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THE ROLE OF SEDIMENTS IN EUTROPHICATION

-- A PRELIMINARY STUDY

by

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F I N A L R E P O R T

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ABSTRACT

THE ROLE OF SEDIMENTS IN EUTROPHICATION -- A PRELIMINARY STUDY

The report is divided into two parts. The first part contains the results of an extensive literature survey concerning the distribution of nutrients in waters and sediments and mechanisms for describing the mobility of phosphate nutrients in aquatic systems. The horizontal and vertical distribution of nutrients for Great Lakes waters in other U.S. as well as foreign lakes and rivers are presented. Phosphate nutrient mobility mechanisms are organized in a single table based upon two types of transformations: special and chemical. Twenty-four possible types of transformation categories are employed based upon the organic or inorganic form of the phosphate itself and the organic or inorganic type of spatial domain in which the phosphate is located.

In the second part a laboratory technique to aid in the study of the hydrodynamic transport of phosphates in saturated soils is described. The technique is based upon a modification of the one dimensional consolidation test and employs radionucleid tracers. Typical test results are presented, though the complete study of the phenomenon is the subject of a subsequent project in progress.

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INTRODUCTION

The objective of this research was to perform a feasibility study to aid in determining the amount and type of association between sediments and phosphate nutrients. The research consisted of two phases. The first phase involved a literature review to determine:

1. The present state of knowledge concerning where phosphates occur in sediments. This included a study of the quantities of phosphates reported in sediments as well as a study of horizontal and vertical distributions within the sediments.

2. Mechanisms by which phosphates are held in sediments and mechanisms that result in mobility of phosphates within the sediments. During the course of the research it became necessary to extend the scope of this aspect of the study to include mobility mechanisms for phosphates in the entire aquatic system because complex interactions rendered the treatment of the fates of phosphates within sediments only unfeasible.

The second phase of the research consisted of the development of laboratory techniques for studying the mobility of phosphates in sediments. The primary objectives of these studies were:

1. to develop capabilities within the UICC laboratories to determine phosphate contents of sediments using colorimetric techniques; and
2. to develop P^{32} tracer techniques to measure transport phenomena of phosphates in sediments.

The objectives of this research were met during the past year and the results are described in this report. In addition, the inter-relationships between this project (A-047) and a current project (A-053, Dynamic Interaction between Phosphate Nutrients and Sediments) are discussed.

PHASE I - RESULTS OF THE LITERATURE SEARCH

A. NUTRIENT CONTENTS IN AQUATIC SYSTEMS

Established Levels of Excessive Nutrient Content

It is generally agreed by ecologists and biologists that phosphorous and nitrogen are two of the most important nutrients required to support growth of aquatic plants (Hutchinson, 1957). Even though it is difficult to clearly define the influence of single elements on the growth rate of aquatic organisms, a body of literature does exist showing that there is a minimum level of nutrient content below which there is little or no growth of aquatic plants. This level may be considered to be a lower limit against which to measure excessive nutrient contents of rivers and lakes. Above this minimum, there is a second level where experiments have shown that accelerated growth of aquatic plants including algae and phytoplankton develops. When nutrient contents exceed these levels, the eutrophication process may accelerate rapidly.

The results of laboratory studies that have been performed to aid in establishing these nutrient levels are shown in Table 1. In general, it may be seen that the minimum phosphorous content needed for growth of algae is below 0.01 mg/l and may even be less than 0.001 mg/l. Phosphorous concentrations in excess of 0.1 mg/l often cause accelerated growth of various types of phytoplankton and algae.

TABLE 1

NUTRIENT LEVELS REQUIRED FOR ALGAE GROWTH

Type of Algae	Lake	Phosphate or Phosphorus Concentration		Nitrogen Concentration		Notes	References
		Min. Needed for Growth	Causing Accelerated Growth	Min. Needed for Growth	Causing Accelerated Growth		
Algal blooms	Madison Lakes	0.01 mg/l (inorganic phosphorus)		0.3 mg/l [inorganic Nitrogen (NH ₃ , NO ₂ , NO ₃)]		Lakes Waubesa and Kegonsa had an excessive amount of inorganic phosphorus at all time of the year, usually 0.25 mg/liter or more. For the other lakes studied, the minima of inorganic phosphorus was less than 0.01 mg/liter.	Sawyer (1947)
Algal blooms		0.015 mg/l (phosphate)		0.3 mg/l (nitrate)			Lackey (1961)
Asterionella formosa	English Lake District	0.06 to 4.2 µg per million cells (phosphorus)		6-12 µg per million cells (nitrogen)		The content of phosphorus varied in both the natural and cultural populations. The ability of the organisms to store phosphorus in excess of their immediate needs.	Lund (1950)
Asterionella formosa		1 microgram/liter or 1 µg/liter (phosphorus)				The only limiting requirement was 0.06 µg of phosphorus/10 ⁶ cells.	Mackereth (1953)
Anabaena flos-aqual	Southern Saskatchewan, Canada	0.15 to 0.3 mg/l (phosphate)				The concentrations of orthophosphate during the period of blooms varied widely.	Hammer (1964)
Microcystis aeruginosa		0 to 0.30 mg/l (orthophosphate)					
Algal blooms	Wisconsin Lakes	0.015 mg/l (inorganic phosphorus)		0.3 mg/l (inorganic nitrogen)		An analysis of the benthic organisms indicated that Chaoborus Chironomus, and Oligochaetes were most numerous in Lake Mendota.	Sawyer (1945)
Pediastrum boryanum	Artificial pond in London garden	0.09-1.8 ppm		2.1-5 ppm			Chu (1942)
Staurastrum paradoxum	Barn Elms Reservoir	0.1-1.8 ppm		2-10 ppm		Collected in Jan. 1939 from the No. 8 Barn Elms Reservoir at Hammersmith.	
Botryococcus baraurii	Small artificial pond, London	0.09-18 ppm		1.4-14 ppm			Chu (1942)
Nitzoschia palea	Stream, London	0.2-1.8 ppm		5-10.5 ppm		Was isolated from the stream leading into the pond in the Cambridge Botanic Garden.	
Fragilaria crotonensis	Isolated from the Barn Elms Reservoir	0.2-1.8 ppm		1.65-10.5 ppm			
Dinobryon divergens		The Lower Limit was less than 0.02 mg/l (phosphorus)	The Upper Limit was less than 0.02 mg/l (phosphorus)			Some algae had a luxury consumption of phosphorus, e.g. Scenedesmus had the ability to accumulate phosphorus beyond its needs and Asterionella, under some circumstances, was able to reproduce merely by using the phosphorus stored within the cell itself.	Rodhl (1948)
Asterionella formosa		The Lower Limit was less than 0.02 mg/l (phosphorus)	The Upper Limit was greater than 0.02 mg/l (phosphorus)				
Scenedesmus quadricornis		The Lower Limit was greater than 0.02 mg/l (phosphorus)	The Upper Limit was greater than 0.02 mg/l (phosphorus)				
Coccolithis pericystis			0.4 mg/l (phosphorus)		13.6 mg/l (Nitrate Nitrogen)		Gerloff (1958)

TABLE I
NUTRIENT LEVELS REQUIRED FOR ALGAE GROWTH (Continued)

Type of Algae	Lake	Phosphate or Phosphorus Concentration		Nitrogen Concentration		Notes	References
		Min. Needed for Growth	Causing Accelerated Growth	Min. Needed for Growth	Causing Accelerated Growth		
Chlorophyceal		2-3% of the dry weight of the cells (phosphorus)		6.5-8.3% of the ash free weight of the cultures of this organism			Ketchum (1954)
Asterionella formosa		1 mg/l or 1 µg/l (phosphorus)				The natural concentration of phosphorus in Lake Windermere varied between 1 µg in Summer to 2 µg in Winter	Mackereth (1953)
Various types		0.05 mg/l (phosphorus)	0.1-2.0 mg/l	0.2 mg/l	1-7 mg/l		Chu (1942)
Green Alga Pediastrum boryanum		0.09-1.78 mg/l (phosphate phosphorus)				When the nitrogen source was ammonia.	Chu (1943)
Various types		0.09-1.8 mg/l [phosphate (PO ₄) phosphorus]		0.9-3.5 mg/l (Nitrate-Nitrogen)			Chu (1943)
Various types		0.009 mg/l (phosphorus)		0.1 mg/l		The growth of algae was limited when the concentrations of Nitrogen and Phosphorus dropped below 0.1 mg/l and 0.009 mg/l, respectively. Concentrations of either nitrogen or phosphorus higher than 45 mg/l produced a marked inhibiting effect on the organisms studied.	
Asterionella gracillima	isolated from the Barn Elms Reservoir & from Lake Windermere	0.18-9 ppm		1.7-17 ppm			Chu, S. P. (1942)
Tabellaria flocculosa	Lake Windermere	0.2-1.8 ppm					Chu, S. P. (1942)
Cyanophyta (blue-green algae)		10 ppb (phosphorus)					Sewage and Industrial Wastes
Sphaerotilus		0.02 mg/l (phosphorus)					Crowley, W. A. (1958)
Chlorella pyrenoidosa, the unicellular green alga		0.05 mg/l (detergent phosphorus)	concentration above 0.1 mg/l of detergent phosphorus			With phosphorus-starved cells.	Maloney, T. E. (1966)

With nitrate nutrients, somewhat higher concentrations seem to be necessary for growth of aquatic plants. Nitrogen contents greater than 0.1 mg/l are necessary for growth, while measured concentrations greater than 1 mg/l have been observed to lead to accelerated plant growth.

An attempt has been made to establish permissible nutrient and pollutant contents in Great Lakes harbors in the Chicago area. The Calumet Area Enforcement Conference established water quality measurement criteria, shown in Table 2. It may be seen that they set a criterion for maximum total phosphorous content of not more than 0.033 mg/l and the maximum permissible level of ammonium nitrogen ($\text{NH}_3\text{-N}$) of not more than 0.12 mg/l. It is interesting to note that total phosphorous levels are one-third the levels permissible for cyanides, indicating the extreme concern expressed by the Conference over lake phosphate contents.

Nutrient Contents in Great Lakes Waters and Sediments

Data have been assembled from the literature giving the quantities and distribution of nutrients in the Great Lakes. The average total phosphorous contents as determined during the 1950's as reported by Beeton (1960) are shown in Fig. 1. It is seen that the phosphorous contents vary from .012 mg/l for Lake Michigan to .0443 mg/l for Lake Erie. The sampling locations and number of samples obtained are given in Table 3. These measurements represent averages and considerable variation was found with position within the Lakes. For Lake Michigan values varied as much as 0.006 mg/l vertically with the highest value frequently found at a depth of 15 meters below the water surface. In Lake Superior a larger variation with position was found with total phosphorous averaging 0.005 mg/l in the open lake and 0.010 to

TABLE 2

CRITERIA ADOPTED BY THE CALUMET AREA ENFORCEMENT
CONFEREES FOR INNER HARBOR BASINS

Water Quality Measurements

<u>Parameter</u>	<u>Criteria</u>
Temperature	Not more than 29.6°C
pH	Within range 7.5-9.0
Dissolved Solids	Not more than 230 mg/l
MBAS	Not more than 0.30 mg/l
Chloride	Not more than 30 mg/l
Sulfate	Not more than 75 mg/l
Total Phosphorus	Not more than 0.033 mg/l
NH ₃ - N	Not more than 0.12 mg/l
Phenol	Not more than 5 µg/l
Cyanide	Not more than 0.1 mg/l

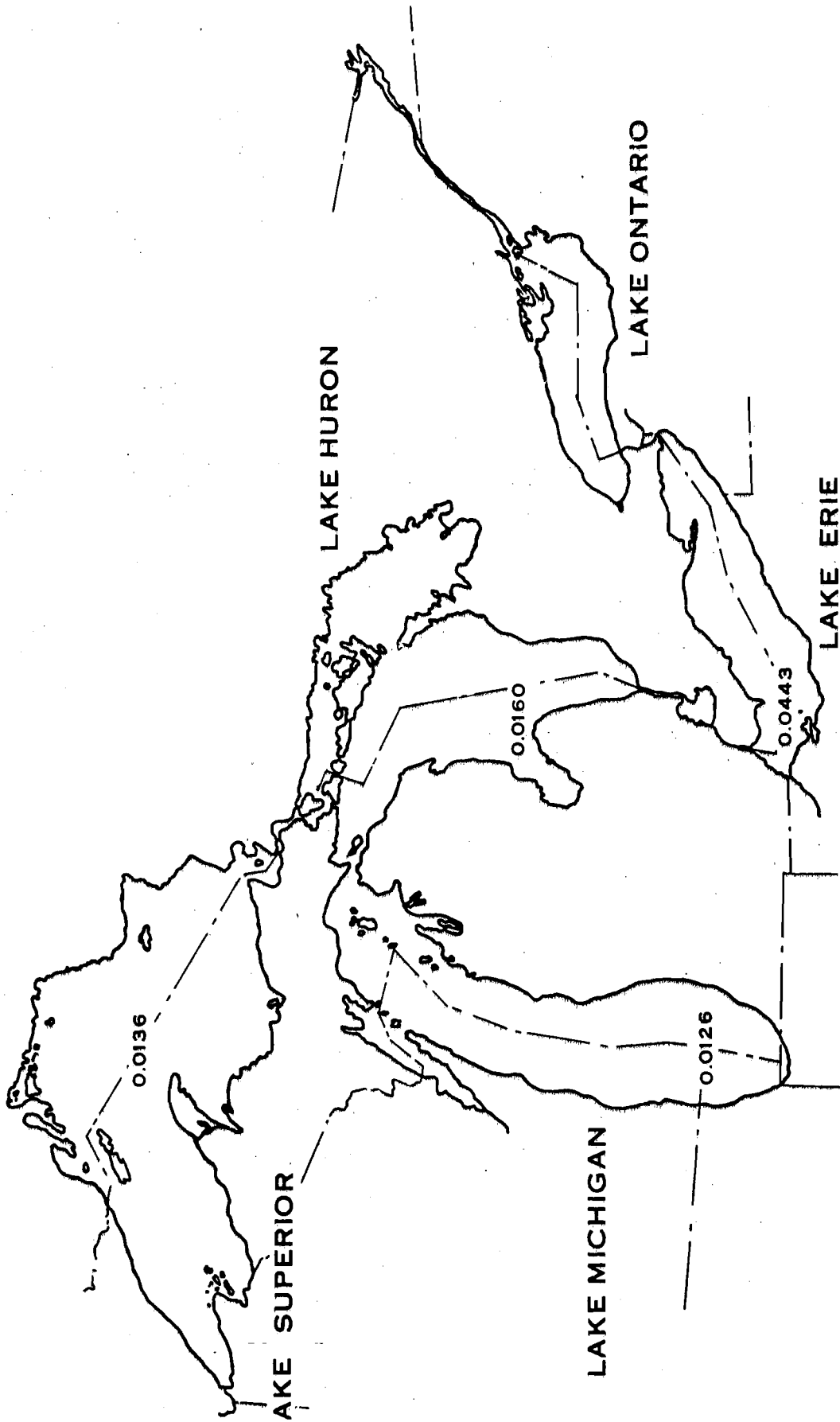


FIGURE 1. AVERAGE PHOSPHORUS CONTENT IN GREAT LAKES WATERS
MEASUREMENTS IN MG/L

TABLE 3
AVERAGE PHOSPHORUS CONTENT IN
GREAT LAKES WATERS

Location and year sampled	Total Phosphorus in mg/l
Lake Michigan 1954 (South basin)	0.0126 (509) ¹
Lake Erie 1958 (West end)	0.0443 (18) ¹
Lake Huron 1956 (Saginaw Bay)	0.0160 (166) ¹
Lake Superior 1953	0.0136 (538) ¹

¹ Number of determinations. (After Beeton, 1960)

0.015 mg/l along the South Shore. More detailed data for nutrient contents in the Great Lakes are given in Table 4. In addition to data reported for phosphorous, there is also data on the nitrogen content of Lake Michigan.

While measurements of the phosphate content in Great Lakes waters have been made by several investigators, scant information exists on the phosphate levels common in central lake sediments. Knowledge of existing nutrient contents in Great Lakes sediments is important for future nutrient level comparisons and for determination of locations where large concentrations exist.

Hartley (1967) has indicated that phosphorous levels in Lake Erie sediments are higher than those in Lake Michigan. Table 5 shows that phosphorous levels on the order of 700 mg per kg exist in central Lake Erie sediments. Schleicher and Kuhn (1970), as shown in Fig. 2, have determined the vertical variation of P_2O_5 content in South-Central Lake Michigan.

Nutrient Contents in Rivers and Harbors Tributary to the Great Lakes

Several investigators have studied the nutrient contents in rivers and harbors tributary to the Great Lakes. Values for the phosphorous content along the shores of Lake Michigan as reported by the FWPCA (1967) are shown in Fig. 3. Variations in phosphorous contents from 0.021 to 0.052 mg/l are shown within a distance of 2000 meters. Similar variations in nitrogen content are shown in Fig. 4.

Additional data for the phosphorous and nitrogen contents in the Waukegan shore region as reported by Beer (1969) are given in Table 6. Again, the average phosphorous content is over twice the average for central Lake waters. Table 7 gives additional data for total phosphorous and for total soluble

TABLE 4

PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - GREAT LAKES

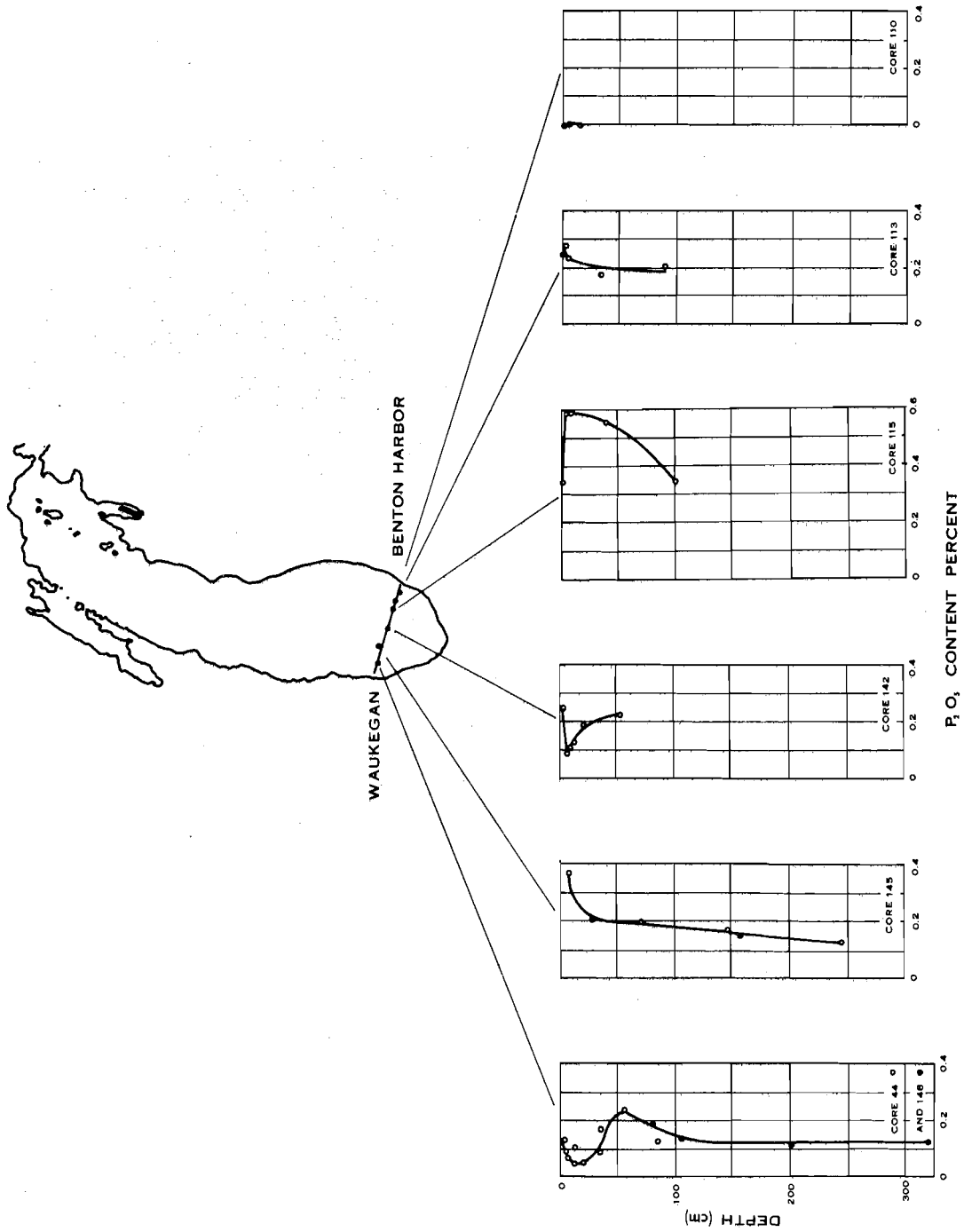
Location	Phosphorus		Nitrogen		Notes	References
	in Water	in Sediments	in Water	in Sediments		
Lake Michigan, Illinois	0.03 mg/l(PO_4)		0.12 mg/l (Ammonia, NH_3) 0.01 mg/l (Nitrates, NO_2) 0.93 mg/l (Nitrates, NO_3)		Non-heated zone: 1850' south of Waukegan outfall. (389' offshore, 1' deep)	Beer, (1969)
	0.03 mg/l(PO_4)		0.07 mg/l (Ammonia, NH_3) 0.01 mg/l (Nitrates, NO_2) 0.93 mg/l (Nitrates, NO_3)		Non-heated zone: 1800' north of Waukegan outfall. (1175' offshore, 11' deep)	
	0.03 mg/l(PO_4)		0.04 mg/l (Ammonia, NH_3) 0.01 mg/l (Nitrates, NO_2) 0.84 mg/l (Nitrates, NO_3)		Heated zone: Waukegan outfall (922' offshore, 13' deep)	
Lake Michigan, Illinois		0.37% (P_2O_5 constituents)			The highest value of P_2O_5 constituents was observed at 0 to 8 centimeters below the mud and 23 miles from shore.	Shimp, et al (1970)
Lake Michigan, (South basin)	0.0126 mg/l (Average Total P)				The highest value frequently occurred at a depth of 15 meters. Phosphorus varied as much as 6 ppb.	Beeton (1960)
Lake Erie (West end)	0.0443 mg/l (Average Total P)					
Lake Huron, (Saginaw Bay)	0.016 mg/l (Average Total P)					
Lake Superior	0.0136 mg/l (Average Total P)				Total phosphorus averaged 5 ppb in the open lake and 10 to 15 ppb along the South Shore.	
Lake Erie	0.040 mg/l Western Basin 0.020 mg/l Central Basin 0.010 mg/l Eastern Basin (Average Total P)				Valves represent average data from 3 depths. Data obtained in 1967.	FWPCA (1968)
Lake Erie	0.02 mg/l	700 mg/kg	0.25 mg/l Organic 0.39 mg/l NH_3 -N 0.84 mg/l NO_3 -N	1,900 mg/kg		Hartley (1967)

TABLE 5

AVERAGE NUTRIENT CONTENT IN CENTRAL
LAKE ERIE WATER AND SEDIMENT

Nutrient	Soil Concentration in mg/kg	Water Concentration in mg/l
Total Phosphorus	700	0.02
Soluble Phosphorus	—	0.003 - 0.066
Nitrogen	1,900	—
Organic Nitrogen	—	0.25
NH ₃ - N	—	0.00 - 0.39
NO ₃ - N	—	0.00 - 0.84

After Hartley, 1967



FROM SCHLEICHER AND KUHN 1970

Figure 2 - Variation of P₂O₅ content with depth in Lake Michigan sediments.

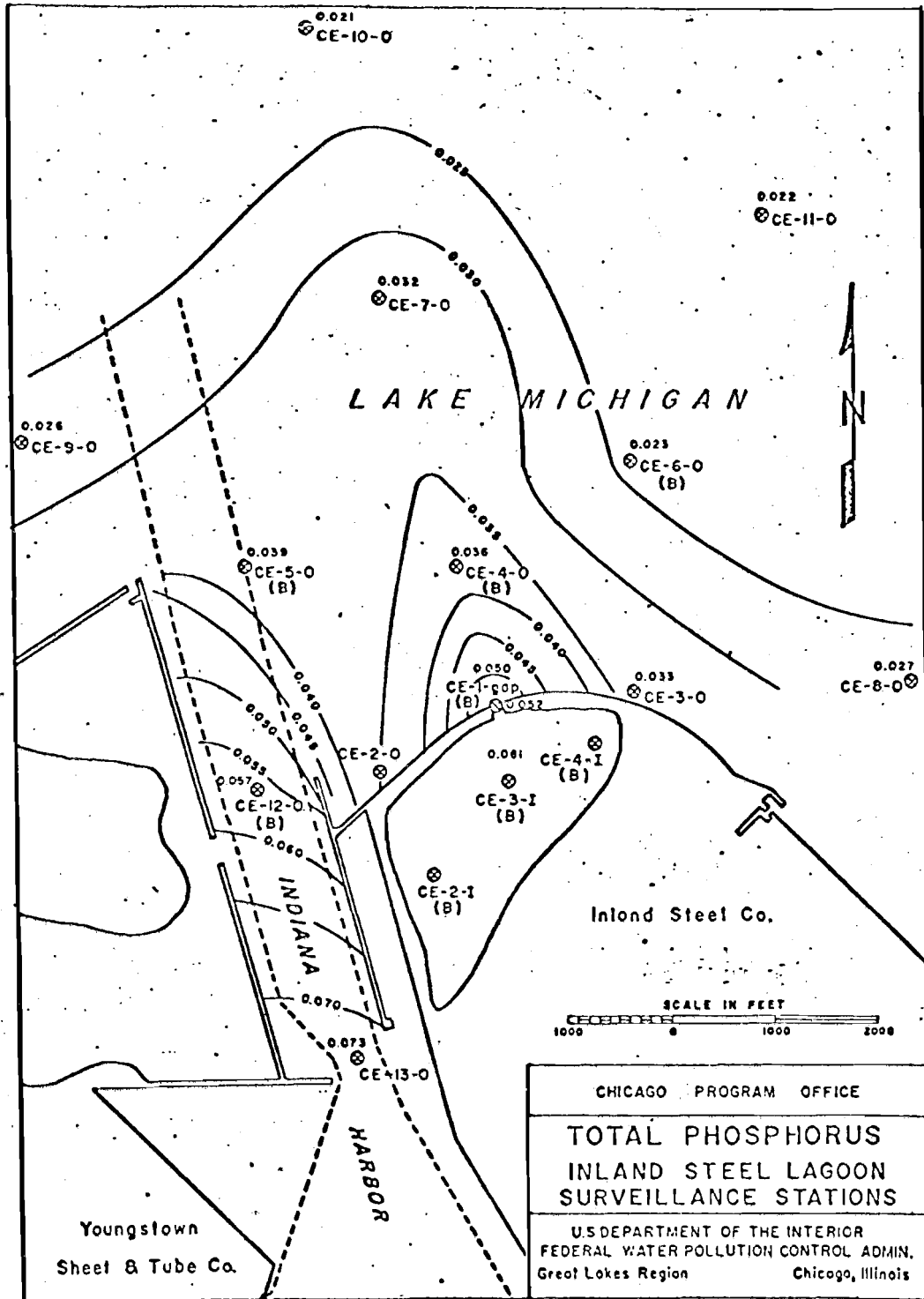


Figure 3. Dispersion patterns in Lake Michigan.

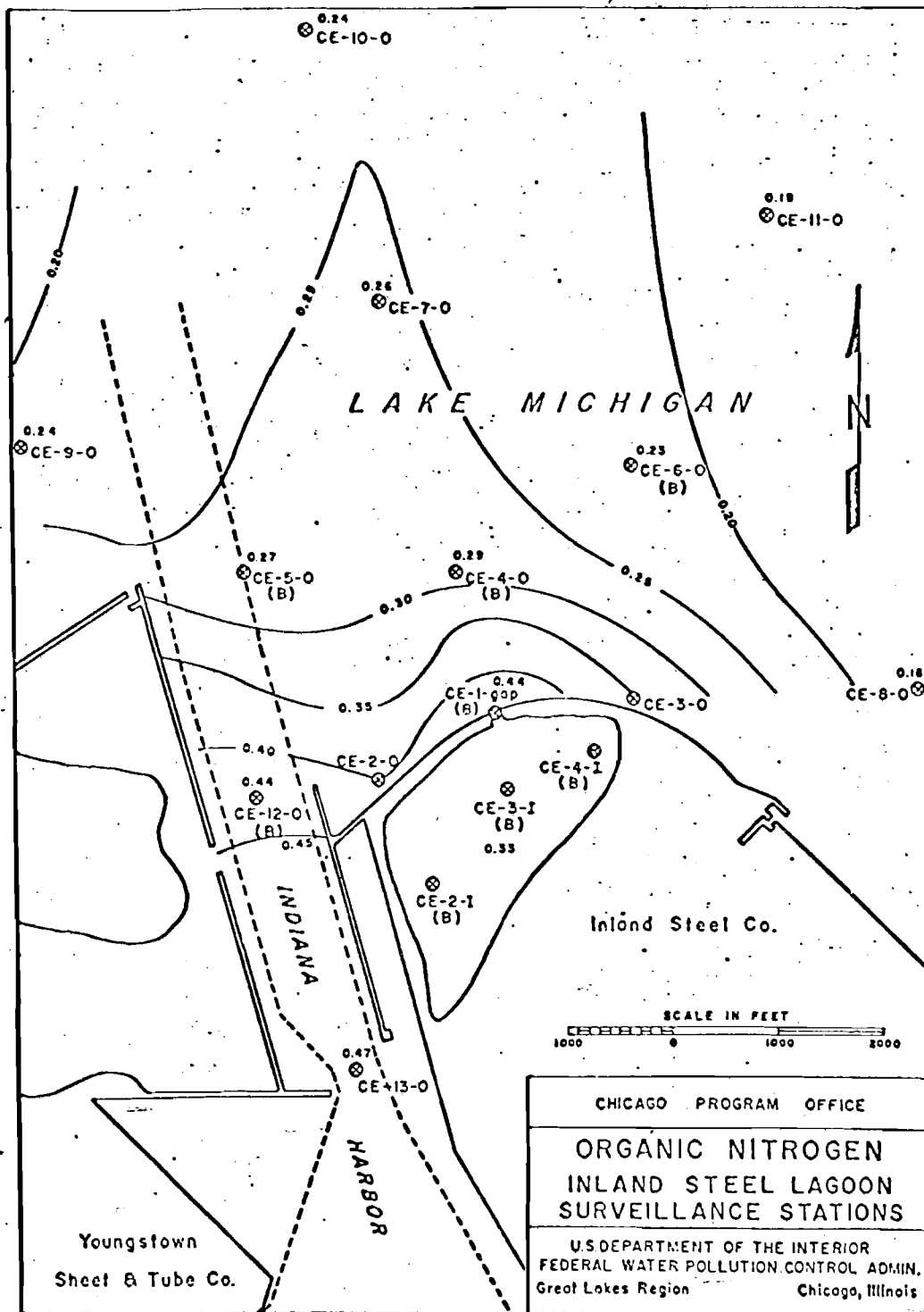


Figure 4. Dispersion patterns in Lake Michigan.

TABLE 6

PHOSPHORUS AND NITROGEN CONTENTS IN LAKE MICHIGAN SHORE WATERS, WAUKEGAN REGION, ILLINOIS

Nutrient	Non-Heated Zone		Heated Zone
	1850' south of Waukegan Outfall (389' offshore, 11' deep)	1800' north of Waukegan Outfall (1175' offshore, 11' deep)	Waukegan Outfall (922' offshore, 13' deep)
Phosphate, PO ₄	0.03 mg/l	0.03 mg/l	0.03 mg/l
Ammonia, NH ₃	0.12 mg/l	0.07 mg/l	0.04 mg/l
Ammonia as N	0.10 mg/l	0.06 mg/l	0.03 mg/l
Nitrates, NO ₂	0.01 mg/l	0.01 mg/l	0.01 mg/l
Nitrates as N	0.003 mg/l	0.003 mg/l	0.003 mg/l
Nitrites, NO ₃	0.93 mg/l	0.93 mg/l	0.84 mg/l
Nitrites as N	0.21 mg/l	0.21 mg/l	0.19 mg/l

After Beer, 1969

TABLE 7

PHOSPHORUS NUTRIENT CONTENT MEASURED IN RIVERS
AND HARBORS TRIBUTARY TO LAKE MICHIGAN

Location	Sampling Date	Phosphorus Content				Notes	Conclusions Reported
		Sediment		Water			
		Total Phosphorus Mg/Kg (dry wt.)	Total Soluble Phosphorus Mg/Kg (dry wt.)	Total Phosphorus Mg/L	Total Soluble Phosphorus Mg/L		
Calumet Harbor and River, Illinois	7/12/67	2,175(max) 447(min)	1.65 2.13	0.107	0.031	Water samples are one month average of measurements taken at different river stations	1. Bottom sediment samples indicate that polluted material is present in high concentration in the Calumet River.
Waukegan Harbor, Illinois	3/29/68	1,070(max) 174(min)	1.64 1.00	0.096 0.092	0.040 0.038	Maximum at Sta. 68-12 Minimum at Sta. 68-1	1. Material within harbor severely polluted. 2. Material in outer channel, NE adversely polluted. 3. Water quality generally satisfactory except for phosphorus which must be prevented from reaching Lake Michigan.
Indiana Harbor Channel, Indiana	12/12/67	786	1.32	0.073	0.023	Station CE 13.0 Nutrient content in water is an average for the period Nov. 11 to Dec. 12, 1967	
New Buffalo Harbor, Mich. (Gallen River)	7/4/68	90.2(max) 9.76(min)	- -	0.004 -	- -	Maximum at Sta. 68-4 Minimum at Sta. 68-1	1. Sediments outside mouth of river free of pollution. 2. Sediments in Gallen River slightly to moderately polluted. 3. River water quality entering Lake Michigan good.
Fox River Channel, Wisconsin	5/4/67	6,500(max) 1,627(min)	132.0 21.5	0.14 0.17	0.09 0.08	Maximum at River Sta. MI 3 Minimum at River Sta. MI 1	1. Bottom sediments in Fox River are heavily polluted. 2. Disposal of dredgings from river into lake would constitute a serious source of phosphate and nitrate. 3. Waters of the river constitute a significant source of pollution.
Green Bay Harbor, Wisconsin	5/21/70	348		0.104			1. One of the heaviest polluted harbors on Lake Michigan. 2. Bottom sediments in Fox River are heavily polluted. 3. Disposal of harbor material in lake would constitute serious source of phosphorus and nitrogen pollutants in lake. 4. Waters of Fox River constitute a significant source of pollution.
Green Bay, Wisconsin	5/4/67	4,104(max) 2,683(min)	109.5 53.5	2.41 0.13	0.14 0.06	Maximum Bay at Sta. mile 1 Minimum at Bay Sta. mile 2	
Kenosha Harbor, Wisconsin	4/24/68	66.5	0.61	0.06	0.04	Samples from outer harbor,	1. Clays show moderate pollution, but do not contain high concentrations of nutrients. 2. Water entering Lake Michigan does not represent a serious pollution source.
Manitowoc Harbor, Wisconsin (Manitowoc R)	4/23/68	672(max) 54(min)	30.44 20.13	0.37	0.13	Maximum at Sta. 68-5 Minimum at Sta. 68-12	1. Bottom sediments in upper part of harbor (river) are polluted and disposal in L. Michigan would constitute significant source of nutrients. 2. Water from Manitowoc R. discharged to Lake Michigan did not meet several criteria. Amount of phosphorus in river should be reduced.
Milwaukee Harbor, Wisconsin	4/24/68	1,121(max) 301(min)	2.43 5.01			Maximum at Sta. 68-8 Minimum at Sta. 68-1	1. Bottom sediments in both the Kinnickinnic and Menominee Rivers in the harbor are severely polluted and dredgings should not be disposed of in Lake Michigan. 2. Pollution from industrial waste and domestic sewage.
Oconto Harbor, Wisconsin (Oconto River)	5/22/68	79.7		0.025			1. Sediments at mouth of river relatively unpolluted. 2. Oconto River water met reasonable quality criteria (May 22).
Pensaukee Harbor, Wisc. (Pensaukee Rv.)	5/21/68	258		0.017			1. Bottom sediments not seriously polluted but have a moderately high concentration of total phosphorus. 2. Water entering Green Bay from river met reasonable water quality criteria.
Port Washington Harbor, Wisc. (Sauk Creek)	4/24/68	8.45	3.00	0.13	0.05	Industrial and domestic wastes. Absence of benthic organisms suggest high concentrations of toxic metals	1. Sediments not severely polluted. 2. Water quality meets reasonable criteria except that amount of phosphorus should be reduced.
Two Rivers Harbor, Wisc. (East Twin R, West Twin R)	4/22/68	469	19.43	0.17	0.08		1. Bottom sediments in inner harbor are seriously polluted and should not be disposed of in Lake Michigan. 2. River water contained significant amounts of pollution, especially nitrogen and phosphorus. Action should be taken to reduce amount of nutrients released to the stream.

phosphorous in rivers and harbors tributary to Lake Michigan. Values as high as 2.41 mg/l are reported in Green Bay Harbor. Green Bay Harbor sediments contained up to 4104 mg/kg phosphorous. Moreover, values as high as 6500 mg/kg total phosphorous are reported in sediments of the Fox River.

The nutrient levels in many harbors were considerably higher than levels found in the central lake and higher than levels considered satisfactory by pollution experts. For example, the phosphate content in the waters of Green Bay, Wisconsin have been measured at 2.41 mg/l which is 200 times the level common in the central lake and 75 times the level generally considered tolerable by the Lake Calumet Conferees.

Data for rivers and harbors tributary to Lake Erie are given in Table 8 after the FWQA (1967). In Great Sodus Bay, total phosphorous contents of 0.17 mg/l in the water are accompanied by values of 33,238 mg/kg in the sediments. Figures 5 and 6 obtained from the FWPCA (1967) show the variation in total phosphorous content of sediments in the Cuyahoga River as it enters Lake Erie.

Nutrient Contents in United States Lakes and Rivers

Data has also been obtained from the literature on the nutrient levels in lakes and rivers in several states. Table 9 summarizes data for Illinois lakes and rivers and shows that phosphorous levels of as high as .3 to .4 mg/l in waters are not uncommon.

Measurements of the phosphorous contents in Illinois waters have been carried out at a variety of locations throughout the state. The locations of these sampling stations are shown in Fig. 7. These measurements, reported by Engelbrecht and Morgan (1959), show concentrations of orthophosphate (P_2O_5)

TABLE 8

PHOSPHORUS NUTRIENT CONTENT MEASURED IN
RIVERS AND HARBORS TRIBUTARY TO LAKE ERIE

Location	Date	Sediment		Water		Notes
		Total Phosphorus mg/Kg (dry weight)	Total Soluble Phosphorus mg/Kg (dry weight)	Total Phosphorus mg/l	Total Soluble Phosphorus mg/l	
Buffalo Harbor, New York	June, 1967	778 (average)	---	0.03 to 0.06	---	Range values measured at different stations
Buffalo River, New York	June, 1967	1,150 (average)	---	0.82 to 0.17	---	Range of values
Cleveland Harbor, Ohio	March 23-30, 1967	2,030 to 850	---	0.55 to 0.08	0.16 to 0.03	Range of values
Cuyahoga River, (Cleveland) Ohio	March 23-30, 1967	6,990 to 1,180	---	1.53 to 0.17	0.30 to 0.05	Range of values
Great Sodus Bay, New York	June 28, 1968	33,238	107.0	0.17	0.12	Samples at station 10

From FWQA (1967)

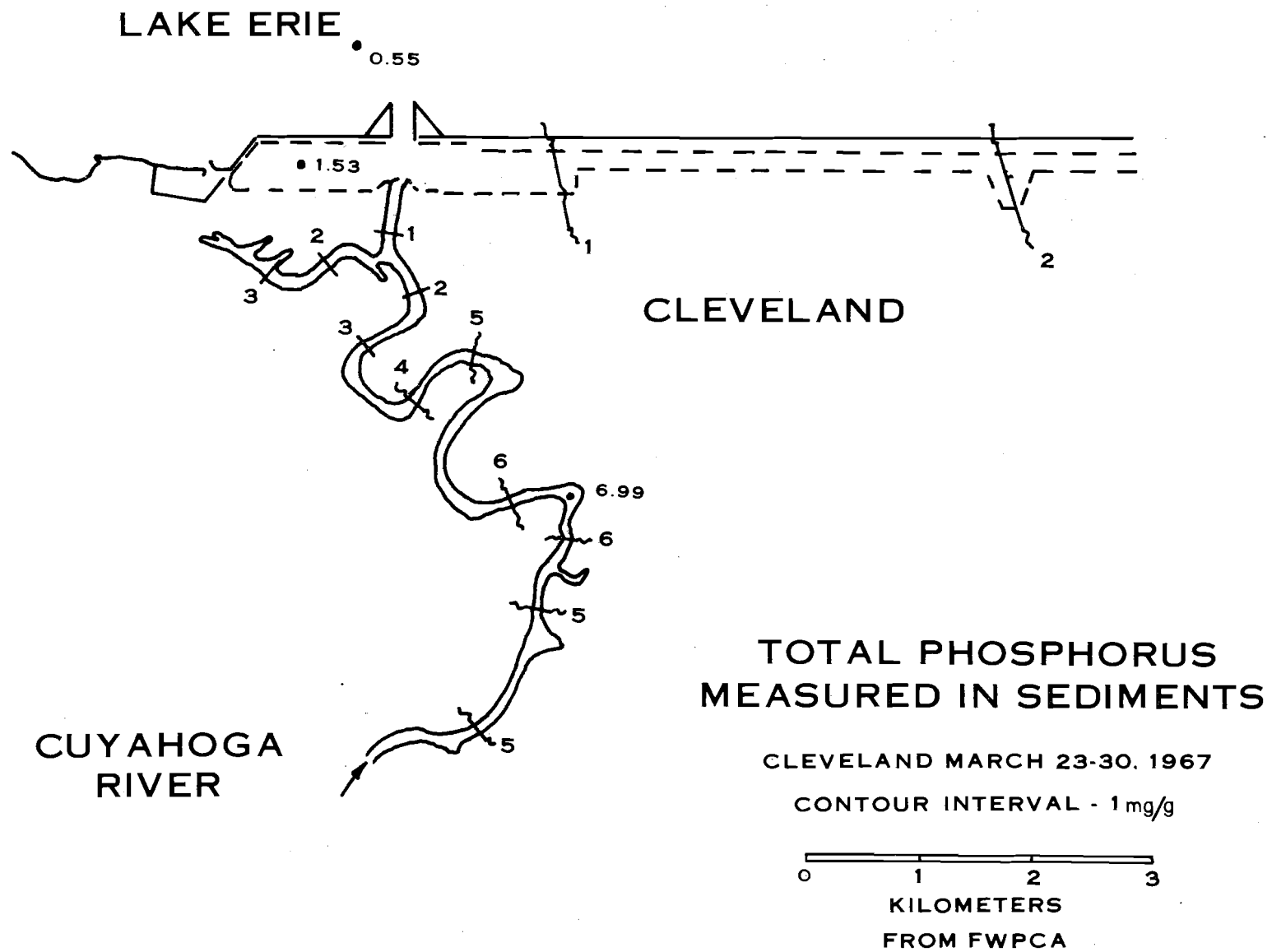


Figure 5 - Nutrient content in Cuyahoga River, Ohio, sediments (Plan View).

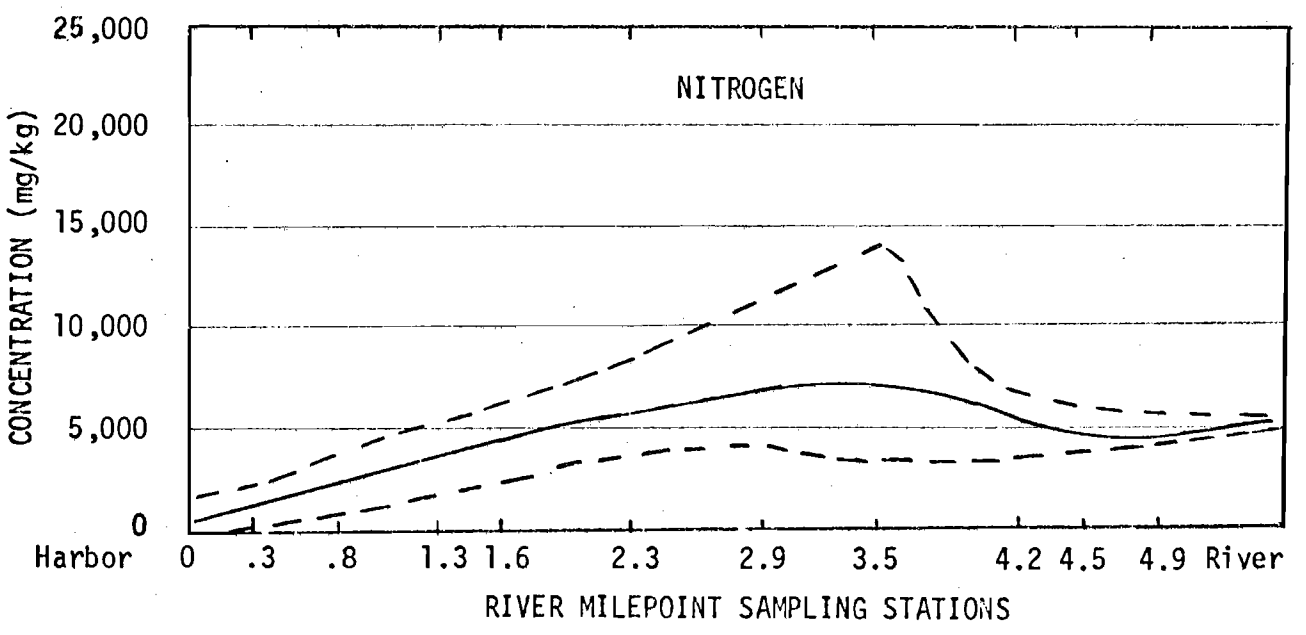
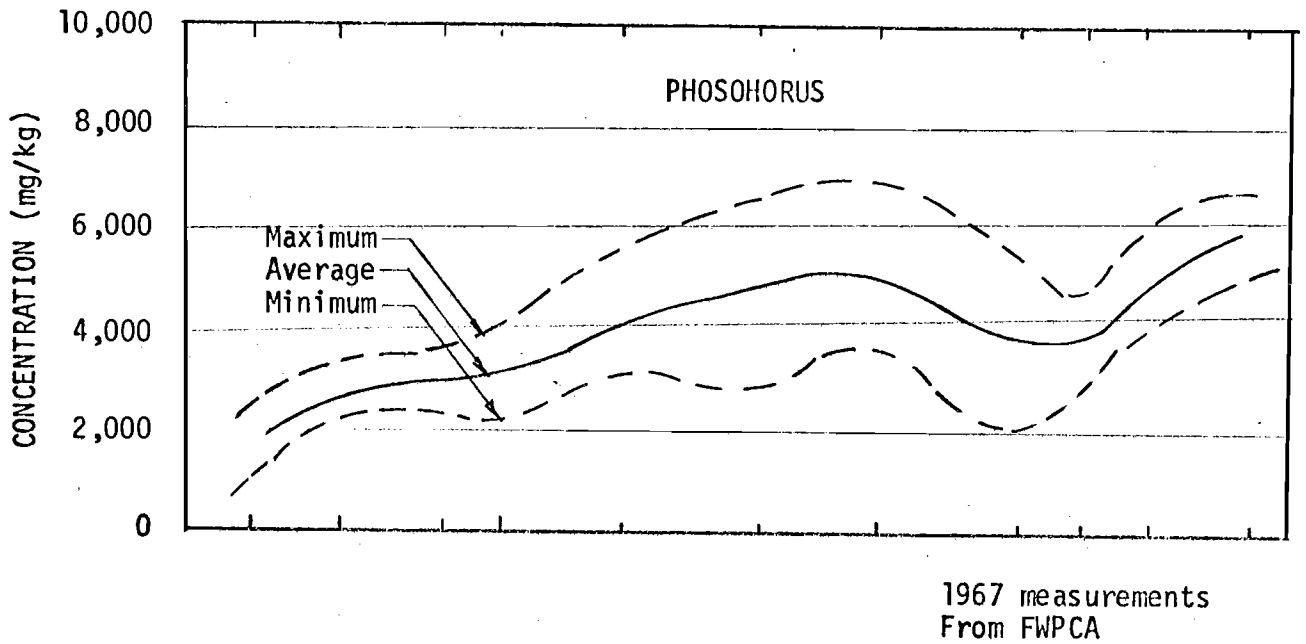


Figure 6 - Nutrient Content in Cuyahoga River, Ohio, Sediments (Profile)

Table 9
PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - ILLINOIS

Location	Phosphorus		Nitrogen		Notes	References
	in Water	in Sediments	in Water	in Sediments		
Embanass River Illinois	0.01788 mg/l (P)				Average orthophosphate	Engelbrocht and Morgan (1959)
Illinois River at Grafton, Illinois	0.2365 mg/l (P)					
Kankakee River Illinois	0.0318 mg/l (P)					
Little Vermilion River, Illinois	0.044 mg/l (P)					
Little Wabash River, Illinois	0.024 mg/l (P)				Average orthophosphate	
Mississippi River, Illinois	0.171 mg/l (P)				Average orthophosphate	
Vermilion River, Illinois	0.3035 mg/l (P)				Average orthophosphate	
Wabash River, Illinois	0.0414 mg/l (P)					
Kaskaskia River, Illinois	0.366 mg/l (P)				From April 1956 to December 1956	
Lake Chantangua, Illinois	61.6 mg/l/cm. thick (Total P) 29.1 mg/l/cm. thick (Soluble P)		12.8 lb/yr/ acre (Total Nitrogen)		Area = 3,500 acres Measured annually	

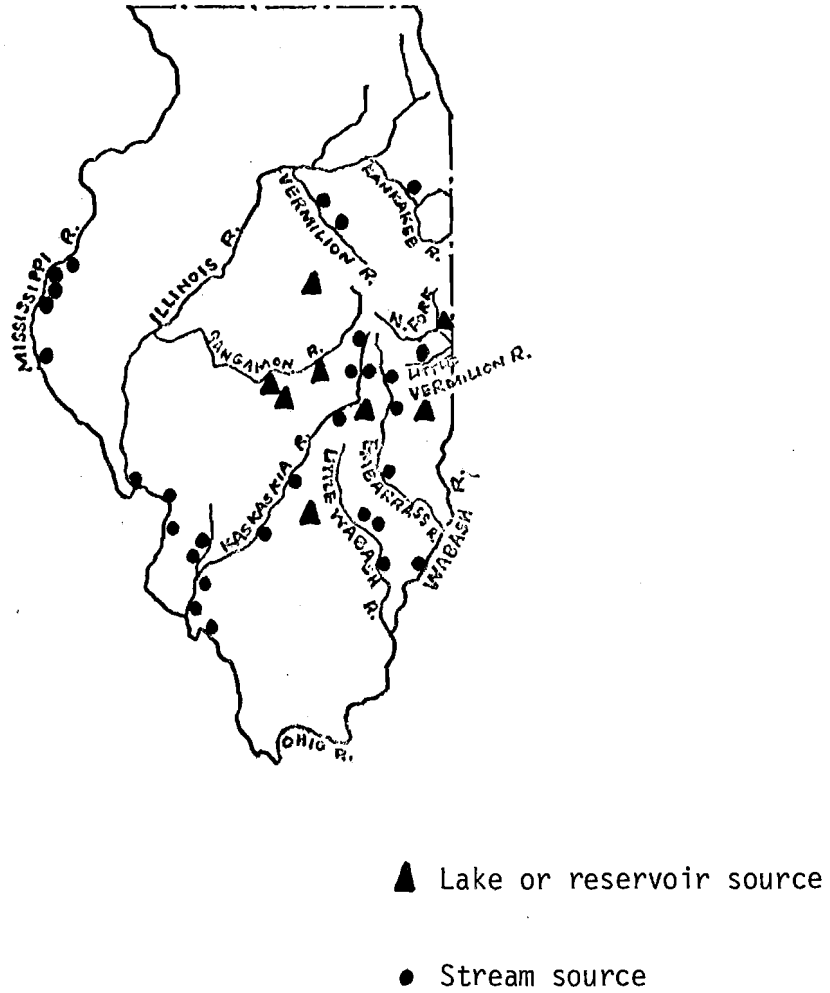


Figure 7. Lake, reservoir, and stream sampling locations in Illinois.

and hydrolyzable condensed orthophosphate which is more commonly referred to as maximum inorganic condensed orthophosphate (MIC).

One extensive set of measurements was made on samples from the Kaskaskia River which flows through Central Illinois and is tributary to the Mississippi River. Water samples were collected at four locations on June 3, 1957. In addition to the usual analyses for orthophosphate P_2O_5 and orthophosphate plus maximum inorganic condensed P_2O_5 , the total P_2O_5 of each sample was determined by wet-ashing. Table 10 lists the results of these measurements and shows that the mean value of maximum inorganic condensed P_2O_5 is 0.20 mg/l. Fifty percent of the phosphate found was in the maximum inorganic condensed form.

The range of values of orthophosphate at the Kaskaskia River sampling stations is indicated in Table 11 and summarized in Table 12. Concentrations of orthophosphate in these samples ranged from 0.01 mg/l to 1.76 mg/l P_2O_5 . Concentrations of orthophosphate plus maximum inorganic condensed P_2O_5 ranged from 0.03 to 4.27 mg/l. Ninety percent of the samples contained less than 0.9 mg/l P_2O_5 of orthophosphate plus maximum inorganic condensed P_2O_5 .

A study of records of rainfall and stream discharge in relation to date of sampling indicated that the quantity of orthophosphate plus maximum inorganic condensed P_2O_5 generally increased with peak rainfalls and stream discharges.

A number of lakes and reservoirs in Illinois has been sampled and the measured orthophosphate concentrations are summarized in Table 13. The mean value of orthophosphate plus MIC P_2O_5 in these waters was 0.081 mg/l P_2O_5 . The mean orthophosphate was 0.036 mg/l P_2O_5 . The average MIC P_2O_5 was 55 percent. The average phosphate content of these samples is considerably higher than for the lake and reservoir sample (Table 14). The average orthophosphate content

TABLE 10
 SUMMARY OF ORTHOPHOSPHATE PLUS MAXIMUM INORGANIC
 CONDENSED PHOSPHATE CONCENTRATIONS FOR
 KASKASKIA RIVER SURVEY, 1956

P_2O_5 Range (mg/l)	No. of Samples in Range	Percent of Total Samples	Cumulative Percent
0-0.1	17	13.6	13.6
0.1-0.2	26	20.8	34.4
0.2-0.3	23	18.4	52.8
0.3-0.4	19	15.2	68.0
0.4-0.5	9	7.2	75.2
0.5-0.6	12	9.6	84.8
0.6-0.7	3	2.4	87.2
0.7-0.8	2	1.6	88.8
0.8-0.9	2	1.6	90.4
0.9-1.0	4	3.2	93.6
1.0-1.1	3	2.4	96.0
1.1-1.2	1	0.8	96.8
1.2-1.3	0	0	96.8
1.3-1.4	1	0.8	97.6
1.4-1.5	0	0	97.6
1.5-1.6	0	0	97.6
1.6-1.7	1	0.8	98.4
1.7-1.8	0	0	98.4
1.8-1.9	0	0	98.4
1.9-2.0	0	0	98.4
2.0-3.0	1	0.8	99.2
3.0-4.0	0	0	99.2
4.0-4.27	1	0.8	100.0

From Engelbrecht and Morgan (1959)

TABLE 11
 MEAN VALUES AND RANGES OF POUNDS PER DAY OF
 ORTHOPHOSPHATE AND MIC P_2O_5 AT
 KASKASKIA RIVER SAMPLING STATION, 1956

Location or Station	No. of Samples	P_2O_5 (lb/day)					
		Orthophosphate			MIC		
		Low	Mean	High	Low	Mean	High
Bondville	27	0.04	0.7	42	0	0.4	3.3
Above Ficklin	24	0	30.0	130.0	0.6	14.2	84.0
Below Ficklin	25	0.4	14.0	73.4	5.2	33.2	199.7
Shelbyville	25	1	911	12,810	0	1,749	36,030
Vandalia	10	21	611	5,167	8	1,858	17,223
Carlyle	7	34	486	1,838	25	477	1,694
New Athens	7	90	884	2,112	54	1,656	5,934

MIC is defined as Maximum Inorganic Condensed.

From Engelbrecht and Morgan (1959)

TABLE 12
 AVERAGE ORTHOPHOSPHATE CONCENTRATIONS
 KASKASKIA RIVER

Location or Source	Orthophosphate P_2O_5 (mg/l)	Orthophosphate plus Maximum Inorganic Condensed P_2O_5 (mg/l)	Total P_2O_5 (mg/l)
Bondville	0.05	0.06	0.09
Above Ficklin	0.14	0.16	0.19
Below Ficklin	0.14	0.23	0.31
Shelbyville	0.18	0.24	0.28

From Engelbrecht and Morgan (1959)

TABLE 13
 ORTHOPHOSPHATE CONTENT OF SAMPLES FROM LAKE AND
 RESERVOIR SOURCES IN ILLINOIS

Location or Source	Phosphate as P_2O_5 (mg/l)	
	Orthophosphate	Orthophosphate plus MIC
Bloomington	0.018	0.226
Danville	0.108	0.195
Danville	0.091	0.113
Decatur	0.016	0.036
Kincaid	0.000	0.000
Mattoon	0.000	0.000
Paris	0.026	0.044
Salem	0.066	0.115
Springfield	0.000	0.000
Mean	0.036	0.081

MIC is defined as Maximum Inorganic Condensed.

From Engelbrecht and Morgan (1959)

TABLE 14

ORTHOPHOSPHATE CONTENTS IN ILLINOIS STREAMS
ANALYTICAL RESULTS FOR GENERAL SURVEY OF ILLINOIS STREAMS

Location or Source	P ₂ O ₅ (mg/l)	
	Orthophosphate	Orthophosphate plus MIC
Embarrass River:		
Oakland	0.013	0.025
Charleston	0.033	0.076
Newton	0.076	0.109
Illinois River:		
Grafton	0.541	1.551
Kankakee River:		
Kankakee	0.073	0.058
Kaskaskia River:		
Vandalia	0.334	0.706
Carlyle	0.371	0.708
Mascoutah	0.584	1.560
Freeburg	2.899	3.402
New Athens	0.380	0.788
Evansville	0.467	0.786
Little Vermilion River:		
Georgetown	0.101	0.082
Little Wabash River:		
Flora	0.061	0.113
Clay City	0.058	0.113
Fairfield	0.077	0.148
Mississippi River:		
Dallas	0.101	0.338
Nauvoo	0.65	0.531
Hamilton	0.157	0.400
Warsaw	0.227	0.603
Quincy	0.310	0.654
Alton	0.621	0.726
E. St. Louis	0.321	0.435
E. St. Louis	0.587	0.715
Chester	0.564	1.352
Vermilion River:		
Pontiac	0.062	0.073
Streator	1.329	1.299
Wabash River:		
Mt. Carmel	0.095	0.149
MEAN	0.411	0.657

From Engelbrecht and Morgan (1959)

of all river samples was 0.411 mg/l P_2O_5 . The average MIC P_2O_5 was 0.246 mg/l, or 38 percent. The highest value of MIC P_2O_5 , 1.01 mg/l, was observed at Grafton on the Illinois River. The highest value of orthophosphate plus MIC P_2O_5 , 3.402 mg/l, was observed at Freeburg on Silver Creek, a tributary to the Kaskaskia River. However, the MIC phosphate in this sample was only 15 percent.

Table 15 summarizes data on phosphate contents in Wisconsin lakes. Discharge of municipal waste and agricultural runoff have degraded the quality of a number of lakes in Wisconsin. A great deal of study has been carried out on several of these lakes, especially Lake Mendota.

Lake Mendota is adjacent to Madison, Wisconsin, located in the South Central portion of the State. It is a rather small lake with a surface area of 15.2 square miles and a maximum depth of 81 feet. The lake is characterized by very hard water, much domestic and cultural drainage and well developed thermal stratification. Murray (1956) found that the common sediment section found in cores taken from water deeper than 20 feet is black sludge resting on buff marl. The sludge is shiny black and locally carries visible calcareous shells and small red worms. The interface between water and sludge is quite sharp both in summer and winter. The sludge ranges from 0 to 14 inches in thickness and rests with a sharp contact on the light buff marl below.

The annual nutrient loading to Lake Mendota and other Wisconsin lakes and streams is often quite high as indicated in Table 16. The total phosphorus loading may normally be anywhere from 140 to 1,160 lb/yr/cu.ft.sec. for the streams sampled but with maximum concentration reaching upwards of 3,000 lb/yr/cfs during the spring.

Stream runoff eventually reaches the lakes and reservoir where it may or may not be retained in high percentages depending on climatic conditions

TABLE 15

PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - WISCONSIN

Location	Phosphorus		Nitrogen		Notes	References
	in Water	in Sediments	in Water	in Sediments		
479 Lakes of Northeastern Wisconsin	0.023 mg/l (mean of Total P)					Juday and Birge (1931)
17 Lakes in Southern Wisconsin	0.01 mg/l (Inorganic P)		0.3 ppm (Inorganic Nitrogen)		At the time of the spring overturn.	Sawyer, C. (1952)
Hummingbird Lake, Wisconsin	0.006 mg/l (Soluble P)				The water soluble phosphorus content of limed and unlimed agitated systems in a laboratory experiment.	Juday and Birge (1931)
Moccasin Lake, Wisconsin	0.008 mg/l (Soluble P)				Phosphorus reported was the amount released by the mud and present as soluble phosphorus in the water phase of the control system.	
Madison, Wisconsin	0.56 mg/l (Total P) 0.22 mg/l (Soluble P)		1.3 mg/l (Organic Nitrogen) 0.44 mg/l (Inorganic Nitrogen)		Storm waters	Lackey and Sawyer (1945)
Lake Mendota, Wisconsin		1,200 mg/kg dry weight (P)		7,300 µg/g dry weight (nitrogen)		Sawyer, et al (1945)
Lake Mendota, Wisconsin	20 mg/l/cm thick (Total soluble P)		302 µg/cm ² (nitrate)		From Oct. 1948-Oct. 1949 On the lake surface. Area -- 3,940 ha; max. depth -- 25.6 m.	Rohlich and Lea (1949)
Lake Mendota, Wisconsin		0.182 % of P ₂ O ₅			Average phosphorus content in sediment as a percent of total sample volume at 6-15 inches below the bottom, and 53 f-et depth of water. Area of Lake -- 15.2 square miles max. depth -- 81 feet	Murray, R.C. (1956)
Lake Monona, Wisconsin		1,070 mg/kg dry weight (P)		7,100 µg/g dry weight (nitrogen)	Area -- 1,410 ha; max. depth -- 22.5 m.	Sawyer, et al (1945)
Lake Wanbesa, Wisconsin		1,070 mg/kg dry weight (P)		9,080 µg/g dry weight (nitrogen)		
Lake Kegonsa, Wisconsin		1,210 mg/kg dry weight (P)		9,060 µg/g dry weight (nitrogen)		
Lakes Wanbesa, Kegonsa, Wisconsin	0.25 mg/l or more (Inorganic P)				At all times of the year Wanbesa -- 824 ha; 11.1 m. max depth Kegonsa -- 1,274 ha; 9.6 m. max. depth	Sawyer, C.N. (1947)
Tisut Lake, Wisconsin	0.147% (average P)				Measured from iron-manganese deposit, and at a water depth of 20 meters. Determined by Mr. James Nicholas in the Chemical Laboratory, Department of Geology, University of Wisconsin	Twenhofel, et al. (1945)

TABLE 16

NUTRIENT LOADING OF SOME WISCONSIN STREAMS

Stream	Nutrient Loading (lb/yr/cfs)		
	Inorganic Nitrogen	Total Phosphorus	Soluble Phosphorus
Crawfish River at Mouth			
Normal	950	1,160	370
March	4,250	1,980	550
Rock River below Jefferson			
Normal	470	990	290
March	4,160	3,280	590
Yahara River and Token Creek			
Normal	457	140	86
March	5,350	512	100
Door Creek			
Normal	7,740	-	115
March	13,350	-	215
Badfish Creek			
Normal	4,616	-	150

(After Mackenthun, 1962)

and the characteristics of the individual lake. Table 17 shows the measured retention in several lakes. It may be seen that nutrient retention is lower during the winter months with the greatest retention in inorganic nitrogen occurring during the periods of greatest biological activity characterized by the warm summer months. Soluble phosphorus retention displays more variability. Table 18 gives the yearly average nutrient loading and retention for several lakes. It may be seen that the annual average percentage retention of inorganic nitrogen is higher than that of soluble phosphorus, especially under the higher loadings.

Nutrients retained in lakes may be stored in several places: in the water, in the sediment or in aquatic plants in concentrations above those needed for immediate growth requirements and therefore available at later times. Murray (1956) determined the phosphorus content of bottom samples from Lake Mendota, at various locations in the lake. His results, shown in Table 19, indicate that the phosphorus content does not change radically with depth in the sediment and an average of .202 percent of P_2O_5 determined by volumetric method for all samples obtained. Data obtained by Mackenthun (1962) shown in Table 20 indicates that this would correspond to a total phosphorus concentration of about 1,2000 mg/kg.

Table 21 presents a summary of phosphorus contents in waters and sediments of Michigan lakes. Table 22 presents similar data for other United States lakes.

Nutrient Contents in Foreign Lakes

Table 23 presents data for concentrations of phosphorus in Canadian lake waters. Data for European lakes is given in Table 24. In addition, Chu (1942) summarized much early literature on phosphorus and nitrogen contents in natural waters. His summary, presented in Table 25, shows the range of values commonly in various types of water bodies.

TABLE 17

SEASONAL VARIATION IN NUTRIENT RETENTION IN WISCONSIN LAKES

	Soluble Phosphorus					Inorganic Nitrogen						
	Period					Period						
	July-Sept.	Nov.-Jan.	Feb.-Apr.	May-Oct.	July-Sept.	Nov.-Jan.	Feb.-April	May-Oct.	July-Sept.	Nov.-Jan.	Feb.-April	May-Oct.
Lake Monona												
Loading (lb/yr/acre)	5	14	20	16	47	85	162	75	47	85	162	75
Retention (%)	87	82	64	89	90	64	37	71	90	64	37	71
Lake Waubesa												
Loading (lb/yr/acre)	55	49	66	63	336	406	394	306	336	406	394	306
Retention (%)	-5	-10	-26	26	89	66	23	70	89	66	23	70
Lake Kegonsa												
Loading (lb/yr/acre)	32	32	67	41	22	57	306	91	22	57	306	91
Retention (%)	1	12	-21	-15	71	74	43	74	71	74	43	74

(After Mackenthun, 1962)

TABLE 18

NUTRIENT LOADING AND RETENTION IN WISCONSIN LAKES (ANNUAL AVERAGE)

Location	Date	Soluble Phosphorous		Inorganic Nitrogen	
		Loading (lb/yr/acre)	Retention ¹ %	Loading (lb/yr/acre)	Retention ¹ %
Lake Mendota	-	0.6		20	
Lake Monona	1942-43	7	64	73	48
	1943-44	9	88	90	70
Lake Waubesa	1942-43	62	-26	422	50
	1943-44	64	25	448	64
Lake Kegonsa	1942-43	34	-21	168	44
	1943-44	38	12	156	61
Lake Koshkonong	1959-60	40	30-70	90	80

¹Annual average percentage retention.

(After Mackenthun, 1962)

TABLE 19

PHOSPHORUS CONTENT IN SEDIMENTS OF LAKE MENDOTA, WISCONSIN

Depth of Water	Depth Below the Bottom	% of $P_2 O_5$ ¹
63 feet	0-12 inches	0.275
	12-18 inches	0.209
	18-25 inches	0.269
35 feet	0 - 8 inches	0.180
	8-14 inches	0.181
	14-21 inches	0.182
53 feet	0 - 6 inches	0.208
	6-15 inches	0.182
	15-21 inches	0.191
55 feet	0 - 5 inches	0.168
	5-12 inches	0.177
	12-21 inches	0.189
69 feet	0-13 inches	0.259
	13-21 inches	0.183
	21-29 inches	0.185

¹Determined by Volumetric Method of Assn. of Official Agricultural Chemists (2.11 and 2.13). (After Murray, 1956)

TABLE 20

PHOSPHORUS AND NITROGEN CONTENT OF BOTTOM MUDS IN WISCONSIN LAKES

Location	Phosphorus in mg per kg ¹	Nitrogen in mg per kg
Lake Mendota	1,200	7,300
Lake Mououa	1,070	7,100
Lake Waubesa	1,070	9,080
Lake Kegonsa	1,210	9,060

¹Based on dry weight.

(After Mackenthum, 1962)

Table 21 PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - MICHIGAN						
Location	Phosphorus		Nitrogen		Notes	References
	in Water	in Sediments	in Water	in Sediments		
Douglas Lake, Northern Michigan	Summer 1950- 1951: 0.012- 0.0175 mg/l (Total P) 0.00266- 0.0041 mg/l (Soluble Inorg. P) 0.00933- 0.0134 mg/l (Total Inor, P) 0.00383- 0.00744 mg/l (Sestonic P) 0.0055-0.006 mg/l (Soluble Organic P) Fall 1950-51: 0.023-0.171 mg/l (Total P) 0.011-0.1205 mg/l (Soluble Inor.P) 0.012-0.0505 mg/l (Total Organic P) 0.0045-0.0435 mg/l (Sestonic P) 0.007-0.0075 mg/l (Soluble Organic P) Winter 1950: 0.0455 mg/l (Total P)				All measurements at a depth of 20 meters. Area of the lake -- 3,735 acres Maximum depth -- 27.1 meters Maximum length -- 3.8 miles Maximum width -- 2.27 miles	Tucker, A. (1957)
Douglas Lake, Northern Michigan (Continued)	0.032 mg/l (Soluble Inorganic P) 0.0135 mg/l (Total Org. P) 0.007 mg/l (Sestonic P) 0.0065 mg/l (Soluble Organic P) Spring 1951: 0.015 mg/l (Total P) 0.005 mg/l (Soluble Inorganic P) 0.01 mg/l (Total Orga. P) 0.0035 mg/l (Sestonic P) 0.006 mg/l (Soluble Organic P)					
Muro Lake, Northern Michigan	0.011-0.0115 mg/l (Total P) 0.001 mg/l (Soluble Inorganic P) 0.01-0.0105 mg/l (Total Organic P) 0.006-0.0065 mg/l (Soluble Organic P)				During Fall of 1950-51, at a depth of 2 meters: Area of the lake -- 512 acres Maximum depth -- 4.2 meters	

Table 21 (cont.)
PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - MICHIGAN (Continued)

Location	Phosphorus		Nitrogen		Notes	References
	in Water	In Sediments	in Water	in Sediments		
Michigan Lakes	Inorganic P-11% Soluble Organic P-48% Seston P-41%				Percentage based on total phosphorus content in sample.	Tucker, A. (1957)
Lancaster Lake Northern Michigan	0.0505-0.098 mg/l (Total P) 0.032-0.0825 mg/l (Soluble Inorganic P) 0.01525-0.0185 mg/l (Total Organic P) 0.0055-0.00575 mg/l (Sestonic P) 0.0095-0.0135 mg/l (Soluble Organic P)				During the Fall of 1950-51, at the depth of 15 meters: Area of the lake -- 51 acres Maximum depth -- 17 meters near the center of the lake	
Vincent Lake, Northern Michigan	0.0165 mg/l (Total P) 0.0005-0.001 mg/l (Soluble Inorganic P) 0.0155-0.016 mg/l (Total Organic P) 0.006-0.0095 mg/l (Sestonic P) 0.006-0.01 mg/l (Soluble Organic P)				During the Fall of 1950-51, at the depth of 2.5 meters: Area of the lake -- 32 acres Maximum depth -- 6 meters	
Lake Lansing, Southern Michigan	0.0248 mg/l (Total P) 0.01283 mg/l (Soluble Inorganic P)				During the Fall of 1950, at the depth of 9 meters: Area of the lake -- 452.5 acres Maximum depth -- 10.7 meters	
Lake Lansing, Southern Michigan (Continued)	0.012 mg/l (Total Organic P) 0.0096 mg/l (Sestonic P) 0.00283 mg/l (Soluble Organic P)					
Silver Lake, Michigan		0.031 mg/kg P (dune sand) 0.01765 mg/kg P (rubicon sand)			At depth of 60 cm. below the mud surface.	Ellis and Erickson (1969)
Lake of Woods, Michigan		0.0292 mg/kg P (rubicon sand)				
Otsego Lake, Michigan		0.0246 mg/kg P (rubicon sand)				
Sturgeon River Michigan		0.025 mg/kg P (Emmett loamy sand)			Purest stream in Michigan. At depth of 60 cm. below the mud surface.	
Au Sable River Michigan		0.016 mg/kg P (Grayling sand) 0.0155 mg/kg P (Roseland sand) 0.01415 mg/kg P (rubicon sand)			River not polluted. At depth of 60 cm. below the mud surface.	

Table 22

PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - UNITED STATES

Location	Phosphorus		Nitrogen		Notes	References
	in Water	in Sediments	in Water	in Sediments		
Kodiak Island, Alaska	-----	1,394 mg/kg (P)	-----	8 ppm	Katmai ash collected from Kodiak Island which laid down by the eruption of Mount Katmai in 1912. Streams coming from the steeper slopes show a lower PO ₄ -P concentration than those coming from shallow slopes as might be expected from runoff-residence considerations. Exactly the opposite is found when the nitrate concentration of these streams is examined, i.e. only the streams arising on steep slopes show appreciable amounts of nitrate.	1. Grigg, R.F. (1920) 2. Shipley, J.W. (1920)
Little Kitoi Lake, Alaska	0.000745 mg/l (PO ₄ -P) 0.002675 mg/l (Soluble Org. P) 0.004575 mg/l (Total P)	1 µg/L (PO ₄ -P) 2.5 µg/L (Soluble Org. P) 5.3 µg/L (Total P)	23.25 µg/L (NO ₃ -N)	-----		Dugdale and Dugdale (1961)
Upper Jennifer Lake, Alaska	0.001105 mg/l (PO ₄ -P) 0.003183 mg/l (Soluble Org. P) 0.00493 mg/l (Total P)	0.8 µg/L (PO ₄ -P) 1.5 µg/L (Soluble Org. P) 4.8 µg/L (Total P)	11.16 µg/L (NO ₃ -N)	-----		
Twenty-nine Palms, California	1.6 mg/l (PO ₄)	-----	213 ppm	-----		Stone and Merrell (1958)
Fresno, California	0.3 mg/l (PO ₄)	-----	-----	-----		
Surface Water of Linsley Pond, North Branford, Conn.	0.021 mg/l (mean of Total P)	-----	-----	-----	Area - 9.4 ha., maximum depth - 14.8 m.	Hutchinson, E. (1941)
Linsley Pond, North Branford, Conn.	0.0017 mg/l (PO ₄ -P) 0.006 mg/l (Org. Sol. P) 0.0133 mg/l (Seston P)	-----	0.0227 mg/l Nitrate Nitrogen	-----	The mean phosphate phosphorus in the surface waters constitutes 8.1% of the mean total, the organic soluble 58.6%, & the mean seston phosphorus 63.3%. The mean of all observation gives a value of 8.98 kilograms of phosphorus in the lake, April to August, 1937.	Hutchinson, G.E. (1941)
Lake Quassapang, Middlebury, Conn.	1.3 mg/l/cm thick per week (Total P)	-----	-----	-----	Rate of output during the maximum rise. Determination made Summer, 1938.	Hutchinson, G. E. (1941)
Lake Zoar, Conn. (1950-51)	0.012-0.041 mg/l average - 0.025 mg/l (PO ₄)	-----	-----	-----		Curry and Wilson (1955)
Housatonic River, Conn.	Less than 0.033 mg/l (Soluble P)	-----	-----	-----	During period of high water.	
Lake Candlewood, Conn.	0.008 mg/l (P)	-----	-----	-----	Measured during the algae season. However, the lake produces no algal bloom of any consequence. It has been suggested that the phosphate is utilized early in the season by diatoms which die, sink to the bottom, removing phosphate from surface waters before the algal season.	
Lake Zoar, Conn.	0.012-0.041 mg/l (P) average-0.025 mg/l (P)	-----	-----	-----		Benoir and Curry (1961)
Linsley Pond, Conn.	-----	1.15 mg/ml mud	-----	-----		Livingston and Boy in (1962)
Deer Creek Reservoir, Utah	0.00871 mg/l at the surface to 0.501 mg/l in the lower waters (P)	-----	-----	-----	Located about 56 km southeast of Salt Lake City, Utah	Gaufin and McDonald (1965)
Green Lake, Seattle, Wash	0.01 mg/l (PO ₄ -P)	-----	0.3 mg/l Nitrate-Nitrogen	-----	640 ha., mean depth of 3.8 meters, maximum depth of 8.8 meters.	Sylvester and Anderson (1964)
Lake Washington, Wash.	0.038 mg/l	-----	-----	-----	Maximum concentration in the hypolimnion and also at 60 meters on Sept. 1955. Previous records:	Edmondson, et al. (1956)

TABLE 23
PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - CANADA

Location	Phosphorus		Nitrogen		Notes	References
	in Water	in Sediments	in Water	in Sediments		
Lake Costello, Ontario	0.012 mg/l (Total P)				Area -- 39 ha; max. depth -- 18 m.	Rigler, F.H. 1964
Lake Opeongo, Ontario	0.007 mg/l (Total P)				Area -- 2,180 ha; max. depth -- 53 m.	
Lake of Two Rivers, Ont.	0.007 mg/l (Total P)				Area -- 296 ha; max. depth -- 45 m.	
Found Lake, Ontario	0.005 mg/l (Total P)				Area -- 13 ha; max. depth -- 31 m.	
Grenadier Pond, Ont.	0.133 mg/l (Total P)				Area -- 16 ha; max. depth -- 6 m.	
Heart Lake, Ontario	0.044 mg/l (Total P)				Area -- 15 ha; max. depth -- 9 m.	
Teapot Lake, Ontario	0.033 mg/l (Total P)				Area -- 0.5 ha; max. depth -- 12 m.	
Lake Mary, Ontario	0.027 mg/l (Total P)				Area -- 13 ha; max. depth -- 16 m.	
Lake Eos, Ontario	0.018 mg/l (Total P)				Area -- 1.5 ha; max. depth -- 6 m.	
Crecy Lake, New Brunswick	0.015 mg/l (P)				General level in the water. Area -- 20.4 ha; max. depth -- 3.8 m.	Smith, M.W. (1945)
Bluff Lake, Halifax, N.S. Canada	0.031 mg/l (Total P)				Average Phosphorus in whole lake. Area -- 10 acres or 4 ha. max. depth -- 7 m. or 22 ft.	Hayes, et al (1952)

TABLE 24

PHOSPHORUS CONTENT IN WATER AND SEDIMENTS - EUROPE

Location	Phosphorus		Nitrogen		Notes	Reference
	in Water	in Sediments	in Water	in Sediments		
Lake West-water, Eng.	0.002 mg/l (Inorganic P)				In surface water; June-August average	Pearsall, W. H. (1930)
Lake Innerdale, England	0.0026 mg/l (Inorganic P)				Average in surface water.	
Lake rammock, England	0.0026 mg/l (Inorganic P)				In surface water; June-August average.	
Lake went-water, Eng.	0.0018 mg/l (Inorganic P)				In surface water; June-August average.	
Ilswater, Lake District, England	0.0014 mg/l (Inorganic P)				In surface water; June-August average. Area -- 900 ha; max. depth -- 63 m.	
owes Water, England	0.0011 mg/l (Inorganic P)				In surface water; June-August average.	
Lake sserthwaite, Eng.	0.0009 mg/l (Inorganic P)				In surface water; June-August average.	
Lake thwaite, Eng.	0.0011 mg/l (Inorganic P)				In surface water; June-August average.	
Esthwaite Water, Lake District, Eng.	0.225 mg/l (Maximum PO ₄)		1.7 mg/l (Nitrate)		Maximum depth -- 16 meters. Limits of water column -- 9 to 14 meters.	
Scottish Loch A		205 mg P% ¹ or 2050 mg/kg(max. P concentration)			Total P required to saturation given volume of mud at 1-2 cm. below the mud surface. γ sat = 1.275 g/l 110 mg. P/100 g. dry wt. = 110 mg%	
Scottish Loch B		212 mg.P% ¹ or 2120 kg/kg(max. P concentration)			Total P required to saturate a given volume of mud at 1-2 cm. below the mud surface. 110 mg.P/100 g. dry wt. = 110 mg%	
Lake Constance or Bodersee (bordering Germany, Switzerland and Austria)	0.002-0.003 mg/l (1950) 0.002-0.004 mg/l (1954) 0.007-0.0095 mg/l (1958-59) All PO ₄ -P)				In 1935 when the first recorded measurement was made, no dissolved PO ₄ -P was present. No measurements of the compound were made after this early study until 1950. Based on the result of increased PO ₄ -P content, the lake change from an oligotrophic to an eutrophic condition between 1935 and 1962.	Kliffmiller (1962)
Alpine Lake, Zurichsee, Switzerland	0.05 mg/l (Soluble P)				At overturn seasons Zurichsee (Unter) -- 6,700 ha. and 143 m. max. depth Zurichsee (Ober) -- 2,000 ha. and 50 m. max. depth	Hasler, A.D. (1947)

TABLE 25

PHOSPHORUS AND NITROGEN CONCENTRATIONS OF NATURAL FRESH WATERS

Water Location	P (in parts per million)	N (in parts per million)	Reference or Source
Lake Superior	-	0.001	Clarke, 1924
Lake Superior	-	0.113	Dole, 1909
Ennerdale	0.0009	0.016	Pearsall, 1930, 1922
	0.01	0.08	
Windermere	0.0007	0.048	Pearsall, 1930, 1922
	0.04	0.2	
Nile	trace	trace	Clarke, 1924
	0.023	0.098	Dole, 1909
Mississippi	-	0.32	Dole, 1909
Mississippi	-	0.61	Collins, 1910
Mississippi	trace	0.05	Wiebe, 1931
	0.065	0.91	
Wharfe	0	trace	West Riding River Board,
	0.022	1.58	1930
Illinois	-	0.023	Koffoid, 1903
	-	2.82	
Illinois	-	9.5	Collins, 1910
	-	11.3	
Thames at Slough	-	3.5	Thresh, et al, 1933
	-	8.7(a)	
Welland	-	1.98	Thresh, et al, 1933
Trent	-	1.65	Pearsall, 1922
Various	trace	-	Atkins, 1923, 1924
	0.54	-	Atkins and Harris, 1924
Lake Wingra	0.02	trace	Tressler and Domagala,
	0.89	0.25	1931
Wisconsin Lakes	trace	-	Juday, et al, 1927, 1931
	0.015	-	
	0.75(b)	-	
Texas Reservoir	0.04	0	Harris and Silvey, 1940
Lakes	0.3	0.44	
English Lakes	0.0005	0.016	Pearsall, 1922, 1930
	0.04	0.2	
Selected typical		trace	Pearsall, 1922, 1930
fresh waters	0.62	2.0	
30 surface waters	0.02	0.8	Metropolitan Water Board,
(f)	0.137	5.0	London, 1937
36 well waters	0.003	0.1	Metropolitan Water Board,
	0.072	11.4	London, 1937
Various collection	trace	trace	Clarke, 1924
	0.65	3.1	
Surface waters (e)		0.8	Thresh, et al, 1933
		8.7	
Average of surface	0.064	0.95	Murray, 1887
waters			
Average of surface	0.2(c)	0.31	Clarke, 1924
waters (g)			

The figures give the range, the upper being the minimum and the lower the maximum; when only one figure is given, it represents an average. (From Chu, 1942)

- (a) River Thames at Staines.
- (b) Maximum P at 20m. depth.
- (c) Figure from Pearsall (1922).
- (d) Including aluminum.
- (e) Exclude Thames at Grays.
- (f) Average of the year.
- (g) Calculated with 152 as the average salinity.

Nutrient Content Profiles in Sediments and Soils

The preceding discussion has presented available data summarizing the measured distribution of nutrients in sediments as they are distributed laterally in different locations. Such information may be used as a guide to determine where large concentrations may be expected and how these concentrations relate to geological and topographic features. Of equal importance however, is the knowledge of how these nutrients are distributed with depth at any given location since this type of information is needed to estimate the total amount of nutrients available or existing at any site.

A general lack of profile data presenting the distribution of nutrients with depth is a general indication of the difficulty involved with sampling, coring and testing of nutrient rich sediments. For example, rather simple and easily handled equipment such as the Ekman or Peterson dredge is suitable for taking representative samples of the first few inches of the sediment surface. Chemical analyses on such samples yield values which might be thought of as average determinations for surface materials. On the other hand, equipment suitable for sampling sediments to any significant depth is difficult to use, often requiring extensive ship support and mechanical assistance to handle the heavy and bulky equipment. Moreover, sample handling and storage is much more complicated and important when dealing with soft sediments than when handling other types of soils. For these reasons, data describing the chemical constituents of sediments with depth is very limited.

The range of information which is available suggests that phosphate concentrations may exist to significant depths in sediments. This is reflected in the results of Hutchinson and Wollack (1940) and Livingston and Boykin (1962) who studied the phosphate distribution in cores from Linsley pond in Massachusetts.

The sampling profile consisted of dark brown and black Gyttja extending from the mudline to a depth of 11 meters. The Gyttja graded into a two meter layer of clay containing a short series of black bands in the upper part and sand layers in its lower part. The clay was underlain by coarse unsorted gravelly sand.

There is some discrepancy as to the total quantity of phosphate present (see Table 26) yet the later work might be a better measure of phosphate content because of the use of analytic procedures that provided more complete release of phosphates from the bottom inorganic soil layers. Fig. 8, which plots the distribution of phosphate with depth in the deposit, indicates that phosphate concentrations increase from an average of about 150 mg/l of wet mud for the upper 8 meters of the profile to a maximum of 1640 mg/l at a depth of 12 meters. It is of interest to note that high values of phosphate were recorded in the organic Gyttja as well as the underlying clay.

The presence of large quantities of phosphates in the lower regions of the deposit may be due to large quantities of allochthonous material deposited in the lake during its early history which might have interfered with the release of phosphate into the water layer. If this were the case it could be expected that succeeding geologic deposition has occurred at such a rate as to trap these high concentrations making them unavailable for subsequent exchange processes.

The distribution of phosphorus with depth across Lake Michigan along a profile between Waukegan and Benton Harbor is graphically represented in Fig. 2. These data, which were obtained by X-ray fluorescence methods, indicate the percentage of total (both organic and inorganic) P_2O_5 by weight of dry sample obtained by measurements of samples taken with 2-inch and 3-inch gravity corers (Schleicher and Kuhn, 1970). For these samples, the nutrient level as measured

TABLE 26

PHOSPHATE CONTENT IN SEDIMENTS OF LINSLEY POND MUD

Depth (m)	Phosphate (mg/ml wet mud)	
	Hutchinson and Wollack (1940)	Livingston and Boykin (1962)
2	0.22	0.18
4	0.23	0.10
6	0.22	0.12
8	0.24	0.20
9	0.18	1.15
10	0.19	1.46
12	0.6	1.64
13	1.05	1.09

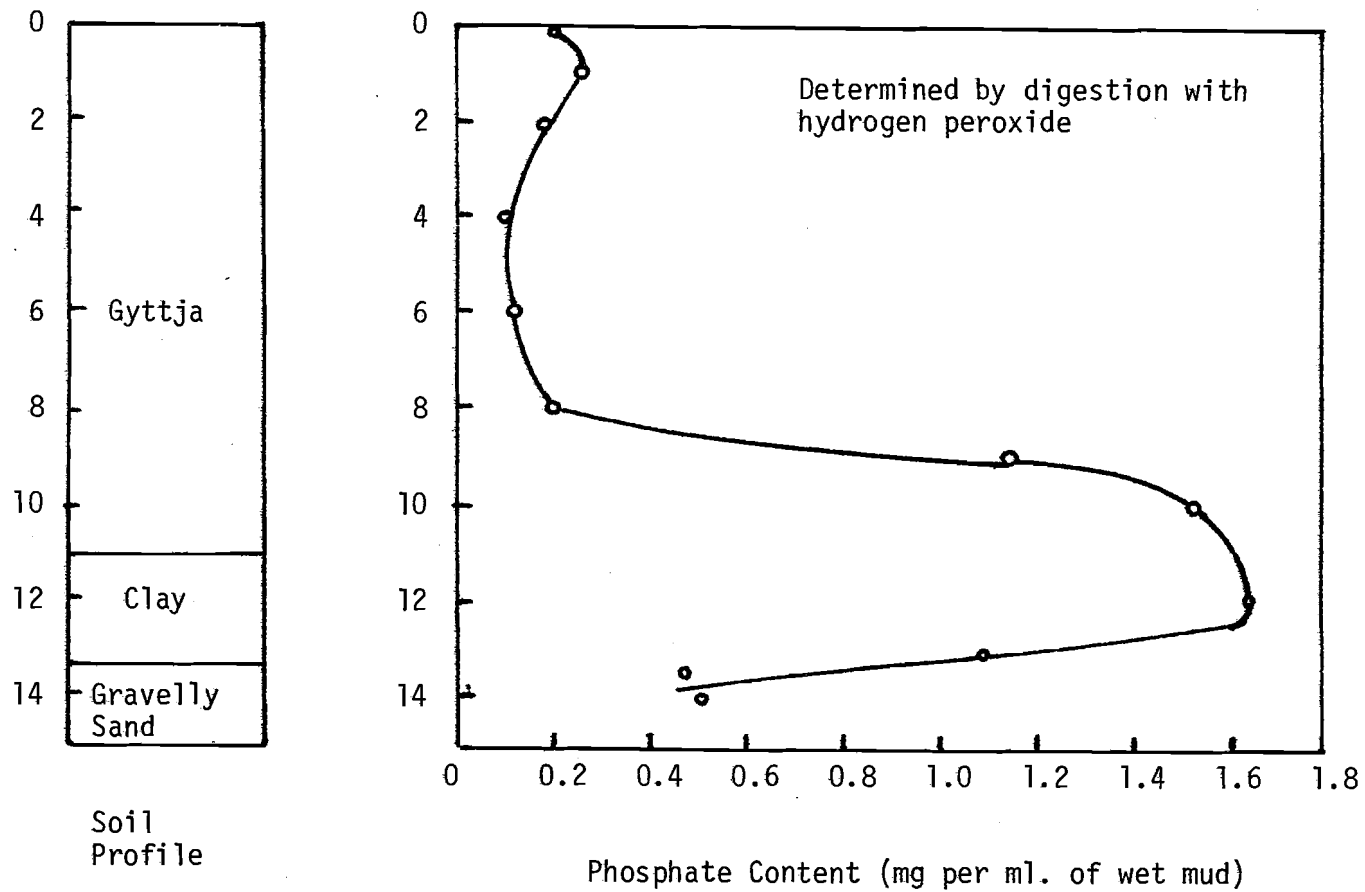


Figure 8 - Phosphorus Content in Sediments of Linsley Pond (after Livingston and Boykin, 1962).

by the P_2O_5 content was high at the surface, decreased in the first 25 centimeters, and then increased again. For the longer cores, it seems that the phosphate level again decreases and remains almost constant to a depth of about 200cm.

Holden (1961) studied core samples from the bottom deposits of productive but unfertilized lochs in Scotland. Measured phosphate concentrations are shown in Fig. 9. The data indicates the ability of the surface layer of mud to accumulate phosphorus, either from solution or from plant and animal debris. Moreover, it was found that these high sediment concentrations were retained in equilibrium with extremely low dissolved phosphate concentrations in overlying water. In loch fertilization experiments, where large quantities of phosphate (about $300\mu\text{g P/cm}^2$ of surface area) were added to the water, mud core samples showed that in some instances the phosphorus had penetrated downwards through the mud for at least 150mm. Holden suggested that downward burrowing bottom fauna organisms might have been partly responsible for some of this downward movement since surface mud samples had phosphate concentration less than previously determined saturation levels.

Extensive study of Lake Mendota have also yielded measurements of the nutrient content with depth. Measurements by Murray (1956) summarized in Table 27 and plotted in Figure 10 show that the high nutrient contents may exist uniformly with depth and need not be confined to only surface materials.

A variety of information exists describing the distribution of nutrients with soil depth in non-aquatic systems. In one such study, Williams and Saunders (1956) measured the distribution of total, total organic, and total inorganic phosphorus in several sandy Scottish soil profiles. In general, they found that the highest P_2O_5 content was located in the first 6 inches and that

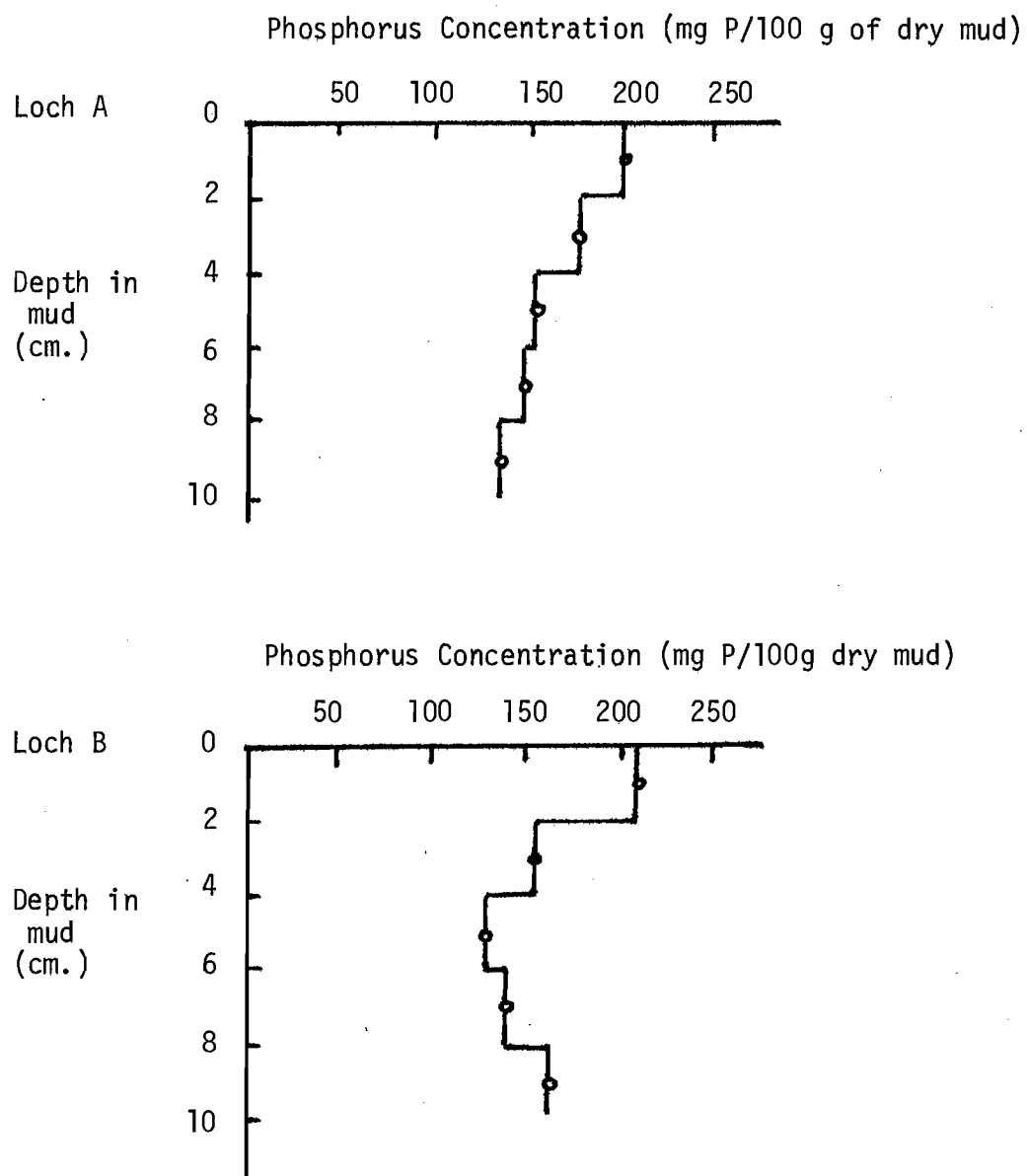


Figure 9 Total phosphorus in mud of two Scottish Eutrophic Lochs.

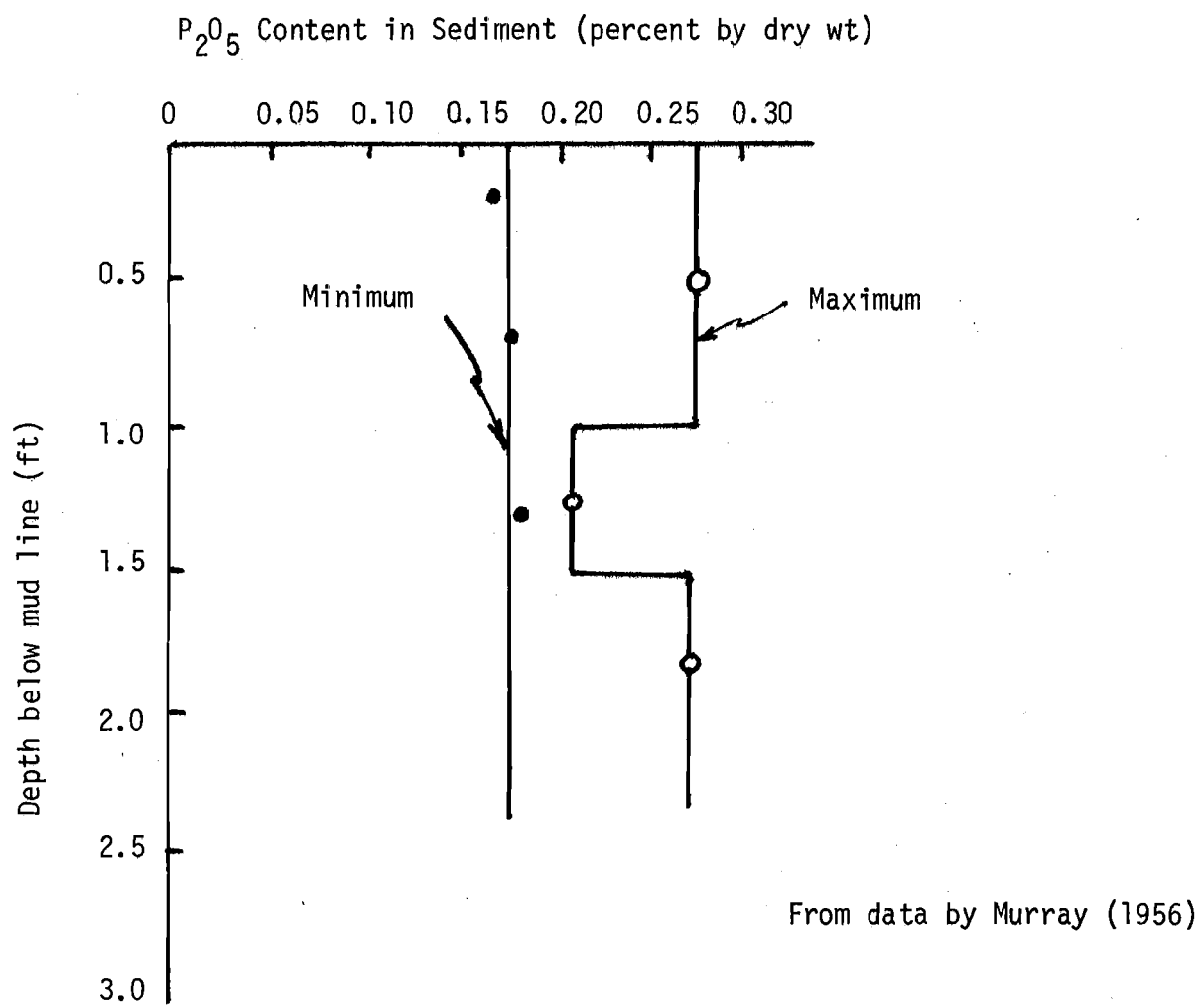


Figure 10 Concentration of Phosphorus with Depth in Sediments of Lake Mendota, Wisconsin.

TABLE 27

PHOSPHORUS CONTENT IN SEDIMENTS OF LAKE MENDOTA, WISCONSIN

Depth of Water	Depth below the Bottom	Percent of P_2O_5
63 feet	0-12 inches	0.275
	12-18 inches	0.209
	18-25 inches	0.269
35 feet	0-8 inches	0.180
	8-14 inches	0.181
	14-21 inches	0.182
53 feet	0-6 inches	0.208
	6-15 inches	0.182
	15-21 inches	0.191
55 feet	0-5 inches	0.168
	5-12 inches	0.177
	12-21 inches	0.189
69 feet	0-13 inches	0.259
	13-21 inches	0.183
	21-29 inches	0.185

After Murray (1956)

this concentration decreased somewhat with depth. It may be seen from Table 28 that total soil phosphorus decreased down all soil profiles yet significant phosphate concentration on the order of 252 mg/P₂O₅/100g of soil were found to exist to depths in excess of 3 feet below the surface. It is interesting to note that the ratio between the quantity of organic and inorganic phosphorus was not constant with depth. For example, the average total phosphorus content of surface soils was divided roughly equally between the organic and inorganic forms, while at depths of about 3 feet, the inorganic form predominated.

More important however, these results also show the effect of permeability on the nutrient content relationships for soil. For example, lower permeability correlates with measurements of lower total phosphorus, much lower total organic phosphorus, and higher values of total inorganic phosphorus. In general, measured phosphorus contents for sands were higher than for clays. This observed behavior may well be due to a combination of effects such as different flow rates, flow quantities and surface activity which characterize the different materials.

Discussion of Nutrient Contents in Aquatic Systems

This section has summarized data describing the occurrence and distribution of nutrients in aquatic systems. In addition, data has been obtained on the relationship between observed nutrient levels and levels which might cause eutrophication.

This investigation has made it clear that there is a general lack of information on the time rate of change of nutrient content in aquatic systems. The limited data that does exist generally represents the results of isolated measurement programs that are not continued with time. Most time studies

TABLE 28
DISTRIBUTION OF PHOSPHOROUS IN PROFILES OF SCOTTISH SOILS

Depth inches	Total P Contents in Soils			Organic P as % of total P
	mg. P ₂ O ₅ /100g Oven-Dry Soil			
	Total	Total organic	Total inorganic	
Freely drained profile on Old Red Sandstone till				
0-6	270	130	140	48
10-14	220	124	96	56
17-21	226	120	106	56
Poorly drained profile on Old Red Sandstone till				
0-6	236	90	146	38
9-13	197	95	102	48
15-19	145	75	70	52
23-27	114	28	86	25
37-41	156	24	132	15
Freely drained profile on basic igneous till				
0-6	413	189	224	46
8-13	340	191	149	56
15-17	252	68	184	27
18-21	181	48	133	27
26-30	141	30	111	21
36-44	252	43	209	17
Poorly drained profile on basic igneous till				
0-6	352	93	259	27
10-14	237	19	218	8
18-22	222	8	214	4
26-30	147	12	135	8
36-42	286	-	-	-
Freely drained profile on granitic till				
0-8	238	168	78	67
10-14	170	93	77	55
14-20	189	9	180	5
27-30	186	20	166	11
41-46	193	10	183	5
Poorly drained profile on granitic till				
0-8	215	105	110	49
11-16	100	10	90	11
22-27	130	10	120	8
33-39	130	4	176	2
Freely drained profile on slate till				
0-8	464	241	223	52
12-18	232	111	121	48
24-30	147	52	95	35
36-40	155	47	108	30

After Williams and Saunders (1956)

have been carried out to investigate the seasonal variation of nutrient contents during a single year. Researchers should, whenever possible be encouraged to reoccupy sampling stations to ensure that measured nutrient contents do not represent the contribution of isolated hydrologic or meteorological events.

A measure of the change in sediment nutrient content with time can be obtained from a knowledge of the distribution of these components with depth. For example, stratigraphic interpretations and radio carbon dating may be used to derive a time scale for dating the approximate age of the sediments and the concentration of the nutrient contents that were present at the time of deposition. Future success using this approach will require more comprehensive sampling programs that provides nutrient content data at adjacent stations as well as with depth at distinct points in the aquatic environment.

In addition, more and better physical-chemical limnologic and soil data is required to properly evaluate the results of nutrient sampling programs. For instance, parameters such as temperature and temperature distribution, current profiles, chemical profiles and biological data are seldom reported but are indispensable if the overall limnologic regime is to be understood and its characteristics added to the nutrient content picture. In many cases, this auxiliary data may be obtained with very little added effort and the range of studies that require such information could generally justify whatever added effort that must be expended.

An additional problem is presented by the variety of units used in reporting data. It is realized that different disciplines favor their own units; nevertheless, sufficient information should be included to aid in converting to other units. For example, converting nutrient contents expressed in terms of dry weight to expression based on wet weight requires a knowledge of the unit weight of the sediment. Such information is almost

always lacking. Here, journal reviewers could insure that such information is provided by the writer.

Finally the results of chemical analyses are often reported relative to some standard test. Yet there is often little thought as to the relevance of the chemical test to the individual system which is to be studied. For example, the standard separation to determine soluble and insoluble phosphorous is with a 45 μ filter. This is a hold-over from potable water determinations which required rapid measures of coliform organisms. Many bacteria, containing large quantities of phosphates, will pass a 45 μ filter, and thus much insoluble phosphate may be reported as soluble. In this example, the analytical breakpoint was chosen arbitrarily in the middle of a range of critical importance.

B. MECHANISMS FOR DESCRIBING MOBILITY OF PHOSPHOROUS NUTRIENTS IN AQUATIC SYSTEMS

Organizational Chart for Mechanisms Reported in the Literature

A variety of mechanisms has been proposed for the phosphate cycle in aquatic systems. However, very little attention has been given to organizing the various mechanisms suggested in terms of basic principles of physics and chemistry. Thus it is very difficult to consider in any comprehensive fashion the phosphate nutrient cycle in such systems. Therefore, an attempt has been made in Table 29 to organize previous research into a single format which is based on such fundamental principles. For each entry in Table 29, a brief description of the mechanism is given along with the literature reference in which the mechanism was discussed. In many cases more than one author has reported studies on a given mechanism.

MECHANISMS FOR FATE OF PHOSPHATES

HETEROGENEOUS CHEMICAL		HOMOGENEOUS SPATIAL		HETEROGENEOUS SPATIAL	
ORGANIC → INORGANIC	INORGANIC → ORGANIC	INORGANIC → INORGANIC	ORGANIC → ORGANIC	INORGANIC → ORGANIC	ORGANIC → INORGANIC
<p>CONVERSION OF INORGANIC AUTOGENOUS/ALLOCHTHONOUS INTO ORGANIC FORM BY MICROORGANISMS (E. MARSH, 1957) IN PLANTS (MOROT DIETARY SUPPLEMENT 1970) DISSOLVING REACTIONS IN MICRO-ORGANISMS (E. MARSH, 1957) CONVERSION OF ORGANIC FORMS INTO ORGANIC FORM BY BACTERIA (A. J. MCELROY, 1951)</p>		<p>ADSORPTION ON CLAY PARTICLES (POKORNY ET AL., 1956; OLSEN, 1964; OLSEN, 1965; THOMAS, ET AL., 1961; GORTIN AND BATHOLIC, 1961)</p>		<p>ADSORPTION BY PLANT ROOTS (BLACK, 1962; HAYES AND PHILLIPS, 1966; WOOD AND JACOBSON, 1970; ORENZIELLO AND 1957; R. N. ROBERTSON, 1951; PATTY AND THORPE, 1968; STANISLAVA AND HILL, 1955; STANISLAVA AND STANISLAVA, 1956; OREBETZ ET AL., 1955; M. A. SLAW, 1955-1964; JERRY AND OREBETZ, 1955; ODM AND RUMINS, 1956; WILKINSON, 1950; A. B. PHIPPS, 1964) ACCELERATION OF THE RATE OF ADSORPTION BY THE SEDIMENT OF THE WATER BY BACTERIA (PHILLIPS, 1968)</p>	
<p>UTILIZATION OF ADSORBED HOMOGENEOUS BY PLANTS (MOROT DIETARY SUPPLEMENT) FORMATION OF ORGANIC COMPOUND IN WATER (LITTE AND HAYES, 1963) UTILIZATION OF ADSORBED HOMOGENEOUS BY MICRO-ORGANISMS (E. MARSH, 1957) CONCENTRATION OF OXYGEN, SULFUR AND OTHER ELEMENTS BY BACTERIA, FUNGI AND PLANTS (MOROT DIETARY SUPPLEMENT) (MOROT ET AL., 1970; HAYES ET AL., 1961; STANISLAVA ET AL., 1955; GORTIN, ET AL., 1961) UPTAKE OF HOMOGENEOUS BY PLANTS TO UTILIZATION OF ADSORBED HOMOGENEOUS BY PLANTS AND PLANTS (MOROT AND MCELROY, 1951; MCELROY, 1951) HOMOGENEOUS BY SPERMATOPHYTES, FLORIDA PLANT, SPERMATOPHYTES (GORTIN ET AL., 1961) BACTERIAL PHOSPHATE MOBILIZATION BY PLANT AND WATER (MOROT, 1958)</p>		<p>UTILIZATION OF ADSORBED HOMOGENEOUS BY PLANTS (MOROT DIETARY SUPPLEMENT) FORMATION OF ORGANIC COMPOUND IN WATER (LITTE AND HAYES, 1963) UTILIZATION OF ADSORBED HOMOGENEOUS BY MICRO-ORGANISMS (E. MARSH, 1957) CONCENTRATION OF OXYGEN, SULFUR AND OTHER ELEMENTS BY BACTERIA, FUNGI AND PLANTS (MOROT DIETARY SUPPLEMENT) (MOROT ET AL., 1970; HAYES ET AL., 1961; STANISLAVA ET AL., 1955; GORTIN, ET AL., 1961) UPTAKE OF HOMOGENEOUS BY PLANTS TO UTILIZATION OF ADSORBED HOMOGENEOUS BY PLANTS AND PLANTS (MOROT AND MCELROY, 1951; MCELROY, 1951) HOMOGENEOUS BY SPERMATOPHYTES, FLORIDA PLANT, SPERMATOPHYTES (GORTIN ET AL., 1961) BACTERIAL PHOSPHATE MOBILIZATION BY PLANT AND WATER (MOROT, 1958)</p>		<p>DECOMPOSITION OF DEAD BACTERIA (LITTE AND HAYES, 1963) LEACHING OF HOMOGENEOUS BY WATER FROM DEAD ORGANISMS (LITTE AND HAYES, 1963) (A. D. WALKER, 1967) DECOMPOSITION OF DEAD PLANT ORGANISMS (LITTE AND HAYES, 1963) (A. D. WALKER, 1967) MOVING OF PHOSPHATE FROM WATER BY DECOMPOSITION OF DEAD PLANT AND ANIMAL REMAINS (LITTE AND HAYES, 1963) ACCUMULATION BY AND FROM PLANT AND ANIMAL REMAINS (LITTE AND HAYES, 1963) ELIMINATION PROCESSES (GORTIN AND FOREST, 1969)</p>	

The table as a whole is designed to demonstrate possible transformations that phosphate can undergo. Two major types of transformations are considered. The first major transformation is a spatial transformation. Such transformations imply that the position of the phosphate in the aquatic system changes. In particular, a distinction is made between phosphate which resides in an organic domain within the lake and phosphate which resides within an inorganic domain within the lake. For example, phosphates which exist in a solution in the water would be considered to be in an inorganic domain, and phosphates which reside within plants or animals would be considered to be within organic domains. Three major classes of spatial translation are considered. The first class of spatial translation actually involves no spatial translation of the phosphate. Thus phosphate which changes its chemical state but still remains in solution in the water would not be considered to have undergone a spatial translation. A second type of spatial translation is termed a homogeneous spatial translation. Homogeneous spatial translation implies that the phosphate undergoes a transition from one spatial domain to another spatial domain but that the two spatial domains are of the same type. Such homogeneous spatial translations can involve going from an inorganic domain to another inorganic domain, or from an organic domain to another organic domain. An example of the latter would be phosphate which resides in a plant being translated into another organic domain through ingestion by an animal. An example of a homogeneous spatial translation from an inorganic domain to another inorganic domain would be phosphate, existing in solution in the water, becoming lodged in the interlattice positions of clay minerals. The third type of spatial translation is a heterogeneous spatial translation. A heterogeneous spatial translation implies that the phosphate goes from a domain of one type to a domain of another type. Possible

heterogeneous spatial translations are inorganic to organic and organic to inorganic. Uptake of phosphate that exists in solution in water by adsorption through cell membranes is an example of an inorganic to organic heterogeneous spatial translation. Phosphate being desorbed by plants would be an example of an organic to inorganic heterogeneous spatial translation.

The second class of transformation to be considered is a transformation in the chemical state of the phosphate. Again, there are three possible types of chemical transformations. The first type involves no chemical transformation and the phosphate remains through the transformation in its original chemical form. A second class of chemical transformation is a homogeneous chemical transformation. Homogeneous chemical transformation involves a change in chemical state but if the phosphate was originally in an inorganic chemical state it remains in an inorganic chemical state. If the phosphate was originally in an organic chemical state, it remains in an organic chemical state. An example of the former would be phosphates released from inorganic compounds to solution in water through reducing conditions. An example of the latter would be digestive processes in animals which result in the transformation of organic phosphorous to a different type of organic phosphorous. The third class of chemical transformation is the heterogeneous chemical transformation. In this type of transformation the phosphate is changed from one chemical form to another by either an inorganic to organic transformation or an organic to inorganic transformation. An example of an inorganic to organic heterogeneous chemical transformation would be the formation of organic compounds from inorganic compounds dissolved in water. An example of an organic to inorganic heterogeneous chemical transformation would be the decomposition of dead bacteria to release inorganic soluble phosphate to the water.

MECHANISMS FOR FATE OF PHOSPHATES

HETEROGENEOUS CHEMICAL		HOMOGENEOUS CHEMICAL		HETEROGENEOUS SPATIAL		
NO SPATIAL	HOMOGENEOUS SPATIAL	NO SPATIAL	HOMOGENEOUS SPATIAL	NO SPATIAL	HOMOGENEOUS SPATIAL	
ORGANIC + INORGANIC	INORGANIC + ORGANIC	ORGANIC + ORGANIC	INORGANIC + INORGANIC	INORGANIC + ORGANIC	ORGANIC + INORGANIC	
<p>DIESTER REACTIONS IN HIGHER ORGANISMS (POMEROY, ET AL., 1963)</p>	<p>CONVERSION OF INORGANIC AND ORGANIC PHOSPHATES TO DIESTERS BY MICROORGANISMS (LEWIS, 1957)</p> <p>DIESTER REACTIONS IN PLANTS (MCCOY AND LAMBERT, 1970)</p> <p>DIESTER REACTIONS IN MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF PHOSPHATES INTO ORGANIC FORM BY BACTERIA (LEWIS, 1957)</p>	<p>DIESTER REACTIONS IN HIGHER ORGANISMS (POMEROY, ET AL., 1963)</p>	<p>DIESTER REACTIONS IN HIGHER ORGANISMS (POMEROY, ET AL., 1963)</p>	<p>UTILIZATION OF ASSIMILATED PHOSPHATES BY PLANTS (HODGSON AND BARRETT, 1970)</p> <p>PHOSPHATE RELEASE FROM PLANTS IN WATER (LAW AND WATTS, 1963)</p> <p>UTILIZATION OF ASSIMILATED PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF DIESTERS INTO PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>DIESTER REACTIONS IN PLANTS (MCCOY AND LAMBERT, 1970)</p> <p>DIESTER REACTIONS IN MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF PHOSPHATES INTO ORGANIC FORM BY BACTERIA (LEWIS, 1957)</p>	<p>DIESTER REACTIONS IN HIGHER ORGANISMS (POMEROY, ET AL., 1963)</p>	<p>UTILIZATION OF ASSIMILATED PHOSPHATES BY PLANTS (HODGSON AND BARRETT, 1970)</p> <p>PHOSPHATE RELEASE FROM PLANTS IN WATER (LAW AND WATTS, 1963)</p> <p>UTILIZATION OF ASSIMILATED PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF DIESTERS INTO PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>DIESTER REACTIONS IN PLANTS (MCCOY AND LAMBERT, 1970)</p> <p>DIESTER REACTIONS IN MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF PHOSPHATES INTO ORGANIC FORM BY BACTERIA (LEWIS, 1957)</p>
	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p> <p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	<p>UTILIZATION OF ASSIMILATED PHOSPHATES BY PLANTS (HODGSON AND BARRETT, 1970)</p> <p>PHOSPHATE RELEASE FROM PLANTS IN WATER (LAW AND WATTS, 1963)</p> <p>UTILIZATION OF ASSIMILATED PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF DIESTERS INTO PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>DIESTER REACTIONS IN PLANTS (MCCOY AND LAMBERT, 1970)</p> <p>DIESTER REACTIONS IN MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF PHOSPHATES INTO ORGANIC FORM BY BACTERIA (LEWIS, 1957)</p>	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	
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	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	<p>UTILIZATION OF ASSIMILATED PHOSPHATES BY PLANTS (HODGSON AND BARRETT, 1970)</p> <p>PHOSPHATE RELEASE FROM PLANTS IN WATER (LAW AND WATTS, 1963)</p> <p>UTILIZATION OF ASSIMILATED PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF DIESTERS INTO PHOSPHATES BY MICROORGANISMS (LEWIS, 1957)</p> <p>DIESTER REACTIONS IN PLANTS (MCCOY AND LAMBERT, 1970)</p> <p>DIESTER REACTIONS IN MICROORGANISMS (LEWIS, 1957)</p> <p>CONVERSION OF PHOSPHATES INTO ORGANIC FORM BY BACTERIA (LEWIS, 1957)</p>	<p>RELEASE OF PHOSPHATE FROM PHOSPHATES - CONTAINING SUBSTRATES BY HETEROTROPHIC BACTERIA (POMEROY, ET AL., 1963)</p>	

The table as a whole is designed to demonstrate possible transformations that phosphate can undergo. Two major types of transformations are considered. The first major transformation is a spatial transformation. Such transformations imply that the position of the phosphate in the aquatic system changes. In particular, a distinction is made between phosphate which resides in an organic domain within the lake and phosphate which resides within an inorganic domain within the lake. For example, phosphates which exist in a solution in the water would be considered to be in an inorganic domain, and phosphates which reside within plants or animals would be considered to be within organic domains. Three major classes of spatial translation are considered. The first class of spatial translation actually involves no spatial translation of the phosphate. Thus phosphate which changes its chemical state but still remains in solution in the water would not be considered to have undergone a spatial translation. A second type of spatial translation is termed a homogeneous spatial translation. Homogeneous spatial translation implies that the phosphate undergoes a transition from one spatial domain to another spatial domain but that the two spatial domains are of the same type. Such homogeneous spatial translations can involve going from an inorganic domain to another inorganic domain, or from an organic domain to another organic domain. An example of the latter would be phosphate which resides in a plant being translated into another organic domain through ingestion by an animal. An example of a homogeneous spatial translation from an inorganic domain to another inorganic domain would be phosphate, existing in solution in the water, becoming lodged in the interlattice positions of clay minerals. The third type of spatial translation is a heterogeneous spatial translation. A heterogeneous spatial translation implies that the phosphate goes from a domain of one type to a domain of another type. Possible

heterogeneous spatial translations are inorganic to organic and organic to inorganic. Uptake of phosphate that exists in solution in water by adsorption through cell membranes is an example of an inorganic to organic heterogeneous spatial translation. Phosphate being desorbed by plants would be an example of an organic to inorganic heterogeneous spatial translation.

The second class of transformation to be considered is a transformation in the chemical state of the phosphate. Again, there are three possible types of chemical transformations. The first type involves no chemical transformation and the phosphate remains through the transformation in its original chemical form. A second class of chemical transformation is a homogeneous chemical transformation. Homogeneous chemical transformation involves a change in chemical state but if the phosphate was originally in an inorganic chemical state it remains in an inorganic chemical state. If the phosphate was originally in an organic chemical state, it remains in an organic chemical state. An example of the former would be phosphates released from inorganic compounds to solution in water through reducing conditions. An example of the latter would be digestive processes in animals which result in the transformation of organic phosphorous to a different type of organic phosphorous. The third class of chemical transformation is the heterogeneous chemical transformation. In this type of transformation the phosphate is changed from one chemical form to another by either an inorganic to organic transformation or an organic to inorganic transformation. An example of an inorganic to organic heterogeneous chemical transformation would be the formation of organic compounds from inorganic compounds dissolved in water. An example of an organic to inorganic heterogeneous chemical transformation would be the decomposition of dead bacteria to release inorganic soluble phosphate to the water.

Discussion of Mechanisms Studied

The primary objective of the literature search was to determine the relationship between phosphate in sediments and phosphates in solution; thus there are presently more entries in the table in transformations that are involved in this particular aspect of the problem of the fate of phosphates.

Therefore, the diligence with which the literature was searched was not uniform amongst the several possible transformation mechanisms. Nevertheless, the format offered by the table should be useful as a vehicle for continued organization of the state of research in the fate of phosphates. It is hoped that other investigators will contribute mechanisms and associated references in the areas that are not strongly represented in the table.

Several patterns emerge in Table 15 which deserve comment. First, many mechanisms have been proposed which involve either no chemical transformation or no spatial translation. The large number of mechanisms studied in these areas results from the simplifying assumption that only a single type of transformation is encountered. Secondly, of the mixed transformation mechanisms, most lie in squares along the upper left to lower right diagonal. This is logical since such squares represent cases where the chemical form of the phosphate is the same as the chemical form of the space within which the phosphate resides. Thus we would not be surprised, for instance, to see an inorganic to organic chemical transformation occurring simultaneously with an inorganic to organic spatial translation. Thirdly, it may be noted that inorganic type mechanisms predominate. This may be the result of bias in the literature search, but it may also reflect a relative underdevelopment of techniques for studying organic mechanisms.

It may also be noted that a wide variety of mechanisms for transformation of phosphates in aquatic systems has been studied. The detail of the studies and their relevance to conditions in natural systems varies. The commonly employed technique of isolating variables has often resulted in too few variables being examined as well as in minimizing the study of interaction between the variables. In particular, the problem of eutrophication is often characterized by a sporadic event such as the occurrence of an algal bloom. Such an event may not depend upon the value of a single parameter but rather on a critical combination of values for two or more parameters. Thus one weakness of the existing literature is a failure to carefully consider the individual and combined effects of a variety of parameters that might influence the mechanism.

A second shortcoming in the literature is the tendency to assign causative significance to what may only be indirect parameters. Thus a correlation may be set between pH and the degree of activity of some mechanism without attempting to assign the specific physico-chemical role of pH within that mechanism.

A third shortcoming in the literature is the failure to fully examine multipath mechanisms in light of the probability of branching to the several alternative mechanisms. Thus if phosphate is known to exist in a given physico-chemical state, one must look at all possible transformations to other states and decide which transformation is most likely to occur. Implicit in this is that the rates of transformation for each possible mechanism must be studied.

This failure to consider the dynamics of the system probably represents the area that can be most fruitfully studied at present. The following

illustration points out one such case. While the total phosphate contained in bacteria is relatively small, the turnover rate is quite high. Thus bacteria acquire phosphate by attacking dead organisms. These bacteria in turn die and sink to the lake bottom. The role of bacteria here is to subdivide phosphate into smaller packets within the system. The spacial translation is organic to organic and the chemical transformation is organic to organic. Nevertheless, phosphate in a bacteria cell is potentially more available than phosphate in a larger organism simply because the bacteria is smaller than the organism.

The bacteria which settle to the bottom of the lake then decompose. The resulting organic to inorganic chemical transformation serves as a potential source of inorganic phosphorous for association with clays in sediments. However, static studies indicate that this reaction can only occur if the decomposed bacteria are in physical contact with the clay. Thus in stationary sediments, this exchange occurs only within the top millimeter or two. Clearly, under such circumstances, the bottom clays cannot act as effective reservoirs for large quantities of phosphate nutrients. However, it is not unusual for clays to hold enough phosphate to initiate hundreds of algal blooms. Thus some mechanism must exist whereby increased contact between dead bacteria and clays occurs. This mechanism appears to be through the dynamic disturbance of the bottom sediments. Typical mechanisms for disturbance of sediments are normal currents, density currents, fish stirring, seiches, underwater landslides, bacterial fermentation, stirring by ship propellers, dredging and other construction. Very little work has been done to date on the dynamics of this important exchange reaction.

PHASE II - LABORATORY TECHNIQUES FOR STUDYING THE MOBILITY OF PHOSPHATES IN SEDIMENTS

Laboratory Techniques for the Determination of Phosphorous

A search of the literature produced two techniques for measuring P in soils and water. Both techniques determine total P by converting phosphate to a phosphomolybdate complex. The intensity of the blue color of this complex is measured colorimetrically by comparison with known standards at 660 m μ .

The details of the techniques appear in "Chemistry Laboratory Manual", Bottom sediments, compiled by the Great Lakes Region Committee on Analytical Methods (1969).

Design of Special Consolidation Test Apparatus

A laboratory testing program has been designed to determine the mobility of phosphates in sediments due to ionic diffusion and mass transport by flowing water. A modification of the consolidation test was chosen for this purpose. In this test, as shown in Fig. 11, a saturated soil sample is confined in a rigid cylindrical tube. The ends of the sample are loaded by a porous rigid plate to which an external force is applied. Initially the entire load is borne by a buildup of pressure in the water in the pores of the soil. The only way in which this pressure can be released is by water flowing out through the porous plates at the end of the sample. This dynamic outflow of water continues until all excess pore water pressure is dissipated. The process of water outflow is termed consolidation.

The consolidation test has distinct advantages for the present study. Since there is a compression force in the soil mass, the outflow of water occurs uniformly from all of the interstitial pores in the soil. This is

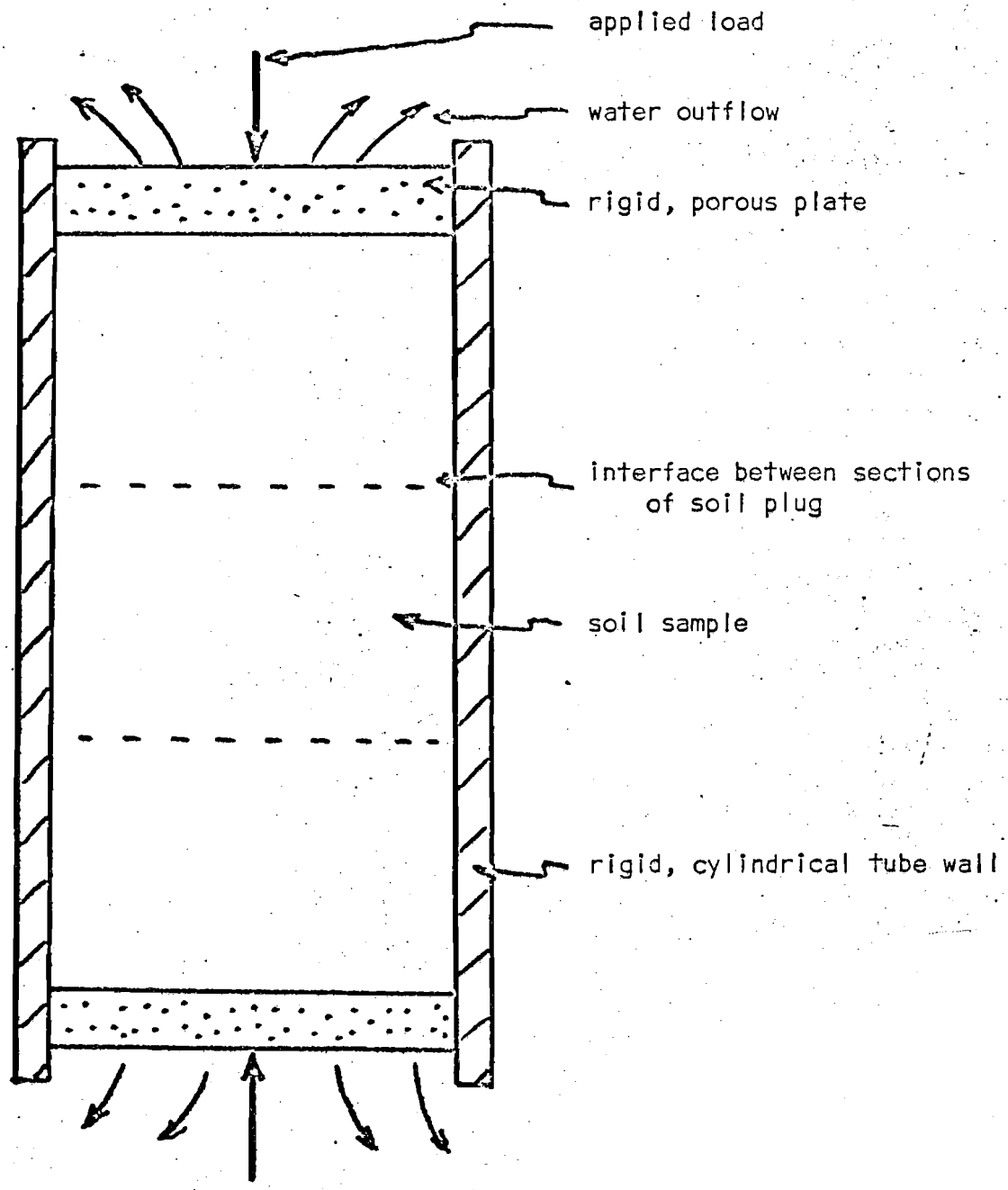


Figure 11 - Schematic of special consolidometer.

in contrast to a simple permeability test where flow has been shown to occur through channels around the periphery of the sample. Moreover, the consolidation process has a built-in time dependency which results in imposing a variable dynamic force on the pore ions.

For purposes of these studies, the triaxial test will be modified to allow the use of radioactive tracer techniques to assist in analyzing the test results. The sample to be used will consist of three subsamples as shown in Fig. 11. The phosphate content throughout the entire sample will be constant; however, the center one third of the sample will contain some radioactive P-32. At the completion of the consolidation phase, the sample will be sectioned into slices approximately 0.01 inch thick and the quantity of radioactive phosphorous, will be determined using standard radionucleid counting techniques. The results of these tests will show the amount of dispersion at the interfaces between the three soil plugs.

A testing program using these techniques is presently being conducted under contract A-053, Dynamic Interaction Between Phosphate Nutrients and Sediments, through the Annual Allotment Program of the Water Resources Center. In this study the mobility of phosphate in illite clay is being determined under five driving forces and for four phosphate concentration levels.

Reduction of Laboratory Data

A computer program has been developed to analyze the data to be obtained from the radionuclied counting apparatus. The program reduces the data and plots the results on a Cal-Comp plotter. The following output normalization options are available:

1. Counts normalization
 - a. display of counts per minute per gram (c/m/g) at a scale to fit within ten inches
 - b. display of c/m/g with sample background count subtracted
 - c. display of c/m/g with sample background count subtracted and average crest of plot normalized to five inches
2. Normalization with respect to position along the sample
 - a. actual distance
 - b. actual distance normalized to ten inches
 - c. actual cumulative weight
 - d. actual cumulative weight normalized to ten inches
3. Normalization with respect to both weight and c/m/g to yield a unit area under the total curve.
4. Correction of c/m/g for decay.

Figure 12 shows typical laboratory data obtained using the experimental techniques developed. The results to date indicate that these techniques will be acceptable for use under contract A-053.

CONCLUSIONS

The initial objectives of this research have been met. The literature review of the present state of knowledge concerning where phosphates occur in sediments produced considerable data as summarized in Tables 1 through 28 and Figures 1 through 10. In many cases it was difficult to convert data presented in the literature into consistent units for comparison purposes.

The literature review of mechanisms by which phosphates are held in sediments and mechanisms that result in mobility of phosphates within sediments

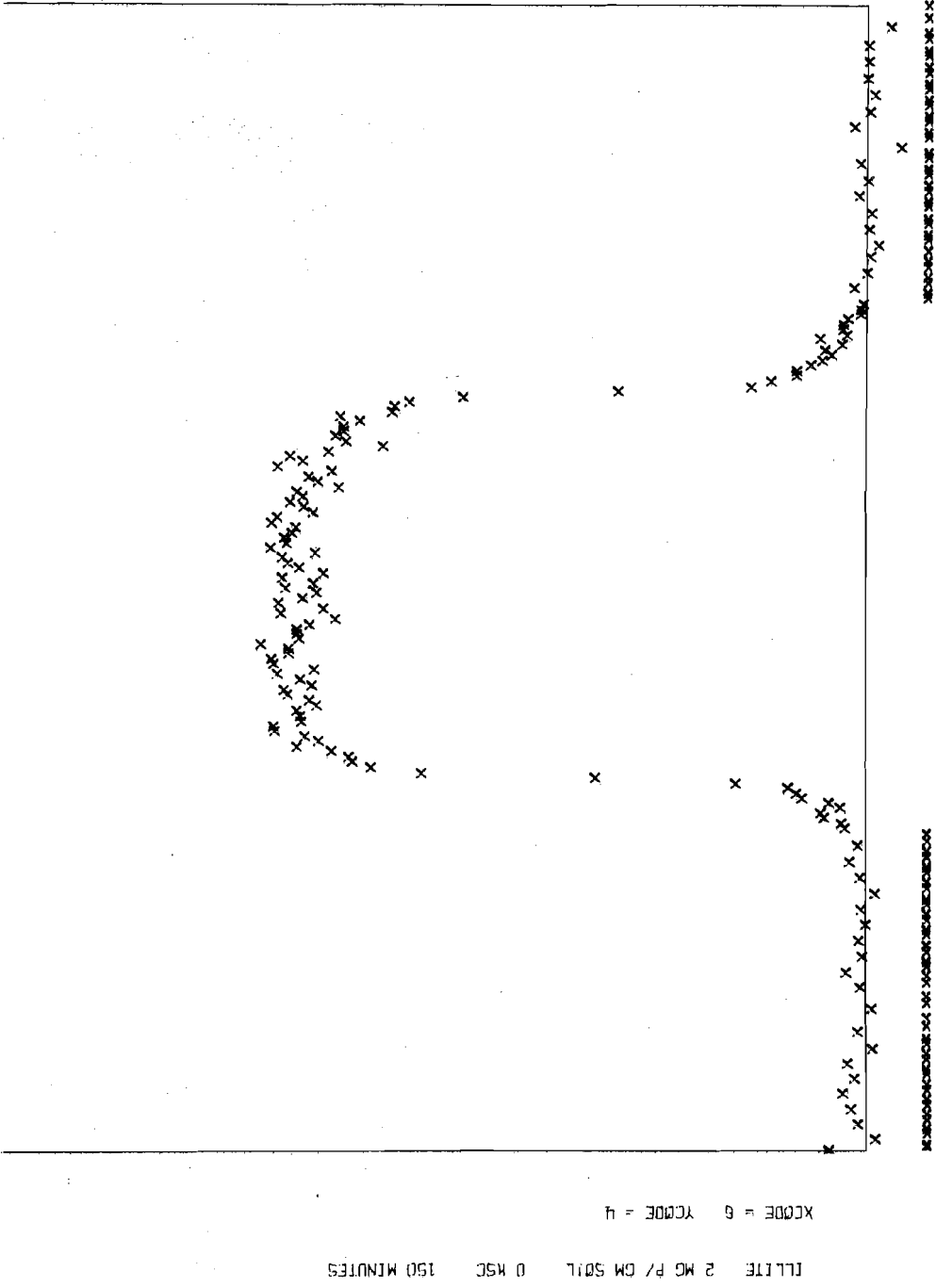


Figure 12 - Typical transport test results.

resulted in extending the scope of the original proposal. It was found that interactions between the sediment and the other components of the aquatic system could not be ignored. Table 29 presents a synthesis of mechanisms for fate of phosphates in aquatic systems compiled from the literature.

The second phase of the research concerned laboratory techniques for measuring transport phenomena for phosphates in sediments. Techniques currently recommended by the Great Lakes Region Committee on Analytical Methods (1969) were found to be acceptable.

A special consolidation test apparatus was designed to allow the use of P^{32} tracer techniques for studying the transport of phosphorous in soils. Initial tests on the apparatus indicate that it will perform acceptably.

RELATIONSHIP TO WATER RESOURCES PROBLEMS

The work performed under contract A-047, The Role of sediments in Eutrophication - A Preliminary Study, is particularly pertinent to the solution of pressing problems in eutrophication. Eutrophication is a process which depletes lake and rivers of oxygen. The process is initiated by nutrients such as phosphorous and nitrogen which cause the accelerated growth of algae. This algae then cuts off sun light which results in a drastic decrease in oxygen production. The depletion of oxygen, in turn, results in the death of animal life.

The purpose of this research was to investigate the extent to which nutrients in sediments might become available for algal growth. The study encompassed the following areas:

1. a literature review determining the present state of knowledge concerning the quantitative distribution of phosphates in sediments. The results of this review indicated that potentially

dangerously large quantities of phosphates and nitrates are stored in some sediments.

2. a literature review of mechanisms proposed by which nutrients are held in sediments and mechanisms that result in mobility of nutrients within the total aquatic system. It was determined that many mechanisms exist that could result in the release of nutrients from sediments into the overlying waters.
3. an experimental portion of the research resulted in the development of special laboratory apparatus to use radionucleid techniques to study the transport of nutrients in sediments.

This investigation was preliminary to a continuing contract A-053, Dynamic Interaction Between Phosphate Nutrients and Sediments. An objective of A-053 is to study the dynamic release of phosphates from sediments and assess the potential of these sediments for supplying nutrients for eutrophication.

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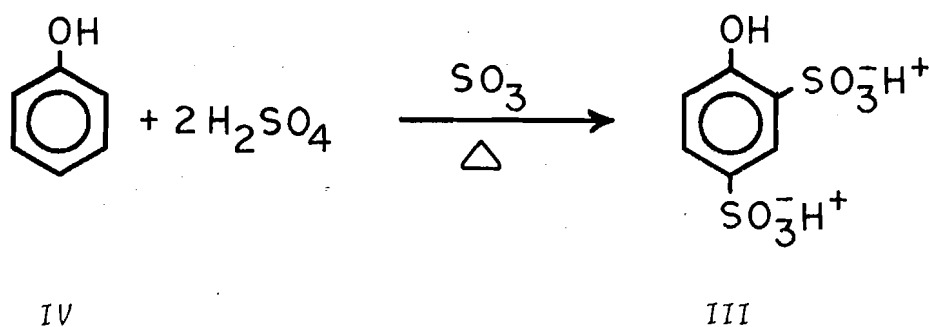
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fuming sulfuric acid and heating the solution for two hours on a hot-water bath.



A water sample is first decolorized, if necessary, with an aluminum hydroxide suspension. Nitrite if present, is converted to nitrate with potassium permanganate in the presence of sulfuric acid. Chloride if present, is removed by precipitation with silver sulfate, followed by filtration or centrifugation. The sample is neutralized to a pH of 7 and evaporated to dryness. The residue is rubbed thoroughly with *III* to prevent any undissolved residue from remaining, and if needed, heated on a water bath for a short period. The solution is diluted with water and the maximum color is developed with the addition of ammonium hydroxide or potassium hydroxide. Any precipitates which may exist are removed by filtration or complexation with EDTA. The solution is diluted to volume and the absorbance is measured at 410 m μ . Standard solutions for comparison are prepared in a similar manner and are stable for a period of several weeks.

Murty and Gopalarao (10) reported a colorimetric method for the determination of nitrate using α -naphtholsulfonic acid. The reagent was reacted with a small amount of nitrate and formed a species that developed an intense yellow color in basic solution. When compared to the phenoldisulfonic acid method, the proposed method could tolerate a larger amount

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