches (Welch, 1936a, b, 1938a, b, 1945, Jewell and Brown, 1929, Gorham, 1931, and others). However, despite the abundance of these lakes in certain regions of northern Michigan and Wisconsin where sports fisheries are extremely important, it has not been until recently that this type of lake has been included in developmental research programs aimed at proper management of bog lakes as sport fishery resources.

several reasons are apparent. Generally, interest shown in utilizing bog lakes as fishery resources has been low. Bog lakes are often very small and perhaps unnotiqed; many do not contain desirable fishes (or perhaps none at all); and they cannot be waded nor approached easily either by foot or boat. But one of the greatest deterrents to giving the bog lake an important position among our fishery resources is its extremely low biological productivity.

rt has been often · observed that a correlation exists between the biological productivity of lakes and the alkalinity of their waters. Ball (1945), reporting on the results of poisoning lakes in Michigan, divided the lakes which were poisoned and for which complete fish recoveries were attempted into three categories of methyl-orange alkali-

nity and observed that the more alkaline categories contained higher average standing crops of fish. It has been suggested, furthermore, that the alkalinity of lake waters be used as an index to productivity. Moyle (1949), in a study of this and several other suggested indices of lake productivity in Minnesota, compared total alkalinity and productivity (based on pond fish yield and test-net catches in lakes) and ,i; reported that 40 ppm. total alkalinity appeared to be a valid separation point between soft-water (less productive) and hard-water (more productive) lakes. He concluded that total alkalinity, along with total phosphorus, appeared to be the most valuable of the indices studied. Since the existence of causal relationships is a possibility, a valid phase of developmental research appears to be an investigation of the use of alkalinizing compounds, such as lime, to increase the alkalinity of lake waters and thus, possibly, biological productivity.

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It is considered appropriate here to define the terms "alkalization" and "alkalinization," as used in this report. "Alkalization" is used as being synonymous with "lime application," and is not meant to imply that the water is necessarily made more alkaline, even though such an effect may be expected; the term "alkalinization" is reserved for the purpose of denoting an actual increase in alkalinity.

It was the purpose of this research program to test the use of lime to increase biological productivity in bog lakes, and to report upon the chemical and biological effects of such treatment. Such a program permits the attempt to answer several questions: (1) What causal factors are involved in the higher production observed in more alkaline waters? (2) What direct effects, if any, would there be upon organisms living in the lake waters? (3) What would be the effect of changing pH levels upon the availability of nutrients? (4) What fac-

tors would reduce the alkalinizing effects of lime treatment, such as calcium loss due to ion-exchange at the mud-water interface?

In agriculture, the use of lime on acid soils is widely recognized as a very necessary management practice. The above questions, posed . about an aquatic medium, have been amply answered about terrestrial soils. More alkaline conditions in soil favor the activities of de- ~· composition bacteria, thus mineralizing nutrients from unavailable organic forms. Phosphorus availability depends upon the level of soil reaction, undesirable levels being at both ends of the pH scale. Direct effects of soil reaction upon soil organisms are known, particularly disease-causing organisms.

However, the use of lime in aquatic production in this country is very small compared to its terrestrial use. In Europe, where the pond production of carp has been practiced for centuries, lime has been used to produce increased fish yields (Neess, 1949). Lime has been added with other fertilizers in pond and lake fertilization experiments, both as a fertilizer itself (Juday and Schloemer, 1938), and for offsetting acidifying effects of ammonium fertilizers (Swingle and Smith, 1939).

In Michigan, a small application of hydrated lime was made to a soft-water, non-bog lake in 1943, expressly for the purpose of increasing alkalinity, and was again treated in 1945 (Ball, 1947), this time with limestone, neither treatment effecting a change in alkalinity; the same lake was again incorporated in an alkalization program of research in the years 1952 through 1955 (Ball and waters, MS), where changes in alkalinity resulted and increases in standing crop of net phytoplankton were observed.

The use of lime in treating bog lakes was investigated in Wisconsin

in 1948 by Hasler, Brypildson and Helm (1951). They offered several suggestions as to the mechanisms by which productivity may be increased by liming in colored bog lakes. The color--caused by humic colloids- would be flocculated and precipitated through combination with calcium, thus permitting deeper light penetration and increasing the volume of the trophogenic zone. Secondly, alkalinization of the water would mobilize nutrients which are fixed in unavailable organic forms in the lake soils. Finally, a higher concentration of bicarbonates would result, offering available carbon dioxide to plants for photosynthesis in higher concentration. Following their experiment, they reported that the lime treatment resulted in clearing the color of the water and improving oxygen conditions for trout in the deeper, cooler levels of the lakes, but showed no striking differences in nutrient content of the water. It was later reported (Johnson and Hasler, 1954) that no apparent increase in production or carrying capacity resulted.

In the summer of 1953, the present research program was initiated upon several bog lakes in the Hiawatha National Forest in the upper peninsula of Michigan. The program consisted essentially or gathering pre-treatment data on limnological conditions, applying hydrated lime to the lakes, and obtaining data on post-treatment conditions to evaluate the changes effected.

Three postulates **were** made regarding the mechanisms by which biological productivity might be increased by the use of lime, and the sampling program was designed to test these postulates: (1) a greater concentration of bicarbonate alkalinity, offering more available carbon dioxide for photosynthesis, would result; (2) phosphorus would be released either by increased decomposition activities or through ion-exchange phenomena in the mud; and (3) the colloidal or-

ganic color would be 'decreased by flocculation and precipitation caused by combination with calcium.

Description of area

The region of the Hiawatha National Forest in Michigan's upper peninsula was selected for this series of experiments due to its abundance of small bog lakes. This region lies near the western edge of the Lake Superior Lowlands, of the Central Lowland Province, and has a relatively deep layer of g acial drift underlain with high-calcium sedimentary rock (Lobeck, 1950). The sedimentary rock immediately below the glacial drift in the Hiawatha National Forest is limestone (Bergquist, 1937), and it would be expected that the glacial drift contain a large proportion of lime stone and limestone flour. This is evidenced by the alkaline characteristics of deep wells, springs and spring-fed lakes in the area, and by the presence of limestone in an area gravel pit; seepage lakes, however, including bog lakes, are acid in nature and very soft. The region contains several large outwash plains and some morainic areas from the Newberry and Munising moraine systems. The outwash plains, particularly, are dotted with many small glacial lakes, known as pit lakes; several appear in morainic regions where they are known as kettle lakes; still others are shared by the edges of both outwash plains and moraines and are then known as fosse lakes.

METHODS

Description of lakes

A limited survey of' small bog lakes in the Hiawatha National Forest was made during the sunnner of 1953 and five of these lakes were selected for experimental purposes. Among the five lakes were three colored bog lakes and two clear-water bog lakes. They were selected for certain desired characteristics, including similarity of

size, chemical and biological conditions, and accessibility. Several characteristics were constant for all lakes selected. All lakes were completely surrounded by an encroaching, acid, sphagnum-leatherleaf bog mat. In addition to Sphagnum and leatherleaf (Chamaedaphne calyculata, Muench), many other typical bog plants comprised the mats of all lakes, including several ericaceous shrubs such as the cranberry, Vaccinium macrocarpon Ait.; bog rosemary, Andromeda glaucophylla Link; bog laurel, Kalmia polifolia Wang.; and labrador-tea, Ledum groenlandicum Oeder; several sedges, including cotton-grass, Eriophorum *spp.;* Carex spp.; and Rhynchospora alba (L.) Vahl; also the pitcher plant, Sarracenia purpurea L.; sundew, Drosera rotundifolia Wang.; and an orchid, swamp-pink, Calopogon pulchellus (Salisb.) R• Br. Aquatic vegetation was scant in all lakes and consisted of Nuphar and/or Utricularia.

All lakes had approximately the same bottom types, consisting of brown fibrous peat near the mat and a fine, gelatinous pulpy peat of brown color in the deeper areas of the lakes; no exposed sand or other inorganic bottom was found in any of the lakes.

starvation Lake

This was a colored kettle lake in the Newberry moraine system. Figure 1 shows a map of marginal outline and bottom contours. Steep slopes were present on the east and west sides. All sides were densely forested, even out upon the bog mat. Spruce and tamarack were found on the mat, with some white pine along the landward edges of the mat. Poplar, cherry and pine were found on the slopes. The encroaching mat was of moderate width on all sides, while a large, connecting bog mat area lay near the south end, apparently draining into the lake. A large, active beaver lodge was present on the edge of the bog mat.

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starvation Lake was 1.7 acres in size with a volume of 32.6 acre-feet and a maximum depth of 42 feet. Despite repeated attempts with gill nets and by angling, no fish of any kind were ever taken, and none were ever observed nor reported by others. See Plate I.

Timijon Lake

This was a colored pit lake in an outwash plain, possessing only shallow slopes on all sides. It was separated from a moderately sized stream, the Big Indian River, by· only a narrow dike of glacial drift of about 50 feet wide; however, no connection between the lake and stream was apparent nor was one believed to exist. The lake was lightly forested on all sides by poplar and birch, and a very few white pines. Spruce and tamaracks were found on the bog mat. The mat was of moderate width on three sides, while an extensive mat area was found *on* the southeast side. Timijon Lake was 2.0 acres in size with a volume of 43.1 acre-feet and a maximum depth of 42 feet. Yellow perch, Perca flavescens (Mitchell), were found to be very common; northern brown bullheads, Ameiurus nebulosus nebulosus (LeSueur), were also found. See map in Figure 2, and Plate II.

Juanita Lake

Juanita Lake was a colored fosse lake with parts of the Newberry moraine on the north and west sides and outwash plain on the remainder of the shoreline. Slopes on the moraine side were .heavily forested with white pine, birch and poplar. An extensive bog mat area was found on the southeast and north sides; the north mat included a small, very shallow pond, separated from the lake by the mat. Spruce and tamarack were found on the bog mat, while Utricularia was very common along the edges of the bog mat. Juanita Lake was 1.4 acres in size with a volume of 35.1 acre-feet and a maximum depth of 34 feet. Yellow perch, Perea

Starvation Lake **PLATE** I.

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Figure 2. Map of Timijon Lake.

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PIATE II. Timijon Lake

flavescens (Mitchell), were found to be common; bullheads were reported in the lake but the species was unknown. See Figure 3 and Plate III.

Irwin Lake

This was a clear-water fosse lake, having the Newberry moraine on the east side and outwash plain on the remainder. It was densely forested on all sides except the west; white pine and birch were predominant. The bog mat was narrow on all sides and held few spruce and tamaracks. Aquatic vegetation consisted of a few patches of Nuphar. Irwin Lake was 10 acres in size and had a maximum depth of 38 feet. The lake originally contained yellow perch, Perea flavescens (Mitchell), but had been poisoned and restocked with brook trout, Salvelinus fontinalis fontinalis (Mitchell). See map in Figure 4, and Plate IV.

Grant' s Lake

This was a clear-water bog lake of the fosse type, having parts of the Newberry moraine on the north and west sides, and outwash plain on the remainder. The surrounding land was moderately forested on all sides with poplar and birch primarily and a few white pines. Only a few spruce and tamaracks were found on the bog mat, and the aquatic vegetation consisted of Nuphar, which was relatively conunon. The bog mat was narrow on all sides. This lake was k rger and shallower than any of the other lakes and did not stratify thermally except in a small depression of deeper water. This lake, originally containing yellow perch, Perea flavescens (Mitchell), had been poisoned and restocked with rainbow trout, Salmo gairdnerii irideus Gibbons, and brook trout, Salvelinus fontinalis fontinalis (Mitchell). Grant's Lake was 13.8 acres in size and had a maximum depth of 30 feet. See map in Figure 5, and Plate *v.*

Figure 3. Map of Juanita Jake.

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PIATE III. Juanita Lake

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PLATE IV. Irwin Lake

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Figure 5. Map of Grant's lake.

PLATE V. Grant **Lake** s

Preliminary laboratory experiments

Two postulates were investigated in the laboratory before any applications of liming materials were made to the lakes. The first was that phosphorus would be released from the bottom organic deposits upon the application of lime; the second was that the calcium from the applied lime would enter into ion-exchange reactions at the mud-water interface and be lost from the lake water. These postulates were tested by conducting experiments involving the addition of hydrated lime at known rates to bottles containing mud and water which had been collected from the three colored bog lakes, and testing the water for dissolved phosphorus and dissolved calcium. A separate series of experiments was conducted for the testing of each postulate. Detailed procedures are included in a later section with the results.

Application of lime

For the application of the lime to the lake waters, a raft-andpump system was employed which mixed the lime with water and discharged the mixture, which was a white, milky suspension, at the surface of' the water. The apparatus consisted essentially of a flat raft ten feet long and six feet wide, supported in back by the edge of the bog mat and in front by two floating 50-gallon drums. Through a rectangular hole in the raft was lowered a plywood mixing tank which allowed the intake of water at the bottom of the front side of the tank; a hopper was constructed on top of the mixing tank through which the lime was introduced. The intake hose *qf* the pump was placed in the mixing tank, where both lime and water were taken up, carried through the mechanism of the pump and through the exhaust hose of the pump, to be finally discharged into the lake (see Plate VI).

Lime application was made to two of the colored bog lakes, re-

PIATE VI. Summer lime application to Starvation Lake,
showing raft-and-pump system.

taining the third colored lake for a control. The two clear-water bog lakes were retained for comparative studies, particularly should the lime have resulted in clearing the color from the treated lakes.

Each of the two treated colored lakes received two separate lime applications, one during the early summer while thermal stratification *i* was present and the second during the autumn after stratification had been destroyed. The summer application to Starvation Lake commenced on July 10, 1954, and ended July 13, 1954; a total of 1650 pounds was applied, which amounted to a rate of 50 pounds per acre-foot, on the basis of the entire volume of the lake (excluding the bog mat). Liming commenced on Timijon Lake on July 19, 1954, and continued throughout the remainder of the summer to August 28, 1954, on which date the last application was made. A total of 1600 pounds was applied for a rate of 37 pounds per acre-foot, on the basis of the entire volume of the lake (excluding the bog mat).

The difference between the methods of applying lime to Starvation and Timijon lakes during the summer was essentially as follows: An application of 50 pounds per acre-foot was made as rapidly as possible in starvation Lake; producing large and precipitous changes in chemical conditions, particularly the elevation of pH. The application of lime to Timijon Lake was made without reference to the rate applied, but rather to the change in pH produced; it was made at such a rate as to keep the pH of the surface waters near neutrality. In both lakes., during the swnmer application, discharge of the lime-water suspension was made near shore immediately in front of the raft (see Plate VI).

The autumn application to Timijon Lake was made on October 17 , 1954. when the lake was nearly homothermous, and consisted of 2700 ~ pounds. The autunm application to Starvation Lake was made on October

19, 1954, consisting of 1650 pounds. These applications brought the total rates of application up to 100 pounds per acre-foot for each lake. For the autumn applications, the lime-water discharge was made near the center of the lake with the use of hoses suspended by buoys (see Plate VII).

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The lime used was high-calcium hydrated lime, furnished by the cutler-Magner Company, Duluth, Minnesota. An analysis of the material showed a determination of calcium of 95% (as $Ca(OH)_2$) and neutralizing power of 90% $Ca(OH)_2$ (122% $CaCO₃$).

Method of sampling

A periodical sampling; program was initiated on all lakes immediately after selection and mapping of the lakes during the summer of 1953. The three colored bog lakes--Starvation and Timijon, which were treated, and Juanita, the control--were sampled every ten days. The two clear-water bog lakes were sampled three times per year.

The sampling station was selected so as to be at or near the deepest part of the lake, usually near the center. At this point in each lake a buoy was anchored securely, and at the time of sampling, the boat was tied to the buoy, obviating the necessity of dropping anchor each time.

For purposes of sampling, four levels were selected. These were: (1) central epilimnion, taken always at three feet; (2) top of thermocline--this depth varied, but was established at each sampling time with a vertical series of temperatures; the mean depths for this level for each of the lakes were, Starvation--7.4 feet, Timijon--9.1 feet, Juanita--7.7 feet, Irwin--11.5 feet, and Grant's--16.5 feet; (3) cen tral hypolimnion, usually 20 feet; and (4) bottom waters, one foot above the mud-water interface.

PIATE VII. Autumn lime application Starvation Lake,
with discharge near center of lake.

Chemical sampling

water samples **were** collected from the four levels described above with a modified Kemmerer water sampler and analyzed immediately for dissolved oxygen by the rapid Winkler method (Ellis, Westfall, and Ellis, 1948) with the Alsterberg (sodium azide) modification ("Standard Methods for the examination of water, sewage, industrial wastes," American Public Health Association, 1955); for free carbon dioxide by the method given by Ellis, Westfall, and Ellis (1948); for alkalinity according to "Standard Methods"; for pH with one of the following: Hellige pH comparator, Coleman Compax pH meter, or Beckman pH meter, Model *N;* and for color with a USGS color kit using standard glass discs calibrated according to the platinum-cobalt color scale. Water tempera**tures were** taken with a pocket thermometer immediately after the sarnple was collected with the sampler; air and surface temperatures were taken directly. Light penetration was measured with a Secchi disk. In addition to the above determinations made in the field, water samples were collected from all four levels and bottled for return to the field laboratory where they were analyzed for total hardness by the EDTA (versenate) method ("Standard Methods") and for conductivity with a conductivity bridge manufactured by Industrial Instruments, Inc. Similar water samples were also collected (excluding 1953) and stored for later determination of total phosphorus, when the method of Ellis, Westfall, and Ellis (1948) was **used** with a Klett-Summerson photoelectric colorimeter.

In addition to the above analyses made of the water, mud samples were collected from the two treated lakes, Starvation and Timijon, to be analyzed for adsorbed calcium in an attempt to determine if introduced calcium from the applied lime was being lost due to ion-exchange ~ at the mud-water interface. The samples **were** collected always at the

sampling station with an Ekman dredge, making sure that the interface was held within the dredge. Approximately the surface three centimeters **were** scooped out, filtered through filter paper \Whatman No. 1), and air-dried for storage. For determination of adsorbed calcium, the method of Cheng and Bray (1951) was used with modifications. The samples were oven-dried at 60° C. and ground to a 200-mesh size. To one gram of this material was added 10 ml. of 23% $NANO₃$ as the extracting solution; this mixture, after shaking for one minute and standing for ten minutes, was filtered through filter paper (Whatman No. 1) and the filtrate was analyzed for total hardness (calcium and magnesium) by the EDTA (versenate) method ("Standard Methods").

Because some of the mud samples collected after alkalization contained free carbonates (fall-out from the autumn application), the method of Hissink (1923) was modified and utilized. Hissink's method consisted of carrying out two leachings upon each sample, assuming that all the adsorbed bases would be removed by the first leaching and that equal amounts of bases would be removed through dissolution of the carbonates by the extracting solution in the two leachings; the second leaching was then subtracted from the first in order to obtain the adsorbed bases. In the samples of the present study, three leachings were made to test the above assumptions (i.e., if the assumptions were valid, the results of the second and third leachings should have been equal) which were found to be invalid. Therefore, calculations of adsorbed calcium were made in the following manner: It was still assumed that all adsorbed calcium was removed in the first leaching, but it appeared that greater amounts of bases, derived from free carbonates, were removed by prior leachings. The third leaching was subtracted from the second, and the difference was added to the second;

this sum was then subtracted from the first leaching, the difference being an estimate of adsorbed calcium.

Biological sampling

Two samples of net plankton were collected from each of the four levels on each sampling date with a Juday plankton trap holding 10 liters, with a net made of No. 20 silk bolting cloth. The contents were stored in one-ounce bottles in a resulting preservative of about ;5 or 4% formalin. In the laboratory, all samples were brought up to a uniform volume of 30 ml. The samples from the two hypolimnial levels were found to contain negligible amounts of plankton (other than Chaoborus) and were not included in the plankton analysis. The samples from the two epilimnial levels were analyzed for volume of net phytoplankton and zooplankton. The method of Dice and Laraas (1936) for graphically comparing several sets of data was employed for all biological data. The standard error of the estimate was computed for each pair of duplicate samples; two standard errors were plotted on each side of the mean as a straight vertical line. In comparing any two sampling dates, if the vertical lines did not overlap horizontally, statistical significance was indicated.

Net phytoplankton

For the determination of volume of net phytoplankton, a Sedgewick-Rafter counting cell was filled with one ml. of the concentrate, and under the microscope, a total of 10 fields per sample were counted, **using** a Whipple ocular micrometer; an average volume per cell was calculated for each species, using measurements made with a calibrated ocular micrometer and approximating the shape of the cell with some geometric figure (method modified from Whipple, 1948, p. 119). From the counts and average volumes, standing crops in terms of volume per

zooplankton

To determine the volume of zooplankton per sample, a different method was used on each of the following two groups comprising the zooplankton: (1) smaller organisms, composed of rotifiers and nauplii, and (2) larger organisms, composed of Cladocera and Copepoda. For the rotifers, a strip of concentrate in the Sedgewick-Rafter cell one milimeter wide and 50 milimeters long was observed and all rotifers and nauplii were counted. For the large crustaceans, the entire area of the Sedgewick-Rafter cell was observed and all cladocerans and copepods were counted. For both groups, an average volume was calculated from measurements for each species, and from counts and these average volumes, the standing crops, as volume per liter, were computed.

RESULTS AND DISCUSSION

Preliminary laboratory experiments

Release of phosphorus

To test for the release of phosphorus, hydrated lime was added to bottles containing water and mud, and after three days, the water was analyzed for dissolved phosphorus. Three mud-water combinations from each of the three colored bog lakes were treated with lime: (1) surface water with mud, {2) bottom water with mud, and (3) surface water without mud (control). Six different rates of lime application were used: 0 (control), 25, 50, 100, 150, and 200 pounds per acre-foot. In all cases, the experimental unit consisted of 50 ml. of mud, taken from the mud-water interface, added at the bottom of one liter of water in a two-quart jar. The lime was added by dissolving previously weighed amounts of lime with water from the experimental bottles and adding

the solution to the bottle. Water samples were extracted for analysis by pipette three days after the lime addition. Dissolved phosphorus was determined by the method given by Ellis, Westfall, and Ellis (1948), using a Klett-Summerson photoelectric colorimeter.

The results are shown in Figure 6, where it can be seen that dissolved phosphorus increased in the series which included mud, with one exception, when the lime application rates increased. The exception, Starvation Lake bottom water, which had an original high concentration of dissolved phosphorus, showed no increase of phosphorus with lime application. In all control bottles (no mud) there was no increase of dissolved phosphorus with lime application, indicating that the released phosphorus in the other bottles did, in fact, come from the mud.

The release of phosphorus upon alkalinization may be due either to (1) raising the pH to a more suitable level for decomposition bacteria, thus mineralizing phosphorus fixed in an organic form, or to (2) an anionic exchange between adsorbed phosphate and introduced hydroxide. No data are shown here to indicate that either of the above phenomena was in operation to the exclusion of the other.

Calcium adsorption

To test for calcium adsorption, experiments were set up with bottles containing water and mud which were treated with hydrated lime; periodical tests for alkalinity and total hardness **were** made, and finally a solution of sodium nitrate was applied and the water subsequently tested for calcium.

Three mud-water combinations were used from each of the three colored bog lakes, the amount of water being one liter in all cases and the amounts of mud being O (control), 50, and 100 ml. Hydrated lime was applied at the rates of 50 pounds per acre-foot for Juanita

and Starvation lakes, and 100 pounds per acre-foot for Timijon Lake. Hydrated lime was added to the bottles in a manner similar to that described above for the phosphorus experiments. Tests for alkalinity and total hardness were made periodically for about five months, at which time the sodium nitrate solution was added to all bottles at the rate of ten times the equivalents of the calcium hydroxide (hydrated lime) originally added. Tests for alkalinity and total hardness were again made 10 days after the addition of sodium nitrate. Alkalinity was determined by methods given in "Standard Methods" and total hardness by the EDTA (versenate) method ("Standard Methods"). (The total hardness test is a determination for both calcium and magnesium, but since the hydrated lime used contained practically no magnesium, this report **is** limited to the discussion of calcium.)

The results show that calcium was lost from the water after lime application, as smaller concentrations of total hardness **were** observed in the bottles containing mud, as shown in Figures 7, 8, and 9. Furthermore, concentrations of total hardness were smaller in the bottles containing the greater amount of mud, indicating that more than the mud-water interface was involved in cation-exchange phenomena. Barrett (1952) after conducting similar bottle experiments with mud and water from another lake, also suggested that more than the interface is active in calcium adsorption. Alkalinity was found to be lower in those botles containing mud than in those without mud.

When the sodium nitrate solution was added, increases of dissolved calcium were observed in all bottles containing mud, indicating that the calcium which had been introduced and adsorbed by the mud was released through cation exchange between calcium and sodium. Alkalinities did not increase to high values after the addition of sodium nitrate because the calcium, after release, was probably in the form of calcium nitrate,

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which does not contribute to alkalinity.

It should be pointed out that the total hardness of the water in the bottles which contained mud increased upon application of sodium nitrate to values above those observed in the control bottles without mud; this increase was due to a greater concentration of released calcium because the volume of water had been reduced through the time of the experiment by withdrawing samples for analysis. The data, therefore, do not show exact quantitative relationships. It was concluded, however, that adsorption of introduced calcium did occur, and that adsorption was greater in the presence of a greater amount of mud .

Field experiments

The immediate effects of the lime application were to raise the pH of the lake water, and to increase the alkalinity, total hardness, i and conductivity. The summer application--while stratification was present--resulted in chemical effects in the epilimnion only; no effects were observed below the thermocline. The autumn application- when the lakes were nearly homothermous--resulted in almost the entire application of the lime, in dissolved form, falling to the bottom levels of the lakes, apparently because of the high density of the lime-water discharge solution; the dissolved lime remained at the bottom for the duration of the experiment (through the following winter and summer). and did not become dispersed throughout the upper levels of water. Plankton responses were observed in starvation Lake soon after the lime treatment, and in both treated lakes the following sunnner. Conditions in the control lake, Juanita, remained essentially constant during the time of the experiment.

Tables containing complete data on the field experiments are to be found in the appendix; graphs and abbreviated tables illustrating the more important effects accompany the following detailed discussions.

starvation Lake

Effects in epilimnion. The summer application to this lake was nade as rapidly as possible and brought about large and precipitous changes in the chemistry of the lake waters; because of the strong thermal stratification, the effects of the treatment were felt only in the epilimnion. The pH rose from arproximately 5.5 to almost ll.0 in the central epilimnion, and then descended more slowly to level off at about neutrality in about 5 weeks, where it remained for the rest of the summer (see Figure 10). The autumn application had little if any effect upon the pH in the epilimnion, and through the summer of 1955 the pH here remained about neutral. In Figure 10 are also shown the data concerning alkalinity, and it can be seen that these data follow what would be expected with the corresponding pH values. Total alkalinity increased from about 4 ppm to 70 ppm in the central epilimnion; some of the alkalinity was in the form of hydroxide immediately after lime application, but this soon changed to normal carbonate and eventually to bicarbonate as carbon dioxide was produced by the respiratory processes of the lake and was made available for combination with the hydroxide and carbonate. Dissolved carbon dioxide was not present, of course, immediately after the application, because of its rapid utilization in combining with the introduced hydroxide; free carbon dioxide appeared again when the pH values descended to about $e_{\bullet}0_{\bullet}$ Dissolved oxygen concentrations did not appear to be affected directly by the lime applicution. Figure 11 shows the changes in total hardness through both years for the central epilimnion, and it can be seen here that the total hardness generally followed the same trends as did total alkalinity. Conductivity, though not in the same units, followed the same general trends as did alkalinity and total hardness (see Figure 11).

The effect of alkalinization upon color in the epilimnion was parti-

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cularly observed in starvation Lake in order to test the postulate which Hasler et al. (1951) supported experimentally in Wisconsin, namely, that the color would be precipitated. In starvation Lake, no decrease in color was observed following the lime application; rather, an increase was observed shortly after the application, and later, the high values fell off to approximately the same as before lime application (see Figure 12). As would be expected, Secchi disk readings were reduced at this time of apparent higher color concentration (see Figure 12). During this time, it was observed in water samples taken in conjunction with chemical analyses made in the field, that strands of brown, mucilaginous-appearing material were present in the water, particularly at the top of thermocline level, where the increase in observed color was even greater than in the central epilimnion. Following the theory of color flocculation and precipitation by calcium, it is suggested that a partial flocculation did take place, producing the brown strands in the water; some precipitation took place also, and a concentration of the material accumulated on top of the thermocline, probably because of the increased water density at that level. Apparently this partial flocculation, with the resulting visible brown strands, effected an apparent increase in color when measured with the USGS color kit. The color at all levels returned to normal values after about four weeks.

Chemical conditions at the top of thermocline, generally followed trends similar to those in thecentral epilimnion, except that changes **were** not as great, and concentrations of dissolved salts did not increase to the high values observed in the central epilimnion.

Effects in hypolimnion. Conditions in the central hypolimnion, and in the bottom waters, did not change until after the autumn application. At the time of the autumn application in October, water tempera-

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tures varied from 49° F. at the surface to 41° F. at the bottom, with no thermocline present. Conditions in the epilimnion did not change upon liming. Conditions in the central hypolirnnion changed slightly but significantly, while changes in the bottom waters were extremely precipitous, being the result of almost the entire lime application falling to the bottom in solution. pH values rose from about 6.0 to 11.0, total hardness from 11 to 118 ppm., total alkalinity from 17 to 128 ppm., and conductivity from 19 to 147 micromhos.

The high density of the solution at the bottom following this autumn arplication apparently made possible a temperature inversion and the fonnation of a monimolimnion. Temperatures at the bottom were increased slightly (even above temperatures found in the next higher level) from 41°F. before alkalization to 44°F. after alkalization; dissolved oxygen also increased at this bottom level from $0_{\bullet}0$; to 2.0 ppm. after liming. These changes were brought about by the use of surface water--which was warmer and contained dissolved oxygen- for mixing with the lime in the mixing tank on the raft. The limewater suspension, containing oxygen and at a higher temperature, was more dense than the coolest water in the lake at the bottom; therefore, when it was discharged into the surface of the lake it immediately fell with little mixing to the bottom levels.

Effects upon phosphorus concentration. As mentioned previously in connection with the laboratory experiments with mud and water in bottles, the phosphorus concentration of the bottom waters in Starvation Lake was high, even before any lime application, and no apparent changes were brought about upon treatment in the bottle. The same results were observed in the lake after the autumn lime application was made. The mean total phosphorus concentration in the bottom waters before the autumn application (1954 only) was 214 ppb., while the mean

after the autumn application (1955) was 244 ppb.; a t-test showed a t-value of 1.88 with 16 degrees of freedom, the t-value not being significant.

The total phosphorus concentration in the central epilimnion apparently increased immediately after the summer application, as shown in Figure 13. (These data, however, are not conclusive; other apparent increases in total phosphorus were observed at different times and levels, and in other lakes, suggesting variation due to causes other than the lime treatment.) The source of released phosphorus was probably in those shallower **areas** of the lake **where** epilimnial waters, containing low concentrations of phosphorus, came into contact with bottom muds; these conditions are essentially those produced in the bottle experiments with "mud and surface water", where the release of phosphorus was observed.

It might be suggested that any observed increase in phosphorus in the epi1imnion was due to phosphorus actually present in the liming material used. However, this was not the case, as an analysis of the hydrated lime showed only a negligible amount of phosphorus present. A lime solution containing 75 ppm. of alkalinity was found to contain only about one ppb. phosphorus (well within the error of the analytical method), while the increase in phosphorus observed in the lake (for an increase of about 75 ppm. alkalinity) was about 40 to 50 ppb. It was concluded, therefore, that there were no increases in phosphorus due to introduction with the lime.

Calcium adsorption by mud. The summer application of lime had no effect upon the adsorbed calcium in the pulpy peat; this vo uld be expected, considering that the summer application did not affect chemical conditions in the bottom waters. The autumn application, however,

. resulted in alkalinization of the bottom waters only, and the mud samples taken after the autumn lime application showed an increase in adsorbed calcium. As per cent calcium on an oven-dried basis, adsorbed calcium was 0.26% before the autumn application (1953 and 1954) and 0.38% after the autumn application (1955). A t-test showed a t-value of 7.74 with 36 degrees of freedom, the t-value being highly significant.

The modification of the scheme of Hissink's (1923) which was used for determining adsorbed calcium in the presence of free calcium carbonates precludes the determination of absolute values of either the percent figures quoted or the degree of inorease. In the starvation Lake mud samples, free carbonates could not be seen (in Timijon Lake, as will be pointed out later, carbonate material could easily be seen in the samples), and that serious interference from free carbonates was encountered is doubtful. The data can probably be accepted to the degree that a significant increase of adsorbed calcium occurred, but exact quantitative values are not implied.

Biological effects. In the analysis of plankton samples, phytoplankton and zooplankton were separated on the presumption that the two groups belonged to different trophic levels. The reason for using different analytical methods for determining the total volume per sample was that in the latter group, zooplankton, the organisms were large but relatively scarce, while in the former group, phytoplankton, the opposite situation prevailed, and a common analytical method would result in extreme variation. Even among the zooplankton, two methods of analy**sis** were necessary because of the presence of rotifers, which were small but more plentiful in relation to the larger copepods and cladocerans. The different analytical methods were employed in order to reduce the

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variation which would result from using, for example, a method designed to sample small, abundant organisms, such as phytoplankton, upon larger, less abundant organisms, such as zooplankton.

Even with this system, a major difficulty presented itself in the presence of a phytoplankter, Peridinium limbatum, which was very large in comparison with other phytoplankters, and which caused an extreme variation in the analytical results. For this reason, data concerning Peridinium limbatum were removed from the volume computations in constructing the graphs of standing crop of net phytoplankton for all lakes. Data on Peridinium limbatum are included, however, in the tabulated results given in the appendix.

The standing crops of net phytoplankton for the central epilimnion are given in Figure 14. It will be noted that net phytoplankton abundance was extremely low during that part of 1953 sampled, and for all of 1954. **^A**decrease in phytoplankton was observed immediately after application, apparently being **the** result of inhibitory effects of the lime suffered by the organisms; Whipple $(1948, p. 405)$ discusses the use of hydrated lime as an algicide and **says** that lethal effects are probably due to the loss of carbon dioxide available for photosynthesis or to changes in hydrogen ion concentration. During 1955, however, large, statistically significant increases in standing crop were observed. The principal organism making up this "bloom" was Dinobryon sertularia.

During 1954, shortly after the summer lime application, a bloom of Microcystis aeruginosa occurred in the epilimnion; this bloom is not shown among the plankton data because the cells were of nannoplankton size and were not collected in the plankton samples, being too small to be retained by the plankton net (No. 20 silk bolting cloth). The bloom was, however, obvious to the eye; it gave a definite greenish color to the water, and collected in windrows of "scum" along the lee shores of the

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lake at the edge of the bog mat. The date when it was most strikingly observed was August 2, 1954, and chemical data for this same date reflected the effects of the bloom. Dissolved oxygen increased markedly from the previous sampling date, from 2.8 to 10.5 ppm.; a rise in pH **was** observed with a corresponding shift in the form of alkalinity from the bicarbonate form to the normal carbonate form, results of carbon dioxide extraction from the bicarbonate (see Figure 10); and the Secchi disk reading was markedly decreased (see Figure 12). The bloom occurred while the phosphorus content of the epilimnion was high (after the release of phosphorus discussed previously) which decreased after the commencement of the bloom (see Figure 13).

Immediately upon lime application the standing crop of zooplankton was markedly reduced, also apparently suffering inhibitory effects from I the lime treatment. During the latter part of 1954, however, the zooplankton appeared to have recovered and an increase was observed, when the standing crop reached levels much higher than observed previously. This may have been due, in part, to the available food supply produced by the bloom of Microcystis aeruginosa. During 1955 the standing crop of zooplankton appears to 'have been high, remaining above pre-alkalization levels through the 1955 sampling season, although statistical significance is not shown for all sampling dates in 1955. standing crops of zooplankton are shown in Figure 15.

A complete list of the species of the plankton found in starvation Lake is given in Table **1.**

Timijon Lake

Effects in epilimnion. The summer lime applic ation in Timijon Lake was made over most of the summer of 1954 and at such a rate as to keep the pH of the epilimnial waters approximately at neutrality; this was

Table 1. List of plankton organisms, Starvation Lake.

Phytoplankton

Chlorophyta Dictyosphaerium pulchellum Wood Dimorphococcus lunatus A. Braun Pandorina sp. Desmidiaceae Desmidium sp. Staurastrum sp. Xanthidium sp.

Chrysophyta Dinobryon sertularia Ehrenberg Bacillariophyceae (diatoms) Asterionella sp.

Cyanophyta Microcystis aeruginosa Kuetz.

Euglenophyta Euglena sp.

Pyrrhophyta Glenodinium sp. Peridinium limbatum (Stokes) Lemmermann

Zooplankton

Rotifera Anuraea cochlearis Gosse

var. macracantha Notholca longispina Kellicott Polyarthra platyptera Ehrenberg (others unidentified)

Cladocera

Bosmina sp. Daphnia sp. Holopedilum gibberum Zaddach.

Copepoda

Cyclops sp. Diaptomus sp.

done in an attempt to avoid the killing of plankton which had been observed in starvation Lake. As a result, the pH values never reached such high values in Timijon Lake as in starvation, nor did alkalinity reach such high concentrations as observed immediately after alkalization in Starvation, although alkalinity values were about the same in the two lakes at the end of the summer season.

At the first small lime application in Timijon, the pH rose from 5.3 to 6.7 in the central epilimnion; subsequent small applications were made as the pH fell below neutrality due to combination with carbon dioxide, each small application usually resulting in a rise of pH to between 7 and 8. At the close of the summer sampling period, the pH in the central epilimnion was 8.5 , and 7.4 in October immediately before the autumn lime application was made. The autumn lime application had only a slight effect on the p H in the central epilimnion, but did have a great effect at the top of thermocline, as well as in both hyplimnial levels. pH values during 1955 remained at about neutrality for the duration of the summer. pH values are shown in Figure 16; for sampling dates upon which lime applications also were made, the data given are those obtained before the applications, rather than after.

Changes in alkalinity are also shown in Figure 16. During the time of lime application in the summer, the total alkalinity increased by jumps as each small application was made, and in October, before the autumn application, total alkalinity was 23 ppm. The autumn application increased the alkalinity slightly in the central epilimnion, but by a greater amount at the top of thermocline. No hydroxide alkalinity was ever .observed in the epilimnial levels, although normal carbonate was found, usually immediately after a lime application. Changes in total hardness and conductivity, shown in Figure 17, followed, in general, those of total alkalinity.

Figure 18 shows the changes in color in both epilimnial levels. The color observed in the central epilimnion did not increase abruptly during or after the summer lime application, as it did in Starvation Lake, nor did it increase after the autumn application. At the top of thermocline, however, where a greater increase in alkalinity and pH values were observed immediately after the autumn lime application, color increased abruptly and significantly, much as it did in starvation Lake; Secchi disk readings were reduced from 9 feet to 6 feet, the lowest ever observed in Timijon Lake. This apparent increase in color and also that observed in Starvation Lake appear to be the result of a large, sudden change in alkalinity with accompanying high pH values, rather than of total change of alkalinity.

Color appeared to have undergone a decrease in both epilimnial . levels during 1955. This was probably due to the small amount of precipitation received during the summer of 1955, which reduced the run-off water carrying allochthonous material responsible for color into the lake.

Effects in hypolimnion. The summer application of lime had no effects upon either of the two hypolimnial levels. However, at the autumn application in October, 1954, when the lake was nearly homothermous (temperatures ranged from 50° F. at the surface to 42° F. at the bottom), the same **event** occurred as in Starvation Lake; that is, the dissolved lime fell to the bottom, in solution, increasing the alkalinity, · pH, total hardness and coriductivity at both hypolimnial levels. **(As** reported above, some effects were also felt in the epilimnion.) pH values rose in the bottom waters from about 6 to 11, total alkalinity increased from 13 to 175 ppm. (including a large proportion of hydroxide alkalinity), total hardness from 11 to 154 ppm, and conductivity from

16 to 286 micrornhos. As in Starvation Lake, a temperature inversion appeared after lime application; temperatures in the bottom waters rose from 42° F. to 46° F., and dissolved oxygen increased from 0 to 5 ppm.

Effects upon phosphorus concentration. No changes in total phosphorus concentration were observed in the epilimnion during or following the summer lime application. In the bottom waters, however, total phosphorus increased after the autumn lime application from a mean during 1954 of 23 ppb. to a mean during 1955 of 156 ppb.; a t-test showed a t-value of 10.99 with 16 degrees of freedom, the t-value being highly significant. This result was essentially the same as obtained in the , laboratory bottle experiments with "mud and bottom water," where the release of phosphorus was observed.

It might be argued that this large increase observed in the bottom waters might not have been due to a release of phosphorus caused by liming. It is still in doubt whether the meromictic conditions which appeared to be so effective in the bottom waters over the winter of 1954-1955 (the high concentration of alkalinity in the bottom waters was not dispersed) were natural conditions or whether the meromixis was induced by the introduction of the layer of dense (alkaline) solution. If the latter case were true, the factors which generally are responsible for a high concentration of phosphorus at the bottom of meromictic lakes might also have been effective in producing the high concentrations observed in this case.

However, certain evidence points to the conclusion that Timijon Lake was meromictic under natural conditions. No analyses of water from the bottom waters ever showed a trace of dissolved oxygen. In the central hypolimnion, which was usually 20 feet above the bottom, oxygen determinations showed only small concentrations, if any, and then only in the **early**

spring. Furthermore, when chemical analyses were made in October, 1954 , just previous to the autumn lime application, thermal stratification had been destroyed, but dissolved oxygen was absent at both hypolimnial levels.

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Finally, the results of the bottle experiments which showed releases of phosphorus from the mud lend supporting evidence to the postulate that liming would release phosphorus in the lake.

Calcium adsorption by mud. The summer lime application had no effects upon the adsorbed calcium in the pulpy peat at the mud-water interface. However, adsorbed calcium, as percent calcium on an ovendried soil basis, increased from 0.24% before the autumn application (1953 and 1954) to 0.34% after liming (1955·). A t-test showed a t-value of 4.81, degrees of freedom being 36, the t-value being highly significant.

Here again, as explained also in the case of Starvation Lake, the assumptions of Hissink's method were not met in the analytical technique. Free carbonates were definitely present and plainly visible to the eye, and probably interfered considerably with the accuracy of results. It is probably safe to conclude that adsorbed calcium did increase, but such a conclusion must be made primarily upon the basis of there being present greater concentrations of calcium available for cation exchange and upon the indirect evidence shown in the results of the bottle experiments which showed definite exchanges of calcium.

Biological effects. In Timijon Lake the same difficulty was encountered with the phytoplankter, Peridinium limbatum, as in Starvation Lake. For the reasons expressed previously in connection with Starvation Lake, this organism was excluded from the data in constructing the graphs but is included among the tabulated data in the appendix.

Figure 19 shows the changes in standing crop of net phytoplankton in the central epilimnion. It can be seen that net phytoplankton was scarce for all sampling dates during 1953 and 1954, but that increases occurred during 1955, although these increases do not approach the very high values found in starvation Lake. The principal organism making up the large standing crop observed in 1955 **was** Dinobryon sertularia, which was the same in the case of Starvation Lake.

Figure 20 shows the changes in standing crop of zooplankton in the central epilimnion. Among the samples of this group, more variation was observed than in net phytoplankton, but in general, the volume of zooplankton was higher in 1955 than during 1953 and 1954. As was the case with starvation Lake, the zooplankton in Timijon appeared to suffer inhibitory effects upon the first lime application during the summer of 1954; a sharp decrease was noted in zooplankton immediately after the first application, and no recovery was observed during the latter part of the 1954 summer twhich was observed in starvation **Lake),** the probable **reason** being that, in the case of Timijon Lake, lime applications **were** continued through the 1954 summer which probably had a continuing inhibitory effect.

All species of phytoplankton and zooplankton are listed in Table 2.

Juanita Lake

Chemical conditions. Generally, the observation made on this lake were constant over the period of the experiment. Table 3 shows mean values for each of the four levels sampled for color, *pH,* bicarbonate alkalinity, total hardness, conductivity, and total phosphorus, and also for light penetration (Secchi disk reading), averaged over the entire time of sampling (August, 1953 through 1955); the detailed data are presented in tabular form in the appendix.

As this lake was the control for the lime application experiments

Table 2. List of plankton organisms, Timijon Lake.

Phytoplankton

Chlorophyta Dictyosphaerium pulchellum Wood Pandorina sp. Desmidiaceae staurastrum sp.

Chrysophyta Dinobryon sertularia Ehrenberg synura uvella Shrenberg Bacillariophyceae (diatoms) Asterionella sp. Tabellaria fenestrata (Lyngb.) Kuetz.

Eugleno phyta Euglena sp.

Pyrrhophyta Glenodinium sp. Peridinium limbatum (Stokes) Lemmermann

Zooplankton

Rotifera Anuraea aculeata Gosse Anuraea cochlearis Gosse **var.** macracantha Notholca longispina Kellioott Polyarthra platyptera Ehrenberg

Cladocera Bo smina sp. Daphnia sp. Holopedilum gibberum Zaddach

Copepoda Cyclops sp.

Table 3. Mean values of color, pH, alkalinity, total hardness, conductivity, total phosphorus, and light penetration,

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carried out on Starvation and Timijon lakes, it was sampled on a schedule similar to those for the treated lakes, and some points should be pointed out as being pertinent. Dissolved oxygen levels remained usually between 4 and 6 *ppm.,* except for some samples in the spring, when cooler temperatures prevailed and oxygen concentrations were somewhat higher; this was probably due to a greater solubility at these cooler temperatures, greater absorption of oxygen from the air because of greater wind-induced turbulence, and to the fact that decomposition processes, more active at warmer temperatures, had not yet conswned dissolved oxygen to a large degree. The amount of color in the water appeared in a stratified manner; that is, less color was present at the shallower levels. A slight increase in pH was found in the bottom waters, while alkalinity also was at a slightly greater concentration at this level. Usually, oxygen was absent from both hypolimnial levels, but occasionally occurred in the central hypolimnion in the early spring in low concentrations, indicating that partial spring circulation had been effective in bringing dissolved oxygen to at least below the level of the thermocline. Dissolved carbon dioxide was always present at all levels, reaching higher concentrations at the deeper levels (it should be pointed out that carbon dioxide determinations cannot be accepted as completely accurate in waters which contain high amounts of colloidal humic materials, which act as humic acids and which may be titrated along with carbonic acid in the carbon dioxide test). Neither hydroxide nor normal carbonate alkalinity was ever observed.

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> Some differences in total phosphorus concentration were observed in the bottom waters, as was the case in Timijon Lake, but the statistical significance of the difference between the values observed in 1954 and those observed in 1955 is doubtful. Mean total phosphorus in the bottom waters for 1954 was 64 ppb., and for 1955 at the same level was

80 ppb. A t-test showed a t-value of 2.60 for 15 degrees of freedom, the t-value being significant at the 5% level only.

Chemical conditions in the two treated lakes were generally the same as those observed in Juanita Lake except for changes brought about by lime application, and it can be concluded that lime application was responsible for chemical conditions that deviated from those observed in Juanita Lake.

Biological conditions. Figure 21 . shows the standing crop of net phytoplankton in the central epilimnion for the entire sampling period. It will be seen that, in general, the standing crop was low and, during 1953 and 1954, was approximately the same as in Timijon and Starvation lakes; during 1955, the standing crop in Juanita Lake was definitely less than in the two treated lakes. It appears that there may have been some increase in net phytoplankton during 1955, but most sampling dates do not show statistically significant differences, except at the close of the summer sampling period. In Juanita Lake, the organisms which accounted for the bloom in the two treated lakes, namely, Microcystis aeruginosa and Dinobryon sertularia, did not appear at all. The data which were used for constructing the graphs, as in the cases of Timijon and starvation lakes, do not include Peridinium limbatum, but data on Peridinium limbatum are included in the tables in the appendix.

If the data concerning Peridinium limbatum were included in the construction of the graphs in Figure 21, an increase would be apparent at the close of the 1955 sampling season, particularly on the last sampling date. No explanation of this increase is offered here, but the significance of such an apparent increase is doubtful in the light of the variation caused by this organism.

Figure 22 shows the changes in standing crop of zooplankton in the central epilimnion, and it can be seen that some apparent increases

occurred during 1955. Not all the differences, however, were statistically significant when compared to earlier data, and were not of as great a magnitude as the changes which occurred in the two treated lakes.

Table 4 lists by species all plankton organisms found.

Irwin Lake

Samples were obtained from Irwin Lake and Grant's Lake, both of which were clear-water bog lakes, for the purpose of making comparisons with the two treated colored lakes, particularly in the event that the lime treatment cleared the color from the treated lakes. The fact that the colored lakes were not cleared upon alkalization precludes a comparison on this basis. However, data on the two clear lakes are included here, and comparisons are made concerning the differences in chemical and biological conditions.

Chemical conditions. Chemical analyses showed that bicarbonate alkalinity, total hardness, conductivity, and pH were approximately the same in Irwin Lake as in any of the colored·lakes before lime treatment. Light penetration (Secohi disk reading) **was** deeper and color concentration less than in the colored lakes. Dissolved oxygen relationships were entirely different in Irwin Lake, in that oxygen was ordinarily found in depths well below the thermocline, even in the bottom waters during times of thermal stratification, and also in that concentrations of oxygen in the epilimnion were generally higher than in the colored lakes. Carbon dioxide concentrations were found to be less at the deeper levels than in the colored lakes, but this may be due, in part, to the absence of humic acids and, in part, to a greater amount of photosynthesis being carried out at these depths. The greater photosynthesis, made possible by the penetration of light through the clearer water to below the thermocline, also accounts for the presence of dis-

Table 4. List of plankton organisms, Juanita Lake.

Phytoplankton

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Chlorophyta Dictyosphaerium pulchellum Wood Desmidiaceae staurastrum sp. Xanthidium sp.

Chrysophyta. Dinobryon bavaricum Inhof Mallomonas sp. Bacillariophyceae (diatoms) Asterionella sp. · Tabellaria fenestrata (Lyngb.) Kuetz.

Euglenophyta Euglena sp.

Pyrrhophyta. Glenodinium sp. Peridinium limbatum (Stokes) Lemmermann

Zooplankton

Rotifera. Anuraea cochlearis Gosse var. macracantha Notholca longispina Kellicott Polyarthra platyptera Ehrenberg (others unidentified)

Cladocera Bosmina sp. Holopedilum gibberum Zaddach

Copepoda Cyclops sp. Diaptomus sp •

solved oxygen below the thermocline. Total phosphorus concentrations were less than in Juanita Lake, at all four levels.

Only one significant change with time was observed, namely, that of color, as shown in Figure 23. Color concentration in the central epilimnion in August, 1953, was about 40; during 1955, color was reduced to about 15 or 20; a similar reduction took place at the top of thermocline. This change was probably due, as in the case of Timijon Lake, to less rainfall during 1955 and a reduction of run-off water carrying colloidal material responsible for the color.

Table 5 shows the mean values of pH, bicarbonate alkalinity, total hardness, conductivity, and total phosphorus for each of the four levels, and also Secchi disk readings, for the entire sampling period. All data are presented in detail in tabular form in the appendix.

Biological conditions. Figure 24 shows the standing crop of net phytoplankton in the central epilimnion over the entire sampling period, where it can be seen that some increases apparently occurred during 1955. *No* changes in the chemistry of lake waters occurred concurrently or **pre**viously to indicate the cause of the increase, although the decrease of color (discussed above) which permitted greater light penetration might have had some causal effect. A desmid, Staurastrum, accounted for the higher standing crop because of its large volume, although present in small numbers.

Figure 25 shows the standing crop of zooplankton for the central epilimnion. No significant changes were observed, but it can be seen that the standing crop of zooplankton was generally higher than that found in the colored lakes.

Table 6 lists all species of phytoplankton and zooplankton found in Irwin Lake.

Table 5. Mean values of *pH,* alkalinity, total hardness, le 5. Mean values of ph, albeitht of, coder has also the conductivity, total phosphorus, and light penetration, Irwin Lake. Level **Central** Top of Central Bottom Epilimnion Thermocline *Hypolimnion Waters $\mu_{\rm H}$ 5.2 5.2 5.0 5.0 5.3 Alkalinity $(Bicarbonate)$ 3 3 3 4 ppm. caco₃ ' Total Hardness 4 4 4 5 ppm. CaCO₃ Conductivity mho X 10⁻⁶ 8 7 8 8 Total Phosphorus 5 7 **12** 49 ppb. **p** Light Penetration (Secchi disk reading, feet) 13.5

Table 6. List of plankton organisms. Irwin **Lake.**

Phytoplankton

Chlorophyta Dictyosphaerium pulchellwn Wood Tetraspora lacustris Lemmermann Desmidiaceae staurastrum sp.

Chrysophyta

Dinobryon divergens Imhof Uroglenopsis americana (Calkins) Lemmermann Bacillariophyceae (diatoms) Asterionella sp. Tabellaria fenestrata (Lyngb.) Kuetz.

Euglenophyta Euglena sp.

Pyrrhophyta Glenodinium sp. Peridinium limbatum (Stokes) Lemmermann

zooplankton

Rotifera **.Apuraea** coohlearis Gosse var. macracantha Polyarthra platyptera Ehrenberg (others unidentified)

Cladocera

Bosmina sp. Daphnia sp. Holopedilum gibberum Zaddach

Copepoda Cyclops sp. Diaptomus sp.

Grant•s Lake

Chemical conditions. Chemical conditions similar to those found in Irwin Lake **were** observed in Grant's Lake. The pH, alkalinity, total hardness and conductivity were almost identical in the two clear-water lakes. Because Grant's Lake did not generally become stratified, dissolved oxygen and carbon dioxide concentrations usually showed little differences with depth. Only three levels were sampled in Grant's **Lake,** because even when stratification was present it was at such a depth that the level of bottom waters was immediately below the thermocline. Color concentrations were very low, being even less than in Irwin Lake, and light penetration was deeper. *No* significant changes with time were observed.

Table 7 shows the mean values of color, pH, bicarbonate alkalinity, / total nardness, conductivity, and total phosphorus for each level, and also of light penetration (Secchi disk readings). The detailed data **are** shown in tabular form in the appendix.

Biological conditions. Figure 26 shows the standing crop of net phytoplankton for the central epilimnion. There **were** no significant changes, but in general, the standing crop was similar to that observed in the colored lakes.

Figure 27 shows the standing orop of zooplankton for the central epilimaion, where it appears that the zooplankton was more abundant than in the colored lakes. At times the standing crop of zooplankton was much greater at the top of thermocline, indicating a photophobic reaction of the . zooplankton, which was probably maximal in Grant's **Lake** because of the extreme clarity of the water.

Table 8 lists all species of phytoplankton and zooplankton found in Grant's Lake.

Central Top of Bottom

Enilimnion Thermocline Waters Level **Epilimnion** 15 Color 15 15 15 25 pH 4.9 5.0 4.8 Alkalinity (Bicarbonate) 2 3 3 ppm. $cacco_3$ Total \sim Hardness **4** 4 4 4 ppm. $CaCO₃$ Conductivity $\frac{1}{2}$ mho x 10^{-6} $\frac{7}{2}$ $\frac{7}{2}$ $\frac{7}{2}$ Total phosphorus 3 5 24 ppb. **p** ,. , Light (Secchi disk reading, feet) 17
Penetration

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Table 7. Mean values of color, pH, alkalinity, total hardness, conductivity, total phosphorus, and light penetration, Grant's Lake.

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Table 8. List of plankton organisms, Grant's Lake.

Phytoplankton

Chlorophyta Desmidiaceae staurastrum sp.

Chrysophyta
1 pinobryon sertularia Ehrenberg Bacillariophyceae (diatoms) Asterionella sp.

Euglenophyta Euglena sp.

zooplankton

Rotifera **,A.nuraea** cochlearis **Gosse** var. tecta Anuraea cochlearis Gosse
var. macracantha Polyarthra platyptera Ehrenberg (others unidentified)

Cladocera

Bosmina sp. Daphnia sp. Holopedilum gibberum Zaddach

Copepoda Cyclops sp. Diaptomus sp.

GENERAL DISCUSSIONS AND CONCLUSIONS

Effects of alkalinity upon phytoplankton production

In considering the question of whether a causal relationship exists between alkalinity and productivity, several concepts must be kept clearly in mind.

First, if a causal relationship does exist, it may be an indirect one. For example, the availability of phosphorus may be greater, causing higher productivity, under conditions of greater alkalinity; it is conceivable that increased phosphorus availability might also be produced under conditions other than those associated with higher alkalinity, in which case a causal relationship between alkalinity and productivity could not be inferred.

Secondly, the observed correlation between alkalinity and productivity appears to be reversed when a certain high level of alkalinity is reached, resulting in the "alkalitrophy" of lakes; this upper limit is possibly as low as 120 ppm., according to Barrett (1953). In Connecticut, Deevey (1940) reported less produotion (on the basis of summer chlorophyll content) in hard-water lakes than in medium-hard-water lakes. From the standpoint of biological productivity, then, alkalinity can be too high as well as too low. In alkalitrophic lakes, very little organic matter is present in the sediments, and phosphorus, rather than being present in an adsorbed form (available to plants through ionexchange reactions), is fixed permanently in inorganic precipitates, probably tricalcium phosphate and associated compounds which are relatively insoluble. According to Barrett, the fate of phosphorus added in fertilizers to alkalitrophic lakes is also in inorganic precipitates.

Finally, the reason for increased productivity in more alkaline waters may be, as suggested by Neess (1948) and Hasler et al. (1951) waters may be, as suggested by Neess (1948) and Hasler et al. (1951)
a greater concentration of carbon dioxide available for photosynthesis

in the bicarbonate form. In this sense, differentiation should be clearly made between what is being utilized by producing plants and what is in short supply in the lake; the former is carbon dioxide, while the latter is calcium. When lime application is made for the purpose of increasing the available supply of carbon dioxide, it is the calcium which is introduced, and not carbon dioxide itself. The calcium than acts as a "chemical carrier" (Coker, 1954, P• 43), holding the carbon dioxide, which **has** been produced by the respiratory activities of the lake, **in** a large "reservoir" of calcium bicarbonate., and the carbon dioxide then remains available for photosynthesis. Thus, alkalization differs from fertilization, where the material introduced is utilized directly as a nutrient by plants; in alkalization, only the "carrier" is introduced.

Free carbon dioxide is not found in high concentrations in surface waters because it is rapidly lost to the atmosphere upon wind-induced agitation. Much of the carbon dioxide produced by the respiratory activities of the lake is lost in this way. "Water, therefore, is automatically prodigal of one of its most important biological assets., and the losses of free carbon dioxide by this means are often great" (Welch, 1935, P• 95). One purpose of lime application is to provide a means of preventing this l0ss, retaining the carbon dioxide in a form available for photosynthesis.

To understand the relationships involved in the limitation of production by carbon dioxide in, for example, a soft-water bog lake, it would be helpful to know, in addition to the concentrations of free carbon dioxide and bioarbonates, the rate of carbon dioxide production by the lake and also the rate of its utilization in photosynthesis under conditions of observed plankton response, i. e., a plankton bloom.

The events which occurred in Starvation Lake in 1954 soon after

the summer alkalization afforded the necessary data to make the above calculations and permitted a test to be made of whether the increased alkalinity was responsible for .increased biological production.

In Figure 10, the graph for bicarbonate alkalinity shows a linear increase between the dates of July 15, 1954, and July 26, 1954, in the central epilimnion, covering a total of five sampling dates. This increase in bicarbonate alkalinity is due to the reaction of calcium carbonate (resulting from alkalization) and carbon dioxide (produced by the lake's respiratory activities). The slope, then, represents the rate of increase of bicarbonate, and, proportionally, the rate of carbon dioxide production. This rate, calculated by means of the ratios of moleoular weights of the compounds involved, was 1.94 ppm. carbon dioxide **per** day.

On August 2, 1954, a phtoplankton bloom, caused by a blue-green alga, Microcystis aeruginosa, was observed with corresponding changes in water chemistry--higher pH, increased oxygen, decreased bicarbonate, and less light penetration. It can therefore be inferred that for the eight-day period from July 25 to August 2, or for an unknown shorter period, phytoplankton increased rapidly and utilized carbon dioxide at a rate more rapid than its production. The utilization of carbon dioxide could then be calculated.

Table 9 shows the "balance sheet" of carbon dioxide for the eightday period. Section A is the carbon dioxide available over the eightday period, being equal to the sum of that present in the form of bicarbonates and free carbon dioxide at the beginning of the period plus the carbon dioxide production for the eight days, or a total of 34.9 ppm. carbon dioxide. The carbon dioxide utilized over the eight-day period by the phytoplankton, section B, is equal to that available (section A) minus that remaining at the end of the period in the form

Table 9. Carbon dioxide utilized by phytoplankton after alkalization compared to carbon dioxide available without alkalization, starvation Lake (as ppm. CO_2). A. CO₂ available over 8-day period............ 34.9 Present at beginning of period, **Free** co² • • • ••••••••••• o.o Half-bound CO2 (bicarbonate) •• *• ¥ .* 19.4 Production in 8-day period • • • • • • 15.5 34.9 $CO₂$ utilized over 8-day period B_{\bullet} 22.6 Available over period (section $A) \bullet \bullet \bullet 34 \bullet 9$ Less CO₂ present at end of period,
Free CO₂ •• • • • • • • • • • • • 0.0 Half-bound co2 (bicarbonate) • •• 12.3 22.6 C. CO_2 available without alkalization. 20.3 **Present at beginning of period,

Free CO₂** • • • • • • • • • • • • 3.0 $H = 0.02 \cdot 360$
Half-bound 002 (bicarbonate). . . . 1.8 Half-bound 002 (bicarbonate). . . . 1.8
Production in 8-day period 15.5 20.3 n. Portion of co2 utilized that was result of **lime** ••• 2.3 CO₂ utilized (section B) . .
Loga de ermileble without \bullet \bullet 22 \bullet 6 Less CO₂ available without alkalization (section \mathfrak{c}).. $20 - 3$ 2.3

bicarbonates and free carbon dioxide, or 22.6 ppm. CO_2 . In section C_2 the carbon dioxide available under conditions of no lime application is' calculated to be 20.3 ppm. $CO₂$, using the production rate computed above, and free carbon dioxide and bicarbonate concentrations found before alkalization. In section Dis calculated the portion of that carbon dioxide utilized by the plankton which was the result of alkalization, which is 2.3 ppm. CO_2 ; it is the difference between the carbon dioxide utilized and that which would have been available if no **lime** application had been made, for the eight-day period, and it is, in that sense, a measure of the effect of alkalization upon phytoplankton production. **(It** should be pointed out that it would not be necessary to know the carbon dioxide production rate in order to calculate the **figure** in section *D,* for it would cancel out in the final subtraction.)

In making the above calculations several assumptions **were** necess**ary;** they were that (1) the carbon dioxide production observed for the 10-day period (July 15 to July 25) was not higher, due to a more alkaline reaction and increased decomposition, than for a similar period of time without alkalization; (2) there occurred no loss of carbon dioxide to the atmosphere during the 10-day period for which carbon dioxide production was calculated, nor during the 8-day period of the plankton bloom (which is probably a valid assumption since normal carbonates were available during both periods for combination with car c^{ℓ} bon dioxide); (3) the increased standing crop of phytoplankton did not raise the rate of carbon dioxide production because of the algae's respiration, and that (4) the period of plankton production and intense carbon dioxide utilization was not less than eight days.

It is interesting to note that if any of the above assumptions were. in fact, invalid, the figure calculated in section D would either be greater or remain the same; the figure calculated, then, is a mini-

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mum value. Furthermore, it would not be expected that the phytoplankton would extract the carbon dioxide from all bicarbonate present; in the eight-day period under consideration, 65% of the available carbon dioxide was utilized. If, in section D of the table, 65% of **the** carbon dioxide available under conditions of no lime application were subtracted from the carbon dioxide utilized, the figure in section D would be even larger (calculated under these conditions, to be 9.4 ppm. $CO₂$).

It can be concluded, therefore, that a causal relationship did exist between the level of bicarbonate alkalinity and phytoplankton production during the eight-day period of the plankton bloom.

During 1955, increases in standing crop of phytoplankton were observed in the treated lakes, particularly in starvation Lake. **Since,** during the time of these high standing crops, no reduction in either half-bound carbon dioxide or free carbon dioxide occurred, it is not possible to infer that bicarbonate alkalinity exerted direct effects upon plankton production **by** making available more carbon dioxide. **If** the plankton responses were the effect of alkalization (and comparison with pre-alkalization and control data indicate this to be true), then it must be concluded that indirect effects (such as greater nutrient availability) must have been responsible.

The effects of alkalinity upon phytoplankton production may be summarized in the following hypotheses which received support from the results of the present study. (1) In soft-water lakes the bicarbonate alkalinity (or "reservoir" of immediately available carbon dioxide) limits the rate of carbon dioxide utilization and thus the rate of phytoplankton production, but does not limit the level to which the standing crop of phytoplankton may reach providing the rate of carbon dioxide utilization is equal to or less than the rate of carbon dioxide production. (2) Due to the acid conditions and meromictic characteristics

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(in some **cases)** present in bog lakes., the rate of carbon dioxide production is probably less than in more alkaline lakes, which then limits the rate of carbon dioxide utilization, or production. (3) Under optimum conditions of alkalinity, the availability of nutrients, such as phosphorus, is improved through various mechanisms, and the availability of such nutrients probably limits, not the rate of phytoplankton production, but the level of total standing crop.

Finally., it is possible now to summarize the reasons for observed differences in production in lakes with different conditions of alkalinity. (1) Hard-water, or alkalitrophic., lakes appear to suffer poor productivity because of the adverse effects of excess calcium upon the availability of nutrients (see Barrett, 1953). (2) Medium-hard lakes with optimum conditions of alkalinity provide large reservoirs of immediately available carbon dioxide in the form of bicarbonates and permit phytoplankton "blooms". These lakes, if located regionally such as to receive nutrients from,for example, fertile soils, will be productive., but if located such that nutrients are not present, optimum alkalinities alone will not cause high biological production. (3) Soft-water lakes., such as bog lakes, do not permit plankton "blooms" because of a lack of high concentrations of innnediately available carbon dioxide in bicarbonates and also limit total production because of the poor availability of nutrients, whether favorably located in fertile regions or not.

Release of phosphorus from lake soils

The release of phosphorus upon alkalinization may be accomplished principally by two mechanisms. The first is by mineralization of organic phosphorus through decomposition. strongly acid conditions, suoh as are found in bog lake waters and muds, have inhibitory effects upon the micro-organisms responsible for decomposition of organic matter and

the subsequent mineralization of nutrients. It is well established that the addition of liming materials, where such acid conditions exist in soils, improves conditions for decomposition micro-organisms by increasing the exchangeable calcium and raising the pH and, therefore, hastens decomposition (see Lyon~ **al.,** 1953, P• 139, and Waksman, 1938, P• 349).

Secondly, phosphate ions may be released through anion exchange; in the case of the addition of lime, an anion exchange between phosphate and the introduced hydroxide radicals is probably the exchange involved. Barrett (1952) in a study of adsorption and regeneration of introduced phosphorus in lakes, hypothesized that the capacity of lake sediments for holding exchangeable phosphate is an inverse function of the ratio of marl to organic matter in the sediments. He reported that in his study lakes where such ratios were low, much of the introduced phosphorus was adsorbed by the sediments and held in exchangeable form. The above ratio, for a bog lake, would be extremely low, indicating a high capacity for the adsorption of phosphate, and it could logically be hypothesized that increasing the alkalinity in bog lakes would result in a release of adsorbed phosphate.

Anion exchange involving phosphorus in soils may concern phosphate adsorbed to clay minerals, organic colloids, and hydrated aluminum and iron oxides. It is not likely that clay minerals will be found in a bog lake, so the sources of exchangeable phosphate are most likely to be colloidal hydroxides and organic matter. Colloidal iron hydroxides are known to exist in lakes (see Ruttner, 1953, P• 74, and Einsele, 1938) and may thus act as a source of adsorbed phosphate; Ohle (1937) observed an increase in dissolved phosphate after adding a solution of calcium bicarbonate to an iron-hydroxide gel, and attributed this increase to a decrease of adsorptive capacity due to higher pH values.

In a general discussion of anion exchange in soils, Wiklander

(1955) describes anion exchange mechanisms in the cases of clay minerals and hydrous oxides, and says, "Humic acids take part in anion exchange, as evidenced by their power of releasing adsorbed phosphate, but the exact mechanism is not lmown."

In the instances cited in this report where a release of phosphorus was observed or thought to have occurred (laboratory bottle experiments and field experiments on Starvation and Timijon lakes), there was no evidence to suggest which of the above two mechanisms were in operation.

The bottle experiments definitely showed phosphorus releases, and results in both Starvation and Timijon lakes indicate releases occurring from the lake muds. The most striking increase of total phosphorus in the field experiments was observed in the bottom waters of Timijon Lake, where concentrations increased from a mean of 23 ppb. in 1954 to a mean of 156 ppb. in 1955. When this increase is considered in the light of that increase observed in the control lake, Juanita, where total phosphorus increased from a mean of 64 ppb. in 1954 to a mean of 80 ppb. in 1955, also in the bottom waters, some doubt may be cast upon the conclusion that the increase in Timijon Lake was due to phosphorus release from the mud as a result of alkalinization. In other words, the question might be posed: If an increase occurred in Juanita Lake, the control, due to natural causes, why could not the increase in Timijon Lake also be due to natural causes and not associated with lime application at all?

A graphic comparison of the increases in both lakes is shown in Figure 28. First of all, the difference in the two years for Juanita Lake is statistically significant at the 5% level only and may possibly be a result of sampling variation alone, while the difference for Timijon Lake is significant far above the 1% level. Secondly, the nature of the increase in Juanita Lake between 1954 and 1955, as seen in Figure 28.

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is what might be expected in a meromictic lake under conditions of naturally accumulating hypolimnial phosphorus, while the increase in Timijon Lake was precipitous and of great magnitude--an increase which, if due to naturally-occurring, meromixis-induced accumulation, would have happened long ago.

The possibility of the increase in Timijon Lake being due to the formation of a meromictic layer (monimolimnion) by the density of the introduced lime solution was discussed in an earlier section, where ' evidence was pointed out leading to ·the belief that the meromictic character of Timijon Lake was naturally-occurring.

It is tentatively concluded, therefore, from the results of both the laboratory and field experiments, that phosphorus would be released from the lake muds when original phosphorus concentrations are low, but not when phosphorus concentrations are originally high; the postulate that phosphorus would be released from lake mud upon alkalinization **is** supported.

From the practical standpoint, the release of phosphorus due to increased decomposition would have greater importance than that due to anionic exchange. In the former mechanism, the source of phosphorus to be mineralized may be almost inexhaustable, while in the latter case, the supply of exchangeable phosphate ions may soon become exhausted, a phenomenon which has been observed in the use of lime to release nutrients in European carp ponds (Neess, 1949).

The value of applying lime to increase phosphorus concentrations in hypolimnial waters, such as occurred in Timijon Lake, when such waters appear never to enter into circulation with upper waters, may be questioned when such methods are applied in lake management. The bottom waters of Starvation Lake (presumably meromictic) held original high concentrations of phosphorus; yet biological productivity in this lake (as

measured by standing crop of plankton) was no greater than in other bog lakes lacking such high concentration of hypolimnial phosphorus. Such phosphorus release can probably best be utilized in lakes which stratify yet still are holomictic, or completely circulating; in these lakes, that phosphorus released in the hypolimnion under deoxygenated conditions during the summer stratification period would be transported to the upper trophogenic zone during fall and spring circulation periods.

Color relations in bog' waters

The postulate made by Hasler et al. (1951) that color would be precipitated by lime treatment, is only partly supported by the results of this study. A partial flocculation apparently did occur in both starvation and Timijon lakes upon alkalization, but this only resulted in an increase of color and reduction of light penetration. As was pointed out previously, the brown strands obvious in unconcentrated water samples in starvation Lake were probably the result of partial flocculation and the cause of the increased color. The color, at the time of the increase, was greater at the top of thermocline, than in the central epilirnnion, indicating a settling of the brown strands to the level of greatest density change, the thermocline. Perhaps if alkalization had been carried out curing times of homothermous conditions in the early spring it would have been possible for the flocculates of organic matter to settle down completely to the bottom, clearing the color.

One phase of the color problem, interesting both fundamentally and from the standpoint of the development of management techniques for controlling or eliminating color, is the determination of the composition and source of the color. In the lakes of the present study, the color was determined to be of organic nature (as opposed to inor-

ganic colloidal iron hydroxides) and composed of particulate matter too small to be retained by a fine, quantitative filter paper (Whatman No. 42) yet large enough to be retained by Seitz bacterial filter discs. Gorham (1931) was also able to remove color with an ultrafilter, and concluded that bog lake reactions were due to colloidal organic matter.

In discussing the source of color it is desirable to include also the subject of acidity, for the two appear to be closely related in their presence together and nay, in fact, have a common source, for the organic colloids causing color may act as weak acids (humic acids). Jewell and Brown (1929), in studies of both acid and alkaline bog lakes in the northern part of Michigan's lower peninsula, concluded that the acidity was due to seepage water flowing through the surrounding acid bog mat, carrying with it organic acids; and that the alkalinity of a basic bog lake was due to alkaline water entering the lake basin without passing through the acid-producing part of the bog margin. Gorham (1931), in studying the same lakes later, took exception to Jewell and Brown's hypothesis and, on the basis of comparisons among the conditions of the lake waters, the lake sediments, and material of the bog margins, believed the source of reaction of the water in both acid and alkaline bog lakes to be the material at the lake bottom, rather than the margins. He believed the colloidal organic matter of the lake water to be derived I from the bottom sediments.

In a discussion of bottom sediments, Ruttner (1953) states the humic matter leached from the vegetation layer of the soil produces color in lake waters as a colloidal solution and, upon precipitation, forms dy, a very finely divided, gelatinous component of the bottom sediments. The humic matter is thus termed allochthonous by Ruttner.

Welch (1936a) agreed with Gorham on the source of the organic col- ~ loidal matter. In discussing a bog lake with highly alkaline waters.

he reported the reaction (alkaline, up to $p_H 8.0$) of subsurface waters observed in near-by springs and other lakes, and also in surface drainage streams around the lake in question, as not approaching the basic reactions of the lake water. He concludes "that an additional contribution of basic-reaction-forming materials must be added after the water enters the lake basin" (italics Welch's), and suggests that the basic bottom sediments are the result of preexisting vegetation (different from the present acid mat) that produced a basic sort of peat. Welch quotes some of Gorham's chemical determinations where methyl-orange alkalinities are given as being mostly above 100 ppm., indicating rather high concentrations of dissolved calcium. pH values are quoted as being mostly between 8 and *9,* and free carbon dioxide concentrations as between 2 and 4 ppm.

In the present study, where the lakes appear to be meromictic, it is difficult to conclude that the organic colloidal material of the upper waters is derived from the bottom sediment, because the lack of circulation precludes this source. Two of the bog lakes studied. · one treated (Timijon) and one untreated (Irwin), underwent a partial clearing of color from the epilirnnial waters which, in the case of Timijon Lake, did not appear to be the, result of alkalization (see Figure 18), and which in the case of Irwin occurred under known natural conditions (see Figure 23). No quantitative atmospheric precipitation data were collected, but the general observations of less rainfall and decreasing lake levels in the summer of 1955 were easily made. Another lake in the same area which was also under study at the same time, and which \degree had recived lime applications in 1952 and 1953, also was observed to decrease in color concentration in 1955 (Ball and Waters, MS). It would appear that the lack of run-off water carrying colored organic matter permitted the decrease in color concentration through natural causes,

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such as decomposition or settling. The evidence in the present study supports the hypothesis of Jewell and Brown (1929) that the source of the organic matter is in the margin, and does not support the conclusion reached by Welch and Gorham.

Whether the acid reaction of bog lakes is due to the colored colloidal organic matter is still in question. On almost all sampling dates for the colored lakes (before alkalization) in the present study a greater concentration of color occurred in the bottom waters, which. was accompanied by a rise in p_H . Also, the clear-water bog lakes with low concentrations of color, contained waters with a reaction as acid as that observed in the colored lakes. Cowles and Brambel (1934) compared tests for acidity by titration and for total carbon dioxide by the manometric Van Slyke method and concluded that about two-thirds of the acidity was due to carbon dioxide and one-third to colloidal organic matter, with the test for inorganic acids negative. Obviously, it is not sufficient merely to state that the acidity (low pH) observed in bog waters is due to organic colloidal matter. The soft waters of most bog lakes are so slightly buffered that probably any acid, even in small amounts, will have a great effect upon the pH.

As was pointed out previously, the glacial drift in the area containing the lakes in the present study, being underlain by limestone, is probably highly calcareous, as evidenced by the presence of limestone in a near-by gravel pit and the alkaline waters of springs and springfed lakes in the area. The low content of calcium in these bog lake waters, then, indicates the presence of an efficient seal against ground water, probably caused by organic matter in the lake basin. An effective seal against alkaline ground water was described in a colored, soft-water lake, presumably located in calcareous glacial drift, by Hooper (1954) who reported seepage from an adjacent acid sphagnum bog

into the lake.

In the lakes of the present study it is concluded that the source of color is in run-off water from the marginal areas of the lake (either the bog mat or uplands in the drainage basin) on the basis of (1) the decrease of color o.ccurring with decreased atmospheric precipitation., (2) the impossibility of the source being the bottom sediments in a meromictic lake, and (3) the apparent seal of the lake basin against ground water.

Comparison of colored and clear-water bog lakes

In the previous sections several pertinent differences between the clear-water and colored bog lakes have been pointed out. These differences will be summarized in this section, where the data from the colored lakes, used in the comparison, will be limited to those from the control, Juanita Lake, and those collected before alkalization from the treated lakes, Timijon and Starvation.

Chemical conditions

Conditions concerning dissolved gases were markedly different in the two types of lakes. Grant's Lake did not stratify, so it would be expected that oxygen and carbon dioxide concentrations would be similar along a vertical series. Irwin Lake stratified in a manner only slightly different from the colored lakes, in that the thermocline was usually about four feet deeper. Despite the stratification, dissolved oxygen was found in concentrations suitable for fish well below the thermocline and, upon several occasions., in the bottom waters. The presence of oxygen below the thermocline indicates light penetration to this depth and the production of oxygen due to photosynthesis. Hasler's et al. (1951) postulate that oxygen conditions would be improved in the hypolimnion if bog color would be removed is here given

indirect support.

Generally, chemical conditions relating to types and concentrations of electrolytes (pH, alkalinity, total hardness, and conductivity) were approximately the same in the clear lakes as in the colored lakes. Total phosphorus appeared to be slightly higher in two of the colored lakes, namely Juanita and Starvation, than in the clear lakes; this may be due, in part, to the higher amounts of suspended organic matter in the colored lakes.

Color was, of course, much lower in the clear lakes and light penetration deeper. Grant's Lake was by far the clearest of all studied, the color usually being about 10 or 15, while Irwin Lake had a color of 40 which was reduced to 15 by the end of the summer of 1955. No chemical' differences were observed which suggested the reason for less color in the clear lakes. In an earlier section concerning color, it was concluded that the source of color was allochthonous organic material derived from the marginal mat or uplands in the drainage basin; it was observed that in the case of the clear lakes the ratio of bog mat to water area was much smaller than in the colored lakes. This suggests that a correlation between the above ratio and the color of the water, and possibly even a causal relationship, may exist, out the data are too few here to attempt such an analysis.

Biological conditions

Qualitatively, there appeared no significant differences among the plankton of the five lakes, with the possible exception of Grant's Lake, where a fewer number of species of phytoplankters were found; the species found in Grant's Lake, however, were also found in the other lakes, both colored and clear.

Quantitatively, also, the standing crop of net phytoplankton ap-

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peared to be about the same in the clear lakes as in the colored, which was low. standing crop of zooplankton, however, appeared to be higher in the clear-water lakes; it is interesting to note that the standing crops observed in the two treated, colored lakes after alkalization were about the same as in the two clear lakes.

Since the fish populations in both clear-water lakes had been altered artificially, no discussion of the differences in fish populations will be attempted except to remark on one point. The possibility of winter-kill in a colored bog lake is increased because of the large amount of suspended organic matter, and in the case of meromictic bog lakes, the deeper waters would not become charged with oxygen at the fall over-turn (see Greenbank, 1945, for discussion of winter-kill). The possibility of winter-kill may explain the absence of fish in Starvation Lake, which **is** highly colored and apparently meromictic. Winter-kill would not be as likely in a clear-water bog lake which would probably have oxygen in the deeper waters at the beginning of the winter period and less suspended organic matter. Johnson and Hasler (1954) reported winterkill in a bog lake which had not been treated with lime while a similar, near-by, lime-treated lake which had undergone a clearing of color did not winter-kill, and suggested that lime treatment may prevent winterkill in marginal cases by clearing of color. such a clearing in the two treated lakes in the present study did not occur, and an evaluation of alkalization on this basis, of course, cannot be made.

- SUMMARY

To investigate the observed correlation between alkalinity and productivity of lake waters and to test the use of lime in bog lakes to inorease biological productivity, lime application was made to two acid, colored bog lakes in the Hiawatha National Forest in the upper peninsula of Michigan, incorporating a third, untreated, colored bog
lake into the sampling program for control purposes. Two clear-water bog lakes were also studied for purposes of comparison with the colored lakes. Lime application was made twice to each of the two colored bog lakes, once in the summer under thermally stratified conditions, and once in the autumn under nearly homothermous conditions, by pumping a limewater mixture into the surface waters. Total rate of lime application $\frac{1}{2}$ was 100 pounds per acre-foot in each treated lake.

The summer lime applications resulted in raising the pH, and increasing alkalinity, total hardness and conductivity in the epilimnion only. The autumn application resulted in similar effects in the lower hypolimnion, due to a fall of the lime solution to the bottom because of greater density, which solution did not later circulate with upper layers.

Lime application did not decrease the or ganic colloidal color, but produced temporary increases of color immediately following application. Color decreased the year following lime application in one treated lake and in one untreated lake, apparently the result of a lack of rainfall and run-off water carrying colored organic colloids into the lake.

Total phosphorus was greatly increased in the bottom waters of one treated lake which had had low original total phosphorus content but did not increase significantly in the bottom waters of the other treated lake where total phosphorus concentrations were originally high. Total phosphorus also apparently increased temporarily in the epilimnion of one treated lake following the summer application.

Estimations of adsorbed calcium in the bottom muds showed increases following the autumn application, indicating losses of dissolved calcium due to cation exchange.

A bloom of nannoplankton (Microcystis aeruginosa) was observed in one of the treated lakes after the summer lime application which. it is shown. because of high bicarbonate content. utilized carbon dioxide **at**

a **rate** which would not have **been** possible without lime application. In both treated lakes the following summer, significant increases in the standing crop of net phytoplankton **were** observed (principally due to Dinobryon sertularia). Increases in standing crop of zooplankton also occurred in the treated lakes.

Chemical and biological conditions remained relatively constant in the untreated control lake, and the two species of algae responsible for the blooms in the treated lakes did not occur at all.

In comparing the clear-water lakes with the colored bog lakes the principal chemical differences lay in the content of dissolved gases. One stratified clear-water lake contained dissolved oxygen sufficient for fish well below the thermocline. Chemical conditions relating to dissolved electrolytes were similar to those in the colored lakes before lime application. Total phosphorus appeared to be greater in the colored lakes. Color, of course, was less and light penetration deeper. Bio- . logically, the clear-water lakes appeared to have approximately the same standing crops of net phytoplankton, but larger standing crops of zooplankton.

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ACKNOWLEDGEMENTS

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APPENDIX

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Table 10. Dissolved oxygen, carbon dioxide, and temperature at

*Description of sampling levels, as given in text and used in tables in the appendix:

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Level 1, central epilimnion Level 2, top of thermocline Level 3, central hypolimnion Level 4, bottom waters

Table 11. **pH** and alkalinity at all four levels,

Table 12. Total hardness, conductivity, color, and light penetration at all four levels, Starvation Lake.

Table 14. Dissolved oxygen, carbon dioxide, and temperature at all four levels, Timijon Lake.

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Table 15. pH and alkalinity at all four levels, Timijon Lake.

Total Conductivity

Hardness mho X 10⁻⁶ Color Penetration mho X 10^{-6} ppm CaCO₃ secchi, feet Date Level Level Level Level 1 2 3 4 1 2 3 4 l 2 3 4 $8 - 16 - 53$ 4 5 5 6 6 6 6 6 6 60 60 80 9.0 $8-31-53$ 5 6 5 6 7 7 7 8 60 80 60 90 10.0 $5-19-54$ 5 5 5 5 6 5 6 6 55 60 50 60 8.5 $6-27-54$ 4 4 5 5 5 5 6 7 55 70 60 90 7.0 **7-** $7-54$ 4 4 5 5 5 5 5 6 7 60 65 60 90 8.5 $7-18-54$ 4 4 5 6 6 7 11 60 60 60 120 8.5 $7-23-54$ 12 5 4 6 12 6 7 9 60 60 60 90 8.5 $7-27-54$ 18 11 5 8 18 11 7 10 60 60 60 110 10.0 $8 - 2 - 54$ 17 11 5 8 15 11 7 11 60 60 60 130 9.0 $8-5-54$ 21 7 6 8 20 8 7 9 60 60 60 110 8.5 $8-12-54$ 21 18 5 7 21 18 8 12 60 60 70 120 11.5 $8-15-54$ 26 21 5 7 28 23 8 12 50 60 60 120 11.0 $8-24-54$ 31 20 6 9 30 19 7 13 50 80 70 120 10.5 $9 - 3 - 54$ 37 21 5 7 30 21 6 11 55 60 70 110 7.5 10-16-54 26 **24** 10 11 27 26 10 16 55 60 70 110 9.0 $10-19-54$ 29 51 48 154 30 53 49 286 55 110 100 100 6.0 $5-9-55$ 32 35 46 86 25 26 31 56 55 55 55 160 $6-15-55$ 30 30 41 80 29 29 40 73 55 55 55 160 10.0 $6-25-55$ 27 30 40 72 27 29 39 65 55 55 55 160 8.0 $7 - 6 - 55$ 27 28 40 70 30 31 44 77 50 55 65 120 8.0 $7-16-55$ 26 31 41 69 26 29 39 67 50 55 60 110 8.0 7-26-55 26 29 42 64 29 31 44 **71** 40 50 60 120 10.0 $8 - 5 - 55$ 25 30 41 67 29 33 46 77 45 50 60 160 11.0 $8-15-55$ 25 27 42 67 30 32 49 82 45 45 55 160 12.5 $8-25-55$ 26 29 42 67 27 30 43 74 45 50 70 150 11.0

Table 16. Total hardness, conductivity, color, and light penetration at all four levels, Timijon Lake.

Table 17. Total phosphorus at all four levels, and

Table 18. Dissolved oxygen, carbon dioxide, and temperature at all four levels, Juanita Lake.

Table 19. *pH, alkalinity, total phosphorus, total hardness,* econductivity, color, and light penetration at all four levels, Juanita Lake.

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Table 20. Dissolved oxygen, carbon dioxide, temperature, pH, alkalinity, total phosphorus, total hardness, conductivity, color, and light penetration at all four levels, Irwin Lake.

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Table 22. Volume of plankton, in oubic milimeters **X** 10⁻³ per liter,

Table 24. Volume of plankton, in cubic milimeters X 10^{-3} per liter,

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LITERATURE CITED

.American Public Health Association

Standard methods for the examination of water, sewage, and industrial wastes. 10th edition, New York, 1955.

Ball, Robert C.
1947 Repor

Ŧ.

- Report on Stoner Lake, Alger-Delta County, Michigan. (Unpublished report).
- 1948 A summary of experiments in Michigan lakes on the elimination of fish populations with rotenone, 1934-1943. Trans. .Am. Fish. Soc., 75:139-145.

Barrett, Paul H.
1952 Furthe

- Further studies on the feasibility of artificial alkalinization of Stoner Lake, Michigan. (Unpublished report).
- 1953 Relationships between alkalinity and adsorption **and** regeneration of added phosphorus in fertilized trout lakes. Am. Fish. Soc., 82:78-90.

Bergquist, Stannard G.
1937 The Cambrian

The Cambrian-Ozarkian contact in Alger County, Michigan. Pap. Mich. Acad. Sci., Arts, and Lett., 22:421-435.

- Cheng, K. L. and R. H. Bray
1951 Determination of Determination of calcium and magnesium in soil and plant material. Soil Sci., 72:449-458.
- Coker, Robert Ervin 1954 Streams, lakes and ponds. Univ. N. c. Press, 1954.

Cowles, R. P. and Charles Brambel

1934 The acidity of the water of a sphagnum swamp. Program for 32nd. annual meeting of Am. Soc. of Zoologists, Abstracts of papers. Anat. Record, 60 (Suppl.):97.

Dice, L. R. and H. J. Leraas
1936 A graphic method f.

A graphic method for comparing several sets of measurements. Contrib. Lab. Vert. Genetics, Univ. Mich., No. 3:1-3.

Einsele, Wilhelm

1938 ther chemische und kolloidchemische Vorgange in Eisen-Phosphat-Systemen unter limnochemischen und limnogeologischen Gesichtspunkten. Archiv für Hydrobiologie, 33:361-387.

Ellis, M. M., B. A. Westfall, and Marion D. Ellis
1948 Determination of water quality. U. S. Determination of water quality. U.S. Dept. Inter., Fish

and Wildlife Serv., Research Rep. 9.

Gorham, W. C.

ÏI.

1931 **A** limnological study of certain bog lakes, with special reference to the macroplankton. (Unpublished doctorate dissertation, Univ. Mich.)

Greenbank, John

1945 Limnological conditions in ice-covered lakes, especially as related to winter-kill of fish. Ecol. Mono., 15:343-392.

Hasler, Arthur D., O. M. Brynildson, and William T. Helm
1951 – Improving conditions for fish in brown-water be Improving conditions for fish in brown-water bog lakes by alkalization. Jour. Wildlife Man., 15:347-352.

Hissink, D. J.
1923 Meth

Methods for estimating adsorbed bases and the importance of these bases in soil economy. Soil Sci., 15:269-276.

Hooper, Frank F.

1954 Limnological features of Weber Lake, Cheboygan County, Michigan. Pap. Mich. Acad. Sci., Arts and Lett., 39:229-240.

Jewell, Minna E. and Harold W. Brown
1929 Studies on northern Michiga studies on northern Michigan bog lakes. Ecology, 10:427-475.

Johnson, Waldo E. and Arthur D. Hasler
1954 Rainbow trout production in Rainbow trout production in dystrophic lakes. Jour. Wild- $\frac{1}{2}$ life Man., 18:113-134.

Juday, C. and C. L. Schloemer
1938 Effect of fertilize Effect of fertilizers on plankton production and on fish growth in a Wisconsin lake. Prog. Fish Cult., 40:24-27.

Lobeck, A. K.
1950 Phy

Physiographic diagram of North America. The Geographical Press, Columbia University, N. y.

Lyon, T. Lyttleton, Harry O. Buckman, and Nyle C. Brady
1953 The nature and properties of soils. Macmillar 1953 The nature and properties of soils. Macmillan *co.,* N. *y.,* 1953.

Moyle, John B.
1949 Some

Some indices of lake productivity. Trans. Am. Fish. Soc., 76:322-334.

Neess, John C.

Development and status of pond fertilization in central Europe. Trans. Am. Fish. Soc., 76:335-358.

Ohle, Waldemar
1937 Kolloidgele als Nahrstoffregulatoren der Gewasser. Die Naturwissenschaften, 25:471-474.

Ruttner, Franz 1953 Fundamentals of limnology. English translation by D. G. Frey and F. E. J. Fry. Univ. Toronto Press, 1953. (Original German edition published by Walter de Gruyter and *Co.,* Berlin, 1952.) Swingle, H. S. and E. V. Smith
1939 Fertilizers for incre $Fertilizers$ for increasing the natural food for fish in ponds. Trans. Am. Fish. Soc., $68:126-135$. Waksman, Selman A• Humus. Williams & Wilkins Co., Bettimore, 1938. Welch, Paul S. 1935 Limnology. McGraw-Hill, N. *Y.,* 1935. 1936a Limnological investigation of a strongly basic bog lake surrounded by an extensive acid-forming bog mat. Pap. Mich. Acad. Sci., Arts and Lett., 21:727-751. 1936b A limnological study of a small Sphagnum-leatherleafblack spruce bog lake with special reference to its plankton. Trans. Am. Micr. Soc., 55:300-312. 1938a A limnological study of a retrograding bog lake. Ecology, 19:435-453. 1938b A limno logical study of a bog lake which has never developed a marginal mat. Trans. Am. Micr. Soc., 57:344-357. 1945 Some limnological features of water impounded in a northern bog-lake mat. Trans. Am. Micr. Soc., $64:183-195$. Whipple, G. C.
1948 Microscopy of drinking water. 4th edition. John Wiley & Sons, Inc., New York, 1948. Wiklander, Lambert 1955 Cation and anion exchange phenomena. Chemistry of the soil, ed. Firman E. Bear, Reinhold publ. Corp., N. Y., 1955.

