

AD-A083 694

WEST VIRGINIA UNIV MORGANTOWN DEPT OF CHEMICAL ENGIN-ETC F/S S/S
BIOLOGICAL AVAILABILITY OF TOTAL PHOSPHORUS.(U)
JAN 79 T LOGAN, F H VERHOFF, J V DEPINTO

DACU49-79-C-0002

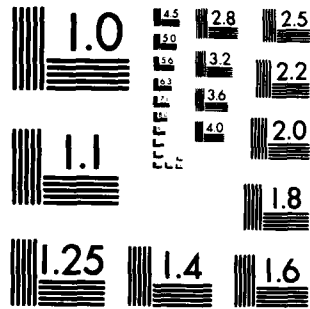
ML

UNCLASSIFIED

1-1
1-1



END
DATE
FILMED
6-80
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ADA083694

DTIC
ELECTE
S MAY 1 1980 D
D

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DO FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ABSTRACT

This paper discusses the bioavailability of Lake Erie tributary sediment phosphate as determined by chemical extraction and algal uptake.

This report will include the following:

1. Review of the literature on procedures to estimate biologically available sediment phosphate (BSP) including sequential chemical extraction, resin extraction, P desorption and various algal bioassay techniques,
2. Sequential chemical extraction of P from suspended sediments in Lake Erie drainage Basin tributaries,
3. Algal uptake of sediment P from several suspended sediments from Lake Erie Basin tributaries,
4. Conclusions from the project studies,
5. Extrapolation and implications for the Lake Erie Basin.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist.	Avail and/or special
A	

DTIC
ELECTE
S MAY 1 1980 D
D

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

BIOLOGICAL AVAILABILITY OF TOTAL PHOSPHORUS

by

**Terry J. Logan
Agronomy Department
Ohio State University**

**Frank H. Verhoff
Chemical Engineering Department
West Virginia University**

Morgantown -

**Joseph V. DePinto
Clarkson College**

January 1979

**Lake Erie Wastewater Management Study
U. S. Army Engineer District, Buffalo
1776 Niagara Street
Buffalo, NY 14207**

DISTRIBUTION STATEMENT A

**Approved for public release;
Distribution Unlimited**

ACKNOWLEDGEMENTS

The efforts of Tom Oloya on the chemical extraction study and Marc Heffner on the algal bioassay are acknowledged. Complete details of the chemical extraction and algal bioassay studies are published separately.

TABLE OF CONTENTS

<u>Subject</u>	<u>Page</u>
LIST OF FIGURES	iv
LIST OF TABLES	v
ABSTRACT	vi
INTRODUCTION	1
LITERATURE REVIEW	4
a. Chemical Fractionation of Sediment Phosphorus	
b. Chemical Measurement of Available P	
c. Bioassay Measurement of Available P	
Allochthonous Material	
Autochthonous Material	
Lake Bottom Sediments	
Summary	
CHEMICAL EXTRACTION OF LAKE ERIE TRIBUTARY SEDIMENT PHOSPHATE	21
a. Methods and Materials	
Sample Collection	
Analytical Procedures	
b. Results and Discussion	
Bioavailable Sediment P	
Total Sediment P Analysis	
Conclusions	
ALGAL UPTAKE OF PHOSPHATE FROM LAKE ERIE TRIBUTARY SEDIMENTS	37
a. Methods and Materials	
b. Results and Discussion	
DO and pH Measurements	
Biological Removal of Phosphorus by Algal Harvests	
Check of Lag Phase	
Chemical Extraction of Sediment Phosphate Before and After	
Algal Uptake	
Conclusions	
CONCLUSIONS	55
REFERENCES	57

LIST OF FIGURES

	Page
1. Lake Erie Drainage Basin tributary sampling sites	26
2. Summary of suspended sediment parameters (mean and standard deviation for samples within each group)	30
3. Dissolved Oxygen and pH Variation as a Function of Time in the Cattaraugus River samples	43
4. Dissolved Oxygen and pH Variation as a Function of Time in the Sandusky River samples	44
5. Percent Phosphorus Removal as a Function of Time in the Honey Creek samples	46
6. Percent Phosphorus Removal by the Algae as a Function of Time in the Sandusky River samples	48
7. Percent Phosphorus Removal by the Algae as a Function of Time in the Honey Creek samples	49
8. Percent Phosphorus Removal by the Algae as a Function of Time in the Broken Sword samples	50

LIST OF TABLES

	Page
1. Characteristics of Lake Erie tributary sampling sites	23
2. Summary of sediment-P characteristics	28
3. Percent bioavailability of sediment-P	32
4. Simple moment correlation coefficients between sediment-P parameters	34
5. Stepwise linear regression equations	35
6. Methods of analysis	40
7. Harvest schedule	41
8. Removal rates for extraction data considering nonalgal suspended solids removal	51
9. Analysis of suspended river sediments before and after algal extraction	52

ABSTRACT

This paper discusses the bioavailability of Lake Erie tributary sediment phosphate as determined by chemical extraction and algal uptake. The main findings are listed below:

1. Sequential chemical extraction showed that there was wide variation in fraction of sediment-phosphorus that was extracted by NaOH, CDB or HCl. Michigan and Ohio sediments were higher in bioavailable sediment P as measured by NaOH or (NaOH + CDB) extractions and New York sediments were lower but highest in HCl-P (apatite).

2. High sediment concentrations and possibly high coarse sediment content of the New York samples appeared to be the main reason for lower bioavailable sediment-P.

3. The algal bioassay study indicated that the New York sediment would not support any algal growth in laboratory incubations.

4. In the Ohio sediments, the pool of available P was not depleted during incubations up to 150 days.

5. Rate of phosphate uptake by algae from sediment was less than 0.4 percent/day and kinetic rate appears to be more of a limiting factor in supply of P to algae by sediment than the total available sediment-P.

6. Bioassay procedures to estimate bioavailable sediment P should measure rate of P uptake, the P associated with the algal bioamass rather than just biomass production, and they should consider the effect of P uptake by indigenous phytoplankton.

7. P extracted by algae from sediment resulted in a removal from all chemical extraction fractions (NaOH, CDB and HCl), but greatest reduction was in the NaOH fraction.

INTRODUCTION

The role of phosphorus in accelerated eutrophication of Lake Erie and other areas in the Great Lakes Drainage Basin has been recognized and documented in recent years. Studies by LEWIS and PLUARG have shown that a major part of the total phosphorus load entering the lakes from tributary drainage is in the form of particulate-P. While it is readily accepted that soluble inorganic-P in drainage water is available to algae and other aquatic vegetation, the bioavailability of sediment-bound phosphate is largely unknown. As a result, one is faced with two extreme scenarios: a) only the soluble inorganic-P is bioavailable or b) all sources of P including sediment-P are available. The first scenario is supported by the findings in New York where soluble inorganic-P was shown to be the dominant form of stream-transported phosphate in stimulating growth of algae (Porter, 1975). On the other hand, Golterman (1977) found that sediment-P in shallow polder lakes in Holland would maintain highly eutrophic conditions even if all external P sources were removed. Recent work by Allan and Williams (1978) demonstrated the importance of biologically available sediment-P in fairly shallow Canadian prairie lakes.

The importance of sediment as a source of P for algae is governed by a number of factors. Streams which carry a low sediment load, and/or sediment of coarse-texture and stream-bank origin will have most of its biologically available P as soluble inorganic-P as a consequence of the lower P content of coarse sediment (Williams *et al.*, 1976). Consideration must also be given to physical lake dynamics. Stream sediments which settle rapidly into deep lakes will only be positionally available to algae in the photic zone for short periods as in the central and eastern basins of Lake Erie, thereby minimizing the significance of sediment-P as a source of biologically available phosphorus. In contrast, we have the situation where streams carry a high load of fine-grained sediment into shallow lakes, a

situation similar to that in the western basin of Lake Erie. In this instance, factors which serve to increase the importance of sediment-P are: the high percentage of the total phosphorus load as sediment-P, the higher content of P in clay-sized sediment, and the longer period in which this suspended sediment load is positionally available to algae in the photic zone.

Procedures to estimate bioavailability of sediment-P from tributary sources must take into account the conditions under which algae obtain P from sediment. Algae can derive some P from sediment in the photic zone for short periods and under aerobic conditions. In addition, available-P is derived from bottom sediments during anoxic regeneration and subsequent lake inversion, a markedly different chemical environment than exists in the photic zone. While much of the P regeneration is from decomposed algal biomass, sediment-P is also released under anoxic conditions. As a result of this dichotomy, bioavailable sediment-P will be viewed here in two ways: a) positionally available, to represent short-term release of P to algae in surface waters, and b) total potentially available, to represent maximum P which can be released over time by all mechanisms. Procedures to estimate sediment-P bioavailability will be discussed in the context of this concept.

This report will include the following:

1. Review of the literature on procedures to estimate biologically available sediment phosphate (BSP) including sequential chemical extraction, resin extraction, P desorption and various algal bioassay techniques.
2. Sequential chemical extraction of P from suspended sediments in Lake Erie drainage Basin tributaries.

3. Algal uptake of sediment-P from several suspended sediments from Lake Erie Basin tributaries.
4. Conclusions from the project studies
5. Extrapolation and implications for the Lake Erie Basin.

LITERATURE REVIEW

Since phosphorus load regulation is generally regarded as the primary means for controlling eutrophication, it is extremely important to have accurate estimates of available phosphorus loadings to the lake in question before contemplating management or abatement measures. Current estimates of total phosphorous loadings to lakes are complicated by the lack of information on the fraction of the P inputs that is available for algal growth or becomes available in a reasonable length of time. The question is particularly important in relation to diffuse runoff sources, which can contain a relatively large fraction of the phosphorus in the particulate form.

The problem can be manifested in the following scenario. Consider a tributary entering a lake. The river water carries a certain total P load based on the flow and concentration. Depending on the source, a substantial fraction of the river phosphorus is particulate. It can be reasonably assumed that most of the dissolved fraction will eventually become available as orthophosphate. As the particulate P fraction enters the lake water environment, it can undergo various physical-chemical and biological reactions including: sorption-desorption, dissolution-precipitation, microbial mineralization of organic P, microbial utilization of particulate P, and coagulation-sedimentation. The factors that will affect the algal availability of this particulate P while it is in the water column are the same ones that govern the above reactions: temperature; soluble inorganic P level in the lake water; lake morphometry, hydrology, and mixing dynamics; size, density and physicochemical characteristics of the particles; phosphorus fractionation (form of P compounds) of the particles; and lake productivity level, including microbial activity and degree of P limitation.

The amount of particulate P made available for algal uptake while the river sediment is in the water column depends not only on the extent and direction of the above reactions but on the respective rates. It is quite conceivable that the river particles may settle to the lake bottom and consolidate before all the potentially available P has been released if the rate of release is slow relative to the settling time. Once the particulate P consolidates in the lake sediments an entirely different set of environmental conditions exist, and estimation of the rate and extent of P availability is a different problem altogether.

In order to correctly estimate the available P loading to a lake one must quantify the above situation. This process involves the measurement or quantification of the rate and extent that allochthonous and autochthonous particulate P is made available for algal uptake and growth as well as the rate of release or uptake of available P from the lake sediments (the internal load). This review is an attempt to bring together the current knowledge on P availability so that better and more meaningful phosphorus loading estimates can be made. Weaknesses or gaps in the current knowledge will be indicated in an attempt to stimulate further research in this area.

Chemical Fractionation of Sediment Phosphorus

The only true measure of algal available phosphorus is a biological assay which determines the amount of phosphorus that an algal community can withdraw from the sample. Since bioassays are often tedious and more variable than chemical methods, however, it would be quite advantageous to relate the biologically determined available P to some fraction of the sediment-P as measured by chemical extraction.

There is a growing body of research on chemical extraction procedures to estimate bioavailable sediment-P (BSP). Much of the early work was done on soils, with more recent studies on lake and stream sediments. Differences in these studies can be attributed, in part, to differences

in the biological and physicochemical characteristics of soils and sediments. A major treatment of the subject is not intended here. However, several major differences between soils and sediments are apparent. First, because of their fluvial transport, sediments are unstructured and generally more fine-grained than the soils from which they were derived. They tend to be enriched in organic matter, and this together with their fine-grained nature results in an enrichment of sediments with phosphate, hydrous oxides of iron and some aluminum, and, in some sediments with carbonates. Suspended stream sediments behave much like their soil precursors except for their P enrichment (Green *et al.*, 1978). Bottom sediments, on the other hand, in both lakes and streams may be subjected to long periods of anoxia with subsequent reduction and solubilization of iron (Patrick and Mahapatra, 1968). Phosphate release from suspended sediments is much more similar to that from soil than from bottom sediments. Discussion of chemical extraction of sediment-P must consider these significant differences.

Any chemical extraction procedure to estimate soil or sediment bioavailability must have the following attributes:

1. Must correlate with biouptake
2. Should be applicable to a wide range of soils or sediments
3. Should be relatively easy to perform and the results should be reproducible.

Early work in soil science was concerned with development of soil test procedures, i.e. chemical extractants to estimate availability of soil-P to agronomic crops. Most of the procedures did one or more of the following:

1. Removed soluble-P held in soil pores
2. Used another anion to exchange with some of the H_2PO_4 adsorbed to soil surfaces
3. Dissolved or hydrolyzed part of the more labile soil-P complex.

Many of the procedures used, in fact, do all three. In the Lake Erie Basin, today, two soil testing procedures for plant-available phosphate are used:

0.5 M NaHCO_3 (Olsen *et al.*, 1954) and the Bray P1 (0.03 M NH_4F + 0.025 M HCl) (Bray and Kurtz, 1945). The Bray procedure is used in all the U. S. Lake Erie Basin states and the Olsen test in Ontario. These tests have also been used to characterize sediment-P (Romkens and Nelson, 1974; McCallister and Logan, 1978).

Workers at Wisconsin (Chang and Jackson, 1957) began to look at sequential chemical extraction to characterize soil-P. Their original theory was that phosphorus in soil occurred as discrete chemical forms which could be selectively removed by sequential chemical extraction. They proposed the following scheme:

<u>Chemical form</u>	<u>Extractant (in sequence)</u>
Saloid-bound P	1 N NH_4Cl
Aluminum-P	0.5 M NH_4F
Iron-P	1 N NaOH
Occluded-P	citrate-dithionite-bicarbonate
Apatite-P	1 N HCl

This theory of discrete P forms in soil has been questioned by Bache (1963, 1964), Bauwin and Tyner (1957) and others. A more prevalent view today is that much of the inorganic-P in soil is chemisorbed to a number of reactive surfaces including iron and aluminum oxides and hydrous oxides, amorphous aluminosilicates and carbonates, or occluded in the matrices of a number of soil mineral forms. Probably only small amounts of apatite in some soils are representative of the discrete P form envisaged by Chang and Jackson (1957). Nevertheless, their scheme for chemical fractionation of soil-P proved to be highly useful in looking at relative differences between soils, and their work proved to be the stimulus for much subsequent research in this area (Logan and McLean, 1973; Fiskell and Spencer, 1964; Robertson *et al.*, 1966).

While the original fractionation schemes were designed to study the effects of soil genesis on soil-P forms, it was quickly adopted by soil chemists as a tool for the study of phosphorus fertilizer reactions in soil, and, more recently, as an indicator of soil potential for water pollution (Reddy et al., 1978). The utility of these schemes is based not on their ability to extract discrete P forms, but because the scheme uses sequential extraction, and because the order of the sequence is from least severe and more selective to more severe and least selective. If one accepts the fact that P is bound to many different surfaces in soil with varying binding forces, and that the P which is held on the weakest sites will be the most environmentally reactive, then this type of sequential extraction, in effect, partitions soil and sediment phosphate on the basis of binding strength.

Major developments in the basic scheme proposed by Chang and Jackson (1957) have been accomplished by Williams and Walker (1969a and b); Williams et al. (1967); Williams et al. (1971a and b); Allan and Williams (1978) for soils and lake sediments. Syers et al. (1972) encountered problems with the NH_4F extractant for aluminum-P and dropped it in favor of NaOH as a single extractant for the combined iron-and aluminum-bound P fractions. Most workers have also dropped the NH_4Cl extraction because the amount of P extracted is very low compared to other fractions. More recently, Williams (Williams et al., 1976; Allan and Williams, 1978) has simplified the scheme for lake sediments even further. He proposes two inorganic sediment-P fractions: non-apatite phosphorus (NAIP) extracted by citrate-dithionite-bicarbonate (CDB), and apatite-P extracted by HCl or H_2SO_4 . Allan and Williams (1978) have proposed that the NAIP fraction be considered bioavailable, based on correlation of CDB extraction with the NTA extraction of Golterman (1976) which was found to estimate sediment-P availability of Scenedesmus.

Although organic P in lake and river sediments has received less attention than the inorganic fraction, it has been found to make up a substantial

proportion of the sediment P (Frink, 1969; Sommers, et al., 1970; Syers, et al., 1973; and Williams, et al., 1976b). In addition certain studies have shown a positive correlation between organic P and organic matter, while finding a lack of relationship between organic P and extractable Fe (Sommers, et al., 1972; Williams, et al., 1971c; Williams et al., 1976a). This suggests that the factors controlling inorganic and organic P levels in aquatic sediment material are relatively independent and that the availability of organic P is governed by the processes affecting organic matter transformations in aquatic systems.

Chemical Measurement of Available P

Because of the known mobility in the various phosphorus fractions in sediments, attempts have been made to relate P availability to chemical fractionation. Armstrong, et al. (1971) attempted to relate the form of P found in Wisconsin lake sediments to the actual or potential amount available for plant uptake. They suggested that potential mobility of sediment inorganic P can best be interpreted in terms of the amounts of "non-occluded" and "occluded" forms and apatite. Using this approach, the interstitial inorganic P and neutral salt extractable is considered chemically mobile. Their data indicated, however, that this form was a small fraction of the total inorganic sediment P (generally < 10%). The "non-occluded" inorganic P (NaOH and citrate-bicarbonate extractable) made up a large fraction of the total inorganic P. This fraction was considered to be surface adsorbed P in equilibrium with soluble inorganic phosphate and, therefore, was potentially mobile. Because of the importance of iron in retaining this fraction, its mobility is likely to be dependent on redox conditions. The remainder of the inorganic P in the lake sediments was either "occluded" P (reductant-soluble) or apatite-P (HCl soluble). This fraction was considered to be immobile. No estimate of the availability of organic P by its mineralization was made at this time.

Later studies by Armstrong, et al. (1977) on the sediments of five major rivers entering the Great Lakes used two different approaches to chemical estimation of plant available P. They measured "available" P in the river suspended sediments as either NaOH-extractable P or exchangeable P (equilibration with an anion exchange resin (Dowex 1X-8)). Based on these analyses "available" P ranged from 3-48% of the total P or 11-64% of the total inorganic P. The lowest "available" P proportions were found in the Namadji River, while the highest fractions were in the Maumee and Menomonee River samples. It should be pointed out that measurement of available inorganic P by this means probably represents an upper estimate of the amount that will actually become available because the conditions of the test strongly favor the release of virtually all adsorbed inorganic P.

A study similar to the one discussed above was conducted on some 30 tributaries to Lake Erie with the intent of refining available P loadings to the lake (Logan, 1978 a,b,c). In this investigation NaOH-extractable P was assumed to be rapidly available, while the total potentially available was assumed to be the NaOH + CDB fraction. Short-term available P (NaOH-extractable) was found to be on the order of 20-25% of the total sediment P for the Michigan and Ohio streams, while an average of only 11% was found for the New York stream sediments. Total available P estimates ranged from an average of 34.5% of total sediment P for the New York streams to an average of 51.7% for the Western Ohio streams.

Another significant result of this study, also found by Porter (1975) and Armstrong, et al. (1977), was that lower stream sediment loads contained more clay and organic matter and, therefore, had a higher sediment P content. Furthermore, size fractionation of sediments by Armstrong, et al. (1977) indicated that available sediment P was higher on the finer sized material. These findings suggest that management schemes designed to reduce sediment load will probably not accomplish a proportional reduction in the available phosphorus load.

An intensive study of the phosphate adsorption-desorption characteristics of sediments in the Maumee River basin revealed that suspended sediments in the river contained higher total P levels than either basin soils or bottom sediments (McCallister and Logan, 1978; Green, et al., 1978). This finding was attributed to enrichment of P in the suspended material by selective erosion of fine particles and adsorption of P during fluvial transport. It was also discovered that calcite precipitate formed in the stream by photosynthetic adjustment of CO₂ had a high capacity to weakly adsorb phosphate. This easily exchangeable phosphorus fraction represents a competition with aquatic plants for soluble P and, thus, a different mode of P transport in the stream.

While the recent chemical evaluations of "available" P have provided several significant insights into the overall problem, they are inherently lacking in two major areas. First, they have really only addressed the question of equilibrium potential availability and have not considered what fraction would actually become available as the stream sediments enter the receiving water body. This involves predicting the response of sediment P to the new and dynamic environmental conditions of the lake as discussed previously.

It also involves predicting the rate at which sediment P becomes available versus the rate of sediment dispersion and deposition. Adsorption-desorption studies such as those performed by Green, et al. (1978), Shukla, et al. (1971), Hwang, et al. (1976), and Edzwald (1977) can assist in this problem but, as discussed previously, there are many other processes which affect the kinetics of P availability. Even if a P exchange process is the dominant mechanism for making P available to algae, the work of Li, et al. (1972) demonstrated that the kinetics of P exchange with lake sediments were not simple. They reported that, while a large fraction of the exchangeable P participated in a rapid first-order exchange reaction (7.4-46 hours⁻¹), the entire process could be resolved into three first-order reactions of differing rates. Amer, et al. (1955) had made the same observation for soils.

The second area of concern deals with the question of what fraction of the organic sediment P becomes available to lake algae before the tributary sediments leave the water column. Very little discussion of this phosphorus fraction is present in the availability literature. Rodel, et al. (1977) did show that hydrolysis of sediment-adsorbed organic P compounds does take place, but at a much reduced rate in comparison to soluble organic P. The above two questions can really only be answered by biological measurements of the kinetics and extent of phosphorus availability, which is discussed in the next section.

Bioassay Measurement of Available P

Allochthonous Material

Recent bioassays of the availability of sediment P for uptake by aquatic plants have simply involved culturing algae in a suspension of river or lake sediments, in which the sediment P is the only possible phosphorus source and other necessary nutrients are in excess supply. Following an incubation period either the algal phosphorus content or the algal biomass (employing a P/biomass conversion factor) is used to estimate the amount of phosphorus that had become available.

Cowen and Lee (1976a) employed the test alga Selenastrum capricornutum to measure the available P in the particulate P portion of urban runoff samples collected in Madison, Wisconsin. After 19-22 day incubation of the Selenastrum in assay flasks containing AAP medium minus P (EPA, 1971) and runoff particulate P, they compared the cell counts obtained to a standard curve of 18 day cell counts versus initial orthophosphate concentration. In this way they converted cell counts to available P. With this procedure they obtained an available P mean value of 30% (range of 8-55%) of the particulate P in the urban runoff. This availability was most closely approximated by the NaOH-extractable fraction, which ranged from 22-27%. Exchangeable P (anion exchange resin extractable) slightly underestimated the algal available fraction by only accounting for 13-17% of the particulate P fraction.

Cowen and Lee (1976 a,b,c) applied the same procedure described above to the assessment of available P in sediment carried by tributaries to Lake Ontario (Niagara, Genesee, Oswego, and Black Rivers). They found that 6 percent or less of the particulate P was available based on growth of Selenastrum. In this case the algal available P was not consistent with base-extractable (mean, 17-25% of inorganic part. P; range, 11-28%) or resin-extractable (mean, 17-25%; range 6-31%). The relatively low availability was, however, consistent with the findings of Logan (1978) on four New York streams and Porter (1975) in Fall Creek, a small New York watershed emptying into Cayuga Lake.

Another finding of the Cowen and Lee (1976 b,c) study was that 26 day dark incubations of sediment P forms in the presence of anion exchange resin yielded resin uptakes that were essentially equivalent to the amount extracted by the resin in short-term, (24 hour) extractions. They interpreted the close agreement between the short- and long-term extractions as indicating that physical-chemical processes were more important than microbial mineralization in governing the release of inorganic P from runoff particles. This interpretation, however, failed to account for the possible storage of available P, originating from inorganic or organic sediment pools, in the microbial biomass which would develop in a 26 day incubation. Phillips (1964) has shown that microorganisms can favorably compete with lake muds in the removal of inorganic P from solution. This microbially immobilized phosphorus could later be released as soluble inorganic P after death and lysis of the microorganisms.

Dorich and Nelson (1978) recently employed an algal growth/available P conversion approach, similar to that of Cowen and Lee, to evaluate the availability of soluble P in Black Creek (Indiana). The Black Creek drainage basin is a subwatershed of the Maumee River. By comparing Selenastrum cell numbers after 4 days growth in filtered creek water with a standard curve of 4-day cell counts in PAAP medium containing known levels of orthophosphate, they concluded that only an average of 50% of soluble P in the water samples

was available for algal uptake. No measurement of actual uptake was made to corroborate these findings.

There are several problems associated with using algal biomass changes, as opposed to actual P uptake, to assess availability. Most of the problems stem from the fact that algae are known to be able to take up P in excess of their immediate metabolic needs, which manifests itself in a highly variable P: biomass stoichiometry intimately associated with the ambient P level of medium and the specific growth rate of the algae (Rhee, 1973).

For example, in the Cowen and Lee (1976 c) study the algal inoculum did not appear to be P-starved. In this case the Selenastrum might not compete as well with other microorganisms for available P. Also, it is quite conceivable that the algae would respond differently in terms of growth rate and cell P quota to a high initial spike of orthophosphate (as is used for the standard curve) then to a slow gradual release of the same P level (as might occur with sediment P). A further complication in the Dorich and Nelson (1978) study, which may explain the low soluble available P results, was the comparison of Selenastrum growth in synthetic PAAP medium as a function of P with growth in the Black Creek water. An entirely different P uptake and growth response might occur in the synthetic medium than in the creek water, particularly if another nutrient were limiting or if an inhibitory toxic compound were present in the creek water. Furthermore, most samples had SIP levels which would cause near maximum algal growth rates, thus a very small decrease in growth rate in the creek water would represent a large difference in estimated available P.

Dorich and Nelson (1978) took a different approach to measuring availability of sediment-bound P in Black Creek. Before and after culturing algae for two weeks in synthetic medium with gamma radiation sterilized sediments as the only P source, they determined the quantity and fractionation of particulate P in the flask. By performing the same procedure for sediment-free algae

culture (containing 0.2 mgP/l as soluble orthophosphate), the extractability of the algal P was analyzed and the results were used to correct the values obtained from the sediment-algal system extractions. This procedure yielded available P values of 20% and 21.4% of the total sediment P for March and June values, respectively. These results represented 27% and 33% of the sediment inorganic P. From the fractionation data, they surmised that most of the algal available P was from the Al- and Fe-bound inorganic fractions; however, these sediments were pre-sterilized by radiation which may have mineralized organic P prior to the initial fractionation and certainly prevented the mineralization of organic P during the two week incubation.

In a recent study Verhoff, et al. (1978) attempted to determine the rate at which an indigenous phytoplankton population could immobilize phosphorus from Lake Erie tributaries. The procedure involved incubation of the algae with the river sediments and periodic harvest of the biological solids. A mass balance performed on total phosphorus and total inorganic solids allowed the calculation of the rate of conversion to available P. In contrast to studies on lake suspended material and lake bottom muds, the rate of algal immobilization of available P from the river sediments was quite low. The conclusion was that a linear availability rate of between 0.2%-0.4% P/day could be expected. This slow rate of release over long time periods suggests that the rate of P release is more important than the ultimate availability. Only bioassay studies can provide information on the release of truly available phosphorus from river sediments.

'Autochthonous Material.' In order to evaluate the total impact of a phosphorus load to a lake, it is necessary to know the fate in internally produced particulate phosphorus in terms of its being reconverted to available P before being deposited in the bottom sediments. Since most of the particulate phosphorus formation in lakes is through primary productivity, the understanding of this aspect of the problem requires an estimate of the rate and extent of

P regeneration (mineralization) from dead or dying algal-related material as it settles through the water column. While this topic is much too broad to be completely covered in this review, some of the more pertinent studies will be outlined. The reader is referred to other reviews for a more thorough coverage (DePinto, 1974; Jewell, 1968; Johannes, 1968; Golterman, 1975; and Kuznetsov, 1970; among others).

The regeneration of phytoplankton phosphorus in the water column of lakes depends upon the decay rate of the algae. Many field studies have indicated that most phytoplankton decay takes place in the water column as opposed to the bottom sediments. Kuznetsov (1968) maintained that the breakdown of a phytoplankton begins only after its death and that 90% of the dead phytoplankton undergo decomposition before leaving the water column. Kajak, et al. (1970) estimated that 63% of the total primary production in several Polish lakes was decomposed in the epilimnion. Jassby and Goldman (1974) used primary productivity and phytoplankton biomass measurements in Castle Lake to estimate that specific loss rates, attributed to cell mortality and decomposition, varied between $0.2-0.8 \text{ day}^{-1}$. In a study of two polar lakes, Kalff, et al. (1975) measured phytoplankton loss rates of 8% per day, 80% of which was the result of decomposition in the water column.

Laboratory studies have attempted to quantify decomposition rates for phytoplankton. In general, darkened batch cultures of unialgal populations or indigenous phytoplankton communities exhibited biomass decay rates of $0.01-0.10 \text{ days}^{-1}$ (base e) (Jewell and McCarty, 1971; Uhlmann, 1971; and DePinto and Verhoff, 1977). The presence of an active microbial decomposer community has led to the higher algal decay rates (Jewell, 1968; DePinto, 1974).

Since it appears that phytoplankton organic matter is more labile (decays at a higher rate) than organic matter associated with river or lake sediments, it follows that the available phosphorus release during the decomposition of algae would be more significant. The net soluble inorganic P released from decayed algae has been measured at anywhere from 12-95% of the initial cell

content (Golterman, 1964; Jewell, 1968; Foree, et al., 1970a; Foree and Barrow, 1970b; DePinto and Verhoff, 1977). The cellular phosphorus, however, that becomes available in a reasonable length of time (one to two months) is generally about 75% (DePinto and Verhoff, 1977).

Just as important as the total available versus refractory phosphorus content of algae is the rate at which phosphorus is regenerated from decaying phytoplankton in the water column. Recent studies have shown that the rate of phosphorus mineralization from decaying algae was governed by temperature, light, pH, dissolved oxygen, algal species and physiological condition (cell age, nutrient content, etc.) and the quality and activity of the microbial decomposer community (Grill and Richards, 1964; Kamatani, 1969; Lee, et al., 1973; Mills and Alexander, 1974; Barsdate and Prentki, 1974; Cranwell, 1976; DePinto and Verhoff, 1977). Barsdate and Prentki (1974) emphasized the importance of the microbial community and also demonstrated that protozoan grazing on bacteria increased the rate of phosphorus mineralization by stimulating bacterial activity, rather than by phosphorus cycling through the grazers themselves. In addition to the importance of bacteria, DePinto and Verhoff (1977) observed that the rate and extent of phosphorus regeneration was dependent upon the phosphorus content of algal cells. In batch regeneration experiments two runs that had the lowest initial cellular P levels (.048 and 0.38% P dry wgt.) produced P regeneration rates of 0.08 and 0.06 ugP/mg algae (dry wgt.)-day. Conversely, the rates for four cultures where the algae appeared to be in a luxury state (cellular P ranging from 0.51-1.21%) ranged from 0.16-0.39 ugP/mg algae-day with an average of 0.24 ugP/mg algae-day.

More recently DePinto, et al. (1978) used a newly designed Dual Culture Diffusion Apparatus to measure rates of algal decomposition and phosphorus regeneration. The P regeneration rates from Scenedesmus sp. in lake water appeared to be a function of both decay rate and internal P content of the algae. First-order rate coefficients varied from 0.01-0.05 days⁻¹ (base e), with higher

rates associated with bacteria-inoculated cultures and those with initially high cell phosphorus levels. Data of this nature can be used to determine the rate at which P becomes available from algal-related organic matter entering lakes in tributaries as well as that being produced within the lake system.

Lake Bottom Sediments. Since lake sediments are a combination of allochthonous and autochthonous material, it is useful to determine the P availability for two reasons. First, it would be useful information in predicting sediment-water interchange in response to varying environmental conditions. Second, it would be useful to compare with availability measurements of lake suspended matter as an estimate of the loss of available phosphorus to the sediments. Furthermore, for systems such as Lake Erie resuspension of sediment particles due to wind generated wave action can be significant (Lam, D.C.L. and Jaquet, 1976), and the P availability of these resuspended sediments must be known in order to determine their true impact.

Bioassay results of the phosphorus availability of lake sediments are inconsistent and difficult to interpret because of the changes in sediments which occur in moving them from the lake bottom to an assay culture. Fitzgerald (1970) found virtually no growth of either Selenastrum capricornutum or Cladophora sp. when exposed to lake muds (in dialysis tubes) as the only source of phosphorus. He suggested that the lack of response was because of the high capacity of the muds to retain sorbed phosphorus under aerobic conditions. On the other hand, Goltzerman, et al. (1969) found Scenedesmus cell count increases of up to 100-fold when incubated in the presence of lake muds as the only P source. They calculated apparent phosphate released from inorganic precipitates and lake muds by comparing log growth rates against those with known orthophosphate concentrations. The results indicated that about 7% of the total P in the mud from one lake was used for cell growth while about 30% was available from a second lake. Using a mean cell P content of 9.1×10^{-8} ugP/cell

to calculate the cell P at the end of an experiment, they found that the phosphorus taken up by the algae from the muds was equivalent to the decrease in the sum of the NaOH-plus H_2SO_4 -extractable forms. Using an approach similar to Golterman's (cell counts and sediment P fractionation), Sagher et al. (1975) showed that 50-80% of sediment inorganic P for Wisconsin lakes was available for use by Selenastrum and indigenous sediment algae. The wide variation of bioassay results for lake sediment P availability is apparent from comparison of the above three studies. There is an obvious need for further studies to determine if the variations are real or simply the result of varying experimental approaches.

Summary

The intent of this review was to evaluate our knowledge of the availability of the various sources of phosphorus to lakes. It has also served to stress the need for further work in developing an assessment methodology for determination of the biologically available phosphorus in both point and non-point sources. Once this problem is solved eutrophication control measures can be directed toward available P forms, thus making more efficient use of water pollution control resources.

In order to obtain a true assessment of algal availability the method must make use of the algae themselves as an indicator of the quantity and rate of available phosphorus production. Furthermore, algal available P should be defined as that quantity actually taken-up by the algae, rather than the growth response under test conditions. It is therefore recommended that an assessment methodology actually measure the amount of P incorporated into the biomass of the test organism.

On the other hand, a chemical assessment technique is desirable from the standpoint of relative ease and quickness of obtaining results. These are very important attributes if one is attempting to evaluate all the tributary sources to one of the Great Lakes, for example. It is therefore necessary for future research to place equal emphasis on both chemical and biological

approaches to assessing P availability. Even more important is the need for future work to attempt to correlate the quantity and the rate of production of biologically measured available P with the chemical tests, which can characterize the forms of the phosphorus in its unavailable state. In other words, every attempt should be made to find an operationally defined chemical extraction which best estimates algal available phosphorus.

CHEMICAL EXTRACTION OF LAKE ERIE TRIBUTARY SEDIMENT PHOSPHATE

A study was conducted by LEWIS in 1977 to determine variation in sediment-P characteristics and sediment-P bioavailability in sediments entering Lake Erie from the U. S. tributaries. A sequential chemical extraction procedure was used to distinguish freely available and non-available forms of sediment-P. The extractions and their interpretations are given below in the order of extraction:

<u>Extraction</u>	<u>Name Used</u>	<u>Interpretation</u>
0.1 <u>N</u> NaOH	NaOH-P	Labile phosphate that can be taken up by algae under oxic and anoxic conditions
citrate-dithionite-bicarbonate	CDB-P	Less available than NaOH-P. Can <u>potentially</u> be released over long periods of time during anoxia
1 <u>N</u> HCl	HCl-P (Apatite-P)	Not biologically available

A summary of the work conducted on this study is given here. Complete details are given in the technical report (Logan, 1978).

The objectives of the study were:

1. To characterize the phosphorus contained in suspended sediments from streams draining into Lake Erie.
2. To study the differences in suspended sediment phosphorus entering Lake Erie in streams from different drainage basins.
3. To estimate the bioavailability of phosphorus to aquatic plants from suspended sediments in streams draining into Lake Erie.

Methods and Materials

Sample Collection

During the period March through July, 1977, a total of 66 samples were collected from 36 tributary locations in the Lake Erie drainage basin on the U. S. side. A summary of the sites, tributaries, sampling dates, etc. are given in Table 1. Six major tributaries in Michigan and two smaller streams with drainage areas ranging from 20 to 1042 mi² (52-2698 km²) were sampled between March 5 and May 16. In Ohio, eight major tributaries and ten smaller streams ranging in drainage area from 0.3 to 6330 mi² (0.8-16395 km²) were sampled between March 10 and July 7. In New York four creeks ranging from 10 to 37 mi² (26-96 km²) were sampled on April 23.

The sites were arbitrarily separated into four groups:

1. Michigan streams
2. Maumee-Portage-Sandusky-Huron river basins in western Ohio
3. Eastern Ohio streams
4. New York streams

This division allows some separation on the basis of land use and geochemistry.

Samples provided were either part of an ongoing monitoring program or were taken for this study. Some samples were pumped while others were grab sampled. Drs. Steve Yaksich, U. S. Army Corps of Engineers Buffalo District and David Baker, River Laboratory, Heidelberg College, Tiffin, Ohio provided most of the samples. Most samples were taken during the period of medium to high flow (Table 1) and so represent the period of maximum sediment transport.

Sample sites are located in Figure 1 by numbers which correspond to those in Table 1.

Analytical Procedures

Complete details of the procedures used are given in the technical report of this study (Logan, 1978). Unfiltered water samples were digested with perchloric acid (Sommers and Nelson, 1972) to give total-P. Samples were

TABLE 1. CHARACTERISTICS OF LAKE ERIE THROUGH SAMPLING SITES (1977)

Map No.	Section No.	Stream	Sampling Site	County	Drainage Area km ²	Sampling Dates	Sample No.	Mean Annual Discharge cfs/sec	Mean Discharge of Month Sampled cfs/sec	Mean Discharge of Date Sampled cfs/sec
Michigan										
1	04100600	Detroit	Michigan	St. Clair	391.09	3/5, 3/29	1, 9	89.0	172, 21	305/345
2	04109200	Black	Pargo	St. Clair	1043.2	3/5, 3/29	17	282.0	692, 43	1120/91.6
3	04105200	Clio	Mr. Clemens	Macomb	1901.06	3/5, 3/29	3, 11	584.0	1324, 322	2665/34.59
4	04102113	Harbor	S. Metropolitan Park		2351.72	3/5, 3/29	19			219
5	04109900	Mill Creek	Avon	St. Clair	437.72	3/5, 3/29	4, 12	92.0		305/265
6	04107500	Madison	Harbor	Macomb	2698.78	3/5, 3/29	5, 13	698.0	1827, 567	2720/1300
7	04102070	Harbor	West Jefferson Bridge	Wayne	1209.53	3/5, 3/29	21			377
8	04106000	Sanctuary Creek	Devotion Plains	Oakland	54.13	3/5, 3/29	7, 15	12.5	72, 8.6	24/21
New York										
9		Amsterdam	Junction	Putnam	6004	3/10, 4/26	25, 38	1702	2916, 1693	
10		Harmon	Independence	DeWitt	2998	3/10, 7/1	26, 41			
11		Clifton	DeWitt	DeWitt	1906	3/10	27			
12	04103500	Harmon	Westerville	Lebanon	16381.7	3/10, 4/26	28, 39	4797.0	13880, 11900	26500, 32900
13	04107200	Poughkeepsie	Westerville	Saratoga	1108.28	7/1	31	308.0	1189, 171	4110
14	04108000	Saratoga	Poughkeepsie	Saratoga	3840.09	3/28, 7/1	34, 47	948.0	2164, 519	1760
						7/1	48			2150/1200

TABLE 1. (Continued)

-24-

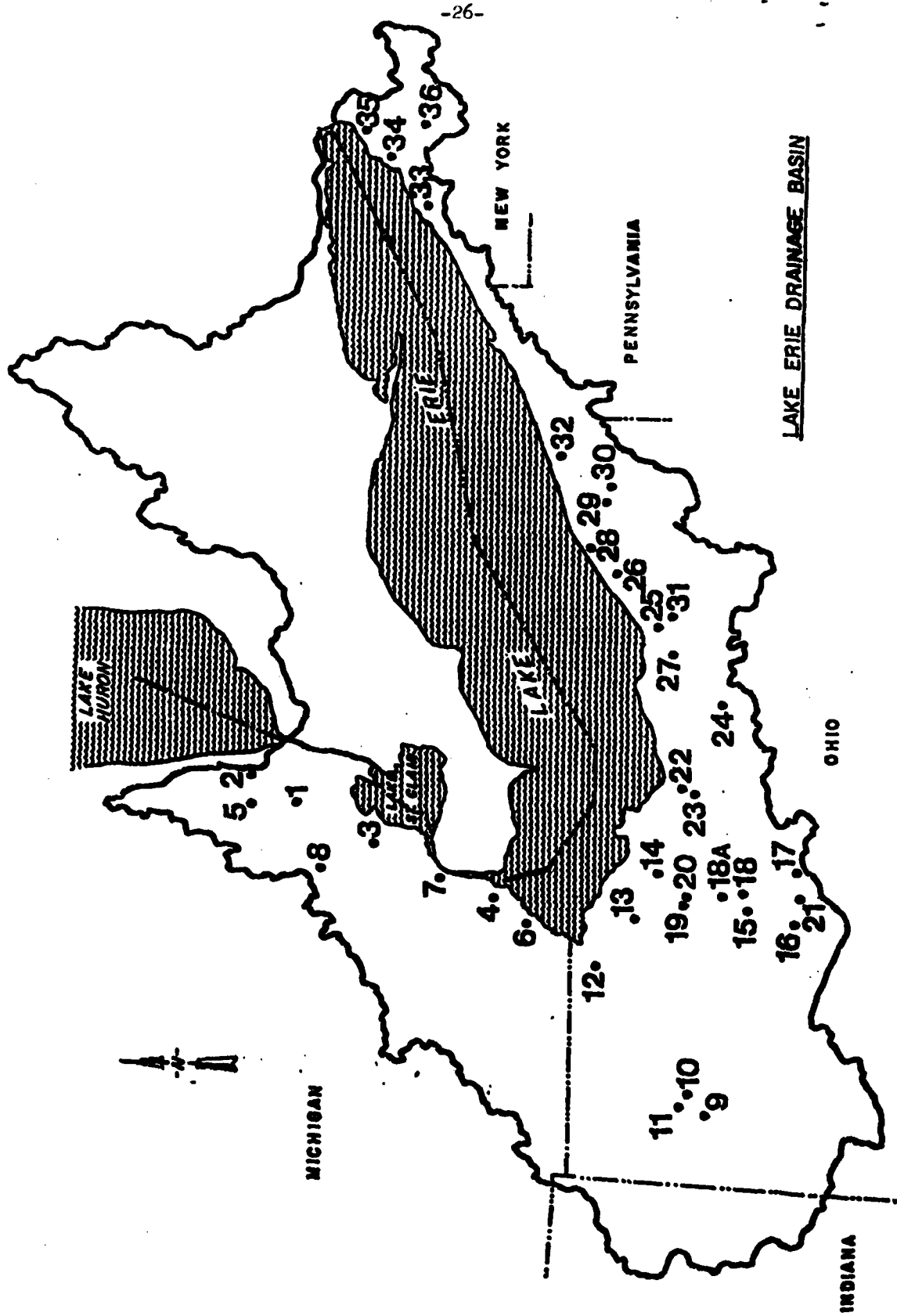
Map No.	Station No.	Stream	Sampling Site	County	Drainage Area, km ²	Sampling Dates	Sample No.	Mean Annual Discharge, cfs/sec	Mean Discharge of Month Sampled, cfs/sec	Year Discharge of Base Set, cfs/sec
Huron-Port Huron-Sandusky-Huron (Continued)										
15	04197000	Sandusky	Merice	Seneca	2004.66	3/28	32	575.0	1401	1153
16	04196500	Sandusky	Upper Sandusky	Wyandot	771.82	3/28	33	241.0	467	295
17	04196000	Sandusky	Bucyrus	Crawford	229.99	3/28	30	64.6	132	112
18	04197100	Romey Creek	Malmore	Seneca	385.91	3/28, 3/28, 4/5, 7/1, 7/2	29, 31, 37, 42	100	321	225
19	04197300	Half Creek	Stiffin	Seneca		7/2	44		44.5	44.7/305
20	04197500	West Branch	Bettaville	Seneca	171.46	7/1	45	42	10.2	127
21	04196800	East Branch	Bettaville	Sandusky	213.42	3/28	36	100	497	1050
22	04199000	Broken Ford	Berada	Wyandot	217.04	7/1	43	70	84	725
23	04199100	Huron	Milan	Erle	960.89	7/1, 7/5	46, 49	295	716	725
24	04199200	Huron	Huron	Huron	12.76	6/6	40	14.37		4.2

TABLE 1. (Continued)

25

Sta. No.	Station No.	Stream	Sampling Site	County	Drainage Area sq. mi.	Sampling Date	Sample No.	Mean Annual Discharge cfs/sec	Mean Discharge of Month Sampled cfs/sec	Mean Discharge of Date Sampled cfs/sec
Eastern Ohio										
24	04139000	Herr Run	Lislesfield	Madison	1.97	6/6	57			2.0
25	04080002	Big Creek	Cleveland	Cuyahoga	91.53	6/6	53	51.4	55.7	71.0
26	04080000	Chagrin	Willingby	Lake	637.14	6/6	54	384	349	866
27	04081100	Becky	Berea	Cuyahoga	691.53	6/6	60	260	80.9	11.0
28	04081200	Grand	Painesville	Clark	1774.15	6/6	59	934	72.4	
29	04082000	Monroville Nitch	Monroville	Cuyahoga	0.75	6/6	58	28		1.50
30	04082100	Madison Creek	Marlinton	Madison	14.04	6/6	56			7.5
31	04082200	Cuyahoga	Lakewood	Cuyahoga	1831.13	6/6	55	789	348	380
32	04082300	Hobart Run	Amherst	Amherst	2.48	7/7	61			0.75
For Year										
33	04081300	Cattaraugus Creek	Cattaraugus	Erie	1118.88	3/28	62		2254	2380
34	04081400	Delaware Creek	Angola	Erie	12.95-	4/23	63	731	1478	8930
35	04081500	18 Mile Creek	E. Boston	Erie	25.9	4/23	64			503
36	04081600	O. Cattaraugus	Getz	Cattaraugus	66.39	4/23	65			3000
						4/23	66			1100

Figure 1. Lake Erie Drainage Basin tributary sampling sites.



filtered through 1.0 μ m Nucleopore membrane filters and sediment concentration measured by weighing sediment recovered. Filtered reactive phosphate (FRP) was determined on the filtrate by the molybdate blue colorimetric procedure of Murphy and Riley (1962). P in filtrate after digestion with perchloric acid gave total filtered-P.

Total sediment in the sample obtained (4 liters) was recovered by sedimentation and centrifugation and then freeze-dried. Aliquots (0.1 g) were then extracted sequentially with:

0.1 N NaOH

citrate-dithionite-bicarbonate (CDB)

1 N HCl (apatite-P)

concentrated perchloric acid (residual inorganic-P)

Separate sediment aliquots were digested with perchloric acid (Sommers and Nelson, 1972), persulfate (Standard Methods, 1975) and NaOH + HCl (Mehta, 1954) to give independent measurements of total sediment-P. In addition, the difference between total-P and inorganic-P after the Mehta digestion is a measure of sediment organic-P. Specifics of these procedures as used in the present study are given in the technical report (Logan, 1978).

Results and Discussion

The data was organized into the four geographical areas discussed previously. The complete data set is given in the final report (Logan, 1978). Summary statistics by area are given in Table 2, and mean and S. D. are presented graphically in Figure 2. Sediment concentrations were significantly higher in the New York samples, with the western Ohio samples intermediate. Filtered reactive-P was highest in the eastern Ohio streams although the variation was quite high. Total P reflected both the high sediment concentrations in New York streams and high FRP in the eastern Ohio streams. Total sediment-P is calculated as the difference between total and total filtered-P divided by sediment concentration. Our data show that these

TABLE 2. SUMMARY OF SEDIMENT-P CHARACTERISTICS

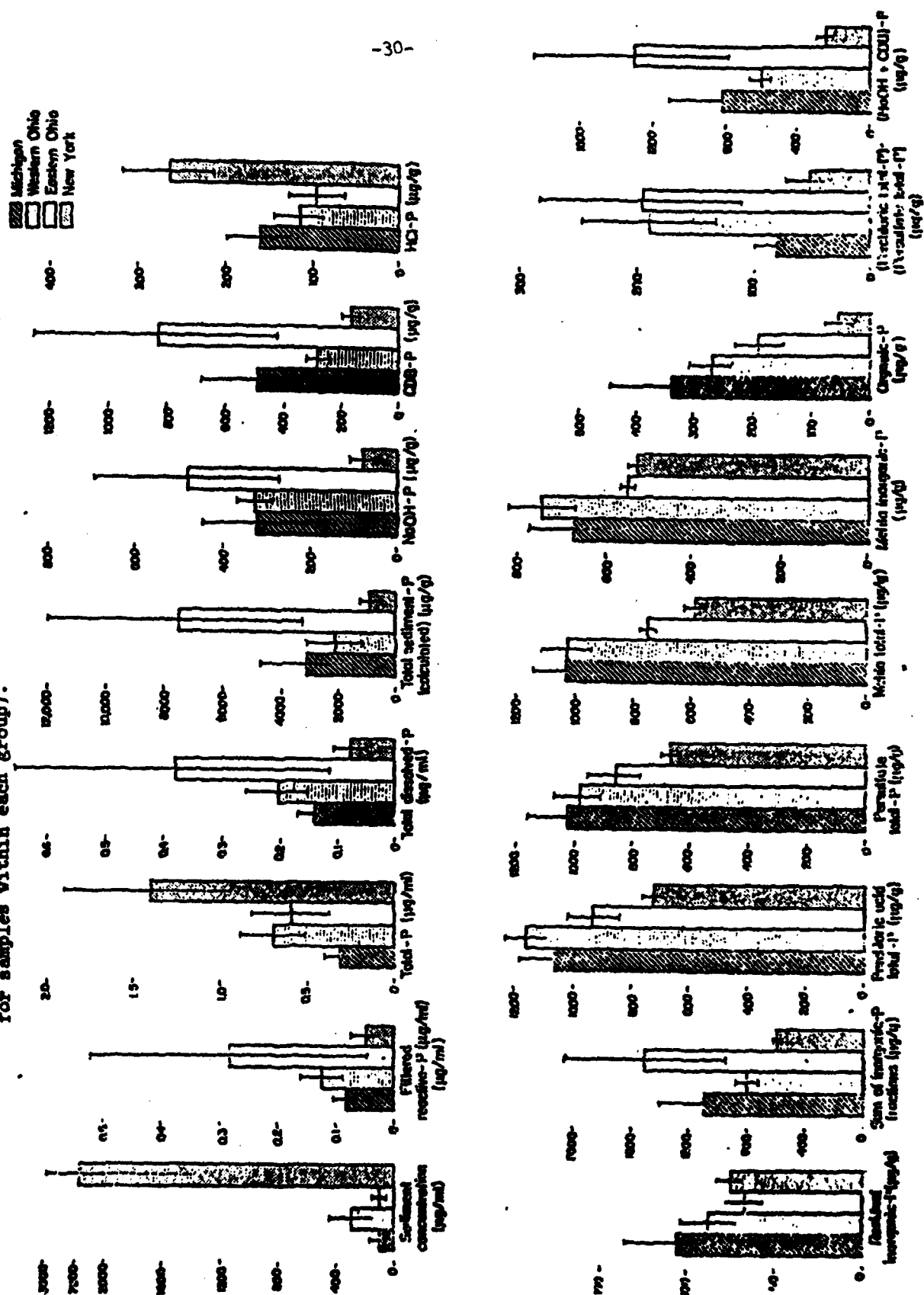
Parameter	No. of Observations	Mean	S.D.	Std. Error of Mean	Minimum	Maximum
Michigan						
Sediment concentration	24	97.5	87.8	17.9	4.0	334.0
Filtered reactive-P	24	0.086	0.043	0.009	0.016	0.151
Total-P	24	0.317	0.170	0.035	0.063	0.606
Total filtered-P	24	0.141	0.054	0.011	0.031	0.278
Total sediment-P	24	3095.0	3168.1	646.7	160.2	15666.7
NaOH-P	24	328.9	238.3	48.7	34.3	1069.4
CDB-P	21	493.7	380.3	83.0	106.2	1614.3
HCl-P	24	162.9	72.2	14.7	40.8	340.6
Residual inorganic-P	21	106.1	58.2	12.7	29.2	245.0
Sum inorganic-P fractions	21	1096.6	603.7	131.7	525.1	2779.7
Perchloric acid total-P	9	1065.5	233.6	77.9	735.0	1477.0
Persulfate total-P	12	1023.5	265.8	76.7	673.2	1524.6
Mehta total-P	11	1032.7	266.2	68.2	668.2	1348.9
Mehta inorganic-P	11	675.0	201.8	60.9	440.6	1118.7
Organic-P	8	341.1	203.3	71.9	96.5	778.4
(Per-Pers) total-P	9	80.1	37.6	12.5	32.4	126.8
(NaOH+CDB)-P	21	825.3	571.0	124.6	332.2	2408.2
Maumee-Portage-Sandusky-Huron						
Sediment concentration	28	348.8	340.0	64.2	48.0	1204.0
Filtered reactive-P	28	0.123	0.074	0.014	0.025	0.374
Total-P	28	0.706	0.365	0.069	0.234	1.452
Total filtered-P	28	0.201	0.107	0.020	0.082	0.505
Total sediment-P	28	2240.5	2447.0	462.4	901.8	13354.2
NaOH-P	28	330.1	79.2	15.0	121.3	480.8
CDB-P	23	282.4	77.9	16.2	159.3	432.8
HCl-P	28	113.2	64.3	12.1	19.6	261.5
Residual inorganic-P	23	86.1	31.0	6.5	39.2	137.2
Sum inorganic-P fractions	23	787.0	153.6	32.0	503.9	1003.4
Perchloric acid total-P	22	1168.4	136.1	29.0	909.0	1380.4
Persulfate total-P	28	978.4	169.4	32.0	663.3	1287.0
Mehta total-P	26	1029.0	170.8	33.5	705.4	1441.3
Mehta inorganic-P	25	751.8	152.5	30.5	475.2	1211.3
Organic-P	23	270.1	72.7	15.2	173.2	475.2
(Per-Pers) total-P	21	190.2	115.8	25.3	37.8	430.9
(NaOH+CDB)-P	23	598.9	112.2	23.4	394.9	762.7

Table 2. (Continued)

Parameter	No. of Observations	Mean	S.D.	Std. Error of Mean	Minimum	Maximum
Eastern Ohio						
Sediment concentration	9	93.6	119.6	39.9	12.0	384.0
Filtered reactive-P	9	0.286	0.492	0.164	0.013	1.485
Total-P	9	0.604	0.518	0.172	0.076	1.749
Total filtered-P	9	0.379	0.555	0.185	0.030	1.768
Total sediment-P	9	7593.0	8613.7	2871.2	1049.5	28555.6
NaOH-P	8	491.5	422.3	149.3	88.6	1332.4
CD8-P	8	834.9	859.3	303.8	181.8	2160.1
HCl-P	8	101.4	61.4	21.7	16.5	180.7
Residual inorganic-P	8	68.5	21.2	7.5	39.2	107.8
Sum inorganic-P fractions	8	1496.2	1134.0	400.9	542.2	3085.6
Perchloric acid total-P	2	934.2	178.5	126.2	808.0	1060.5
Persulfate total-P	3	867.1	224.4	129.5	732.6	1126.1
Mohta total-P	2	742.5	52.5	37.1	705.4	779.6
Mohta inorganic-P	2	551.9	31.5	22.3	529.6	574.2
Organic-P	2	190.6	84.0	59.4	131.2	250.0
(Per-Pers) ^a total-P	2	196.7	171.5	121.3	75.4	318.0
(NaOH+CD8)-P	8	1326.4	1090.4	385.5	393.8	2798.3
New York						
Sediment concentration	5	2163.2	1631.1	729.4	292.0	3666.0
Filtered reactive-P	5	0.048	0.051	0.023	0.016	0.138
Total-P	5	1.402	0.985	0.441	0.479	2.954
Total filtered-P	5	0.077	0.053	0.024	0.044	0.170
Total sediment-P	5	973.8	673.2	301.0	309.9	2054.8
NaOH-P	5	83.2	56.4	25.2	36.1	180.1
CD8-P	5	169.9	60.3	27.0	93.9	249.1
HCl-P	5	265.8	99.1	44.3	115.2	357.7
Residual inorganic-P	5	76.4	13.7	6.1	58.8	91.9
Sum inorganic-P fractions	5	595.4	49.2	22.0	546.6	661.3
Perchloric acid total-P	5	720.5	71.0	31.8	664.9	841.6
Persulfate total-P	5	669.2	60.5	27.0	613.8	772.2
Mohta total-P	5	587.2	71.1	31.8	519.8	668.2
Mohta inorganic-P	5	532.6	33.1	14.8	495.0	574.2
Organic-P	5	54.6	41.8	18.7	14.9	104.6
(Per-Pers) ^a total-P	5	51.2	41.2	18.4	1.6	110.0
(NaOH+CD8)-P	5	253.1	103.2	46.2	165.0	479.2

^a Perchloric total-P minus persulfate total-P.

Figure 2. Summary of suspended sediment parameters (mean and standard deviation for samples within each group).



values are overestimated at low sediment concentrations when compared with direct measurement of total P on sediment. Errors in the three parameters which are used to calculate total sediment-P may contribute to this difference.

The NaOH-P was essentially the same for Michigan and Ohio streams and these were significantly higher than the New York samples. CDB-P showed the same trend; the eastern Ohio streams had significantly higher values than western Ohio and New York was again lower than the other three areas. On the other hand, HCl-P (apatite) was highest in the New York streams; apatite-P was lowest of three fractions in the Ohio and Michigan streams and highest in the New York tributaries. Sum of the two fractions that are considered to be available (NaOH + CDB) was highest in the eastern Ohio samples, significantly higher than western Ohio and New York. New York was lower than the other three areas.

Total-P determined by perchloric acid digestion was higher than that by persulfate digestion in all cases. The difference between the two methods was highest in Ohio streams.

The sum of inorganic fractions (NaOH + CDB + HCl + residual) correspond quite well to Mehta inorganic-P for New York and western Ohio streams but not for the other two areas. The discrepancy is due to the incomplete data set for Michigan and eastern Ohio streams (because of limited amount of recovered sediment rather than analytical error).

Organic-P decreased from west to east, reflecting the organic matter content of soils in the Basin (more organic soils in Michigan) and the high sediment loads in the New York streams (organic-C content tends to decrease as sediment concentration increases).

Bioavailable Sediment-P

For the purpose of this study, bioavailable-P will be considered in two ways: short-term and total. The NaOH-P will be considered to be short-term bioavailable because it is known that this fraction contains the most

labile or exchangeable phosphate (Logan and McLean, 1973) and has been shown by Sagher *et al.* (1975) to be correlated with algal uptake. (CDB + NaOH)-P can be considered as a measure of the total available fraction which is potentially releasable over a long period of time (years). Table 3 expresses bioavailable-P as a percentage of the total sediment (perchloric acid method). Eastern Ohio had the highest amounts of both fractions (Table 2) but on a percentage basis they were the same. The high incidence of point sources in these two areas should be investigated further as a possible relationship with high bioavailable-P.

Table 3 . Percent Bioavailability of Sediment-P*

	NaOH-P	CDB-P	(NaOH + CDB)-P
Michigan	30.0	45.0	75.0
Western Ohio	41.9	35.9	77.8
Eastern Ohio	32.8	55.8	88.6
New York	14.0	28.5	42.5

* Expressed as percent of total sediment inorganic phosphorus

New York samples were lowest in both NaOH-P and CDB-P and would be expected to support much less algal growth than the streams to the west. On a percentage basis, NaOH-P was lower than other areas. Studies in Fall Creek, New York (Porter, 1975) used a desorption technique to measure readily available phosphorus and concluded that about 4% of the total sediment-P was available by this technique.

Actual bioavailability of sediment-P is strongly dependent on equilibrium kinetics: the rate at which sorbed P is released when a demand or sink (algal uptake) is in operation, and the period during which the sediment is positionally accessible to the algae. In deep lakes with significant stratification, as in the eastern, and to a lesser extent, the central Lake

Erie basins, sediment may be in contact with algae for short periods only, during which time NaOH-P will be most important. During anoxia and subsequent lake inversion, P released from the CDB fraction will become significant. Therefore, chemical fractionation data must be interpreted in light of dynamics of the receiving lake.

Simple moment correlations were run between all parameters and Table 4 gives those correlations which were significant at the 5% level of probability or better. Sediment concentration was positively correlated with total-P (ug/ml) and HCl-P, and negatively correlated with NaOH-P, total sediment-P and organic-P. A closer examination of the data set (Logan, 1978) indicates that many of these relationships are reflecting the influence of the New York samples, a number of which were the highest in suspended solids found in the study. The results, however, are supported by the work of Porter (1975), and Logan (1978) who found that, at lower sediment concentrations, the sediment that is transported contains more clay and organic matter and is higher in sediment-P. Armstrong et al. (1977) used a chemical fractionation scheme to characterize suspended sediments from Great Lakes tributaries. They fractionated the sediment into various particle size fractions and showed that available sediment-P was higher on the finer textured material.

Both NaOH-P and CDB-P were correlated with total sediment-P as expected. Step-wise linear regression correlations were run on the various fractions and these are given in Table 5. None of the equations had very high R^2 values. However, a few trends were apparent. CDB-P and (CDB + NaOH)-P were negatively related to sediment concentration, while HCl-P was positively correlated. Total filtered-P was positively correlated with each fraction except CDB-P, and NaOH-P was positively correlated with organic-P. The relationship of this fraction with organic-P is not unexpected since NaOH is known to extract organic material; although only the inorganic-P in the NaOH extract was

Table 4. Simple moment correlation coefficients between sediment-P parameters λ

SEDIMENT	FRP	SDRP	TRP	MACRP	CDRP	NCIP	NCOTP λ / FRALP λ / FRCTP	FRCTP	MACRP λ / MACRP λ / CRCP	DIFFP	SUM
FRP		0.74°		-0.30		0.37°	-0.49°	-0.40°	-0.31	-0.52°	-0.31
SDRP	0.31		0.94°		0.39°		0.15°		0.32		0.47°
TRP	0.31	0.37°				-0.20		-0.30	-0.40°	-0.37	
MACRP	0.94°	0.37			0.96°		0.10°	0.64°	0.75°	0.46°	0.44
CDRP	-0.30				0.34°	0.42°	0.77°	0.60°	0.30	0.60°	0.79°
NCIP	0.37°		0.96°	0.34°		0.27	0.94°	0.40	0.49°	0.60°	0.94°
NCOTP						-0.14°				-0.40	-0.45°
FRALP	-0.26			0.42°	0.27		0.42°	0.51°		0.47°	0.36°
FRCTP	0.43°		0.40°	0.77°	0.94°	0.42°		0.83°	0.70°	0.60°	0.99°
MACRP	0.30		0.46°	0.66°	0.40	-0.43°	0.42	0.67°	0.81°	0.36°	0.83°
CDRP	-0.40°			0.61°	0.61°	0.51°	0.83°	0.86°	0.58°	0.46°	0.82°
NCIP	-0.33°		-0.42°	0.75°	0.49°		0.70°	0.81°	0.65°	0.65°	0.79°
NCOTP				0.38	0.61°	0.47°	0.68°	0.58°	0.61°		0.70°
FRALP	-0.38	-0.37	0.46°	0.60°		-0.40		0.46°	0.65°		0.48°
FRCTP			0.39			-0.43°					
MACRP	-0.31	0.47	0.44°	0.79°	0.94°	0.36°	0.99°	0.82°	0.79°	0.70°	0.40°

λ All coefficients given are significant at the 5% level or better. Those with "°" are significant at the 1% level.

λ Diff P = Percentile diff P (FRCTP) - Percentile P (FRCTP)

λ Sum = MACRP + CDRP λ / MACRP = Residual (sum - P) FRALP = Sum of (sum - P) MACRP = MACRP total - P MACRP = MACRP total - P

measured, it is possible that the NaOH may be extracting a part of the inorganic-P that is bound to organic matter or there may be extraction of polyphosphates with subsequent hydrolysis to inorganic reactive-P.

Table 5 . Stepwise Linear Regression Equations

$$\text{NaOH-P} = 333.1 \text{ total filtered-P} + 0.26 \text{ organic-P} - 0.60 \text{ HCl-P} + 217.3 \quad R^2 = 0.57$$

$$\text{CDB-P} = 1.52 \text{ residual inorganic-P} - 0.04 \text{ sediment conc.} + 169.2 \quad R^2 = 0.39$$

$$\begin{aligned} \text{HCl-P} = & 0.03 \text{ sediment concentration} + 162.9 \text{ filtered} \\ & \text{reactive-P} + 205.8 \text{ total filtered-P} - 0.30 \text{ NaOH-P} \\ & - 0.23 (\text{Perchloric acid total-P} - \text{persulfate acid} \\ & \text{total-P}) + 182.2 \end{aligned} \quad R^2 = 0.56$$

$$\begin{aligned} (\text{NaOH} + \text{CDB})\text{-P} = & 600.7 \text{ total filtered-P} + 20.3 \text{ residual} \\ & \text{inorganic-P} - 0.06 \text{ sediment concentration} \\ & - 0.57 \text{ HCl-P} + 373.4 \end{aligned} \quad R^2 = 0.63$$

Total Sediment P Analysis

One of the objectives of this study was to compare the persulfate method of total-P analysis with perchloric acid digestion used in soil analysis. O'Connor and Syers (1975) showed that when water samples contain significant amounts of mineral sediment, persulfate digestion fails to recover all of the P present. They attributed the difference between persulfate and the more rigorous perchloric acid digestion to highly resistant inorganic-P forms.

Our data (Table 2) showed that perchloric acid does extract more P than persulfate in all cases. The difference in sediment-P extracted was positively correlated with total filtered-P and negatively correlated with HCl-P. Step-wise linear regression gave the following equation:

$$\begin{aligned} \text{Difference in total-P} = & 517.9 \text{ total filtered-P} - 0.38 \text{ CDB-P} - 0.67 \text{ HCl-P} \\ & + 258.2 \end{aligned} \quad R^2 = 0.42$$

The R^2 was quite low but confirmed the negative correlation with HCl-P.

Evidently the perchloric acid is extracting some form of P in the samples from Ohio and Michigan not seen in the New York samples and that this form is not organic-P or residual inorganic-P since these did not correlate.

Conclusions

1. Bioavailable sediment-P as estimated by NaOH extraction was on the order of 30-40% of total inorganic sediment-P for suspended sediments in Michigan and Ohio. New York sediments were only half as much, about 14%.
2. New York sediments had the highest content of apatite-P and were lowest in total-P.
3. Persulfate gave lower total sediment-P values than perchloric acid in all cases; this difference was negatively correlated with apatite-P but was not correlated with organic-P or residual inorganic-P.

ALGAL UPTAKE OF PHOSPHATE FROM LAKE ERIE TRIBUTARY SEDIMENTS

Previous studies in the Lake Erie system indicated that P bound to tributary sediments might be released to algae in relatively short time periods, i.e. 1 month. The experiments described here were designed with that assumption. However, the study showed that total phosphorus was not similar to that found in lake sediments and that the fraction of total phosphorus biologically available was not as important as the rate of utilization of total phosphorus by microbial populations.

The experimental procedure involved incubation and separation. At time equal to zero samples of water from various rivers were placed in lighted tanks. The initial concentrations of total phosphorus, orthophosphate, suspended solids, and other parameters were measured. The incubation with the indigenous microbial population was then initiated. The microbial growth was observed and after a significant microbial population had accumulated, it was harvested. The microbes were centrifuged from the water which was decanted from the incubation tanks. Most of the inorganic suspended solids remained in the tank. Further, any microbial growth which accumulated on the sides of the tank was removed by scraping. The total phosphorus and the inorganic suspended solids in the solids removed from the tank were then determined. The water was returned to the tank and the incubation was continued. The dissolved oxygen concentration and the pH in the tank were monitored during the entire incubation period.

The basic concept involved in the experiments is the conservation of mass on the two major quantities of interest, total phosphorus and inorganic suspended solids (fixed solids). The initial quantities of these two materials were determined and the amount removed during each harvest was measured. From these numbers it was possible to calculate the amount of total phosphorus which was converted to microbial biomass. From the time between harvests, the rate of conversion could be calculated.

The differences between this availability study and most previous ones can be attributed to the harvesting procedure and the mass balance calculations. The harvesting procedure gave semi-direct measurements of the total phosphorus incorporated into the microbial population. Secondly, the harvesting procedure permitted a time succession of microbial species, each specie growing and extracting phosphorus when conditions were best for it. The mass balances could then be applied to calculate rate of conversion of total sediment phosphorus to total phosphorus taken up by algae.

Although the experiments utilized indigenous microbes, it was not intended to mimic the exact conditions in a lake or bay. However, the conditions used in the experiments should reasonably approximate some conditions under which this total phosphorus would be converted to biomass in natural waters. Probably the laboratory conditions would give a high estimate of the phosphorus conversion rate in a lake.

Methods and Materials

Five-gallon glass pickle jars with their necks removed were used as culture vessels and are referred to hereafter as tanks. Florescent work bench lamps were suspended at a height such that they would supply 400 foot candles at the liquid surface. The sides of some of the tanks had been darkened but this didn't appear to influence the phosphorus conversion by the microbes.

At the starting time the samples were placed in the tanks, usually a few days after the samples had been removed from the river. All time references relate to time equal zero when the water was put into the tanks. Samples from four different rivers were obtained. They are designated as the Cattaraugus sample, taken from that river in New York State, the Broken Sword sample, the Honey Creek sample, and the Sandusky sample, all taken from the Sandusky River Basin in Ohio.

The variables analyzed and methods used are summarized in Table 6 . The first two of these, DO and pH were checked frequently by immersing the respective electrode into the growth tank then gently swirling the electrode and reading the meter value. The other tests were performed on aliquots drawn from the original sample.

The following laboratory procedures were followed with the test samples:

1. Twelve to fourteen liters of sample were poured into a test tank. This tank was then incubated at room temperature (20°C - 25°C) in 24 hour light conditions. A light intensity of approximately 400 foot-candles at the sample surface was provided by flourescent bulbs. The tanks were covered with clear plastic to inhibit both evaporation and the entry of insects into the samples.
2. Aliquots of the original sample were taken to establish base data. All the variables in Table 6 were determined.
3. DO and pH were checked frequently using the technique mentioned previously.
4. Harvests were made when visual observations suggested they were necessary. A centrifuge capable of handling 1.5 liters of sample at one time at speeds up to 12,000 RPM were first used. This was a rather tedious process, so when a continuous centrifuge became available it was used. Some operational difficulties were encountered with the continuous centrifuge and a snapped tube resulted in a 5-liter loss from the Sandusky Tank 2 sample during the 9/13/77 extraction. It was found that a speed of 10,000 RPM was suitable once the continuous centrifuge was in working order. In the Honey Creek and Broken Sword samples, growth on the sides of the test tank and a crusty layer on the surface of the settled solids became noticeable and was collected using acid washed razor blades and rubber gloves once the tank was drained. Using the above techniques, the harvest schedule shown on Table 7 was followed. Harvests were analysed for solids and phosphorus.

DO	YSI Model 51 Oxygen Meter
pH	Beckman Model 3500 Digital pH Meter
Phosphorus	Persulfate Digestion Method (Std. Mthds. 425 C, III) Stannous Chloride Method (Std. Mthds. 425 E)
Solids	Total Residue Dried @ 103-109°C (Std. Mthds. 208 A) Total Volatile & Fixed Residue @ 550°C (Std. Mthds. 208 E)
Nitrite	Nitrogen (Nitrite) (Std. Mthds. 420)
Nitrate	Nitrate Electrode Method (Std. Mthds. 419 B)

Reference: Standard Methods (1975)

Table 6 . Methods of Analysis

Table 7. HARVEST SCHEDULE (Growth in the Cattaraugus tanks were insufficient to harvest)

DATE	DAY # SAND	DAY # HC & BS	SANDUSKY			HONEY CREEK			BROKEN SWORD		
			TANK 1	TANK 2	TANK 3	TANK 1	TANK 2	TANK 3	TANK 1	TANK 2	TANK 3
3/23	36	-	6 L @ 10,000 RPM *								
3/29	42	-	6 L @ 10,000 RPM *								
**											
9/13	57	-	6 L @ 18,000 RPM								
10/16	80	23	9 L @ 10,000 RPM			9 L @ 10,000 RPM					
10/17	-	34				12 @ 10,000 RPM Scrape Sides	Scrape Sides and Bottom		12 @ 10,000 RPM Scrape Side	Scrape Sides and Bottom	
11/9	-	36				12 @ 10,000 RPM	Scrape Bottom				
11/24	129	72	Scrape Sides			12 @ 10,000 RPM					
12/6	143	84			12 @ 10,000 RPM	12 @ 10,000 RPM			12 @ 10,000 RPM		
12/20	-	98					Scrape Sides				

* Centrifuge run for 10-15 minutes

** All centrifuge work done after this point was done with the continuous centrifuge

*** Growth in the Cattaraugus samples was insufficient to harvest

5. At the end of the experiments an effort was made to aerate our samples after NaNO_3 addition to maximize growth. Aeration was for 3 weeks in Sandusky Tank 1 and for 1 week in the other test tanks.

6. Aliquots from each sample were taken and analyzed for remaining solids and phosphorus.

Results and Discussion

DO and pH Measurements

DO and pH were monitored continuously throughout this experiment. For each sample, values were taken in each tank and these three values were averaged together to yield the data points shown on Figures 3 and 4 which are characteristic of the New York sample and the Ohio sample respectively.

The DO curves in these figures exhibit lag time before maximum DO is reached. If DO levels are an indicator of photosynthetic activity one would then assume that there is a lag time of approximately 15 to 35 days before a steady state microbial activity is reached. Another point brought out by the DO in the Cattaraugus curve (Figure 3) is the lack of microbial activity in the vessel. This unchanging dissolved oxygen (DO) agrees with the absence of algal activity noted in the sample over the duration of the experiment.

The pH data shows that the samples rose above the 8.5 maximum recommended in the Algal Assay Procedure Bottle Test (1971). No attempt was made to artificially lower the pH when it exceeded this value, thereby letting the system be more self-regulating by allowing it to respond naturally to the situation. As the figures indicate the pH did finally return to the 8.5 range.

Biological Removal of Phosphorus by Algal Harvests

Phosphorus and solids were initially measured on the river water in the tank. This base data provides the starting points for the extraction data. For time equals zero, the total suspended solids (mg/l) and phosphorus (mg/l) were multiplied by the sample volume in the tank to give the initial

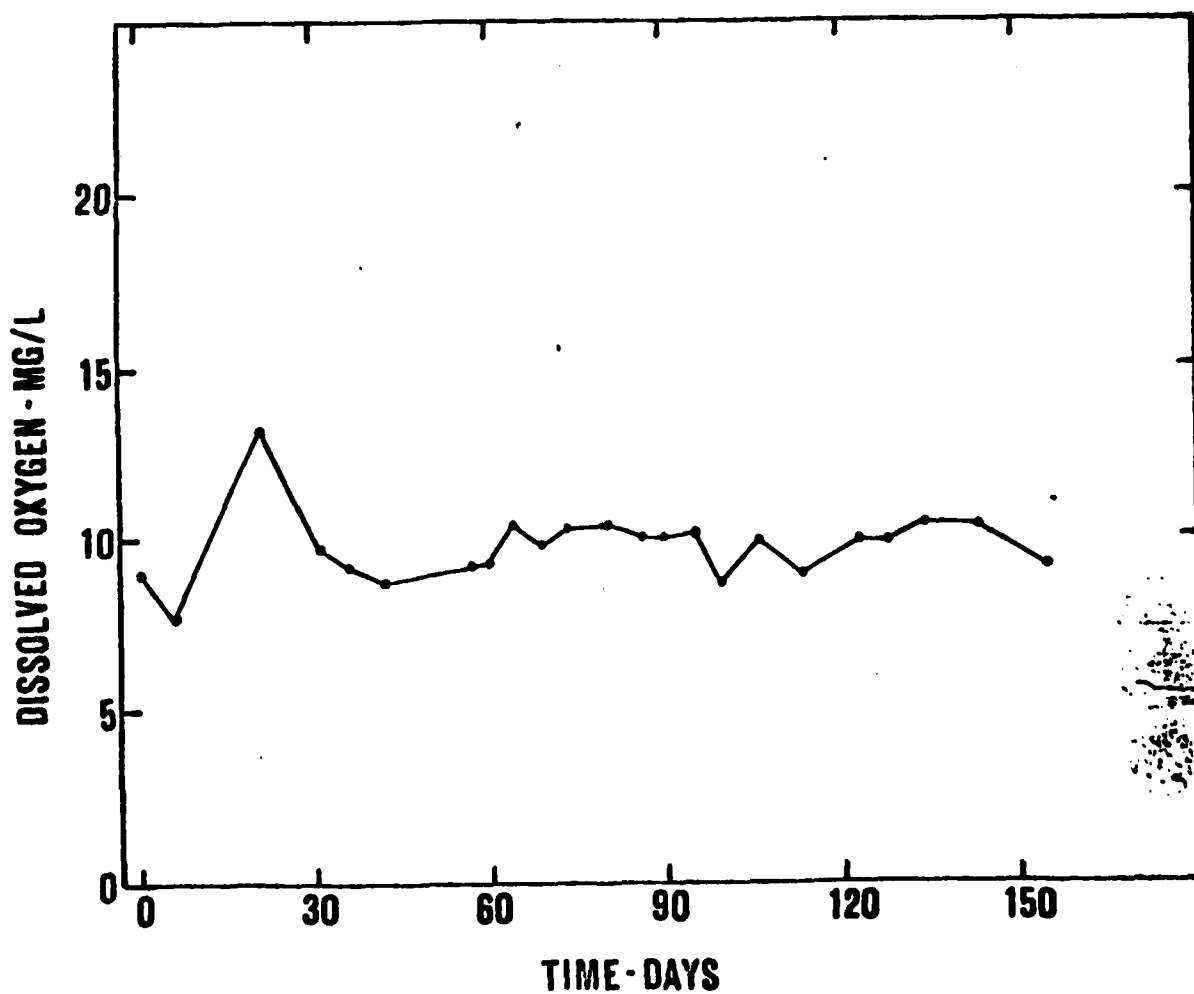
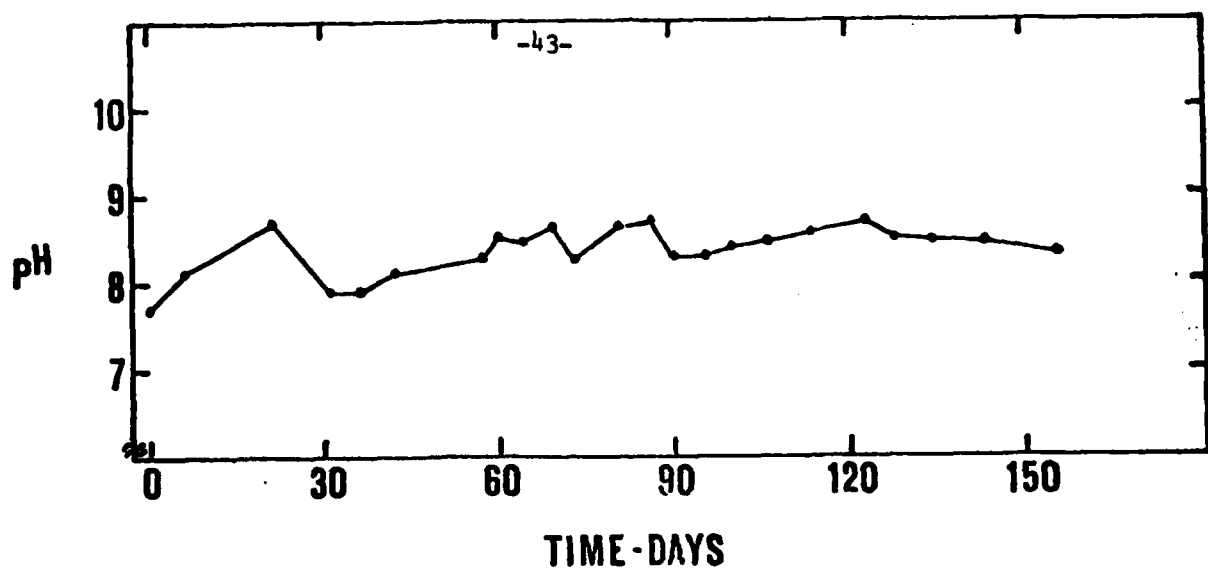


Figure 3 . Dissolved Oxygen and pH Variation as a Function of Time in the Cattaraugus River samples

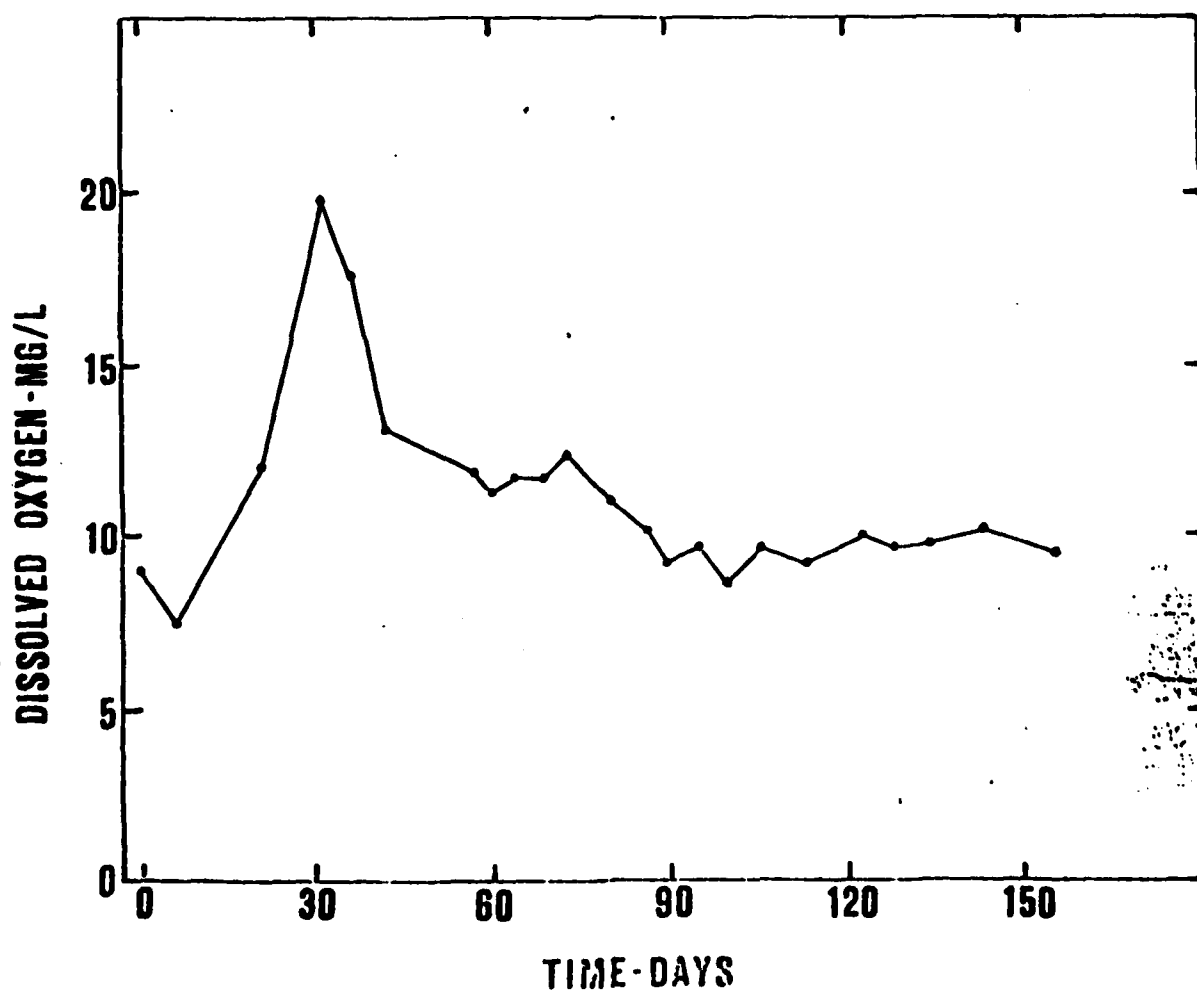
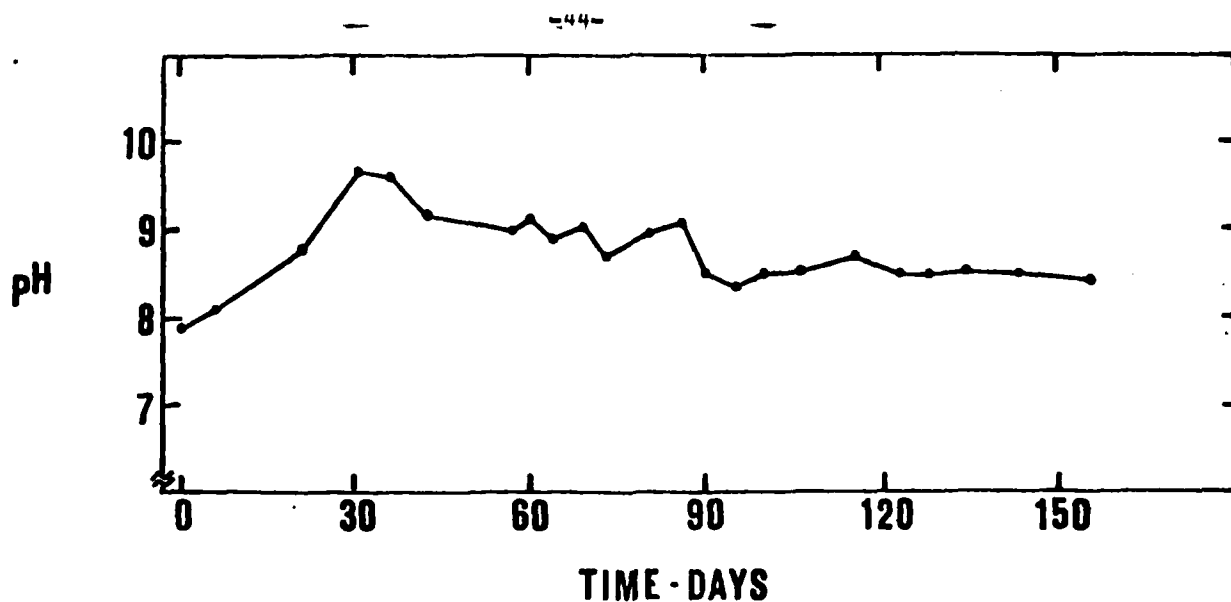


Figure 4 . Dissolved Oxygen and pH Variation as a Function of Time in the Sandusky River samples

fixed solids and phosphorus contents of the tank in milligrams. As an extraction was made according to the schedule shown in Table 7 the following calculations were made:

$$\frac{\text{Wt. Volatile Solids Removed}}{0.75} = \text{Wt. Algae Removed}$$

This calculation is based on previously collected experimental data which indicated that pure algae was approximately 75% volatile solids.

After the weight of algae removed was calculated, the weight of nonalgal suspended solids removed could then be found:

$$\text{Wt. Nonalgal Suspended Solids Removed} = \text{Wt. Suspended Solids Removed} - \text{Wt. Algae Removed}$$

$$\frac{\text{Wt. Nonalgal Suspended Solids Removed}}{\text{Wt. Suspended Solids at T = 0}} \times 100 = \% \text{ Nonalgal Suspended Solids Removed}$$

$$\frac{\text{Wt. Phosphorus Removed}}{\text{Wt. Phosphorus at T = 0}} \times 100 = \% \text{ Phosphorus Removed}$$

The data were analyzed in a series of plots in which the cumulative % Phosphorus removed was compared with time. Figure 5 shows this plot for the Honey Creek sample. A least square analysis of the form $y = ax$ in which a , the slope, is equal to the removal rate was made for each sample. The 90% confidence interval was calculated and appears on Figure 5 in the form of broken lines.

This method of analysis presumed that all the total phosphorus was associated with the microbe when in fact some of it was removed in the nonalgal suspended solids portion of the extractions. To account for phosphorus in these nonalgal suspended solids the assumption that the sediment associated phosphorus¹ originally in the sample was evenly distributed among the suspended solids in the sample was made. This meant that the percent nonalgal suspended solids removed also represented the percent sediment associated phosphorus removed in the nonalgal suspended solids and allowed the following calculation to be made:

$$P \text{ removed by algae} = P \text{ removed} - P \text{ associated with nonalgal suspended solids removed}$$

¹ Sediment associated phosphorus equals initial total phosphorus concentration minus the initial orthophosphorus concentration.

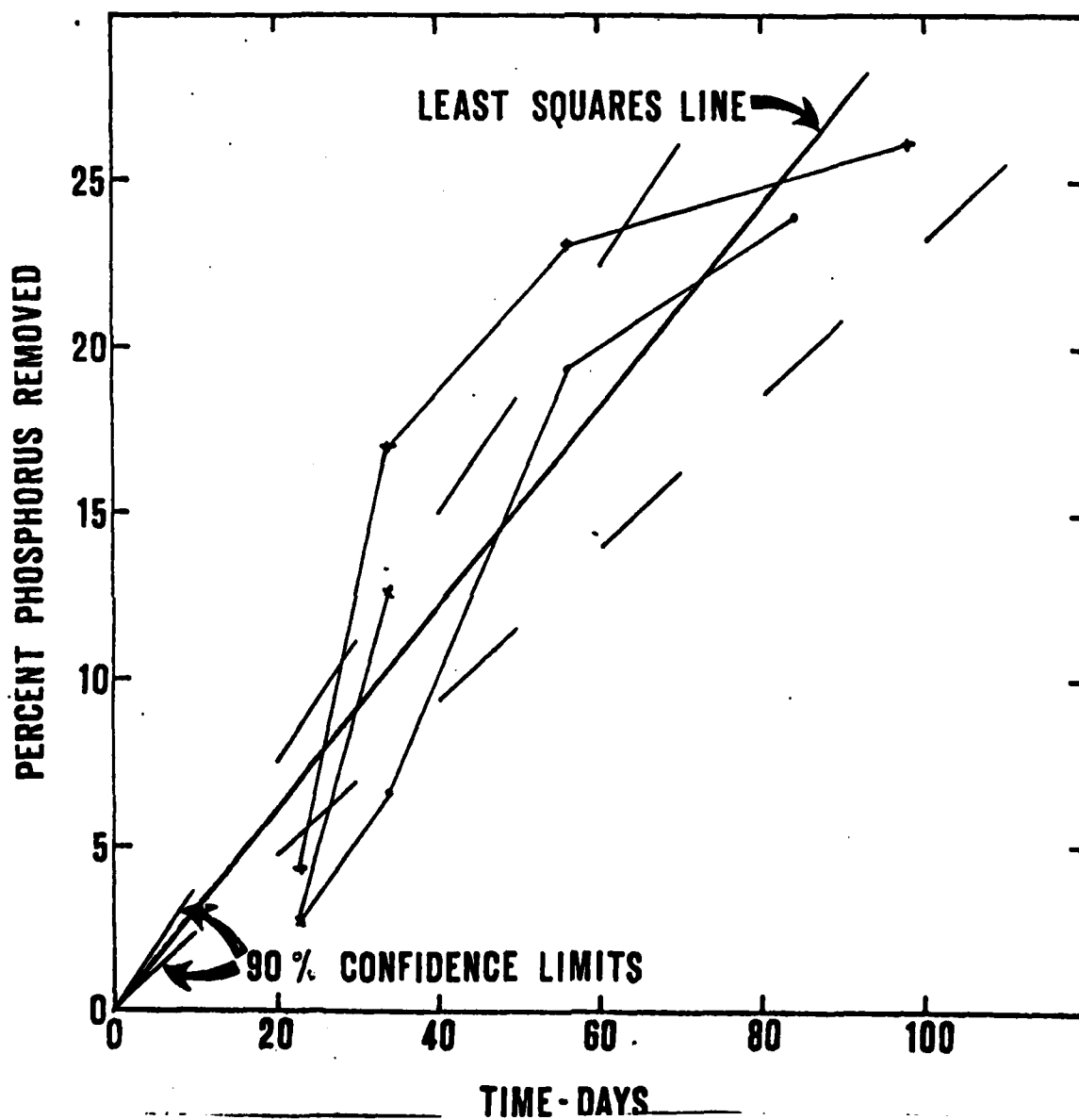


Figure 5 . Percent Phosphorus Removal as a Function of Time in the Honey Creek samples (• = Tank 1; x = Tank 2; + = Tank 3)

A series of plots comparing the cumulative %P removed by the algae and time was then made for each sample (Figures 6-8). The same least squares and 90% confidence interval as was used previously were then calculated and drawn on Figures 6-8. This method of calculation seemed more reasonable so a further calculation to find an uptake rate in terms of $\frac{\text{mg P removed by algae}}{\text{gm fixed solids}}/\text{day}$ was made using the formula:

$$\text{uptake rate} \left(\frac{\text{mg P removed by algae}}{\text{gm fixed solids}}/\text{day} \right) = \frac{\% \text{ P removed by algae}}{\text{day}} \times \frac{\text{mg P}}{\text{gm fixed solids (in tank at time zero)}}$$

The % removal rates and uptake rates are both summarized in Table 8 .

Check of Lag Phase

A check of the Honey Creek "a" value using the least squares formula of $y = ax + b$ was then made to check the $y = ax$ fit for accuracy. This type of formula would provide better fit if the lag were significant. The "a" value of .226 and "b" value of =.13 for the $y = ax + b$ test as compared to the "a" value of .268 and "b" value of 0 for the $y = ax$ test seems to indicate that the assumption of $b = 0$ was valid.

Chemical Extraction of Sediment Phosphate Before and After Algal Uptake

The four sediments used in the algal bioassay study were fractionated according to the procedure described previously in this report. Fractionation before and after algal extraction was used to identify the fraction or fractions most utilized by the algae. During the algal uptake study, there was some loss of sediment solids during harvesting and at the end of the incubation period there was still significant amounts of algal biomass in the sediment. These factors must be taken into account in any interpretation of the fractionation data. Table 9 gives the fractionation data as well as total, filtered reactive-P (ortho-P) and suspended solids content. In all cases, there was a significant reduction in suspended solids which is probably due to that lost in harvesting in the case of Broken Sword, Honey Creek and Sandusky sediments.

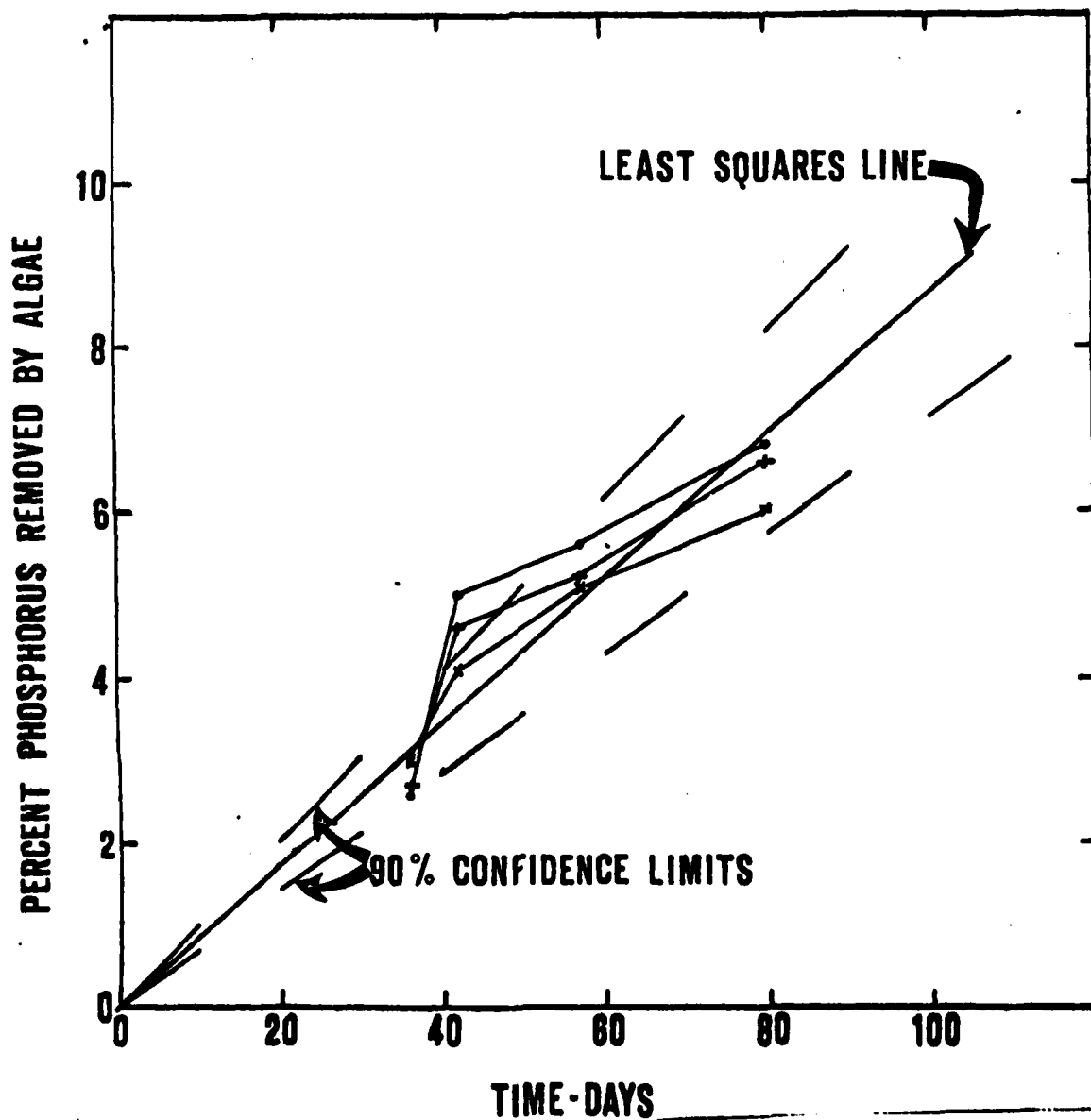


Figure 6 . Percent Phosphorus Removal by the Algae as a Function of Time in the Sandusky River samples (• = Tank 1; x = Tank 2; + = Tank 3)

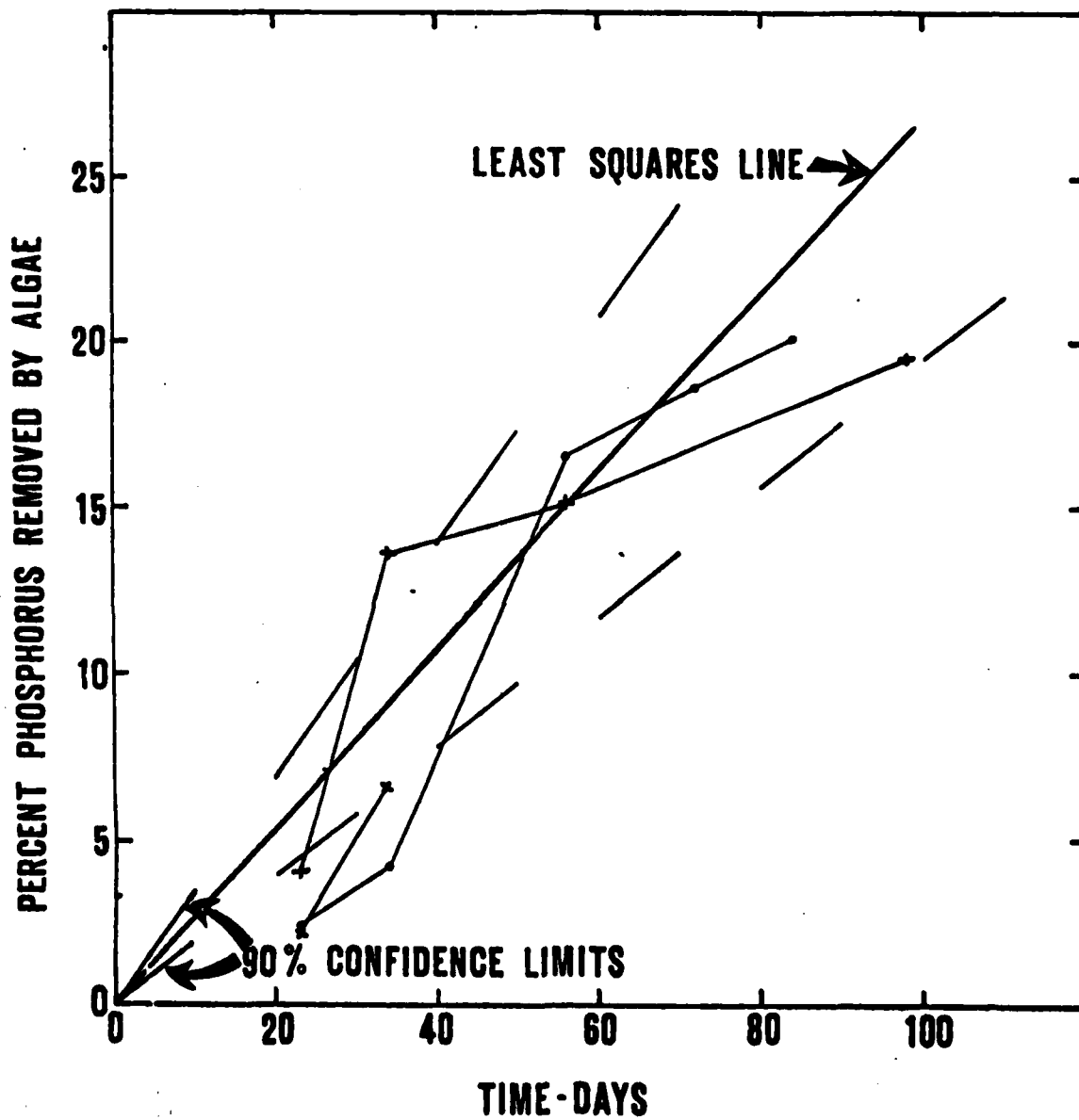


Figure 7. Percent Phosphorus Removal by the Algae as a Function of Time in the Honey Creek samples (\bullet = Tank 1; \times = Tank 2; $+$ = Tank 3)

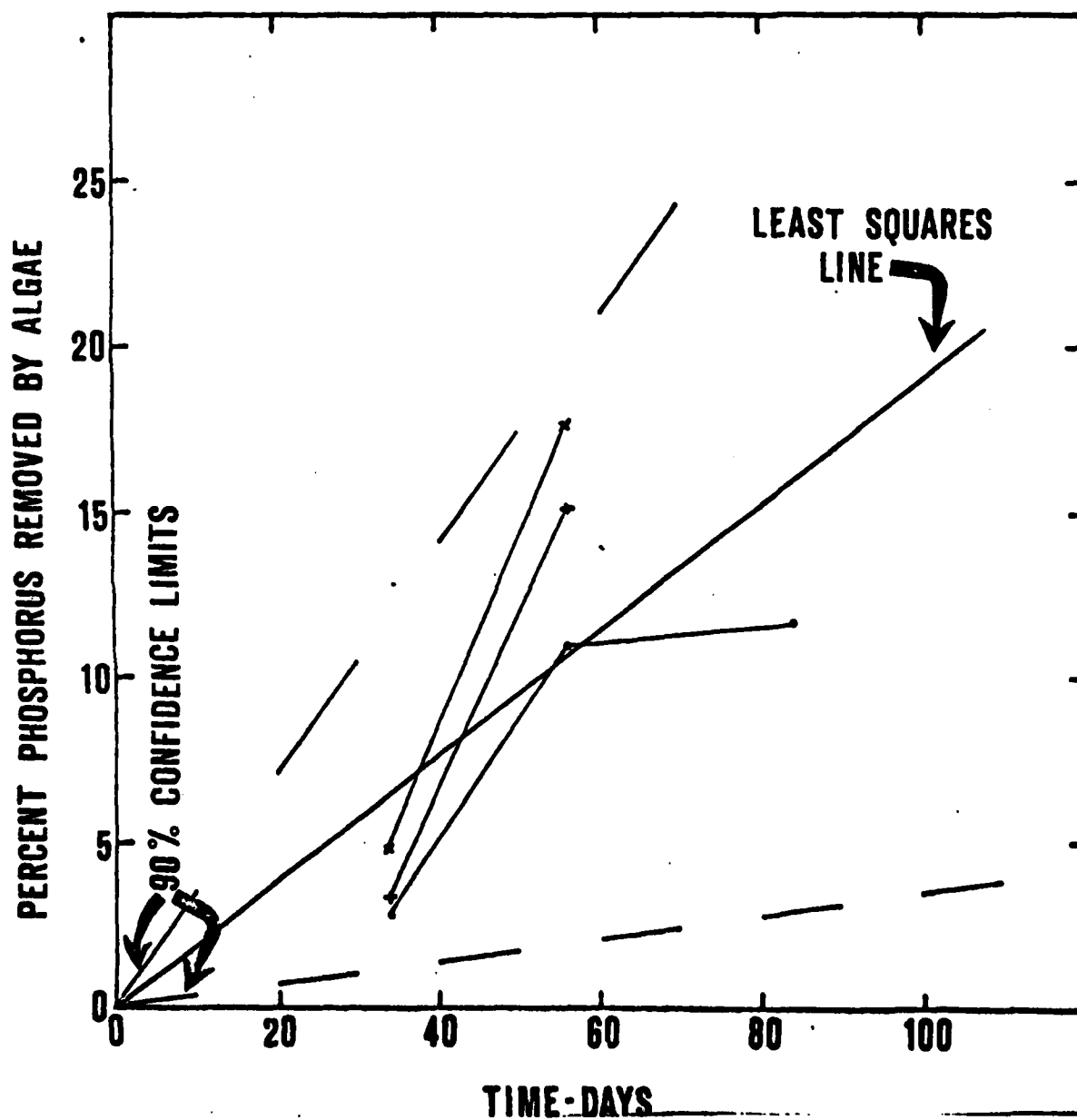


Figure 8 . Percent Phosphorus Removal by the Algae as a Function of Time in the Broken Sword River samples (• = Tank 1; x = Tank 2; + = Tank 3)

	Sandusky	Honey Creek	Broken Sword
Removal Rate ($\frac{\% \text{ P removed by Algae}}{\text{day}}$)	.087	.268	.191
95% Confidence Interval	.072 - .102	.194 - .324	.035 - .347
Uptake Rate ($\frac{\text{mg P removed by Algae}}{\text{gm solids day}}$)	.092	.191	.144
90% Confidence Interval	.076 - .108	.138 - .244	.026 - .261

Table 8. Removal Rates for Extraction Data Considering Nonalgal Suspended Solids Removal.

Table 9 . Analysis of suspended river sediments before and after algal extraction

Sediment conc.	ug/ml		ug/g				
	Ortho-P	Total-P	NaOH-P	CDB-P	HCl-P	Total sediment-P	Organic-P
<u>Broken Sword</u>							
Before	1203						
After	774	1.452	332.3	177.5	31.2	1035.2	180.7
Difference	-430	1.206	209.5	539.0	58.8	909.0	250.0
		-0.246	-122.8	361.5	27.6	-126.2	69.3
<u>Honey Creek</u>							
Before	1184						
After	1030	1.358	354.1	204.2	23.3	1228.8	284.0
Difference	-154	1.326	330.5	444.8	46.6	909.0	217.8
		-0.032	-133.6	240.6	23.3	-319.8	-67.8
<u>Sandusky</u>							
Before	730						
After	330	0.979	290.6	310.3	68.6	1058.8	-*
Difference	-400	0.619	272.0	383.8	71.1	1262.5	-
		-0.360	-18.6	73.5	2.5	176.7	-
<u>Cattaraugus</u>							
Before	3602						
After	2002	2.954	71.1	93.9	350.4	690.2	22.3
Difference	-1600	3.074	42.9	204.2	332.0	656.5	180.7
		0.120	-28.2	110.3	-18.4	-33.7	158.4
		-0.005					

* Insufficient sample for analysis.

The lower solids content of the Cattaraugus sample is not explained since there was no growth in this sample sufficient to harvest. Ortho-P increased and total-P decreased for those samples which supported algal growth, and there was little change in the Cattaraugus. Total-P reduction represents solids reduction and P removal by algae, while ortho-P increase probably represents P released from senesced algae after termination of the study.

In the three Sandusky River sediments (Broken Sword and Honey Creek are tributaries to the Sandusky), NaOH-P was reduced, CDB-P increased and apatite (HCl-P) increased slightly. Several authors (Sagher et al., 1975; Cowen and Lee, 1976) have observed depletion of NaOH-P fraction during algal P uptake, and this is confirmed by the limited data presented here. Another contributing factor may be the preferential loss of fine suspended sediment during the harvesting operation. Armstrong et al., (1977) have shown that finer particles are higher in NaOH-P and lower in apatite-P than coarser particles. This is supported by the increase in HCl-P in the samples analyzed here after the algal uptake study. Similar effects were noted in the Cattaraugus sample. Since no harvesting occurred in this case, the only explanation is that there was enough unobserved growth in the sample to cause some sediment-P changes. The organic-P data was inconsistent, two samples showing an increase and one a slight decrease. Increased organic-P would be predicted if there were significant algal biomass remaining in the sample after incubation. Organic-P reduction would be predicted if organic-P levels were initially high and algal-P remaining in the sample were low. The Honey Creek sample which gave decrease in organic-P did have the highest initial organic-P level.

Conclusions

1. The absence of harvestable growth and the lower DO and pH values for the Cattaraugus samples indicate that the Cattaraugus River water was far less suitable for biological activity than the Sandusky, Honey Creek,

and Broken Sword waters. Presumably the total phosphorus in the Cattaraugus is less available than that of the other streams.

2. Phosphorus removal by the algae appears to take place at a rate less than 0.4% P/day. This is significantly less than the value of 5 to 10% P/day often given for lake sediments. This slow rate implies that biological activity is capable of utilizing total phosphorus from river storm flows for a year or two after it has flushed into the lake. This long time period indicates that the rate of release of total phosphorus is more important than the ultimate total availability of the total phosphorus.

CONCLUSIONS

Monitored tributary loads of sediment to Lake Erie in recent years have shown that most of the sediment is transported during storm events. These sediments are primarily of surficial soil origin; during deposition and resuspension cycles in the river, the sediments undergo sorting, and chemical and biological interaction with point source discharges. The result is that stream sediments are higher in total P content than their soil precursors and a higher percentage of this P is biologically available. Other sources of sediment such as streambank erosion and urban runoff are of lesser significance in terms of their contribution to the total load. PLUARG-Task C studies in the Menomonee River Basin and work by Cowen and Lee (1976 a,b,c) in New York and Wisconsin indicate that urban sediments have phosphorus characteristics similar to those from agricultural areas.

Sediment-P bioavailability as measured by chemical extraction, bioassay or other techniques reflects, for the most part, native soil phosphorus levels in Basin soils and its chemical and biological reactivity, fertilizer phosphorus additions, the degree to which sediment is enriched in P because of preferential clay transport, and the adsorption of point source soluble inorganic P by stream sediments.

Based on these considerations, sediments from the more urbanized tributary areas in Michigan and eastern Ohio and those from the high clay agricultural basins in western Ohio should have the highest BSP per unit sediment load. The high total annual sediment load in the Maumee, Portage and Sandusky basins together with high BSP point to these areas as the major contributors of BSP. In addition, the discharge of these sediments into the shallow western basin of Lake Erie make their impact on algal production even more significant. As one proceeds into the central and eastern basins, the significant contribution of sediment-P to algal growth is diminished for two reasons: lower sediment loads and BSP, and shorter contact time between algae and sediment because of settling.

Reductions in total sediment load to the Lake in concert with point source phosphorus reductions have been proposed. Sediment load reductions in the Ohio region of the Lake basin should receive greatest attention. In this regard, two points should be made: 1) While total fertilizer P additions since modern chemical fertilization began about 40 years ago have only increased soil-P levels by about 10%, these additions have a higher BSP than native soil-P. Logan (1978) found that Lake Erie Basin agricultural soils had available-P levels sufficient for optimum crop production and state extension programs should strive to maintain these levels rather than increase them further. 2) sediment-P reductions will not be as great as sediment reduction when conservation programs are implemented, because these programs are more efficient at preventing the loss of coarse-grained sediment than the fine sediment with its higher P content. The results of Armstrong et al. (1977) indicate that BSP will also diminish slower than sediment reduction.

The net result, then, of both point source P reduction and erosion control will be to reduce the total biologically available sediment-P load with no measurable change in the percentage of sediment-P that is bioavailable.

The algal bioassay study reported here indicates that the rate of P removal from sediment by algae is more likely to be limiting to algal growth in the Lake on an annual basis than the total capacity of tributary sediments to supply P. The capacity factor as measured by chemical extraction is useful as an index of total potential BSP in situations such as the central basin where significant anoxic regeneration occurs, and, to a lesser extent, in the western basin where sediments are continuously resuspended. The kinetic control of sediment-P release to algae suggests that dynamic phosphorus lake models may be more significant in predicting future change in the individual basins than static P loading models.

REFERENCES

1. Allan, R.J. and J.D.H. Williams. 1978. Trophic status related to sediment chemistry of Canadian Prairie Lakes. Jour. Envir. Qual. 7(1):99-106.
2. Amer, F., D.R. Bouldin, C.A. Black and F.R. Luke. 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P32 equilibration. Plant Soil 6:391-408.
3. Armstrong, D.E., M.A. Anderson, J.R. Perry, and D. Flatness. 1977. Availability of pollutants associated with access to the Great Lakes. Unpublished. EPA Progress Report. Wisconsin.
4. Armstrong, D.E., R.F. Harris and J.K. Syers. 1971. Plant available phosphorus status of lakes. Final Tech. Comp. Report. OWRRB-022-W15.
5. Bache, B.W. 1963. Aluminum and iron phosphate studies relating to soils: 1. Jour. Soil Sci. 14:113-123.
6. Bache, B.W. 1964. Aluminum and iron phosphate studies relating to soils: 2. Jour. Soil Sci. 15:110-116.
7. Barsdate, R.J. and L.T. Prentki. 1974. Phosphorus cycle of model ecosystems: Significance for decomposer food chains and effect of bacterial grazers. Oikos 25:239-251.
8. Bauwin, G.R. and E.H. Tyner. 1957. The nature of reductant soluble phosphorus in soils and soil concretions. Soil Sci. Soc. Amer. Proc. 21:250-257.
9. Bray, R.H. and L.T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. Soil Sci. 59:39-45.
10. Chang, S.C. and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84:133-144.
11. Cowen, W.F. and G.F. Lee. 1976a. Algal nutrient availability and limitation in Lake Ontario tributary waters. Ecological Research Series. EPA-600/3-76-094a.
12. Cowen, W.F. and G.F. Lee. 1976b. Phosphorus availability in particulate materials transported by urban runoff. Jour. WPCF. 48:580-591.
13. Cowen, W.F., G.F. Lee and K. Sirininh. 1976c. Nitrogen availability in urban runoff. Jour. WPCF 48:339-345.
14. Cranwell, P.A. 1976. Decomposition of aquatic biota and sediment formation: Organic compounds in detritus resulting from microbial attack on the alga Ceratium hirundinella. Freshwater Biology 6:41-48.

15. DePinto, J.V. 1974. Studies on phosphorus and nitrogen regeneration: The effect of aerobic bacteria on phytoplankton decomposition and succession in freshwater lakes. Ph.D. dissertation, Notre Dame University, West Bend, Ind.
16. DePinto, J.V. 1978. Water column and decomposition of phytoplankton: An experimental and modeling review. In Perspectives on Ecosystem Modeling. Ann Arbor Sci. Press, Ann Arbor, Mich.
17. DePinto, J.V. and F. H. Verhoff. 1977. Nutrient regeneration from aerobic decomposition of green algae. *Envir. Sci. Technol.* 11:371-377.
18. Dorich, R.A. and D.W. Nelson. 1978. Algal availability of soluble and sediment phosphorus in drainage water of the Black Creek watershed. Unpublished report. Purdue Agric. Exp. Sta.
19. Edzwald, J.K. 1977. Phosphorus in aquatic systems: The role of the sediments. In Fate of Pollutants in the Air and Water Environments. I.H. Suffet, Ed. Part 1, Vol. 8, John Wiley and Sons.
20. Fiskell, J.G.A. and W. R. Spencer. 1964. Forms of phosphate in Lakeland fine sand after six years of heavy phosphate and lime applications. *Soil Sci.* 97:320-325.
21. Fitzgerald, G.P. 1970. Aerobic lake muds for the removal of phosphorus from lake waters. *Limnol. Oceanog.* 15:550-555.
22. Foree, E.G., W. J. Jewell and P.L. McCarty. 1970a. The extent of nitrogen and phosphorus regeneration from decomposing algae. In Advances in Water Pollution Research. Vol. 2. Pergamon Press, N.Y.
23. Foree, E.G. and R.L. Barrow. 1970b. Algal growth and decomposition: Effects on water quality, Phase II. Nutrient regeneration, composition, and decomposition of algae in batch culture. OWRR, Report No. 31. Kentucky Water Res. Inst., Lexington, Ky.
24. Frink, C.R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. *Soil Sci. Soc. Amer. Proc.* 33:369-372.
25. Golterman, H.L. 1964. Mineralization of algae under sterile conditions or by bacterial breakdown. *Verh. Int. Verein. Theor. Angew. Limnol.* 15:544-548.
26. Golterman, H.L. 1975. *Physiological Limnology: An approach to the physiology of lake ecosystems.* Elsevier Scientific Publishing Co., Amsterdam.
27. Golterman, H.L. 1976. Sediments as a source of phosphorus for algae growth. In H.L. Golterman (Ed.). *Interactions between sediments and freshwater.* Proc. 51L-UNESCO Conf. Junk and Pudoc, The Hague, Netherlands.
28. Golterman, H.L. 1977. Forms and sediment associations of nutrients, pesticides and metals. Nutrients-P. In Proc. Workshop on Fluvial Transport of Sediment-associated Nutrients and Contaminants. H. Shear, Ed. IJC-PLUARG, Windsor, Ontario.

29. Golterman, H.L., C.C. Bakels and J. Jakobs-Mogelin. 1960. Availability of mud phosphates for the growth of algae. *Verh. Int. Verein. Limnol.* 17:467-479.
30. Green, D.B., T.J. Logan and N.E. Smeck. 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin of Ohio. *Jour. Envir. Qual.* 7:208-212.
31. Grill, E.V. and F.A. Richards. 1966. Nutrient regeneration from phytoplankton decomposing in seawater. *J. Mar. Res.* 22:51-57.
32. Huang, C.P., T.H. Lackie and P.M. Huang. 1976. Adsorption of inorganic phosphorus by lake sediments. *Jour. Water Poll. Cont. Fed.* 48:2754-2760.
33. Jassby, A.D. and C.R. Goldman. 1974. Loss rates from a lake phytoplankton community. *Limnol. Oceanog.* 19:618-627.
34. Jewell, W. 1968. Aerobic decomposition of algae and nutrient regeneration. Ph.D. dissertation, Stanford Univ., Stanford, Calif.
35. Jewell, W. and P.L. McCarty. 1971. Aerobic decomposition of algae. *Envir. Sci. Tech.* 5:1023-1031.
36. Johannes, R.E. 1968. Nutrient regeneration in lakes and oceans. In *Advances in the Microbiology of the Sea*. Vol. 1. M.R. Droop and E.J.F. Wood, Eds. Academic Press, N. Y.
37. Kajak, Z., A. Hillbricht-Irkowska and E. Pieczynska. 1970. Production in several maxurian lakes. Prelim. papers for UNESCO-IBP Symposium on Productivity Problems of Fresh Waters, Kazimierz Dolny, Poland. pp 173-189.
38. Kalff, J., H.J. Kling, S.H. Holmgren and H.E. Welch. 1975. Phytoplankton growth and biomass cycles in an unpolluted and in a polluted polar lake. *Verh. Int. Veorsin. Limnol.* 19:487-495.
39. Kamatani, A. 1969. Regeneration of inorganic nutrients from diatom decomposition. *J. Oceanogr. Soc. Japan.* 25:63-68.
40. Kuznetsov, S.I. 1968. Recent studies on the role of microorganisms in the cycling of substances in lakes. *Limnol. Oceanog.* 13:211.
41. Kuznetsov, S.I. 1970. The microflora of lakes and its geochemical activity. Ed., C.H. Oopenheimer, U. of Texas Press, Austin, Texas.
42. Lam, D.C.L. and J.M. Jaquet. 1976. Computations of physical transport and regeneration of phosphorus in Lake Erie. Fall 1970. *Jour. Fish. Res. Board Canada.* 33:550-563.
43. Lee, G.F., W. Cohen, and N. Sridharan. 1973. Algal availability and limitation in Lake Ontario during I*YGL. EPA 660/3-73-021.

44. Li, W.C., D.E. Armstrong, J.D.H. Williams, R.F. Harris and J.K. Syers. 1972. Rate and extent of inorganic phosphorus exchange in lake sediments. Soil Sci. Soc. Amer. Proc. 36:279-285.
45. Logan, T.J. and E.O. McLean. 1973. Nature of phosphorus retention and adsorption with depth in soil columns. Soil Sci. Soc. Amer. Proc. 37:351-355.
46. Logan, T.J. 1978a. Available phosphorus levels in Lake Erie Basin soils. LEWMS Final Technical Report. Corps of Engineers, Buffalo District, Buffalo, N. Y.
47. Logan, T.J. 1978b. Maumee River Basin pilot watershed study. PLUARG Task C. Summary Technical Report. IJC, Windsor, Ont.
48. Logan, T.J. 1978c. Chemical extraction as an index of bioavailability of phosphate in Lake Erie Basin suspended sediments. Final Report. LEWMS, Corps of Engineers, Buffalo, N. Y.
49. McCallister, D.L. and T.J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. Jour. Envir. Qual. 7:87-92.
50. Mehta, N.C., J.O. Legg, C.A.I. Goring and C.A. Black. 1954. Determination of organic phosphorus in soils. 1. Extraction method. Soil Sci. Soc. Amer. Proc. 18:443-449.
51. Mills, A.L. and M. Alexander. 1974. Microbial decomposition of species of freshwater planktonic algae. J. Environ. Quality. 3:423-428.
52. Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27:31-36.
53. O'Connor, P.W. and J.K. Syers. 1975. Comparison of methods for the determination of total phosphorus in water containing particulate material. J. Envir. Qual. 4:347-350.
54. Olsen, S.R., C.V. Cole, F. Watanabe and L.A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939.
55. Patrick, W.J. and I.C. Mahapatra. 1968. Transformation and availability of nitrogen and phosphorus in waterlogged soils. Advan. Agron. 20:323-359.
56. Phillips, J.E. 1964. The ecological role of phosphorus in waters with special reference to microorganisms. In Principles and Applications of Aquatic Microbiology. H. Neukelekian and N.C. Dondero eds. John Wiley and Sons, New York p. 61-81.
57. Porter, K.S. 1975. Nitrogen and phosphorus, food production, waste and the environment. Ann Arbor Science, Ann Arbor, Mich. 372 pages.

58. Reddy, G.Y., E.O. McLean, G.D. Hoyt and T.J. Logan. 1978. Effects of soil, cover crop, and nutrient source on amounts and forms of phosphorus movement under simulated rainfall conditions. Jour. Envir. Qual. 7:50-54.
59. Rhee, G. 1973. A continuous culture study of phosphate uptake, growth rate and polyphosphate in Scenedesmus sp. Jour. Phycol. 9:495-506.
60. Robertson, W.K., L.G. Thompson, Jr. and C.E. Hutton. 1966. Availability and fractionation of residual P in soils high in aluminum and iron. Soil Sci. Soc. Amer. Proc. 30:446-451.
61. Rodel, M.C., D.E. Armstrong and R.F. Harris. 1977. Sorption and hydrolysis of added organic phosphorus compounds in lake sediments. Limnol. Oceanog. 22:415-422.
62. Romkens, M.J.M. and D.W. Nelson. 1974. Phosphorus relationships in runoff from fertilized fields. Jour. Envir. Qual. 3:10-14.
63. Sagher, A., R. F. Harris, and D.E. Armstrong. 1975. Availability of sediment phosphorus to microorganisms. Univ. of Wisconsin Water Res. Cent. Tech. Report WIC WRC 75-01. Wisconsin.
64. Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong and R.F. Harris. 1971. Sorption of inorganic phosphate by lake sediments. Soil Sci. Soc. Amer. Proc. 35:244-249.
65. Sommers, L.E., R.F. Harris, J.D.H. Williams, D.E. Armstrong and J.K. Syers. 1970. Determination of total organic phosphorus in lake sediments. Limnol. Oceanog. 15:301-304.
66. Sommers, L.E., R.F. Harris, J.D.H. Williams, D.E. Armstrong and J.K. Syers. 1972. Fractionation of organic phosphorus in lake sediments. Soil Sci. Soc. Amer. Proc. 36:51-54.
67. Sommers, L.E. and D.W. Nelson. 1972. Determination of total phosphorus in soils: A rapid perchloric acid digestion procedure. Soil Sci. Soc. Amer. Proc. 36:902-904.
68. Standard methods for the examination of water and wastewater. 13th Edition. 1975. American Public Health Assoc. Washington, D. C.
69. Syers, J.K., R.F. Harris and D.E. Armstrong. 1973. Phosphate chemistry in lake sediments. Jour. Envir. Qual. 2:1-14.
70. Syers, J.K., G.W. Smillie and J.D.H. Williams. 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride. 1. Implication to inorganic P fractionation schemes. Soil Sci. Soc. Amer. Proc. 36:20-25.
71. Uhlmann, D. 1971. Influence of dilution, sinking and grazing rate on phytoplankton populations of hyperfertilized ponds and microecosystems. Mitl. Internat. Verein. Limnol. 19:100-124.

72. Verhoff, F.H., M. Heffner and W.A. Sack. 1978. Measurement of availability rate for total phosphorus from river waters. Final Report. LEWMS, Corps of Engineers, Buffalo, N.Y.
73. Williams, J.D.H., T.P. Murphy, and T. Mayer. 1976b. Rates of accumulation of phosphorus forms in Lake Erie sediments. J. Fish. Res. Board Can. 33:430-439.
74. Williams, J.D.H., J.K. Syers, and T.W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Sci. Soc. Amer. Proc. 31:736-739.
75. Williams, J.D.H., J.M. Jaquet and R.L. Thomas. 1976a. Forms of phosphorus in surficial sediments of Lake Erie. Jour. Fish. Res. Board Can. 33:413-429.
76. Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1971a. Fractionation of inorganic phosphate in calcareous lake sediments. Soil Sci. Soc. Amer. Proc. 35:250-255.
77. Williams, J.D.H., J.K. Syers, D.E. Armstrong, and R.F. Harris. 1971b. Characterization of inorganic phosphate in noncalcareous lake sediment. Soil Sci. Soc. Amer. Proc. 35:556-561.
78. Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris and D.E. Armstrong. 1971c. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Envir. Sci. Technol. 5:1113-1120.
79. Williams, J.D.H. and T.W. Walker. 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic soil profiles: 1. Soil Sci. 107:22-30.
80. Williams, J.D.H. and T.W. Walker. 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic soil profiles: 2. Soil Sci. 107:213-219.