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PLANKTONIC PHOTOSYNTHESIS AND THE ENVIRONMENT
OF CALCIUM CARBONATE DEPOSITION IN LAKES

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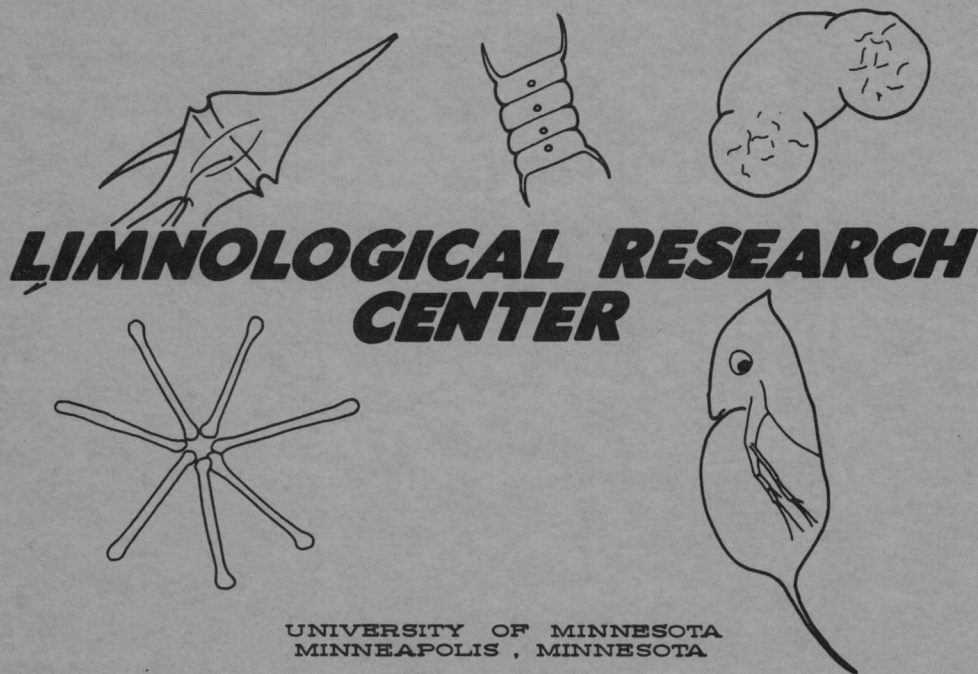
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Preface

This paper describes one facet of a regional limnological survey of Minnesota that has been initiated by the Limnological Research Center at the University of Minnesota.

No two lakes in a region are identical, because of subtle differences in depth, area, water chemistry, and biology. Nevertheless, lakes in a region share many common features that reflect the interactions of the regional geology, vegetation, and climate. Thus, because each lake in a region is unique and at the same time related to its neighbors, lakes are very difficult to compare with each other and with lakes in other regions.

Since 1965 the facilities of a mobile limnological laboratory have been used in northern Minnesota to perform periodic experiments that measure the rates of photosynthesis by planktonic algae. The photosynthetic rates at various depths in the lakes reflect the interactions of all the factors affecting the abundance and activity of the plankton, irrespective of the species that are present. Photosynthesis is the ultimate source of the organic matter that serves as food for animals in lakes, including fish. Furthermore, as illustrated in this paper, the water chemistry of lakes may be influenced profoundly by the biochemical reactions associated with the production and destruction of organic matter. The measurements of photosynthesis are obtained relatively efficiently, and they provide an index for comparing lakes within a region with each other and with lakes in other regions.

This interim report has been prepared primarily as an informal progress report for the information of individuals and agencies

who are concerned with limnology in Minnesota. The purpose of the Interim Report series is to disseminate information prior to formal publication in technical journals. Thus, although it is hoped that the information and ideas in this report will be useful for other limnological projects now in progress, authors are cautioned not to cite this report without permission from the author.

Additional interim reports describing regional variations of water chemistry, the distribution of algae in Minnesota lakes, and the use of photosynthesis experiments as bioassays of lake pollution are in preparation, and other reports will appear as various projects are completed.

PLANKTONIC PHOTOSYNTHESIS AND THE ENVIRONMENT
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Abstract

The calcium and alkalinity concentrations increase in a productive lake during the winter and the water at all depths becomes undersaturated with calcium carbonate. Soon after the ice melts, the entire water column becomes oversaturated with calcium carbonate, and the calcium and alkalinity concentrations decrease during spring, summer, and autumn. After the lake becomes thermally stratified, carbonate oversaturation increases at depths in which photosynthesis occurs, but the water at greater depths becomes undersaturated. Carbonate saturation therefore appears to be controlled by the balance between carbon dioxide assimilation by planktonic photosynthesis and carbon dioxide release by respiration. The seasonal changes of calcium concentrations are balanced by chemically equivalent alkalinity changes, but magnesium concentrations do not fluctuate, which also suggests biogenic precipitation and solution of carbonate.

Photosynthesis occurs in both the epilimnion and the metalimnion of a deeper, less productive lake, and these are the only depths oversaturated with calcium carbonate during the open-water season.

Daily rates of calcium depletion per m^2 of lake surface are computed to provide estimates of calcium carbonate precipitation in 6 lakes. The daily rates of calcium depletion are directly proportional to the mean daily rates of planktonic carbon assimilation. The molar ratios of calcium depletion to net carbon

assimilation are approximately 0.25 in 4 of the 6 lakes, and the ratios in 2 lakes are 0.1 and 0.4. The ratios indicate that approximately 1 mole of calcium carbonate is precipitated for every 4 moles of carbon assimilated by the phytoplankton. The empirical rate of calcium depletion is lower than the potential rate predicted by an equation for photosynthesis in an equi-molar mixture of calcium and magnesium bicarbonates, which is approximately the ionic ratio in the lakes studied.

CONTENTS

Introduction	<u>1</u>
Origin, composition, and distribution of carbonate in lacustrine sediments	<u>3</u>
Methods	<u>9</u>
Geographic setting of the lakes	<u>12</u>
Ionic composition of the lake waters	<u>16</u>
Limnology and productivity of Itasca and Long lakes	<u>20</u>
The environment of carbonate deposition in Itasca Lake	<u>28</u>
The environment of carbonate deposition in Long Lake	<u>35</u>
Discussion and conclusions	<u>36</u>
References	<u>45</u>
Figure	
1. Locations of the lakes	<u>13</u>
2. The Headwaters Region of the Mississippi River	<u>14</u>
3. Morphometry of Itasca Lake	<u>21</u>
4. Morphometry of Long Lake	<u>22</u>
5. Seasonal chemical changes in Itasca Lake, 1965-1966	<u>23</u>
6. Seasonal chemical changes in Long Lake, 1966-1967	<u>25</u>
7. Photosynthetic carbon assimilation and rates of calcium depletion in six Minnesota lakes	<u>37</u>
Table	
1. Location and morphometry of the lakes studied	<u>15</u>
2. Concentrations and proportions of the major ions in surface water from the lakes	<u>17</u>
3. Ionic concentrations, pH, and ionization constants of carbon dioxide in Itasca and Long lakes in July, 1964	<u>18</u>

4. Primary productivity of the lakes	<u>27</u>
5. Calcium and alkalinity budgets for Itasca and Long lakes	<u>31</u>
6. Daily rates of calcium change in Itasca and Long lakes	<u>33</u>

INTRODUCTION

Large quantities of calcium carbonate are precipitated from lake water during photosynthesis by aquatic plants. The leaves and stems of rooted aquatic plants in the littoral zones of lakes commonly are encrusted heavily with carbonate, and the sediments beneath them may contain more than 90% carbonate. Profundal sediments also may contain appreciable quantities of carbonate, which many investigators assume are produced by the macrophytes and redeposited from the littoral sediments. However, the contribution of macrophytes to the total carbonate generated by photosynthesis should be proportional to their share of the total photosynthesis in a lake. Thus in large, deep lakes, where the area of the littoral zones and the biomass of aquatic macrophytes are relatively small, most of the photosynthetic carbonate precipitation is probably performed by phytoplankton instead of macrophytes.

The purpose of this paper is to describe the environment of carbonate sedimentation in 6 lakes in Minnesota, with particular emphasis on the relations between planktonic photosynthesis and calcium carbonate precipitation. Rates of carbonate formation are estimated from calcium and alkalinity depletion rates in lake water during spring and summer. The depletion rates are then compared with rates of photosynthetic carbon dioxide assimilation by natural phytoplankton populations.

This project was supported by funds provided by the United States Department of the Interior as authorized under the Water Resources Research Act of 1964, Public Law 88-379; the Minnesota Resources Commission; and the Hill Family Foundation. The

initial field work in 1964 was supported by a postdoctoral research stipend at the University of Minnesota Itasca Biological Station from National Science Foundation Grant GB-749. The author's interest in carbonate sedimentation was stimulated by K.S. Deffeyes, who also contributed data on carbonate chemistry in Table 3. The assistance of K. Kromer, who made quantitative algal counts, and D. Hall, P. Richmond, and L. Henrickson, who assisted in the field and laboratory is gratefully acknowledged. The author is also grateful to Dr. W.H. Marshall, Director of the University of Minnesota Biological Station at Lake Itasca, for permission to utilize the facilities of the Station. The morphometric maps for Itasca Lake and Long Lake (Figs. 3 and 4) are based on maps compiled by the Minnesota State Department of Conservation.

ORIGIN, COMPOSITION, AND DISTRIBUTION
OF CARBONATE IN LACUSTRINE SEDIMENTS

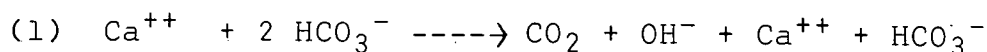
Kindle (1927) observed that many kinds of aquatic plants other than macrophytes were capable of carbonate precipitation. Three genera of blue-green algae and 10 genera of diatoms were identified in marl concretions from Mink Lake, Ontario. Fifteen genera of diatoms were found in the film of carbonate precipitated on a metal spoon suspended in a lake for 2 months. He also noted that there was a film of carbonate on part of the spoon that was not associated with algae. It appeared to be direct carbonate precipitation "which has resulted from the abstraction of CO_2 from the water by diatoms and other plankton plant life". He thought that the entire epilimnion was saturated with carbonate, which was deposited on the bottom more rapidly than it could be dissolved by the slightly acid water in the hypolimnion.

Ohle (1952) demonstrated that the quantity of suspended carbonate in lakes and ponds in northern Germany was greater than in seawater. Oversaturation persisted in filtered water samples from Grosser Plöner See that were stored in the laboratory for a month; aeration and vigorous mechanical stirring did not cause precipitation of carbonate from the samples. These samples evidently contained about 10 mg/l colloidal calcium carbonate. The alkalinity at mid-depth in a small, shallow lake decreased from 3.43 me/l in February to 2.32 me/l in August as a result of photosynthetic carbon dioxide consumption and carbonate precipitation. Although the alkalinity decreased during this time the quantity of suspended carbonate increased from 0.36 to 1.95 me/l. Thus 84% of the alkalinity in August was suspended carbonate. Ohle concluded that carbonate oversaturation of this magnitude probably inhibits

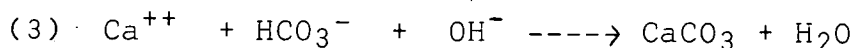
photosynthesis because suspended calcium carbonate cannot be utilized as a carbon source. Hutchinson (1967, p. 308-310) suggested, however, that much of the colloidal and suspended carbonate observed by Ohle may have been in the form of carbamino carboxylic acid complexes of calcium, whose role in natural waters was described by Smith et al. (1960). These organic complexes are readily assimilated by algae. Ohle also concluded that biogenic oversaturation of calcium carbonate was far more important than oversaturation caused by inorganic processes in freshwaters.

Biogenic carbonate precipitation in seawater is generally considered to be less important than carbonate formation by physicochemical means, by crystal secretion about algal cells, by deposition of animal skeletons, or by microbial reduction of sulfate and nitrate (reviews by Graf 1960, Cloud 1962, Revelle and Fairbridge 1957), even though photosynthetic rates are usually very high in environments with rapid carbonate deposition.

The mechanism of photosynthetic carbonate precipitation has been demonstrated in the laboratory (Arens 1936, Ruttner 1947, Steeman Nielson 1947, 1960). The genera Elodea, Potamogeton, Valisneria, Myriophyllum, and presumably most other macrophytes except aquatic mosses in alkaline water utilize bicarbonate ions as a source of carbon for photosynthesis. Bicarbonate enters leaves on both surfaces, and it is dissociated into CO_2 , which is utilized photosynthetically, and OH^- , which is released on the upper surfaces of leaves:



The removal of carbon dioxide and liberation of hydroxyl ions induces carbonate precipitation:



The green algae Scenedesmus and Chlorella may also utilize bicarbonate, and presumably any planktonic alga that can grow under conditions of high pH may utilize bicarbonate and precipitate carbonate if calcium concentrations are high enough.

The carbonate content of sediments is usually highest in the littoral zones of lakes, although considerable quantities also may occur in profundal sediments. Sediments in depths less than 10 m in Tippecanoe Lake, Indiana, typically contain 80% carbonate, whereas sediments in depths as great as 33 m usually contain between 50 and 75% (Wilson and Opdyke 1941). A similar gradient, from more than 90% carbonate in water depths less than 2 m to 40-50% in depths of 12-23 m occurs in the surficial sediments of Winona Lake, Indiana (Mueller 1964). Marl and copropelic marl occur at depths of 16 m and 36 m in Cedar Lake, Minnesota (Swain 1956) and at 23 m in Long Lake, Minnesota (Swain et al. 1964, and this paper). The carbonate content of the marl beneath the surficial sludge (sapropel?) of Lake Mendota, Wisconsin, decreases from 65-80% in shallow water to 50-60% in depths greater than 20 m, although the carbonate content of the surficial sludge is lower in shallow than in deep water because of dilution by clastics from the watershed (Murray 1956).

Carbonate sediments from the littoral zones of lakes commonly contain shells of ostracodes, mollusks, fragments of rooted aquatic plants, and calcified oogonia from the benthic green alga Chara. Profundal calcareous sediments rarely contain shells or large plant fragments, although chitinous Cladocera shells and siliceous diatom frustules are common (Swain 1956; Davis 1900, 1901). The carbonate in sediment samples taken in depths between 10 m and 18 m in Lake Mendota was calcite grains

with diameters between 1.0 and 0.1 μ (Murray 1956). In Kabekona Lake, a few miles east of the Itasca lakes that will be described in this paper, the littoral deposits are molluscan, ostracodal sands and shell marl with organic detritus; the marl consists of flakes deposited around stems of Characeae and other macrophytes. The profundal deposits in depths of 15 to 20 m, on the other hand, are pure fine-textured marls (Swain 1961).

The carbonate gradient, from high concentrations in littoral sediments to low concentrations in profundal, has often led to the conclusion that most of the carbonate in profundal sediments was originally precipitated by the aquatic plants in the littoral zone and then redeposited in deep water. Wilson (1937) noted that 47% of the original area of the basin of Tippecanoe Lake was shallower than 6 m (20 ft) deep, yet this area had received only 30% of the total sediments in the basin. It should be noted, however, that 32% of the basin is now filled with sediment; therefore much of the area outside the 6-m contour could no longer receive sediment. Swain (1956) also was of the opinion that the hypolimnetic marl in Cedar Lake, Minnesota, was redeposited.

That redeposition does indeed occur is probably best indicated by the numerous fossil chydorid Cladocera in profundal sediments. Although the Chydoridae inhabit the littoral zones of lakes, more than 10,000 shells per gram dry weight sediments commonly occur in the profundal zone. By the use of sediment collectors Mueller (1964) demonstrated that the offshore redeposition of chydorid shells is not restricted to periods of overturn but also occurs while a lake is stratified. Turbulence capable of redepositing fossil Cladocera obviously could transport carbonate crystals also. Mueller suggested that a study of

fossil Cladocera in a transect of sediment collectors might be the most effective means of studying the phenomenon of re-deposition in lakes.

At the moment the magnitude of carbonate redeposition from the littoral zone is unknown, but there is reason to believe that it has been seriously overestimated. Wilson (1937) computed that the volume of sediments in the basin of Winona Lake and in the 3 basins of Tippecanoe Lake are very nearly proportional to the surface areas of the basins. Although he acknowledged the role of redeposition, the correspondence between surface area and volume indicates that carbonate sediment is formed equally in all parts of lakes.

Recalculations of data for Tippecanoe Lake presented by Wilson (1937) and Wilson and Opdyke (1941) also indicate that it is likely that most of the carbonate in profundal sediments did not originate in the littoral zone. The volume of profundal sediments, i.e. of sediments deposited in the hypolimnion at depths greater than 10 m, is $8.8 \times 10^6 \text{ m}^3$. The average carbonate content of these sediments is 65%, which is equivalent to $5.8 \times 10^6 \text{ m}^3$. This is 51% of the total carbonate deposited in the basin ($11.1 \times 10^6 \text{ m}^3$). Thus more than one-half of the carbonate in the basin of Tippecanoe Lake is not associated with the rooted aquatic plants, most of which grow in depths less than 6 m. The tremendous quantities of carbonate in deep-water sediments can be accounted for readily with the hypothesis that most of the carbonate is precipitated from all areas of the epilimnion by planktonic photosynthesis. In this connection it is of interest to recall the observation that "the relative quantities of sediment produced in these lakes are

fairly proportional to the amounts of sunlight falling on them" (Wilson 1937). Littoral sediments in some lakes contain carbonate, but profundal sediments often apparently do not (Graf 1960), evidently because the carbonate that falls into the hypolimnion is dissolved by high concentrations of carbon dioxide produced by organic decomposition.

METHODS

A mobile limnological laboratory has been designed (Megard and Shapiro 1966) that enables photosynthesis experiments and associated chemical and biological analyses to be performed in ideal laboratory conditions at any lakes accessible by roads.

The primary productivity of the lakes was measured by use of oxygen light- and dark-bottle experiments. The basic principles and limitations of the method have been critically reviewed by Strickland (1960), who lists many of the earlier studies that used the method, and the general procedure has been described by Strickland and Parsons (1965). The potentials of this method for physiological and ecological analysis have been effectively exploited by Talling (1965, 1966).

The oxygen method was used in this study instead of the more sensitive carbon-14 method (Steeman Nielson 1952), because the sensitivity of the oxygen method is adequate for eutrophic lakes and because it is much simpler than the carbon-14 method. The oxygen method measures both community respiration and photosynthesis, and thus both gross production during daylight and net production during a full 24-hr day may be computed. The carbon-14 method was inadequate for this study because it does not measure respiration and it therefore cannot be used to estimate daily net production; it also underestimates gross photosynthesis by an amount that depends upon the rate of carbon-14 recycling and upon the rate of carbon-14 loss by excretion and respiration. Recycling, excretion, and respiration all vary with conditions of illumination and the physiological state of the organisms, and none of these processes is measured

(Thomas 1961, Barnett and Hirota 1967). Thus in productive lakes where the oxygen changes are large enough, the light- and dark-bottle method is uniquely suited both to measure total daily plankton metabolism and to evaluate the net effect of plankton metabolism on the chemistry of lake water. It is the latter aspect of the method that is explored in this paper.

The carbon exchange between the environment and organisms during the experiments is computed from oxygen changes. However, the ratio of oxygen to carbon exchanged is variable, depending upon the photosynthetic products of the phytoplankters. For heterogeneous assemblages a somewhat arbitrary oxygen-carbon ratio (photosynthetic quotient) of 1.2 is recommended (Strickland 1960) and is utilized in this paper.

Incubation periods of 24 hours were used initially in this study to elicit large oxygen changes, but analysis of the oxygen budget during 24-hr experiments indicates that the oxygen change in light bottles during 24-hr experiments can be no greater than 50% larger than during 6-hr experiments begun at noon. Incubation periods were therefore shortened to 6 hr to minimize the unnatural consequences of enclosing plankton in bottles (discussed by Pratt and Berkson 1959). The results of 6-hr experiments begun at noon are used to compute carbon exchange during a 24-hr day by assuming that there are 12 hours of daylight, that the amount of photosynthesis after noon equals the amount before noon, and that the respiration in light is the same as in darkness. Gross photosynthesis after 24 hr (G_{24}) must equal gross photosynthesis after 12 hr (G_{12}), which is twice the gross photosynthesis after 6 hr (G_6). Hence,

$$(1) G_{24} = G_{12} = 2 G_6.$$

Net photosynthesis after 24 hr (N_{24}) must equal net photosynthesis after 12 hr ($2 N_6$) minus respiration during the night ($2 R_6$):

$$(2) \quad N_{24} = 2 N_6 - 2 R_6.$$

The azide modification of the Winkler oxygen analysis was used to determine the oxygen concentrations in the light and dark bottles with a precision of ± 0.03 mg/l ($\pm 9 \mu\text{g/l}$ carbon with a photosynthetic quotient of 1.2). Vertical temperature and oxygen profiles were determined respectively with a thermister thermometer and a galvanic cell oxygen analyser. Alkalinity, calcium, magnesium, and other ions were determined by standard methods (Amer. Pub. Health Assoc., 1965). The relative degree of calcium carbonate saturation of the water at the various depths was measured with a carbonate saturometer (Weyl 1961), in which the degree of saturation (Figs. 5 & 6) is indicated by the pH change (Δ pH) after crystalline calcite is placed in contact with the glass electrode in a water sample. The saturometer used is a modification of a design by K.S. Deffeyes, who also developed a computer program for determining the apparent ionization constants of carbon dioxide and the relative proportions of $\text{CO}_2 + \text{H}_2\text{CO}_3$, HCO_3^- , and $\text{CO}_3^{=}$ from acid-base titration curves. Subsamples of the water used in each experiment were preserved with Lugol's solution for the quantitative phytoplankton counts later made with an inverted microscope.

Organic and inorganic carbon content of sediments was determined by wet oxidation, absorption of carbon dioxide with barium hydroxide, and back-titration with acid by utilizing the apparatus and procedure described by Züllig (1956).

GEOGRAPHIC SETTING OF THE LAKES

The locations of the lakes are shown in Figures 1 and 2. The lakes studied most intensively are the north basin of Itasca Lake, which is the source of the Mississippi River in northwestern Minnesota, and Long Lake, which lies 8 km northwest of Itasca Lake and also drains into the Mississippi (Fig. 2).

Four other lakes (Mary, Elk, Sallie and Francis) have been studied in less detail. Mary Lake is less than 1 km south of the east basin of Itasca Lake and drains into it via a short stream. Elk Lake also drains into Itasca, but into the west basin, via a short stream. Itasca, Elk, Mary and Long Lakes are in a region of mixed deciduous-coniferous forest. However, Sallie Lake, about 70 km (45 mi) southwest of the Itasca region, is in a narrow band of open deciduous forest that lies between mixed deciduous-coniferous forest to the east and prairie to the west. Francis Lake is near the southern margin of deciduous forest in southeastern Minnesota, about 320 km (200 mi) from the Itasca region.

The lakes range in area from 23 to 528 ha, in mean depth from 3.5 to 12.9 m, and in volume from 1.3 to $32.7 \times 10^6 \text{ m}^3$ (Table 1). The basins of all the lakes are in calcareous drift deposited during late-Wisconsin glaciation.

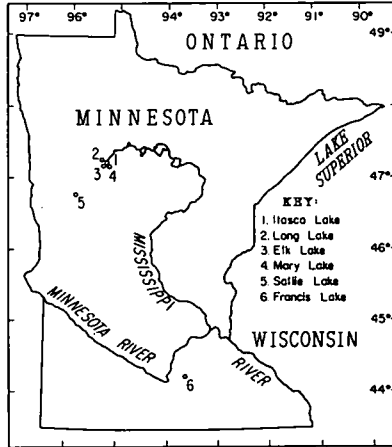


Fig. 1. Locations of the lakes

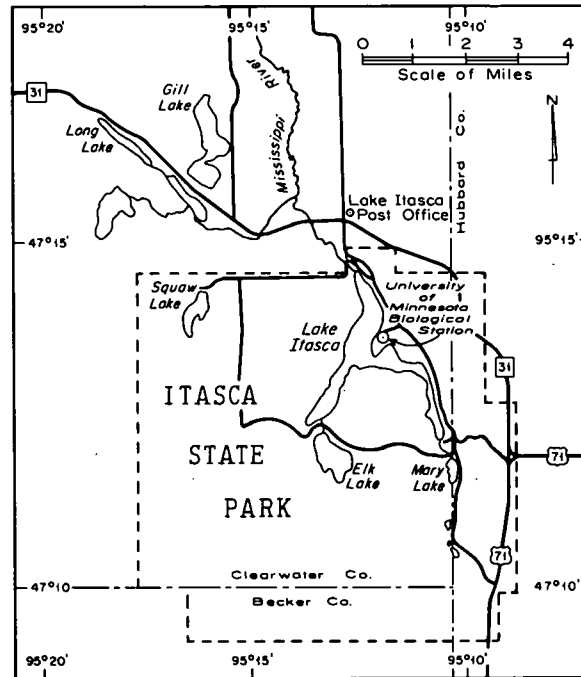


Fig. 2. The Headwaters Region of the Mississippi River, showing the location of Itasca Lake, Long Lake, Elk Lake, and Mary Lake

Table 1. Location and morphometry of the lakes studied

Lake	Latitude and longitude	Area (ha)	Maximum depth (m)	Mean depth (m)	Volume ($m^3 \times 10^6$)
Itasca (total)	47°14'N, 95°10'W	436	14	5.2	22.9
Itasca (north basin)					
Long	47°17'N, 95°16'W	117	11	5.0	5.8
Mary	47°11'N, 95°10'W	60	24	12.9	7.6
Elk	47°12'N, 95°12'W	23	12	5.7	1.3
Sallie	46°46'N, 95°55'W	101	30	11.0	11.2
Francis	44°13'N, 93°43'W	528	13	6.2	32.7
		370	15	3.5	12.9

IONIC COMPOSITION OF THE LAKE WATERS

The concentrations and proportions of the major ions in surface waters of the lakes are shown in Table 2. The data for Itasca and Long Lakes are of particular interest because the limnology of these lakes will be discussed in detail. The water from both lakes is virtually a dilute solution of calcium and magnesium bicarbonate. Total cations in Itasca Lake amounted to 3.48 me/l, of which 55% was calcium and 36% was magnesium during the 1966 spring circulation period. Total cations in Long Lake were somewhat less (3.40 me/l) than in Itasca. Calcium concentrations were also lower than in Itasca Lake, but magnesium concentrations were higher. Sodium and potassium together amounted to only 9% of the total cations in Itasca Lake and 6% in Long Lake. The alkalinity (i.e. bicarbonate) content of the lakes was similar, 3.48 me/l in Itasca and 3.16 me/l in Long Lake. Sulfate and chloride, of the other major anions usually found in fresh-water lakes, amounted to only 1 or 2% of the total anions in both lakes.

The composition of the alkalinity in these two lakes in July 1964 is shown in Table 3. Carbonate carbon constituted more than 95% of the alkalinity at all depths in both lakes. Furthermore, between 95 and 98% of the carbonate carbon in the epilimnia of the lakes was bicarbonate. In the deep water of Itasca, where oxygen concentrations were low, bicarbonate decreased to 91%, while $\text{CO}_2 + \text{H}_2\text{CO}_3$ increased to almost 9% of the total carbonate carbon. In Long Lake bicarbonate amounted to between 95 and 97% of total carbonate carbon at all depths. Significant quantities of carbonate ion occurred only in the epilimnion of

Table 2. Concentrations and proportions of the major ions in surface water from the lakes

		Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	Sum cations	Alka- linity	SO ₄ ⁻	Cl ⁻	Sum inorg. anions
Itasca Lake North Basin 3 May 1967	mg/L	38.1	15.3	6.4	1.6			2.6	0.8	
	me/L	1.90	1.26	0.28	0.04	3.48	3.20	0.04	0.02	3.26
	equivalent proportions	0.55	0.36	0.08	0.01		0.98	0.01	0.01	
Long Lake 9 May 1967	mg/L	33.6	18.5	4.0	1.6			2.0	0.09	
	me/L	1.67	1.52	0.17	0.04	3.40	3.16	.06	.03	3.25
	equivalent proportions	0.49	0.45	0.05	0.01		0.97	.02	.01	
Elk Lake 5 May 1967	mg/L	38.4	11.7	7.7	1.8				0.8	
	me/L	1.92	0.97	0.33	0.04	3.26	3.00			
	equivalent proportions	0.59	0.30	0.10	0.01					
Mary Lake 24 March 1966	mg/L	37.4	11.1							
	me/L	1.87	0.91				2.66			
	equivalent proportions									
Sallie Lake 11 May 1967	mg/L	32.8	27.5	10.8	4.4			15.4	33.7	
	me/L	1.64	2.26	0.47	0.11	4.47	3.49	0.24	0.95	4.68
	equivalent proportions	0.37	0.51	0.10	0.02		0.74	0.05	0.21	
Francis Lake 3 May 1966	mg/L	39.7	10.0							
	me/L	1.98	0.82				2.68			
	equivalent proportions									

Table 3. Ionic concentrations, pH, and ionization constants of carbon dioxide in Itasca and Long lakes in July, 1964. The ionization constants and proportions of carbonate carbon components were computed by K.S. Deffeyes.

	Depth M	Temp °C	moles/ L O ₂	me/L		Alka- linity	me/L Carbonate Carbon				pH	pK ₁	pK ₂
				Ca ⁺⁺	Mg ⁺⁺		Total	CO ₂ ⁺ H ₂ CO ₃	HCO ₃ ⁻	CO ₃ ⁻⁻			
Itasca Lake, North Basin 24 July 1964	0	26.7	.266	1.08	1.46	3.014	2.992	.028	2.928	.034	8.11	6.09	10.03
	2	26.3	.275	1.08	1.46	3.201	3.002	.036	2.934	.031	8.16	6.24	10.12
	4	25.7	.256	1.06	1.42	3.129	2.798	.034	2.741	.022	8.13	6.22	10.22
	6	21.5	.041	1.52	1.50	3.754	3.768	.200	3.562	.005	7.46	6.20	10.23
	8	18.1	.010	1.68	1.50	3.841	3.595	.114	3.471	.009	7.68	6.19	10.20
	10	16.6	.000	1.70	1.74	3.993	3.687	.322	3.362	.002	7.09	6.07	10.23
Long Lake, 9 July 1964	0	23.5	.287	1.37	1.68	3.561	3.391	.045	3.323	.022	8.09	6.22	10.26
	3	23.2	.290	1.40	1.63	3.593	3.438	.030	3.372	.034	8.29	6.24	10.28
	9	14.2	.330	1.46	1.65	3.607	3.447	.027	3.385	.033	8.29	6.20	10.29
	15	7.4	.265	1.52	1.66	3.667	3.724	.075	3.637	.011	7.72	6.03	10.21
	23	6.4	.122	1.56	1.69	3.953	4.230	.261	3.849	.009	7.41	6.24	10.02

Itasca Lake and in both the epilimnion and metalimnion of Long Lake, where it constituted approximately 1% of the total carbonate carbon.

The ratios of calcium to magnesium vary seasonally. The ratios (equivalents) in spring (1967) were 1.51 and 1.10 in Itasca and Long lakes respectively. Lower ratios (0.74 and 0.82) occur in summer (1964).

Partial analyses for Elk and Mary Lakes (Table 2) indicate that they are both similar to Itasca Lake, into which they drain. The calcium and magnesium concentrations of Francis Lake are similar to those of the Itasca lakes, and they are almost balanced by the alkalinity, implying that the concentrations of the other ions are similar to those of the Itasca lakes. Sallie Lake has somewhat lower concentrations of calcium and higher concentrations of all other ions than the other lakes.

Sediments from a water depth of 11 m in the north basin of Itasca Lake contain 9.3% organic carbon (loss on ignition at $450^{\circ}\text{C} = 24.4\%$) and 5.4% inorganic carbon (equivalent to 44% CaCO_3). Sediments from the other lakes contain variable quantities of carbonate, but they have not been analysed.

LIMNOLOGY AND PRODUCTIVITY OF ITASCA AND LONG LAKES

Itasca Lake has three distinct basins (Fig. 3). All the data discussed are from the north basin.

The north basin is exposed to the prevailing southwesterly winds in spring and summer, so the lake does not become thermally stratified until water temperatures exceed 13-15° C (Fig. 5). The epilimnion is usually 5-7 m thick, and the metalimnion includes depths between 5-7 m and the bottom.

Maximum gross photosynthetic rates occur between 0 and 1.5 m, and they vary between 1.4 and 1.7 mg/l O₂ per day. Net photosynthesis generally occurs only above 6 m, but a secondary zone with low net photosynthesis may occur at 7-8 m in mid-summer. Consequently there may be more dissolved oxygen in deep water in mid-summer than in early summer (cf. photosynthesis and oxygen profiles for 28 June and 21 July 1966, Fig. 5).

Differential algal counts on subsamples of the water used for the photosynthesis experiment on 21 July 1966 showed a well-defined algal stratification, with population densities at 7-8 m much greater than in the epilimnion (K. Kromer, unpublished data). The dominant algae in the epilimnion were Cyanophyta (mostly Aphanocapsa and Synechococcus) and Chlorophyta (mostly Ankistrodesmus). The dense populations in the deep water were mostly Cyanophyta (chiefly Merismopedia, Synechococcus, Microcystis, and Spirulina) and Cryptomonas.

Five photosynthesis experiments (Table 4) yielded a mean net productivity of 0.44 g C/m₂ and a gross productivity of

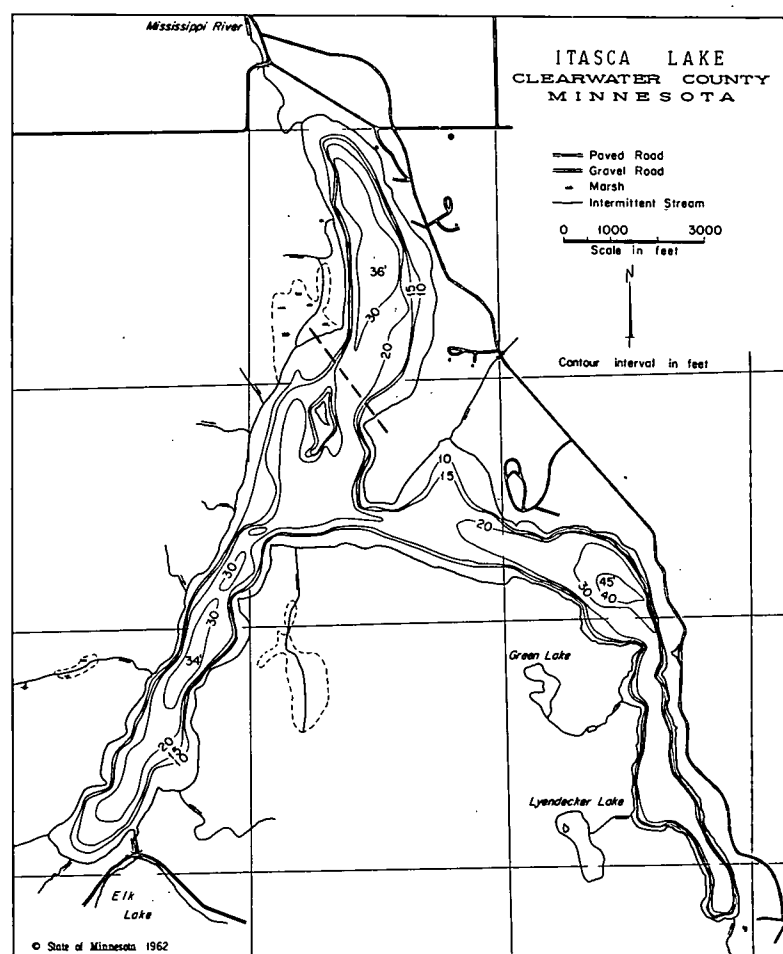


Fig. 3. Morphometry of Itasca Lake. Broken line across the south end of the North Basin indicates the boundary used for computing the volume of the North Basin.

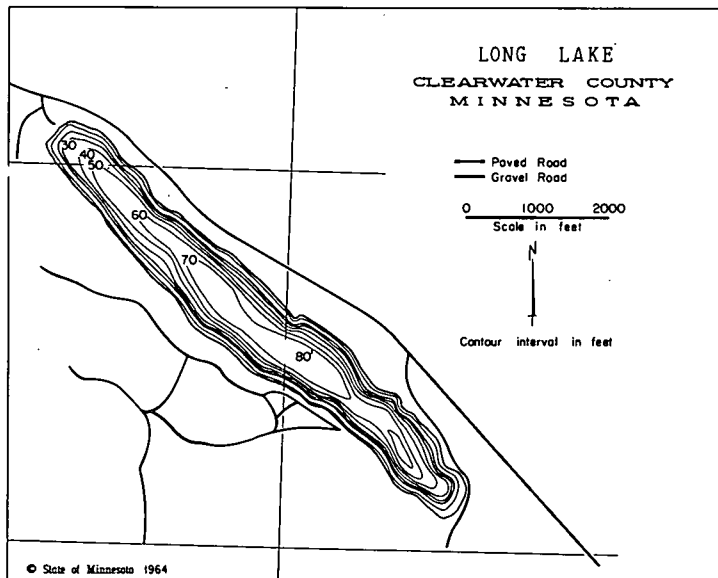


Fig. 4. Morphometry of Long Lake

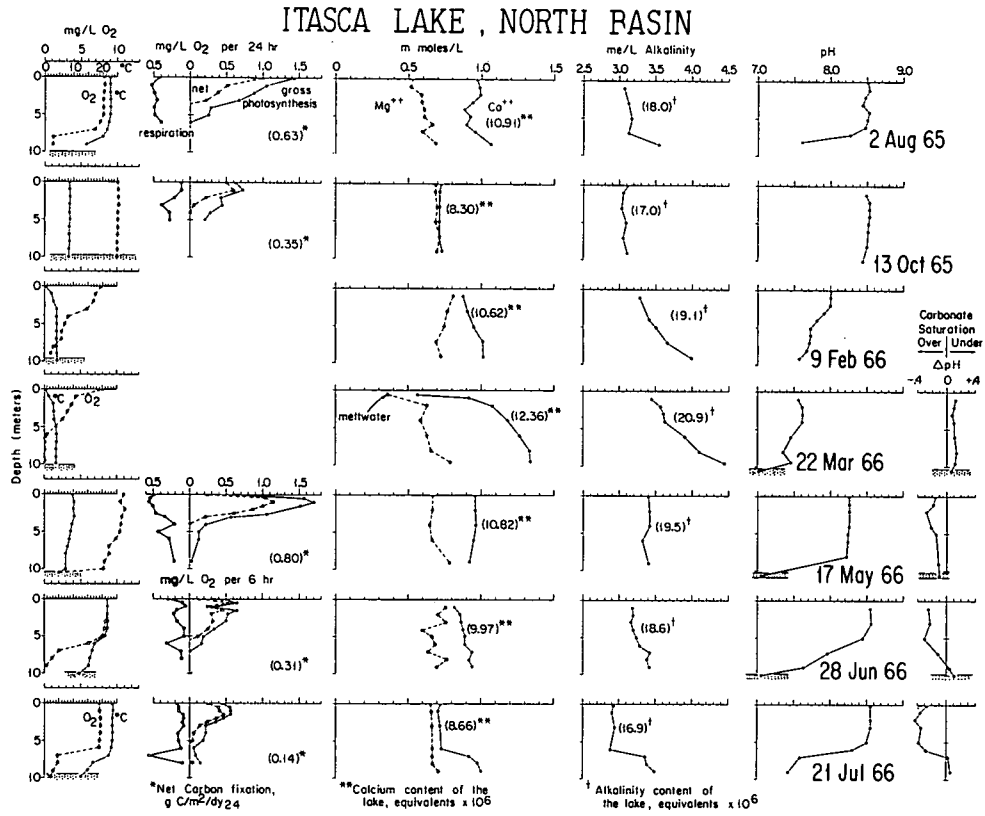


Fig. 5. Seasonal chemical changes and photosynthetic rates in Itasca Lake, 1965-1966

1.24 g C/m₂ per 24-hr day.

In the winter, biochemical oxidation depletes oxygen beneath the ice; oxygen concentrations in late winter may decrease to less than 4 mg/l above 5-m depth, and oxygen may be absent below 6 m (22 Mar 1966, Fig. 5).

Long Lake is very different limnologically from the north basin of Itasca. The volumes of the two water bodies are similar, but Long Lake has slightly less than ½ the area and slightly more than twice the mean depth of the north basin of Itasca Lake (Table 1). Thus, Long Lake is deep enough to have a well-defined hypolimnion (Fig. 4).

The transparency of Long Lake is much greater than in Itasca, and consequently measurable photosynthesis may occur in depths of 12-15 m (Fig. 6). Indeed, the highest photosynthetic rates in summer do not occur in the epilimnion but in the metalimnion at depths of 9-11 m, where rates of gross photosynthesis may amount to 1.6 mg/l O₂ per day (photosynthesis profile for 7 July 1966, Fig. 6). On 7 July 1966, rates were low in the epilimnion, higher near the top of the metalimnion at 5 m, and highest near the bottom of the metalimnion at 11 m. The depths with the highest photosynthetic rates were also richest in dissolved oxygen.

Quantitative counts of algae (K. Kromer, unpublished data) in water samples used for the photosynthesis experiment on 7 July 1966 indicated well-defined algal stratification, with greater population densities in the metalimnion than in the epilimnion. The dominant algae were Chlorophyta and Chrysophyta, with Stichogloea doederleinii most abundant at 5 m and

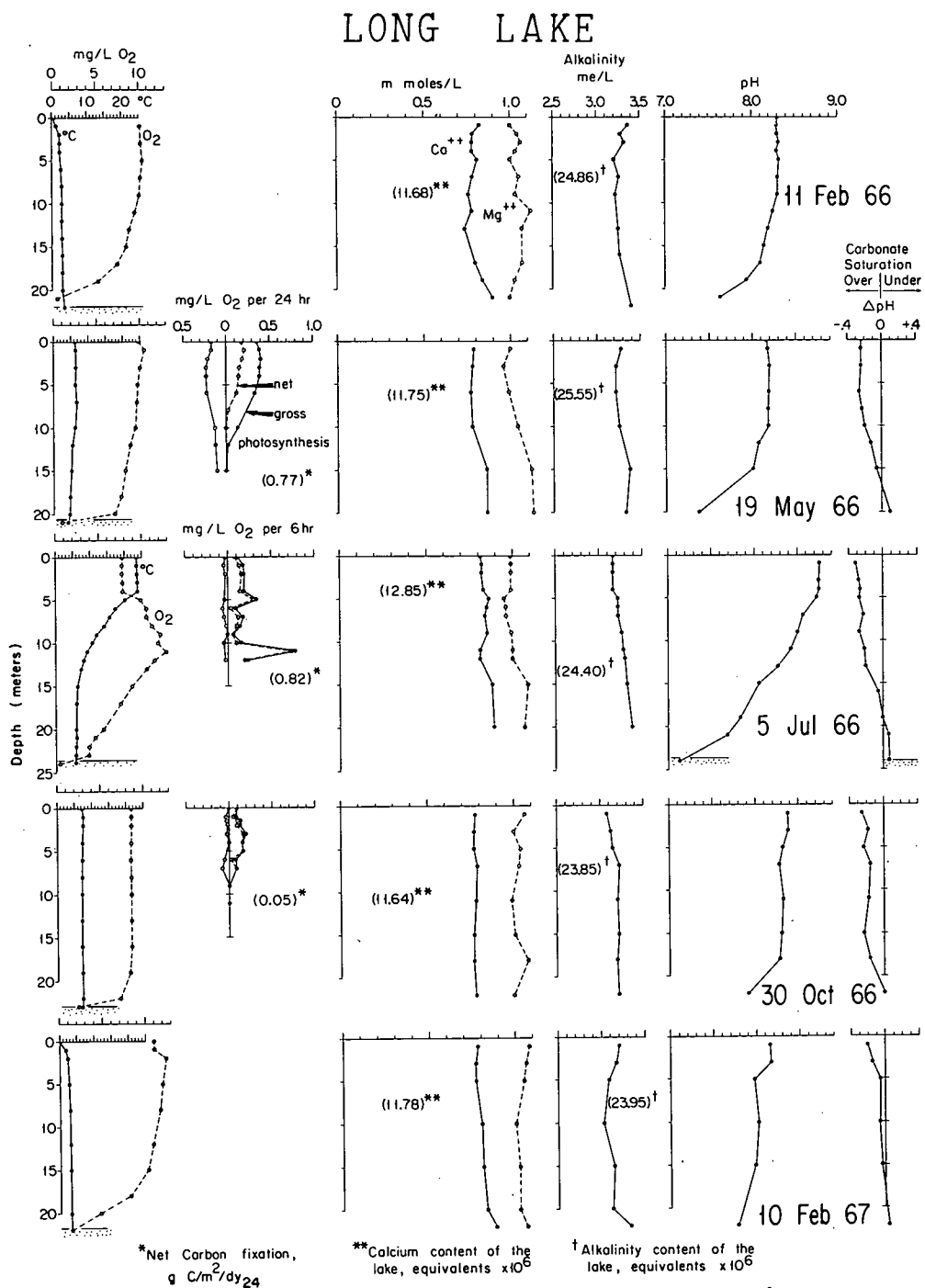


Fig. 6. Seasonal chemical changes and photosynthetic rates in Long Lake, 1966-1967

Asterionella formosa most abundant at 11 m. Other common algae in the metalimnion were Ankistrodesmus falcatus, Sphaerocystis schroeteri, Cruciginea rectangularis, and Oocystis solitaria.

Although photosynthetic rates per unit volume in Long Lake are typically lower than in Itasca Lake, the quantity of carbon assimilated per unit surface area in the lakes is similar because photosynthesis occurs at much greater depths in Long Lake (Table 4). Four experiments yielded a mean gross productivity of 1.03 g C/m^2 , which is lower than in Itasca, and a mean net productivity of 0.50 g C/m^2 , which is higher than in Itasca. The high net productivity of Long Lake is due to the low respiration rates, which are probably related to its lower population densities than in Itasca Lake.

In contrast to Itasca Lake, oxygen remains relatively abundant in the deep water of Long Lake in winter.

Table 4. Primary productivity of the lakes

Lake	Date	Net Photosynthesis (24 hours)			Gross Photosynthesis (24 hours)		
		g O ₂ /m ²	gC/m ²	$\bar{\Sigma}$ g C/m ²	g O ₂ /m ²	g C/m ²	$\bar{\Sigma}$ g C/m ²
Itasca	2 Aug 65*	2.02	0.63		3.78	1.18	
	13 Oct 65*	1.13	0.35		2.36	0.74	
	17 May 66*	2.56	0.80	0.44	4.64	1.45	1.24
	28 Jun 66	1.00	0.31		4.92	1.53	
	21 Jul 66	0.46	0.14		4.22	1.32	
Long	5 Aug 65*	1.08	0.36		1.78	0.56	
	19 May 66*	2.47	0.77	0.50	3.02	0.95	1.03
	7 Jul 66	2.60	0.82		5.72	1.78	
	30 Oct 66	0.18	0.05		2.70	0.84	
Elk	11 Jul 66	1.39	0.43	0.27	3.36	1.05	0.76
	29 Oct 66	0.36	0.12		1.40	0.47	
Mary	9 Jul 65*	0.45	0.14	0.14	1.26	0.39	0.38
	14 Oct 65*	0.43	0.14		1.23	0.38	
Sallie	13 Jul 66	2.12	0.66	0.66	7.76	2.42	2.42
Francis	18 Jul 65*	0.82	0.26		3.22	1.00	
	3 May 66*	0.90	0.28	0.29	1.74	0.54	0.87
	6 Jun 66*	0.54	0.17		1.98	0.62	
	23 Sep 66	1.44	0.45		4.20	1.32	

*24-hour experiments, begun at noon. All others 6 hours duration, begun at noon.

THE ENVIRONMENT OF CARBONATE DEPOSITION IN
ITASCA LAKE

The lowest concentrations of calcium and alkalinity in Itasca Lake occur in autumn (Fig. 5). Calcium concentrations during the autumnal circulation period (13 October, 1965) were slightly more than 0.7 m moles/l at all depths, and alkalinity concentrations were slightly less than 3.0 me/l. The pH at this time was near 8.5 at all depths.

Both calcium and alkalinity concentrations began to increase in winter. The rate of increase was highest in the water adjacent to the sediments, and the rate accelerated after oxygen disappeared from the deep water in February (see below). Calcium concentrations in the deep water rose to more than 1.3 m moles/l and alkalinity to more than 4.4 me/l in late March. In contrast, the pH decreased consistently during the winter, to about 7.6 above 5 m and 7.4 below, where oxygen was absent. The water at all depths in late March was undersaturated with calcium carbonate. The trends begun early in the winter probably continued until the ice melted during the last week in April.

As a consequence of the increases during the winter the calcium and alkalinity concentrations during the spring circulation period were much higher than during the previous autumn. Calcium concentrations were uniformly about 0.9 m moles/l and alkalinity about 3.4 me/l on 17 May, 1966. The pH had increased abruptly to more than 8.2, and the water had become oversaturated with calcium carbonate, with greatest oversaturation in the depths where there was net photosynthesis.

In summer the water above 5 m lost calcium and alkalinity rapidly, but oversaturation with calcium carbonate increased. These were also the depths in which photosynthesis was the dominant metabolic process. Respiration was dominant below 6 m, however, and both calcium and alkalinity increased, pH decreased, and the water became undersaturated with carbonate as oxygen became deficient.

These data suggest that the seasonal fluctuations of calcium and alkalinity in Itasca Lake may be attributed to biogenic calcium carbonate deposition and re-solution. Water in which photosynthetic carbon dioxide consumption occurs is the only water that is oversaturated with calcium carbonate. Conversely, water in which respiration exceeds photosynthesis is the only water that is undersaturated. All depths are oversaturated during spring and probably also autumn circulation periods because all the water in the lake may be transported into depths with sufficient illumination for photosynthesis. In summer only those algae circulating in the epilimnion receive enough illumination to maintain oversaturation. On the other hand, carbon dioxide released by respiration induces carbonate undersaturation in the deep water in summer and at all depths in winter.

It is also apparent that carbonate saturation in Itasca Lake is not controlled by calcium concentrations. Only the epilimnion is oversaturated in summer, and this is where calcium concentrations are lowest. Conversely, undersaturation occurs in environments with high calcium concentrations.

It is unlikely that oversaturation is induced by temperature increases. The water became oversaturated in May even though

water temperatures were only 3-5° warmer than in March.

It may be concluded that calcium carbonate saturation in this lake is controlled by the balance between carbon dioxide consumption during photosynthesis and its release during respiration.

If the concentrations of calcium and alkalinity in the north basin of Itasca Lake during 1965 and 1966 were altered by biogenic precipitation and re-solution of calcium carbonate, then (a) the calcium changes should be balanced by equivalent changes in alkalinity and (b) the rate of calcium depletion beneath a unit area of lake surface should be proportional to the daily rate of net photosynthesis. If these conditions are not satisfied or if the content of other ions, such as magnesium, in the lake changed, then the calcium and alkalinity changes must have been caused by evaporation or dilution of the lake water or by inorganic carbonate precipitation.

To determine whether or not the calcium and alkalinity fluctuations were equivalent, the total quantity of each ion in the lake on each date was computed by multiplying the volume of water in successive depth intervals by the mean concentrations in those intervals and totaling the products. The computed budgets (Table 5) indicate that calcium changes were usually nicely balanced by alkalinity changes and that condition (a) appears to have been satisfied. For the interval 2 August-13 October, however, the computed rate of calcium depletion appears to have been much larger than the rate of alkalinity depletion. This is probably due to an analytical error in the calcium and magnesium titrations for 2 August, in which calcium was systematically over-estimated and magnesium under-estimated. The basis for this conclusion is that

Table 5. Calcium and alkalinity budgets for Itasca and Long lakes

	Interval	Initial Σ Ca ⁺⁺ (equiv.x10 ⁶)	Δ Ca ⁺⁺ (equiv.x10 ⁶)	Initial Σ alkalinity (equiv.x10 ⁶)	Δ alkalinity (equiv.x10 ⁶)
Itasca Lake 1965-66	2 Aug-13 Oct	10.91	-2.6*	17.99	-1.0
	13 Oct-9 Feb	8.30	+2.3	16.97	+2.1
	9 Feb-22 Mar	10.62	+1.7	19.07	+1.9
	22 Mar-17 May	12.36	-1.5	20.94	-1.5
	17 May-28 Jun	10.82	-0.8	19.46	-0.9
	28 Jun-21 Jul	9.97	-1.3	18.58	-1.7
	21 Jul	8.66		16.90	
Long Lake 1966-67	11 Feb-19 May	11.68	+0.1	24.86	-0.3
	19 May-5 Jul	11.75	+1.1	25.55	-0.2
	5 Jul-30 Oct	12.85	-1.2	24.40	-1.2
	30 Oct-10 Feb	11.64	+ .1	23.85	+0.6
	10 Feb	11.78		23.95	

*Probably erroneous because calcium was overestimated on 2 August.

magnesium concentrations for this date were consistently lower than for any other date (Fig. 5). With this exception there were no significant magnesium fluctuations. Therefore it seems unlikely that evaporation and dilution altered the total ionic concentration of the water during the year.

Other aspects of carbonate sedimentation may be inferred from computations of the daily rate of calcium change per square meter of lake surface (Table 6). The rate of increase in early winter (13 October-9 February) was $8.3 \text{ m moles/m}^2/\text{dy}$. The slopes of the calcium curves (Fig. 5) indicate that most of the calcium entering the water during that period came from the sediments. Later (9 February-22 March), after oxygen disappeared from the deep water, the calcium content of the lake increased faster, at a rate of $18 \text{ m moles/m}^2/\text{dy}$. Data were not obtained immediately before the ice melted in late April, but calcium probably continued to increase at about the same rate as in March, or possibly even faster, until the lake probably contained about $270 \times 10^6 \text{ g}$ calcium on May 1. If the estimate for the calcium content on May 1 is correct, then the lake lost calcium at a rate of $62 \text{ m moles/m}^2/\text{dy}$ during early May. The rate of depletion decreased to only 8.3 during late May and June, and increased again in July to 23.

The high rate of calcium depletion inferred for early May was probably only partly biogenic. The carbon dioxide that accumulated in the water during the winter was able to escape to the atmosphere when the ice melted. The combined loss of carbon dioxide to the atmosphere and the rapid carbon assimilation indicated by the high rates of photosynthesis (Table 4, 17 May) would induce massive carbonate formation.

Table 6. Daily rates of calcium change in Itasca and Long lakes

	Interval	Days	Initial ⁺⁺ total Ca ⁺⁺ (g x10 ⁶)	ΔCa ⁺⁺	
				(g x10 ⁶)	(m moles/m ² /dy)
Itasca Lake North Basin 1965-66	2 Aug-13 Oct	43	218.3	-52.4	-26
	13 Oct-9 Feb	120	165.9	+46.6	+8.3
	9 Feb-22 Mar	42	212.5	+35.3	+18
	22 Mar-1 May	39	247.8	+21.5*	+18*
	1 May-17 May	17	269.4**	-53.3	-62
	17 May-28 Jun	43	216.1	-16.7	-8.3
	28 Jun-21 Jul	24	199.4	-25.6	-23
	21 Jul		173.8		
Long Lake 1966-67	11 Feb-19 May	97	233.6	+1.4	+0.6
	19 May-5 Jul	47	235.0	+22.8	+20.2
	5 Jul-30 Oct	117	251.8	-25.3	-9.0
	30 Oct-10 Feb	95	232.5	+3.4	+1.5
	10 Feb		235.9		

*Assumed to be the same rate as during the previous interval.

**Computed from the daily rate assumed for the previous interval.

In June and July rates of calcium depletion and photosynthesis were both lower than in May; 0.4 moles calcium were lost per mole carbon assimilated by phytoplankton.

THE ENVIRONMENT OF CARBONATE DEPOSITION
IN LONG LAKE

It is evident from the data in Figure 6 that both the vertical gradients and seasonal changes of calcium and alkalinity in Long Lake are more subtle than in Itasca Lake.

As in Itasca, the calcium and alkalinity content of Long Lake increased in winter (cf. data for 30 October 1966 and 10 February 1967, Table 5). In contrast to Itasca, however, the calcium content of Long Lake continued to increase during spring and early summer (cf. data for 19 May and 5 July, 1966).

The intensity of biological activity in Long Lake during much of the year is evidently insufficient to offset hydrological factors, particularly the influx of groundwater which, according to analyses from wells and springs in the vicinity, contains about twice as much calcium as the lake water. No streams enter Long Lake; it is fed partly by runoff from a very small watershed, partly by several small springs, and mostly by seepage. Most of the calcium entering the lake in winter and spring probably comes from groundwater and not from the sediments, because most depths remain oversaturated at least until February (Fig. 5), and there is probably very little re-resolution of calcium carbonate from the sediments. Carbonate precipitation probably occurs in spring as a result of carbon dioxide evasion to the atmosphere and consumption by photosynthesis, but the losses of calcium by these mechanisms are less than the increases from groundwater.

Although the trends of calcium and alkalinity in spring did not coincide, both the calcium and alkalinity content of

Long Lake decreased 1.2×10^6 equivalents between July and October. The rate of decrease was $9 \text{ m moles/m}^2/\text{dy}$ (Tables 5 and 6). On 5 July the water at depths to 15 m was oversaturated, and these were also the depths in which photosynthesis occurred. Greater depths were at equilibrium with calcite or weakly undersaturated (Fig. 6). The influx of groundwater calcium was probably less during summer than spring, with the result that there was a net loss of calcium and alkalinity. Net photosynthetic carbon assimilation, as indicated by two experiments in July and October, was about $36 \text{ m moles/m}^2/\text{dy}$. Thus the rate of calcium depletion was 0.25 moles per mole carbon assimilated by the phytoplankton.

DISCUSSION AND CONCLUSIONS

It has been demonstrated that calcium changes are accompanied by equivalent alkalinity changes, probably during all seasons in Itasca Lake and in summer in Long Lake. The concentrations of magnesium are comparatively stable, and therefore the calcium and alkalinity fluctuations may be attributed to precipitation and re-solution of calcium carbonate. Biological consumption and release of carbon dioxide is indicated to be an important cause of the calcium and alkalinity changes, because water in which photosynthesis occurs tends to reach equilibrium or to become undersaturated with calcium carbonate. This is only indirect evidence for the role of organisms, however.

For a conclusive demonstration of photosynthetic carbonate precipitation it is necessary to show that there is a quantitative relationship between photosynthesis and calcium depletion. To demonstrate this, rates of calcium depletion per m^2 of lake surface during various time intervals (Fig. 7, see caption) were

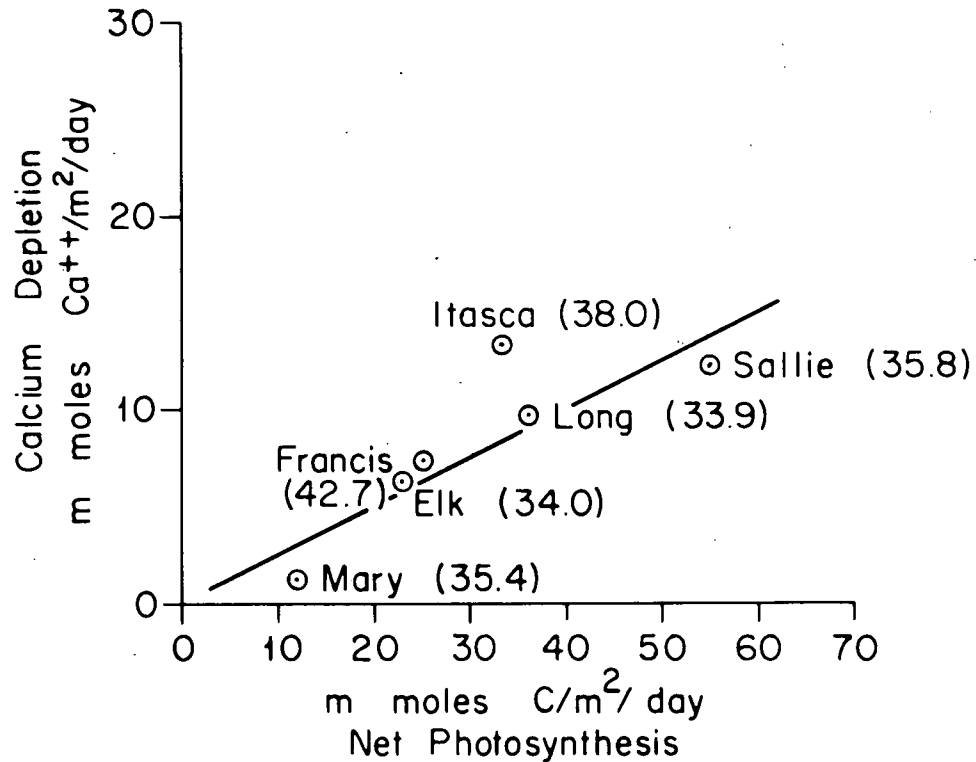


Fig. 7. Photosynthetic carbon assimilation and rates of calcium depletion in six Minnesota lakes. The mean calcium concentrations (mg/l Ca⁺⁺) at the beginning of the depletion interval are shown in parentheses after the name of each lake. The time intervals are as follows: Mary Lake, 9 July-14 October, 1965; Elk Lake, 11 July-29 October, 1966; Francis Lake, 3 May-22 September 1966; Long Lake, 5 July-30 October, 1966; Sallie Lake, 13 July-27 October, 1966; Itasca Lake, 17 May-21 July, 1966.

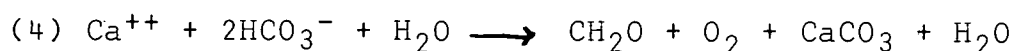
computed for the six lakes in this study. The calcium depletion rates were then plotted against the mean of photosynthesis experiments performed at the beginning and end of the time intervals, except that there were three experiments during the time interval for Itasca and only one for Sallie Lake; subsequent experiments at Sallie Lake indicate that the high rate measured is typical of the lake's productivity, however.

It is apparent that rates of calcium depletion increase as rates of photosynthesis increase (Fig. 7). In four of the six lakes approximately 0.25 moles of calcium were lost per mole of carbon assimilation. In the least productive Mary Lake the rate was only 0.12, and in Itasca the rate was 0.40. Because the hydrologic differences among the lakes would be expected to influence the calcium budgets, and because of the variable crop of rooted macrophytes that are usually considered to precipitate much or most of the carbonate in lakes, it is somewhat surprising that the ratios of calcium depletion to carbon assimilation by phytoplankton should fall within such a narrow range.

The narrow range of values for these ratios indicates that they may depend upon a simple but fundamental stoichiometric relationship that is distorted only slightly by the hydrologic balance of lakes or by macrophyte photosynthesis. The curve along which the data are arrayed (Fig. 7) has a slope of 0.25. In other words, four moles of carbon must be consumed to precipitate one mole of calcium.

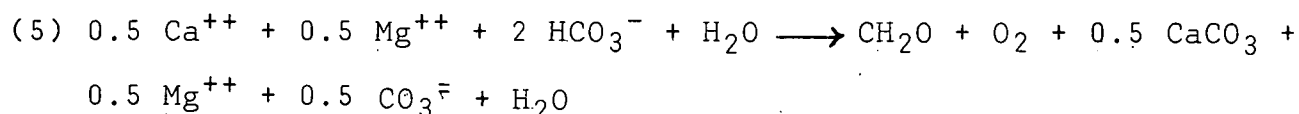
An equation that describes the relationship between photosynthesis and carbonate precipitation in a solution of calcium bicarbonate may be derived by combining equations 1, 2, and 3

(p. 4):



Thus, one mole of carbon consumption induces one mole of carbonate formation in a solution containing only calcium bicarbonate.

Such a relationship would not be expected in these lakes, however, because the waters are actually mixtures of calcium and magnesium bicarbonates. If calcium carbonate is formed it tends to precipitate because of its low solubility, whereas magnesium carbonate is relatively soluble and would not precipitate. Thus a general equation should take into account the proportions of magnesium or any other cations that form soluble carbonates. The proportions of calcium and magnesium in these lakes vary seasonally. In spring the proportion of calcium equivalents is generally higher than that of magnesium, whereas the reverse is true in summer. It is therefore not an unrealistic simplification to write an equation for photosynthesis in solutions that are equimolar with respect to calcium and magnesium:



In such a solution the expected ratio of calcium depletion to carbon consumption would be 0.5, which is to be compared with ratios between 0.1 and 0.4 observed in the lakes. Obviously the empirical rate of carbonate precipitation is substantially lower than the potential rate if equation 5 represents approximately the relationship between carbon consumption and calcium carbonate formation in these waters. The carbonate that precipitates out of solution is only a portion of the carbonate that is formed. This, however, may account for the observations that calcium carbonate oversaturation may persist in water samples stored for weeks in the laboratory.

In other words, only about one-half of the calcium carbonate that is formed is actually precipitated. The colloidal and organically complexed carbonate that remains in suspension also permits lake waters to remain oversaturated in winter even if there is no evident net photosynthesis (Fig. 6).

Also it should be noted that the rates of calcium depletion may be underestimates of total calcium carbonate precipitation because unknown quantities of calcium were delivered to the lakes during the time intervals by ground water and surficial drainage. The influx of calcium from these sources would thus lower the calcium depletion ratios.

Finally it is desirable to assess the relative importance of inorganic factors of carbonate precipitation. The high rates of calcium and alkalinity depletion during the two weeks after the ice melted in Itasca Lake have been attributed to evasion of carbon dioxide to the atmosphere. High photosynthetic rates by phytoplankton undoubtedly also contributed to carbonate formation during this interval, but water temperatures increased only 3 - 5°, and warming was probably of little importance. Another indication that temperature may be relatively unimportant is that calcium depletion rates were relatively low in Francis Lake, which is far south of the other lakes. There also appears to be no relationship between rates of calcium depletion and the concentration of calcium (Fig. 7).

If the rates of calcium depletion in these lakes represent most of the calcium carbonate precipitation, then it is apparent that phytoplankton photosynthesis is sufficient to account for most of the calcium carbonate formed in summer. The role of macrophytes may be relatively minor simply because their biomass

and photosynthesis are relatively small by comparison to those of the phytoplankton. However, the relatively high ratio of calcium depletion to plankton photosynthesis in Itasca Lake may be the effect of the abundant macrophytes in that lake. The role of macrophytes in carbonate precipitation is probably often overestimated because they provide surfaces for crystal nucleation.

Although the data discussed here indicate that the rate of carbonate precipitation in lakes may depend primarily upon phytoplanktonic productivity, it should be emphasized that the carbonate content of sediments depends upon both the rate of carbonate precipitation and the environment of preservation. Thus large quantities of carbonate are deposited in the sediments of Itasca Lake, but a large proportion is re-dissolved in winter. In lakes like Itasca, the ultimate deposition of the carbonate formed in a summer probably does not occur until the following spring, when biological, chemical, and physical features are all conducive to carbonate formation and preservation. Although the rate of carbonate precipitation in Long Lake appears to be lower than in Itasca Lake, the sediments of Long Lake probably contain more carbonate than sediments in Itasca because the environment in deep water is more favorable for carbonate preservation.

The results of this investigation suggest that future studies of the genesis of carbonate sediments, both in the sea and in lakes, would be incomplete without in situ measurements of planktonic photosynthesis and also without evaluating the impact of photosynthesis on water chemistry. An illustration of the potentials of this approach may be derived by utilizing data

obtained by Cloud (1962) during an intensive study of carbonate sedimentation on the Great Bahama Bank west of Andros Island.

As water moves across the Bahama Bank, from the Florida Straits eastward towards Andros Island, it loses approximately 1.0 me/l Ca^{++} and 0.97 me/l CO_3^{--} , which represents a net loss of 50 mg/l CaCO_3 . It was computed that 222 grams CaCO_3 are deposited per m^2 during the 2-month period required for a mass of water to move across the bank, although Weyl (1963) contended that the estimate of transit time may have been inaccurate because tidal displacement was not computed. Examination of sediments indicated that perhaps 20% of the calcium carbonate in the sediments was derived from skeletons of marine animals and plants. It was estimated that an additional 5 - 15% of the CaCO_3 in the sediments was precipitated by the activities of nitrate- and sulfate-reducing bacteria. The remaining 60-75% was attributed to physico-chemical precipitation primarily as a consequence of evaporation and temperature increase, and secondary biochemical precipitation, primarily as a consequence of planktonic photosynthesis. It was concluded, however, that physico-chemical precipitation was usually much more important than secondary biochemical precipitation, i.e. photosynthetic precipitation, although the effects of photosynthesis were acknowledged to be important locally, particularly in patches of water known as "whitings" that are very turbid because of suspended carbonate crystals (aragonite).

In connection with observations at one of the whitings, which was about 0.5 km wide and 1.5 km long, a very high rate of oxygen production was observed in bottles placed on the sea floor, where the water depth was apparently 2-3 m. Sisler (in Cloud, 1962,

p. 67) measured oxygen production rates of 1.5 ml/l per daylight hour and oxygen consumption of 0.1 ml/hr in darkness. This represents a net oxygen production during a 24-hr day of 16.8 ml/l (=24.0 mg/l). Although it was noted that this was an extremely high rate of photosynthesis, which incidently is about 50% higher than any rates measured in a series of lakes now being studied in Minnesota, the full implications of this high rate were not described.

A daily net production of 24 mg/l oxygen represents almost 7.5 mg/l photosynthetic carbon assimilation, assuming a photosynthetic quotient of 1.2. Thus, the plankton removed 7.5 mg/l carbon or 1.2 me/l per day from the alkalinity supply in the seawater, which amounted to only 2.5 me/l (=123 mg/l in Table 6, Cloud 1962). The experiment suggests, therefore, that the phytoplankton in the seawater over the Bahama Bank may utilize more than 48% of the alkalinity supply in a single day! Furthermore, most of the unused alkalinity must have been converted to carbonate and therefore rendered virtually unavailable for photosynthesis. The proportion of the carbonate that would precipitate as CaCO_3 is unknown, but it was observed, that suspended CaCO_3 drystals (aragonite) in the whiting water amounted to 11.9 mg/l (=0.24 me/l) or about 10% of the alkalinity. It is apparent that algal photosynthesis in the waters over the Bahama Bank would be limited by acute carbon deficiency within a very few days if it were not for continuous regeneration of the alkalinity supply, both from the atmosphere and from bacterial re-solution of carbonate in surface sediments.

This experiment can only serve to illustrate the magnitude of photosynthetic carbonate precipitation in shallow marine environments. It may be an underestimate because the bottles were incubated at a depth of several m in turbid water, or it may be an overestimate because photosynthetic rates were abnormally high in the area where the experiment was performed. However, even if the average rate of photosynthesis is only 50% of that measured, photosynthetic carbonate precipitation is probably the dominant mechanism for carbonate precipitation over the Grand Bahama Bank. Obviously future investigation of the carbonate problem should utilize photosynthesis experiments extensively; also pH, alkalinity, conductivity and carbonate formation in the bottles should be measured.

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