MASTER

SILICA AND NITRATE DEPLETION
AS RELATED TO RATE OF EUTROPHICATION IN
LAKE MICHIGAN, LAKE HURON, AND LAKE SUPERIOR¹

by

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ABSTRACT

Eutrophication of the Laurentian Great Lakes is accelerated by inputs of phosphorus from combined sources on land. Silica and nitrate nitrogen are depleted by phosphorus inputs due to an imbalance between the proportions of these nutrients required by phytoplankton assemblages and the proportions in either polluted tributary inputs or supplies in the lake. A model is used to relate increased phosphorus inputs, silica depletion, and nitrate depletion and to predict the trophic state or rate of eutrophication in Lakes Huron, Michigan, and Superior. Water quality is affected by inputs of phosphorus because standing crops of phytoplankton increase and because dominant groups of phytoplankton may change as the result of nutrient depletion. Silica depletion results in a shift from the characteristic diatom assemblages to blue-green or green algae and nitrate depletion favors assemblages with blue-green algae that fix nitrogen.

INTRODUCTION

The Laurentian Great Lakes represent an important and valuable natural resource in North America and, as a result, there has been increasing concern about problems related to water quality. One of the chief problems associated with degradation of water quality for municipal water supplies, recreational purposes, commercial and sport fisheries, and other uses is accelerated eutrophication. Accelerated eutrophication is caused by inputs of nutrients from man's activities on land, a relationship which has been recognized for at least 25 years by ecologists (Hasler, 1947).

Accelerated eutrophication of the Laurentian Great Lakes of North America has been publicized widely from reports about Lake Erie, the most publicized, polluted, and eutrophic of the lakes. Of the Great Lakes, only the two most eutrophic (Erie and Ontario) have hypolimnetic oxygen depletion throughout the lake in summer, although Green Bay on Lake Michigan and Saginaw Bay on Lake Huron also exhibit such a depletion and, like Lakes Erie and Ontario, reflect a high degree of industrialization and land use. Comparatively, Lake Superior is the most oligotrophic lake because it is surrounded largely by undeveloped land, not heavily industrialized, and sparsely populated, with few urbanized areas. It is also the deepest and largest of the lakes, with the greatest capacity for dilution of pollutants--including nutrients.

Chemical and biological changes associated with eutrophication of the Great Lakes have been well documented (Beeton, 1965, 1969). Beeton has shown

that concentrations of sodium, chloride, sulfate, and total dissolved solids have increased in all of the Great Lakes except Lake Superior. In this paper, I will be concerned mainly with increases of phosphate, which control eutrophication (Schelske and Stoermer, 1971a); decreases in soluble nutrients (silica and nitrate nitrogen), which accompany eutrophication; and presentation of a model for relationships among these nutrients which can be used to assess changes in the trophic state and rate of eutrophication in the three upper lakes (Michigan, Huron, and Superior).

Using a model based on chemical changes to assess trophic state has advantages and disadvantages over classical biological methods. The advantages are that today, particularly with automated methods, chemical data can be obtained quickly and precisely, and with computer techniques, large amounts of data can be processed rapidly and incorporated in predictive models. Disadvantages are that the status of the biological community, such as shifts in species composition associated with eutrophication, must be known in order to assess water quality and these changes can be determined only from biological studies. Undoubtedly, both approaches must be utilized to obtain the best understanding of the system.

The chemical approach is applicable because the large size and volume of the upper lakes simplifies interpretation of data. Because of the physical characteristics, water in the lakes has long renewal times and offshore waters are composed of water masses that are identifiable for periods of months. Therefore, to establish trends, measurements are not needed as frequently as would be the case for lakes with shorter renewal times, or for lakes which have large seasonal changes in chemical characteristics.

MORPHOMETRY AND TOPOGRAPHY OF THE LAURENTIAN GREAT LAKES

The Laurentian Great Lakes of North America have a combined surface area of $246 \times 10^3 \text{ km}^2$ (Table 1) and a combined volume of $23 \times 10^3 \text{ km}^3$ (Table 2), which equals the volume of Lake Baikal--the world's largest freshwater lake (Beeton and Chandler, 1963; Hutchinson, 1957). However, Lake Superior, northern and western most of the Laurentian Great Lakes, has the largest surface area ($82.4 \times 10^3 \text{ km}^2$) among the world's freshwater lakes and the third largest volume ($12.2 \times 10^3 \text{ km}^3$)--nearly half the combined volume of the Laurentian Great Lakes. The entire chain of lakes covers 3000 km from the mouth of the St. Lawrence to the western end of Lake Superior, all of which can be traversed by ocean-size vessels, with the aid of locks at Niagara Falls and the St. Mary's River (Figure 1).

The drainage pattern (Figure 1) begins at Lake Superior, which has the highest elevation of the Great Lakes, draining through the St. Mary's River into Lake Huron. Lakes Huron and Michigan have the same elevation, and together with Lake Superior comprise the upper Great Lakes (Table 1). From the upper lakes, water flows out of Lake Huron through the St. Clair River, Lake St. Clair, and the Detroit River into the two lower lakes, Erie and Ontario, respectively, with the Niagara River forming the link between these lakes. From Lake Ontario, the water flows through the St. Lawrence River to the Atlantic Ocean. Movement of water from the upper lakes through the lower lakes is analogous to a river system. The volume of discharge increases as water moves down the chain of lakes to a maximum mean discharge of $6630 \text{ m}^3/\text{sec}$ as the water leaves Lake Ontario via the St. Lawrence River

Table 1. Dimensions of the Great Lakes.*

Lake	Area		Ratio of Drainage Basin to Water Surface	Average Surface Elevation Above Mean Sea Level Since 1860 (m)
	Water Surface (10 ³ km ²)	Drainage Basin (10 ³ km ²)		
Superior	82.4	207	2.51	183.55
Michigan	58.0	176	3.02	176.95
Huron	59.6	188	3.16	176.95
St. Clair	1.27	19.2	15.2	175.22
Erie	25.7	84.2	3.27	174.45
Ontario	19.5	90.1	4.63	74.99
TOTALS	246.	764.	3.12	

*Adapted from Beeton and Chandler (1963).

Figure 1. Map of the Laurentian Great Lakes.

(Table 2). Unlike most tributary systems, however, the surface area of the lakes comprises a significant fraction (25%) of the drainage basin (Table 1).

Furthermore, the simple analogy of the Great Lakes as a river system does not adequately illustrate the physical complexities of water movement and transport within each lake. In studies of eutrophication, such features as water circulation patterns, thermal stratification, or residence time of the water in each lake are important and complex considerations. Renewal time (volume divided by outflow) can be used as a crude estimate of residence time (Rainey, 1967), and reflects the average depths and surface areas of the lakes. In the Great Lakes, the renewal times range from 190 years, in Lake Superior, to 3 years, in Lake Erie (Table 2).

Table 2. Morphometric and discharge data for the Great Lakes. Renewal time is volume divided by outflow.*

Lake	Mean Depth (m)	Volume (10^3 km^3)	Outflow (km^3/yr)	Renewal Time (years)	Discharge ($10^3 \text{ m}^3/\text{sec}$)
Superior	148	12.2	65	190	2.08
Michigan	84	4.87	49	100	1.56
Huron	59	3.53	159	22	5.04
Erie	18	0.453	175	3	5.52
Ontario	86	1.68	208	8	6.63
TOTAL		22.			

*Adapted from data in Beeton and Chandler (1963).

METHODS AND LIMITATION OF DATA

Conclusions in this paper are based on data from three sources: (1) nutrient enrichment experiments conducted by the Great Lakes Research Division, The University of Michigan, (2) monitoring of water chemistry and productivity conducted on research and student training cruises of The University of Michigan, and (3) data from the literature. These data have two limitations: (1) in total there are few data of any type and (2) there is a problem of comparability among the many sources. I have relied heavily on the first two sources because these data were collected and analyzed under my supervision and control, using the same techniques. Other data were selected mainly because of the applicability of the data to the questions of interest and the availability of large data sets.

Data on concentrations of nutrients during the past 50 years are limited. Moreover, these data must be interpreted carefully if they are to be utilized for comparison, since different methods and techniques have been used and some data are unavailable (e.g., Beeton [1969] has no data for silica concentrations in Lake Superior). Some of the early water samples for silica analyses were stored in glass bottles (Beeton and Moffett, 1965), and dissolution of the bottles could increase silica concentrations during long-term storage. The pH of Lake Michigan water was lower on the average when glass bottles were used for storage than presently, so the effect was not as great for that data as it would be today. Available phosphate data may not be reliable because there is a possibility of large relative errors from contamination and from slight carelessness in the procedures used to measure the small concentrations in the lakes.

Because the objective of my paper is not to present results of original research, no information on specific methods is included in this paper. Methods used to obtain the data are given in the papers that have been cited, and it is doubtful if all of the results cited are comparable. Conclusions made in this paper are valid even though some of the results, particularly on concentrations of nutrients, may be questioned due to the different methods of collection, storage, and analysis.

NUTRIENTS IN PHYTOPLANKTON

Not only the absolute quantity or concentration of nutrients but also the relative amounts must be considered to evaluate the effect of specific nutrient inputs on the process of eutrophication. If nutrients are not supplied proportionately to amounts required by phytoplankton, an imbalance results or one (or more) nutrient becomes limiting.

In phytoplankton, proportions of the three major nutrients--carbon, nitrogen, and phosphorus--are 106:16:1 (Redfield, Ketchum, and Richards, 1963). Ratios of N:P vary depending on the physiological state of the cells, particularly with regard to stored phosphate, and may vary from 20:1 to 10:1. In the Great Lakes, diatoms dominate phytoplankton assemblages, and consequently, the amount of silica in phytoplankton assemblages is an important consideration.

Mean silica concentrations for 10 species of diatoms range from 26 to 63% as dry weight (Lund, 1965). Based on these data and my calculations (Table 3), the ratio of SiO_2 :C in diatoms should vary by a factor of five, from 0.7 to 3.5:1, and SiO_2 :P ratios should range from 70 to 370:1. Using data on *Asterionella formosa* (Lund, 1969; Hutchinson, 1967) of $140 \mu\text{g SiO}_2/10^6$ cells and $1.0 \mu\text{g P}/1.6 \times 10^7$ cells, I calculate a SiO_2 :P ratio of 2240:1 and a SiO_2 :C ratio of 21:1. This SiO_2 :P ratio, quoted by Schelske and Stoermer (1971a), is much too large because the mean concentration of SiO_2 in *A. formosa* is 45% as dry weight (Lund, 1965) and a cell that contained 45% SiO_2 with a 21:1 SiO_2 :C ratio would contain only 2.1% carbon as dry weight. The ratio for SiO_2 :P is probably large due to the extremely low

Table 3. Values for SiO_2 :C ratios of diatoms, assuming cells are composed only of silica and organic matter containing 50% carbon. Ratios of SiO_2 :P based on a C:P ratio of 106:1.

SiO_2 As a Percentage Dry Weight	C As a Percentage Dry Weight	Ratio of SiO_2 :C	Ratio of SiO_2 :P
10	45	0.22:1.0	23:1
26	37	0.70:1.0	74:1
33	66	1.00:1.0	106:1
50	25	2.00:1.0	212:1
63	18	3.50:1.0	371:1
67	17	4.00:1.0	424:1
80	10	8.00:1.0	848:1
90	5	18.00:1.0	1910:1

value used for the concentration of phosphorus in cells or to unaccounted supplies of silica in the data from Mackereth's experiments (Mackereth, 1953). Other data cited by Hutchinson for phosphorus concentrations range from 0.28 to 0.81 $\mu\text{g P}/10^6$ cells. Based on these data, the range for $\text{SiO}_2:\text{P}$ ratios is 170 to 500:1.

Obviously, a range of $\text{SiO}_2:\text{P}$ ratios must be considered due to variations in the proportion of silica among different species, to variations in chemical composition of individual species as a result of different environmental conditions, and probably to the lack of good data on chemical composition. The range of values reported in this section (70-500) should encompass most of the $\text{SiO}_2:\text{P}$ ratios that would occur in diatom assemblages in nature.

INPUT OF MAJOR NUTRIENTS TO LAKE MICHIGAN

The only study of inputs of materials, including major nutrients, to Lake Michigan has been summarized by Ayers (1970). Data were available to calculate inputs from tributaries and the output through the Straits of Mackinac. Based on these data the major nutrients--phosphorus, silica, and nitrogen--are not transported out of the lake, but are stored in the lake basin (Table 4). Ultimately, sediments are the major sink for these biologically important elements. In contrast, a large proportion of the conservative elements (elements not affected by biological and chemical processes) was transported out of the lake with the outflow, as evidenced by data for chloride (Table 4).

Summing inputs from the major tributaries, as was done in Table 4, does not provide information on specific sources of nutrient input. Data for individual tributaries indicate that more than 80% of the total phosphorus loading was attributable to six rivers: Burns Ditch, St. Joseph, Kalamazoo, and Grand, which drain into the southeastern part of the lake, and the Fox and Menominee, which drain into Green Bay in the northern end of the lake (Figure 2, Table 5). Of the six rivers, the Fox, Grand, and St. Joseph contribute more than half of the phosphorus loading. It is significant to note that with the exception of Burns Ditch, the major sources of loading are from rivers with the highest mean flow rates (Table 5), which tend to dilute the concentrations of these significant inputs of nutrients. Data on major sources of loading do not indicate all of the areas that may have excessive loadings of phosphorus. Large concentrations of phosphorus in

Table 4. Estimated long-term inputs and outputs from Lake Michigan.*

Nutrient	Input**	Output**
NH ₃ -N	55.9	4.54
NO ₃ -N	44.1	2.27
Org-N	39.5	ND [†]
Tot Sol PO ₄ -P	5.91	1.06
SiO ₂	550.	199.
Cl	1430.	926.

*Results summarized by Ayers (1970) from data collected by FWPCA (1968) between April 1962 and July 1964. Includes Ayers' corrections for ungauged streams.

**Values in metric tons/day⁻¹.

[†]No data.

Figure 2. Map of Lake Michigan showing locations of major tributaries.

Table 5. Contributions of total soluble PO_4^* and silica to Lake Michigan by 19 tributaries (1963-64).

River	Mean Flow (m^3/sec)	Mean Concentrations (mg/l)		Ratios $\text{SiO}_2:\text{P}$	Loading (metric tons day^{-1})	
		Tot Sol PO_4	SiO_2		Tot Sol PO_4	SiO_2
Boardman	5.26	0.20	7.5	114:1	0.125	4.69
Manistique	23.9	0.04	5.8	574:1	0.082	12.00
Manitowoc	2.35	0.62	5.7	28:1	0.125	1.16
Sheboygan	3.73	0.40	3.9	30:1	0.129	1.26
Milwaukee	5.41	0.61	2.8	14:1	0.285	1.31
Burns Ditch	4.24	1.8	10.	17:1	0.661	3.68
St. Joseph	58.4	0.24	6.4	82:1	1.21	32.3
Kalamazoo	32.3	0.21	5.9	86:1	0.586	16.5
Grand	53.8	0.52	5.3	31:1	2.42	24.7
Muskegon	49.0	0.06	5.6	285:1	0.254	23.8
Pere Marquette	16.1	0.03	7.8	796:1	0.041	10.9
Fox	125.0	0.28	9.4	103:1	3.03	101.8
Oconto	22.4	0.17	9.2	166:1	0.329	17.8
Peshtigo	25.2	0.08	9.8	375:1	0.174	21.4
Menominee	92.1	0.11	4.4	122:1	0.877	35.0
Ford	9.54	0.04	7.0	536:1	0.033	5.77
Escanaba	28.8	0.06	7.0	357:1	0.149	17.5
Rapid	2.27	1.59	3.1	58:1	0.311	0.61
Whitefish	6.43	0.18	5.7	97:1	0.100	3.17
TOTALS					10.9	335.

* PO_4 values should be divided by 3.06 to convert concentrations to phosphate as phosphorus.

** Data from FWPCA (1968) as presented by Ayers (1970).

rivers with small flows may produce nutrient concentrations in the lake large enough to significantly enrich a smaller area than the rivers with larger flows. The Milwaukee River, for example, apparently produces more eutrophic conditions near Milwaukee than are found near Ludington, where the major tributary is the unpolluted Pere Marquette River (Fee, 1971).

In unpolluted rivers, such as the Manistique, Pere Marquette, Peshtigo, Ford, and Escanaba, concentrations of total soluble phosphorus were lowest, ranging from 0.03 to 0.08 mg/liter (Table 5), whereas the largest concentrations (1.59 and 1.8 mg/liter) were in Burns Ditch, a tributary from a highly industrialized area, and the Rapid River, a tributary to Green Bay. Both of these rivers have low flows and have smaller loadings than most of the rivers with larger flows, indicating again that large loadings are diluted where sufficient flow is available and that data on both flow and concentration are necessary to evaluate a potential source of nutrients.

Ratios of $\text{SiO}_2\text{:P}$ also vary greatly among the tributaries because concentrations of silica vary much less than concentrations of total soluble phosphorus (Table 5). Ratios range from less than 20:1, for Burns Ditch and Milwaukee River, which have relatively large concentrations of total soluble phosphorus, to more than 500:1, for the Manistique, Pere Marquette, and Ford rivers, which have relatively small concentrations of total soluble phosphorus.

The ratio of $\text{NO}_3\text{-N:PO}_4\text{-P}$ is only 7:1 for the estimated long-term inputs to the lake (Table 4), suggesting a deficiency of nitrogen. But if all forms of nitrogen are included, the ratio is 24:1, indicating that nitrogen is present in excess relative to phosphorus. All forms of nitrogen should be

considered, especially since combined inorganic nitrogen, primarily in the form of nitrates, is the basic form of nitrogen in the open waters of the three upper lakes. Nitrites are not stable chemically in the oxygenated waters, and ammonia is apparently cycled very rapidly since large concentrations are not present in the open water.

Similar proportions of nitrate and phosphate have been reported by other workers. Stephenson and Waybrant (1971) found that the Grand River discharged 1.03×10^6 kg total $\text{PO}_4\text{-P}$ and 4.00×10^6 kg $\text{NO}_3\text{-N}$ annually. The N:P ratio is 4:1 (less than reported by Ayers in Table 4, partly reflecting the fact that total soluble phosphate was measured instead of total phosphate). Input of total soluble $\text{PO}_4\text{-P}$ from the Grand River was 0.29×10^6 kg annually (Table 5), or about 30% of the input of total $\text{PO}_4\text{-P}$ measured by Stephenson and Waybrant (1971).

These data indicate that since $\text{SiO}_2\text{:P}$ ratios are greater than 500:1 (Table 5) in the unpolluted tributaries to Lake Michigan, there is an excess supply of silica relative to supplies of phosphorus, and that phosphorus is limiting. Likewise, other tributaries have excess amounts of phosphorus from pollution sources with ratios of $\text{SiO}_2\text{:P}$ that are less than 50:1. Where $\text{SiO}_2\text{:P}$ ratios are low, diatoms in the phytoplankton assemblages will be limited by supplies of silica, and excess supplies of phosphorus can then be used by green and blue-green algae.

Inputs of phosphorus to Lake Michigan are smaller than might be predicted on the basis of population distribution, because most of the domestic wastes from Chicago, the largest population center, are not released into

the lake. These wastes are diverted via the Chicago Sanitary Canal to the Illinois River and ultimately go into the Mississippi River.

CONTROL OF EUTROPHICATION BY PHOSPHORUS

In the early stages of eutrophication, phytoplankton growth and primary production are limited by supplies of phosphorus. Several lines of evidence to support this statement are available from recent studies at the Great Lakes Research Division, The University of Michigan. Direct evidence is available from nutrient enrichment studies in the field (Schelske and Stoermer, 1971a; Schelske et al., 1972) and from unpublished results of laboratory studies at the Division. The fact that these studies provide direct evidence that phosphorus limits algal growth in Lake Superior and Lake Michigan is significant in itself. These results agree with the statement by Lee (1970) that the open waters of Lakes Huron, Michigan, and Superior have phosphorus-limited algae. Other evidence for control of eutrophication by inputs of phosphorus is provided by relationships between concentrations of phosphorus and primary productivity, chlorophyll α , and Secchi disc transparency.

Effects of phosphorus, silica, and nitrogen on phytoplankton assemblages in Lake Michigan were tested by experimentally simulating nutrient inputs from tributaries. Experiments were conducted by adding nutrients to clear plastic bags containing lake water and natural phytoplankton assemblages. The bags were anchored in the lake to simulate in situ light and temperature conditions. In these experiments, added phosphorus increased the growth of phytoplankton, but phosphorus produced a greater effect when added in combination with silica. Added silica was important because phytoplankton assemblages were composed mainly of diatoms. Nitrogen supplies were adequate

and did not limit phytoplankton growth even in the presence of added supplies of phosphorus, silica, or both. Results are significant in relation to nutrient inputs since effects were produced with added phosphorus concentrations of 20 $\mu\text{g/liter}$ in Lake Michigan (Schelske and Stoermer, 1971a) and of less than 10 $\mu\text{g/liter}$ in Lake Superior (Schelske et al., 1972).

Primary productivity and standing crops, as reflected by chlorophyll α concentrations and Secchi disc transparency, appear to be controlled by phosphorus (Table 6). Concentrations of chlorophyll α from the open lake stations are lowest in Lake Superior, larger in Lake Huron, and largest in Lake Michigan, with phosphorus having the same relationship among the three lakes. There is nearly an order of magnitude range of rates of primary productivity for Lake Superior and Lake Michigan. Lake Huron has intermediate values of primary productivity. Data on primary productivity (Table 6) agree with other available data that have been reviewed previously (Schelske and Callender, 1970). Secchi disc transparency, like chlorophyll α , a function of standing crop, is inversely related to the other parameters that increase as concentrations of phosphorus increase.

The need for data on total phosphate or total particulate phosphate in relation to phytoplankton production in phosphorus-limited waters has been indicated previously (Schelske and Callender, 1970). These two forms of phosphate are the ones that can best be used to determine trophic state. If phosphate is limiting, luxury consumption of phosphate should be minimized, and most of the available phosphate will be incorporated in phytoplankton as particulate phosphorus. Under this condition one would expect a smaller percentage difference between particulate and total phosphorus

Table 6. Averages and standard deviations for chlorophyll, primary productivity, Secchi disc transparency and total phosphorus in the Great Lakes. Data collected by Great Lakes limnology class from The University of Michigan's Biological Station, except as noted.

Location	Chlorophyll <i>a</i> (mg m ⁻³)	Primary Productivity (mg C m ⁻³ hr ⁻¹)	Secchi Disc Transparency (m)	Total P (mg m ⁻³)
Superior				
Near shore	1.5 ± 0.14(5)	0.73 ± 0.20(4)	6.6 ± 1.1 (5)	
Open lake	0.66 ± 0.42(27)	0.37 ± 0.17(18)	12.6 ± 3.4 (30)	2.5 ± 1.5(14)*
All	0.78 ± 0.49(32)	0.44 ± 0.22(22)	11.8 ± 3.8 (35)	
Huron				
Open lake	0.79 ± 0.47(18)	1.1 ± 0.45(13)	8.0 ± 2.4 (18)	4.6 ± 2.7(11)*
Saginaw Bay	6.5 ± 3.5 (7)	30. ± 19. (5)	2.5 ± 1.8 (7)	
Michigan				
Northern	1.3 ± 0.62(7)	2.2 ± 0.9 (4)	4.8 ± 0.6 (6)	6-7 [†]
Southern		3.6 ± 2.3 (14) [†]		7-13 ^{††}
Erie				
W. basin (north)	3.7 ± 1.3 (5)	10. ± 3.1 (3)	2.0 ± 0.4 (5)	
W. basin (south)	12.1 ± 3.8 (7)	59. ± 19. (5)	2.0 ± 0.53(7)	55. ± 46. (15) [§]
C. basin	7.3 ± 6.7 (8)	24. ± 15. (5)	4.4 ± 1.2 (8)	28. ± 25. (15) [§]
All	8.1 ± 5.7 (20)	34. ± 25. (13)	3.0 ± 1.5 (20)	

* CCIW (1968), Limnological Data Report No. 1, Lake Huron Cruise 68-201 (August 5-13); Lake Superior Cruise 68-301 (August 18-28).

** Schelske and Callender (1970).

[†] Holland (1969). No standard deviations for averages.

^{††} Risley and Fuller (1965). No standard deviations for averages. Data omitted for southern-most stations.

[§] CCIW (1968), Limnological Data Report No. 1, Lake Erie Cruise 68-102 (May 17-24); 68-104 (June 15-19); and 68-108 (July 29-August 3). Limnological Data Report No. 2, Lake Erie Cruise 68-109 (August 31-September 3); 68-111 (September 28-October 4); 68-112 (November 4-10).

than if phosphate were not limiting and that concentrations of particulate or total phosphate in the water would be correlated with standing crop.

Data in Table 6 and data from nutrient enrichment studies lead me to conclude that of the upper Great Lakes, Lake Superior is the most oligotrophic lake and Lake Huron is more eutrophic than Lake Superior but not as eutrophic as Lake Michigan. Furthermore, the data leads me to conclude that phosphorus controls eutrophication, which also increases the demand for silica and nitrogen as standing crops of phytoplankton increase.

Role of Silica

The role of silica is important because diatoms that dominate the pristine phytoplankton flora of the upper Great Lakes require silica for frustule formation. Because silica is utilized by diatoms, concentrations in the water would be expected to decrease as greater and greater standing crops are produced or as eutrophication is accelerated. Without silica, diatoms cannot compete with other groups of algae, particularly greens and blue-greens, for available pools of nutrients. It has been concluded recently that silica depletion in Lake Michigan is the result of inputs of phosphorus and that as a consequence of silica depletion, phytoplankton assemblages in Lake Michigan will shift from those dominated by diatoms to those with increasing proportions of blue-green and green algae (Schelske and Stoermer, 1971b). Such a change in primary producers was predicted to have adverse effects on the ecosystem due to associated changes at other trophic levels.

For diatoms to dominate the phytoplankton assemblage during accelerated eutrophication, supplies of silica would have to be adequate to compensate

for the increased inputs of phosphorus. For example, if the $P:SiO_2$ ratio in diatoms is 300:1, then with an input of 30 μg P/liter, 9.0 mg SiO_2 /liter will be utilized by diatoms. Based on data in Table 5, silica supplies in the Great Lakes are inadequate to support diatom populations in the waters from many tributaries, given the present loads of phosphorus. In addition, Redfield, Ketchum, and Richards (1963) have stated that phosphorus and nitrogen are cycled more rapidly than silica, indicating that conclusions based on ratios of $SiO_2:P$ underestimate the effect of increased inputs of phosphorus. In Lake Erie, standing crops of diatoms did not increase proportionately to other forms of algae as eutrophication progressed (Hohn, 1969; Davis, 1964, 1966), indicating that silica supplies were not adequate for diatoms to compete with other algae for available pools of other nutrients.

Role of Nitrogen

Like silica, nitrogen depletion associated with eutrophication also affects the composition of the phytoplankton populations. However, depletion of nitrogen, unlike the depletion of silica, cannot be compensated for by a shift to producers that do not require nitrogen. Instead, producers shift to those that can fix free nitrogen, including several species of blue-green algae. Many of these blue-green algae are indicative of poor water quality.

Nitrate reserves in the surface waters, as indicated by differences in concentrations between bottom and surface waters, are related inversely to trophic state in the upper Great Lakes (Table 7): Lake Superior has the greatest reserve of nitrate; Lake Michigan, the smallest. Reserves of

Table 7. Average concentrations of soluble silica and nitrate nitrogen in the Great Lakes. Bottom values are from samples taken below the photic zone.

Locations	No. of Stations	SiO ₂ (ppm)		NO ₃ -N (ppb)	
		Surface	Bottom	Surface	Bottom
Lake Michigan					
South, July 1969 [*]	16	0.15 ± 0.07	1.63 ± 0.49	101 ± 18	218 ± 29
North, August 1969 [*]	16	0.26 ± 0.07	1.26 ± 0.16	116 ± 7	216 ± 36
Superior					
July 1969 [*]	20	1.87 ± 0.11	2.01 ± 0.14	269 ± 21	276 ± 16
Open lake, July 1970 ^{**}	25	2.28 ± 0.07	2.28 ± 0.20	254 ± 14	264 ± 7
Huron					
Open lake, July 1970 ^{**}	19	0.87 ± 0.22	1.79 ± 0.16	139 ± 29	175 ± 46
Erie					
W. basin, July 1970 ^{**}	7	0.66 ± 0.26	0.85 ± 0.20	86 ± 33	125 ± 51
C. basin, July 1970 ^{**}	8	0.25 ± 0.10	1.36 ± 0.76	34 ± 24	103 ± 57
Saginaw Bay, July 1970 ^{**}	7	1.03 ± 0.28	1.06 ± 0.21	36 ± 43	82 ± 52
Green Bay, August 1969 [*]	3	0.26 ± 0.07	2.73 ± 0.93	39 ± 13	190 ± 46

^{*}Data from Schelske and Callender (1970).

^{**}Unpublished data collected by class in Great Lakes limnology from The University of Michigan's Biological Station, Summer 1970.

nitrogen in the photic zone are depleted through utilization of nitrogen by phytoplankton. In very eutrophic situations such as Green Bay, Saginaw Bay, and western Lake Erie, nitrogen reserves are relatively smaller (Table 7) and may be depleted.

Nitrogen reserves are no longer useful in the assessment of eutrophication when significant amounts of nitrogen are fixed biologically. Usually nitrogen fixation would not be important in the early stages of eutrophication. There is neither indication nor evidence that nitrogen fixation is a significant factor in Lake Superior or in the main bodies of Lake Michigan and Lake Huron. Nitrogen fixation by blue-green algae must occur in very eutrophic situations such as Saginaw Bay, Green Bay, and western Lake Erie because the low nitrate concentrations provide relatively small supplies of nitrogen for growth of phytoplankton (Table 7). Large blooms of blue-green algae are common in Lake Erie during the summer, particularly in the western basin. Sources of nitrogen for the relatively large populations of phytoplankton must be either from ammonia, nitrite, or nitrogen fixation, and supplies of ammonia and nitrite are not adequate for the large standing crops that must be present (Table 6). It is also possible that nitrogen fixation by blue-greens occurs in some areas of Lake Michigan. Low nitrate values (less than 0.010 mg/liter) have been observed at a nearshore location (Schelske, Stoermer, and Feldt, 1971). In the open waters of the three lakes, there is presently no need for nitrogen fixation because nitrogen reserves are sufficient for the amounts of nitrogen presently being utilized by phytoplankton (Table 7). Concentrations of nitrate vary little in the surface

waters of Lake Huron (Figure 3), with the exception of Saginaw Bay, and, as indicated in Table 7, provide large reserves of nitrogen for the present supplies of phosphorus (Table 6).

Discussion of combined inorganic nitrogen in the open lake can be restricted on a quantitative basis to nitrate because concentrations of ammonia and nitrite are small. Nitrogen in the water of the upper three lakes is more conservative than either phosphorus or silica. Silica is not as conservative as nitrogen because it is required by diatoms in amounts 4 to 30 times greater than nitrogen based on $\text{SiO}_2:\text{P}$ ratios of 70:1 to 500:1 and a N:P ratio of 16:1. Increases in standing crops due to early stages of accelerated eutrophication have been primarily diatoms. Nitrate, therefore, is not depleted as rapidly as silica by inputs of phosphorus. In nutrient enrichment experiments, silica was reduced from 1.7 mg SiO_2 /liter to limiting or nearly limiting concentrations by additions of 0.020 mg $\text{PO}_4\text{-P}$ /liter, but nitrate was not depleted and was reduced from 0.35 to 0.09 mg $\text{NO}_3\text{-N}$ /liter (Schelske and Stoermer, 1971a). In this experiment, 6 to 7 times more silica was utilized than nitrate nitrogen.

Figure 3. Isopleths of surface nitrate nitrogen (mg/liter) in Lake Huron, August 1968. Contours drawn from data in CCIW (1968).

DEPLETION OF SILICA IN THE UPPER GREAT LAKES

The relationship between silica depletion and growth of diatoms in Lake Michigan has been recognized by several investigators (Risley and Fuller, 1965; Powers and Ayers, 1967). Lund (1965) stated that one of the first signs of increasing fertility is the appearance of a seasonal, usually vernal, decrease in the silica content, and that the data of Ayers et al. (1968) for southern Lake Michigan were a striking example. Schelske and Stoermer (1971b) have predicted that silica depletion will cause phytoplankton assemblages to shift from diatoms to green and blue-green algae. Kilham (1971) stated that quantity of silica utilized by diatoms could be related to the degree of eutrophication. Owens (1970) also has reviewed the role of silica in eutrophication.

Lake Michigan

Gradual depletion of silica is indicated from data collected at municipal water intakes at Chicago (Figure 4). In 1926, the average concentration of silica was apparently 6 to 8 mg/liter. Reliability of these early data may be questioned, but recent data on concentrations in tributary inputs (Table 5) indicate that 6 to 8 mg/liter is not unreasonable. There is no reason to suspect that the concentration of silica in tributaries has changed greatly in the past 40 years (Table 5); yet, in 1969, average silica concentrations in the bottom waters were less than 2.0 mg/liter (Table 7). The average concentration and the total amount of silica appear to have decreased by more than 75% during the past 40 years, depleting the net silica reserve.

Figure 4. Yearly average concentrations of silica (mg/liter) at municipal water intakes in Lake Michigan (from Powers and Ayers, 1967).

As early as 1955, synoptic surveys in Lake Michigan indicated a relationship between the depletion of silica and the degree of pollution (Ayers et al., 1958, Figures 33 and 46). Surface silica values in August were generally lower in the southern part of the lake than in the northern part and as low as 0.6 mg/liter in a small portion of the southern basin. Data from 1962-64 (Table 8) also indicate an increasing concentration of silica in surface waters from south to north and that average concentrations in the southern part of the lake were as low as 0.4 mg/liter. More recent values for silica concentrations in surface waters (Schelske and Callender, 1970) indicate a range from 0.1 to 0.4 mg/liter. Lower concentrations were present in the southern parts of the lake in July than in the northern parts in August (Table 7).

Lake Huron

Synoptic surveys of Lake Huron from August 1954 and August 1968 provide data on silica distribution that can be compared with those from Lake Michigan. In August 1954, concentrations of silica in surface waters ranged from 1.4 to 2.4 mg/liter over much of the lake (Ayers et al., 1956, Figure 39). In the extreme southern end of the lake, south of Saginaw Bay, concentrations were generally from 1.6 to 2.0 mg/liter. In August 1968, concentrations of silica in the southern end, south of Saginaw Bay, were 1.0 mg/liter or less, ranging as low as 0.6 mg/liter (Figure 5). Furthermore, except for a small area in the northern end of the lake, where Lake Superior water enters Lake Huron, concentrations of silica were generally less than 1.1 mg/liter, or about half the concentrations measured in 1954. Water entering Lake Huron

Table 8. Concentrations of total phosphate, nitrate nitrogen, and silica in southern Lake Michigan, 1962-64. Data presented are averages and ranges of all data collected and averages for silica by depths and seasons.* Data are in ppm.

Nutrients	41°30' - 41°45'		41°45' - 42°00'		42°00' - 42°15'		43°30' - 43°45'	
	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range
PO ₄ (Total)	0.06	0-0.57	0.04	0-0.29	0.02	0-0.16	0.02	0-0.08
NO ₃ -N	0.12	0-0.84	0.09	.01-0.38	0.10	.01-0.29	0.19	.02-0.27
SiO ₂	1.7	0.4-3.7	1.6	.50-3.0	1.9	.70-4.2	2.90	1.80-5.1

SiO ₂	Spring	Summer	Fall	Spring	Summer	Fall	Spring	Summer	Fall	Spring	Summer	Fall
Surface	1.3	1.5	1.4	1.9	1.2	1.5	2.8	1.4	1.7	2.6	2.1	---
Middle	---	1.4	1.4	2.7	2.1	1.6	2.4	1.2	1.9	2.7	3.5	---
Bottom	---	2.7	2.0	2.8	2.6	1.6	3.5	2.4	1.9	2.7	3.8	---

* Risley and Fuller (1965), Tables 1A, 3.

from Lake Michigan at the Straits of Mackinac had silica values of less than 0.6 mg/liter (Figure 5), indicating the low silica concentrations of this water which may be partly mixed with Lake Superior water.

Data presented in Table 9 indicate the reduction in silica concentrations which has been occurring in Lake Huron, and, like Lake Michigan, indicate that the reserve of silica is being depleted since the concentrations of silica in surface and bottom water have decreased over the past 14 to 16 years. In contrast to Lake Michigan, however, the difference in concentrations between surface and bottom water samples is less in Lake Huron, reflecting the more eutrophic state of Lake Michigan.

Lake Superior

Lake Superior has the largest concentration of silica of the three lakes, about 2.0 to 2.2 mg/liter in surface waters (Table 7). Available data indicate that there is no more than a 0.2 mg/liter difference between surface and bottom waters. Again, let me point out that in Lake Superior, where surface and bottom silica concentrations differ the least, the slowest rate of eutrophication exists.

Relation to Seasonal Cycle

In small lakes, the seasonal cycle of silica has been used to explain the periodicity of diatoms (Lund, 1954). In these lakes, silica is regenerated from diatoms or the sediments in the hypolimnion when oxygen is depleted during periods of stagnation in summer and winter (Mortimer, 1941, 1942), and the supply is then replenished during the fall and spring overturns.

Figure 5. Isopleths of surface silica (mg/liter) in Lake Huron, August 1968. Contours drawn from data in CCIW (1968).

Table 9. Silica and nitrate in open waters of Lake Huron (values in ppm).
Bottom depths represent samples taken below the photic zone.

Year and Sample Size	SiO ₂		NO ₃ ⁻ N	
	Surface	Bottom	Surface	Bottom
1954 (42) [*]	1.83 ± .32	2.37 ± .58	---	---
1956 (16) ^{**}	1.6 ± .12	2.6 ± .13	---	---
1968 (57) [†]	1.07 ± .15	1.76 ± .29	0.202 ± .019	0.249 ± .016
1970 (9) ^{††}	0.87 ± .22	1.79 ± .16	0.139 ± .029	0.175 ± .046

^{*} Ayers et al. (1956), August 25, 1954.

^{**} Allen (1964), August 3 and September 15, 1956. Only six samples for bottom depths.

[†] CCIW (1968), August 5-13, 1968.

^{††} Unpublished data collected by class in Great Lakes limnology from The University of Michigan's Biological Station, August 28-30, 1970.

A similar cycle does not occur in the upper Great Lakes because there is no hypolimnetic oxygen depletion. A seasonal cycle occurs in Lake Michigan because during the fall turnover, silica-rich water from the aphotic zone is mixed with surface water, increasing the concentration in the surface waters (Table 8). In contrast to small eutrophic lakes, the differences in concentration are due more to mixing depleted surface waters with bottom waters than to increased concentrations in the bottom waters from regeneration of silica. Risley and Fuller's data for Lake Michigan represent the best set of data (Table 8) to show seasonal variations in silica concentrations. Smaller seasonal differences occur in Lake Huron, and differences in Lake Superior are even less, as can be seen from the data in Table 7.

EUTROPHICATION ASSESSMENT MODEL

Eutrophication is accelerated by inputs of phosphorus and controlled by concentrations or levels of phosphate in the upper Great Lakes. Inputs of phosphorus promote growth of algae and utilization of silica by diatoms and nitrate by diatoms and other components of the phytoplankton assemblage. Net utilization of silica and nitrate by phytoplankton assemblages in the euphotic zone during summer stratification is related to the differences between concentrations of either nutrient in bottom and surface samples (Table 7). Concentrations in the aphotic zone or in bottom samples represent the concentration in the spring and also represent the average winter concentration for the entire lake or portions of the lake less the amount utilized by phytoplankton during spring circulation.

Data on silica and nitrogen, therefore, can be modeled to determine the state and rate of eutrophication: (1) trends in the average bottom concentrations for each year are a measure of whether or not the total reserve and total supply of either nutrient is changing, and if so, whether it is increasing or decreasing; (2) trends in net utilization in the photic zone indicate whether or not production of phytoplankton is changing and if so, whether it is decreasing or increasing. Net utilization cannot be calculated from differences in concentrations alone but must be calculated as total net utilization, which equals the integral of the change in concentration with depth for the volume of the photic zone. The volume of the photic zone must be considered since it may vary from year to year. For the model to be valid, a significant part of the photic zone obviously cannot be in the hypolimnion.

In each lake, the slopes of the lines for average bottom concentrations and for total net utilization with time are functions of the rate of eutrophication, whereas the bottom concentration or the quantity of either nutrient utilized (total net utilization) is a measure of trophic state. The limits of these models have been discussed under the section on roles of silica and nitrogen.

For the model proposed, consideration of net utilization is adequate because (1) the total quantity of nutrients in the lakes is large compared to either inputs from tributaries or to losses with outflows; (2) data for total net utilization for each year are based on measurements for that year only; (3) data used are the integrated results of all the environmental dynamics affecting nutrient supply and demand, including physical, chemical, and biological processes; and (4) net losses, as measured by differences between inputs and outflows (Table 4), are due to environmental processes, mainly biological processes. Much higher concentrations of silica and nitrate in tributaries (Table 5) than in the lake (Table 7) indicate that nutrients are lost eventually to the sediments but do not indicate that the lake has reached an equilibrium concentration based on the higher concentrations of silica and nitrogen in the inputs.

Future decisions regarding pollution control of the Great Lakes could be evaluated from the proposed model. Limitations on inputs of phosphorus from removal of increased amounts at sewage treatment plants, from elimination or reduction of phosphates in detergents or from other restrictions and controls on practices that utilize phosphates, could decrease or reverse the rate of eutrophication. Some of these practices may significantly alter

the chemical composition of inputs and possibly nullify some of the assumptions inherent in the model.

For example, if silica were substituted for phosphates in detergents, the inputs of phosphorus would be decreased, while the inputs of silica would be increased. In this example, the results probably would not affect the utility of the model because the amount of silica added via detergents, unlike the present amounts of phosphorus added, would be only a small fraction of the large concentrations of silica normally present in tributaries. Silica results would be biased, but probably on the order of 10%. If silica were changed significantly, then the model would have to be based on nitrate only.

A situation similar to that described for silica could occur if compounds containing nitrogen were substituted for phosphorus in detergents. Because concentrations of nitrogen in tributaries are smaller than those for silica, the relative effect on the model might be larger than in the case of substitution of silica for phosphorus.

The most serious effect on the model would be if both silica and nitrogen substitutes were used for phosphates in detergents. The major effect, however, would be on the average bottom concentrations with time and not on the net utilization of silica or nitrate because total net utilization is determined yearly and would not be affected significantly by changes in inputs.

CONCLUSIONS

The following is a list of conclusions I have drawn from the evidence presented in this paper, supported by current research efforts.

- (1) Of the major nutrients, phosphorus is the limiting nutrient in the upper Great Lakes; thus, phosphorus inputs and supplies control the rate of eutrophication.
- (2) Silica utilization is a good measure of rate of eutrophication, but because phytoplankton assemblages in the Great Lakes are composed mainly of diatoms, silica depletion, given current inputs and supplies, occurs sooner than the depletion of nitrate nitrogen.
- (3) Nitrate-nitrogen utilization is also a valid measure of rate of eutrophication until nitrogen is depleted or until significant nitrogen fixation occurs. Both probably occur more or less simultaneously and are accompanied by blooms of blue-green algae.
- (4) Silica and nitrate-nitrogen depletion are conditions which eventually favor the growth of green and blue-green algae and not diatom assemblages.

- (5) Inputs of phosphorus and depletions of silica and nitrate nitrogen can be used in a model to predict and assess the rate and state of eutrophication. Utilization of silica and nitrate nitrogen can be used in the model as long as the nutrient of interest is not depleted in the photic zone during the summer, or if it is depleted, the time of depletion must be known.

NEED FOR ADDITIONAL RESEARCH

One of the severe limitations of the data I have presented is the limited number of collections in space and time. Many of the chemical data are available only for surface and bottom samples, and data from municipal water intakes, of course, are from one depth only, but represent the only data collected regularly over long periods of time. Even with the temperature profile and what limited data is available, it is difficult, if not impossible, to extrapolate a chemical profile, which is needed for calculations of total net utilization, and a nutrient budget based on increases or decreases in the total amounts of different nutrients in the lakes. For lakes whose average depths range from 60 to 145 km (Table 2), such a lack of data would introduce large errors for the lake as a whole.

Another serious limitation in any of the data for the upper lakes is the lack of seasonal studies and frequent collections. Few data, except those from municipal water intakes, are available from the winter. In recent years, some of these shortcomings have been corrected. Notable among these are the year-round monitor surveys by the Canada Centre for Inland Waters, Burlington, Ontario; but, unfortunately, these cruises have been restricted to Lakes Erie and Ontario, which are the most eutrophic. Such data are needed to determine the total quantity of any given nutrient in the lake at any given time and to calculate the net utilization of any given nutrient during a specified period of time.

As has been pointed out previously, seasonal data are needed in models that could be used to predict and assess the rate and state of eutrophication.

Other, more detailed and complex mathematical models are needed to predict the rate of eutrophication based on changes in nutrient concentrations, including inputs of phosphorus, and on inputs and losses of soluble nutrients from the system.

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