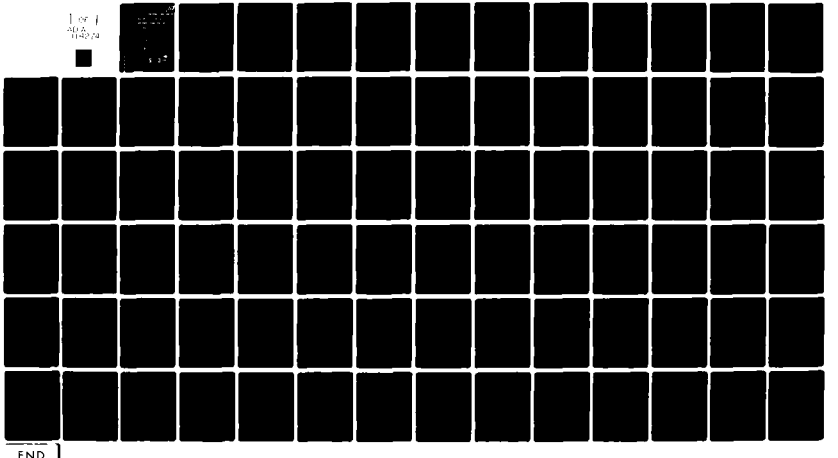
AD-A118 274 CLARKSON COLL OF TECHNOLOGY POTSDAM NY DEPT OF CIVIL--ETC F/G 6/6
EFFECTS OF ANAEROBIC CONDITIONS ON AVAILABILITY OF PARTICULATE --ETC(U)
JUN 82 J P MCAULIFFE, T C YOUNG, J V DEPINTO DACW49-81-C-0045

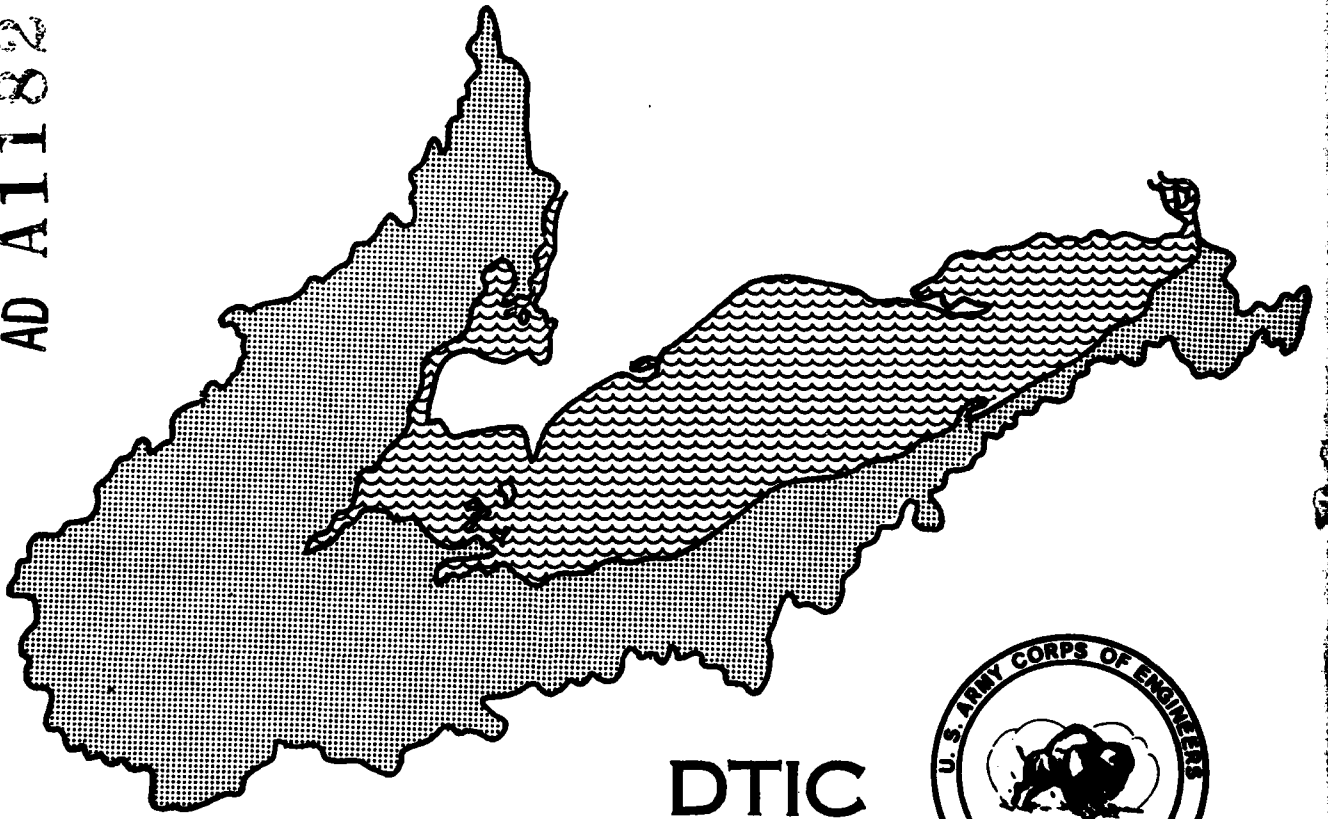
UNCLASSIFIED NL



END
DATE FILMED
9-82
DTIC

TECHNICAL REPORT SERIES

EFFECTS OF ANAEROBIC CONDITIONS ON AVAILABILITY OF PARTICULATE PHOSPHORUS FROM TRIBUTARIES TO LAKE ERIE



PREPARED FOR THE
LAKE ERIE WASTEWATER
MANAGEMENT STUDY
U.S. ARMY ENGINEER DISTRICT, BUFFALO

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A118 274	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Effects of Anaerobic Conditions on Availability of Particulate Phosphorus From Tributaries to Lake Erie		5. TYPE OF REPORT & PERIOD COVERED FINAL
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John P. McAuliffe, Thomas C. Young, Joseph V. DePinto/Clarkson College of Technology		8. CONTRACT OR GRANT NUMBER(s) DACW49-8]-C-0045
9. PERFORMING ORGANIZATION NAME AND ADDRESS Clarkson College of Technology Potsdam, N.Y.]3676		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Engineer District, Bflo. 1776 Niagara St. Bflo., N.Y. 14207/ Water Quality		12. REPORT DATE June 1982
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Copies are available from NTIS
Springfield, VA 22161

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

phosphorus
Lake Erie
Anaerobic
bioassy
chemical fractionations

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

In summary, the bioassay and fractionation data gathered in this study indicate that after tributary sediments are deposited, exposed to anaerobic conditions and resuspended, they will release no more phosphorus than if they had remained suspended.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

EFFECTS OF ANAEROBIC CONDITIONS ON AVAILABILITY OF PARTICULATE PHOSPHORUS FROM TRIBUTARIES TO LAKE ERIE

FINAL REPORT

by

John P. McAuliffe, Graduate Research Assistant
Thomas C. Young, Assistant Professor
Joseph V. DePinto, Associate Professor

Department of Civil and Environmental Engineering
Clarkson College of Technology
Potsdam, New York 13676

for

Water Quality Branch
Buffalo District
U.S. Army Corps of Engineers
1776 Niagara Street
Buffalo, New York 14207

June, 1982

EFFECTS OF ANAEROBIC CONDITIONS ON AVAILABILITY OF PARTICULATE PHOSPHORUS FROM TRIBUTARIES TO LAKE ERIE

ABSTRACT

After deposition, sediments are often exposed to a period of anoxia, followed by resuspension. In order to determine the effect of anoxia on the bioavailability of phosphorus associated with suspended sediments, samples from four Lake Erie tributaries were subjected to a period of anaerobic incubation, reaerated, and bioassayed. The available phosphorus released from these post-incubation bioassays was compared to the release from the same samples not exposed to the anaerobic period. Sequential chemical fractionations were run concurrently to identify the changes in particulate phosphorus fractions.

A concentrated slurry anaerobic incubation did cause low oxidation reduction potentials which resulted in the solubilization of inorganic phosphorus. Upon aeration a major portion of the soluble reactive phosphorus was resorbed. During the anaerobic incubation and aeration changes were observed in some of the chemical fractions. These changes, especially the consistent loss from the residual fraction, can generally be associated with microbial activitiy.

The bioassays on the anaerobically incubated sediments consistently showed less phosphorus release than the bioassays on the control sediments. However, the changes in the total sediment phosphorus during the bioassays indicate that release

from the anaerobically incubated sediments was nearly identical to the release from the control sediments. Since the changes in total phosphorus were the same during the post-incubation and control bioassays, it appears that the changes seen in the fractionations during the anaerobic incubations were due only to rearrangement of the available phosphorus among the fractions.

Overall, the bioassay and fractionation data gathered in this study indicate that after tributary sediments are deposited, exposed to anaerobic conditions and resuspended, they will release no more phosphorus than if they had remained suspended.

ACKNOWLEDGEMENTS

This investigation was sponsored by the Buffalo District, U.S. Army Corps of Engineers through a grant (# DACW49-81-C-0045) to Clarkson College of Technology. The assistance provided by Dr. Dave Baker from Heidelberg College for sample collection is greatly appreciated. The Project Officer, Dr. Steve Yaksich of the Water Quality Branch, Buffalo District, is gratefully acknowledged for his interest in the work.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Eutrophication, the increased growth of primary producers due to nutrient enrichment, causes unsightly conditions, loss of lakes for recreation and drinking water, and a shift of the lakes organisms to species that thrive under low dissolved oxygen conditions. Since phosphorus is essential to the metabolic functions of all organisms and exists in the hydrosphere in small amounts relative to other necessary nutrients and structural components, it is often shown to be the limiting nutrient to primary production. Reduction of phosphorus inputs that are caused by man's inefficient use of phosphorus for agricultural, industrial, and domestic purposes should result in a decline in the growth of primary producers and a decrease in the rate of eutrophication in aquatic systems.

In an effort to reduce the rate of eutrophication in the Great Lakes, the International Joint Commission has determined that phosphorus loading must be reduced. To control point sources, effluent concentration limits of 1 mg $P \cdot L^{-1}$ have been established for treatment plants discharging into the Lower Great Lakes. However, the largest phosphorus loads are from diffuse sources which enter the lakes through tributaries, and comprise approximately 50% of the total phosphorus load to Lake Erie and 40% of the load to Ontario (Chapra and Sonzogni, 1979). It is important to realize, that since more than 90% of this diffuse source phosphorus may be in sediment-bound forms, it is not all available for algal growth. The availability of the sediment

phosphorus depends on the physical and chemical characteristics of the particles, as well as the lakes' productivity level, soluble inorganic phosphorus level, morphometry, hydrology, temperature, and biological activity. By determining what fraction of this particulate phosphorus is available and its rate of release, a cost-effective attempt can be made to decrease the phosphorus loads to lakes from diffuse sources.

The fraction of the particulate phosphorus that does not become available in the photic zone will be deposited at the lake bottom along with the sediments. This fraction, estimated at 60-95% of the total particulate phosphorus (DePinto et al., 1982), will accumulate in the sediments along with organic phosphorus from dead biomass that will be decomposed and hydrolyzed. Obviously, the exchange of this sediment phosphorus with the overlying water and its degree of availability are important considerations in determining a phosphorus budget for the lower Great Lakes.

The exchange of phosphorus between the sediments and the overlying water is affected by mineral-water equilibria, sorption processes, redox interactions, and the activities of bacteria and other organisms. However, at the critical mud-water interface, the factor controlling the exchange mechanisms is the oxygen concentration. As dead particulate organic matter that has settled from the epilimnion is degraded, oxygen is consumed, and must be replaced from the overlying water. In aerobic lakes oxygen will penetrate a few centimeters into the sediments, and this oxidized layer will provide an effective trap for iron and

manganese which may diffuse from deeper within the sediments. However, as the lake becomes stratified, oxygen is not circulated in the water column, the oxidized layer will become thinner, and the mud-water interface will become increasingly more anoxic. Under anoxic conditions, Fe^{+3} will be reduced and will result in the solubilization of some of the sediment-bound phosphorus adsorbed to or occluded within ferric hydroxides (Mortimer 1941, 1942).

During later circulation and exposure to aerobic conditions some of the solubilized phosphorus will be incorporated in or adsorb to hydrated iron oxides as Fe^{+2} is oxidized to Fe^{+3}. Additionally, resuspended bottom sediments will be oxidized and provide further adsorption sites to bind the phosphorus that was solubilized under anaerobic conditions. When the phosphorus is resorbed it may be relatively loosely bound, and may have a different biological availability than before it was exposed to anaerobic conditions.

Therefore, this study was undertaken to investigate the effects of anaerobic conditions on the suspended solids from tributaries to the western basin of Lake Erie. Samples from the Cuyahoga, Maumee, and Sandusky Rivers and Honey Creek were incubated anaerobically and analyzed for biological available phosphorus using a direct bioassay procedure. The samples were also characterized with respect to pH, redox potential, soluble phosphorus, and particulate phosphorus fractionations at strategic points in the procedure. Through this investigation, the following specific objectives were addressed:

1. To determine the extent to which anaerobic conditions stimulate release of algal-available phosphorus from suspended sediments beyond that released under aerobic conditions.
2. To determine the extent to which anaerobic conditions alter the chemical forms of phosphorus associated with suspended sediments, especially the forms considered to be bioavailable.

The knowledge of the effect of anaerobic conditions on Lake Erie tributary sediments will help to form a more complete picture of the phosphorus budget in the Lower Great Lakes. By understanding Lake Erie's phosphorus budget and its effects on primary productivity, an attempt can be made to identify the most significant and economically feasible approach to limiting eutrophication.

CHAPTER 2

LITERATURE REVIEW

2.1 Importance of Sediment Phosphorus

To control and reverse eutrophication in the Lower Great Lakes, it is necessary to reduce phosphorus loading. However, estimates of the effect of the loads on eutrophication are not well-established, because the fraction of the phosphorus input that will be available for growth of primary producers is not well defined. Since most soluble forms of phosphorus are readily converted to inorganic phosphate which is readily available to algae (Wetzel, 1975), it is the bioavailability of the sediment bound phosphorus that must be defined.

2.2 Forms of Sediment Phosphorus

Sediment phosphorus is found in both organic and inorganic forms with varying degrees of availability. Sediments may bind organic phosphorus compounds directly through interaction with organic portions of the molecules or through the phosphate group (Sommers et al., 1972). The organic phosphorus, which often correlates with organic matter (Williams et al., 1971b), becomes available when the organic matter is decomposed and hydrolyzed (Sommers et al., 1970). This available, inorganic phosphorus can then be utilized for cell production or sorbed by the sediments.

Since a large portion of sediment phosphorus is inorganic, a major emphasis will be placed on inorganic P mobility. Depending on the manner in which P is bound to the sediments, it is described as apatite or non-apatite inorganic P. Apatite P is

bound within the crystal latices of discrete calcium compounds, and is considered generally unavailable. Phosphorus release from the apatite form is predicted by solubility product relationships and is influenced by solution ion concentrations and pH (Stumm and Morgan, 1981). The relatively more available non-apatite P is sorbed on the surfaces or present within the matrices of sediment Fe, Al, Mn, and Ca. However, Williams et al. (1971b) showed iron to be the metal most strongly correlated with phosphorus binding. When non-apatite P is sorbed on the surfaces of P retarding compounds (non-occluded-P), usually iron-rich gel-complexes (Shulka et al., 1971), it is generally more available than the non-apatite P present within the crystalline matrices of iron oxides and hydroxides (occluded P) (Syers et al., 1973).

2.3 Chemical Fractionations to Estimate Availability

In order to determine the specific forms of inorganic phosphorus present in soil samples, Chang and Jackson (1957) introduced a sequential chemical extraction procedure. The extraction sequence consisted of treatment with NH_4F, NaOH, H_2SO_4, citrate-dithionite, and NH_4F again to selectively remove aluminum phosphate, iron phosphate, calcium phosphate, occluded iron phosphate, and occluded aluminum phosphate, respectively.

Williams et al. (1971a) found that the NH_4F extraction was actually not removing just aluminum phosphate, but also phosphorus in association with iron. Also, during the NH_4F extraction of calcarious sediments, CaF_2 formed and bound some of the P released during the extraction. Therefore, it was suggested that the NH_4F

extraction be eliminated, and the NaOH fraction be used to estimate P associated with both aluminum and iron (non-occluded P).

Recent studies (Williams et al., 1980; Heiltjes and Lijklema, 1980) found that calcium bound phosphates (non-apatite) were not completely extracted with sodium hydroxide (NaOH) or citrate-dithionite-bicarbonate (CDB), and a large portion of the hydroxyapatite-P was extracted. This lends some doubt to the effectiveness of the extraction procedure by Chang and Jackson (1957) or any of the modifications (see Logan, 1978) for actual separation of inorganic sediment P into discrete non-occluded, occluded, and apatite forms.

However, the extraction sequence does indicate the degree to which P is bound to the sediments. Since the sequence begins with the most selective extractant and proceeds to the least selective; the least tightly bound, most-available phosphorus will be removed first. Logan (1978) interprets the significance of his fractionations as follows: NaOH, mobile phosphate that can be taken up by algae; CDB, less available P that can be released over long periods of time; and HCl, non-biologically available P.

Although chemical fractionations are quick and reproducible, use of the fractions for estimating sediment phosphorus availability must be qualified (Logan et al., 1979). Factors such as receiving water characteristics and availability of organic P are not addressed by the chemical extractions. Furthermore, these methods do not allow for determination of the rate of release, which is necessary to predict the amount of P that

will be released before the sediments are deposited. In order to overcome these difficulties, bioassay techniques are used to measure the truly available P, and comparisons can then be made between the two methods.

2.4 Bioassays to Measure Availability

Many bioassay studies have been conducted to measure the bioavailability of sediment phosphorus and to determine the chemical fractions that become available. Most studies involve growing algae in a suspension of lake or river sediments with the sediments as the only source of phosphorus and the other nutrients in excess. After the incubation, the available sediment P is determined by measuring algal phosphorus content or algal biomass (employing a P/biomass conversion) (Logan et al., 1979).

However, since algae are capable of taking up phosphorus in excess of their immediate metabolic needs, the use of a P to biomass ratio may be unreliable (Sagher, 1976). Also, it is possible that the algal growth rate and cell P quota will respond differently to the orthophosphate spike used to develop standard curves than to the gradual release of P from sediments (Logan et al., 1979). To overcome these disadvantages, bioassay methods that allow direct measurement of P uptake and periodic harvesting are being used (Verhoff et al., 1978; DePinto, 1982).

To measure the rate and extent of sediment phosphorus release, DePinto (1982) proposed the use of a device called a Dual Culture Diffusion Apparatus (DCDA). The DCDA allows the sediment suspension and P-starved algal cultures to be placed in connecting vessels, separated only by a 0.4 μm polycarbonate

membrane. As the sediment P is solubilized, it diffuses across the membrane and is utilized by the algae. Since the rate of solubilization is the slowest step in the transfer from sediment to biomass, the rate of accumulation of algal P should be the same as the rate of release from the sediments. By periodically removing the algae and analyzing their P uptake, the sediment P release kinetics can be determined.

The rate of release from the bioassay is characterized by fitting a first order saturation function, similar to the BOD equation, to the actual data points for accumulated P release over time (DePinto, 1982). Amer et al. (1955) used the same basic model, but the overall curve was resolved into component curves representing simultaneous reactions with different rates.

The ultimately available phosphorus is also shown on the accumulated P release curve by extrapolating to the horizontal asymptote. For suspended sediments from five tributaries to the Lower Great Lakes, DePinto et al. (1981) found that the average ultimately available P ranged from 6% to 36% of the total sediment P. This is in agreement with the range found during other studies on similar samples (Dorich et al., 1980).

Although much of the phosphorus found to be ultimately bioavailable will be released in the water column (Young et al., 1982), there is still a large amount of potentially available sediment-bound phosphorus being deposited. The availability of this phosphorus obviously is very important in determining the cycling of P in the lakes and the impact of efforts to control eutrophication.

2.5 Mobility of Deposited Sediment Phosphorus

The mobility of sediment phosphorus is generally controlled by two interrelated factors. First, the oxidation reduction potential, which is dependent on oxygen concentration, controls the oxidation state of iron and thereby affects the release of inorganic P. Secondly, rates of diffusion and the extent of mixing control the physical transport of oxygen into the sediments and phosphorus into the overlying water (Lee, 1970).

2.5.1 Effects of Oxygen on Sediment Phosphorus. During periods of thermal stratification, dissolved oxygen is no longer being circulated to the sediments. However, dead particulate matter will continue to settle and be degraded by bacteria requiring oxygen. It has been estimated that 88% of the hypolimnetic oxygen consumption in the central basin of Lake Erie is due to degradation of settling algae (Burns and Ross, 1971). Obviously, the rate of this oxygen depletion will be dependent on the rate of organic loading (Wetzel, 1975).

As the hypolimnetic oxygen concentration is depleted, other compounds will serve as electron acceptors. In natural waters the major electron acceptors, in decreasing ease of reduction, include O_2, NO_3^-, MnO_2, Fe^{+3}, and SO_4^{-2} (Stumm and Morgan, 1981). In deoxygenated lake bottoms Mortimer (1941, 1942) found high levels of Fe^{+2} and dissolved inorganic P, and suggested that the reduction of Fe^{+3} was involved in the release of inorganic phosphorus from sediments. Although not clearly understood, phosphorus retention is attributed to sorption on a gel-complex consisting largely of hydrated iron oxides along with smaller

amounts of organic matter, aluminum, and associated $Si(OH)_4$ and inorganic P (Shulka et al., 1971; Williams et al., 1971b). Under reducing conditions characterized by the absence of oxygen and low redox potentials, ferric oxyhydroxide gains an electron and is solubilized, thereby releasing its bound phosphorus (Patrick and Khalid, 1974).

The degree of reduction will depend on the pH and redox potential of the system. Although pH increases with decreasing redox potentials, the maximum release of iron and phosphorus occurs at low pH values and low redox potentials (Patrick et al., 1973). Since nitrate and manganese oxides will be reduced before iron compounds, their concentration will affect the onset of iron reduction. Working with flooded soils, Patrick (1964) found that the concentrations of soluble Fe^{+2} began to increase linearly when the redox potential was lowered below 200 mV, and that the phosphorus concentration responded in a similar fashion.

2.5.2 Transport of Soluble Phosphorus. Both diffusion and turbulent mixing contribute to exchange between the sediments and the overlying water. Lee (1970) suggests, that for the exchange of inorganic P, mixing may be more significant due to slow rates of phosphorus diffusion. It has been shown that the sediment depth affected may range from a few millimeters to a few centimeters depending on the degree of turbulence and the compaction and density of the sediments (Montimer 1941, 1942; Lee, 1970). When the oxygen concentration in the overlying water is sufficient, it will be transferred into the upper sediment layer. This oxidized layer, therefore, will serve as an

effective trap for the Fe^{+2} and phosphorus that diffuses upward from the lower reduced sediments (Wetzel, 1975).

However, the oxygen in this layer is consumed by microbial respiration and by oxidation of reductants such as Fe^{+2} (Howler and Bouldin, 1971). Therefore, when the oxygen is not replenished in the overlying water, the oxidized layer will disappear and inorganic P and Fe^{+2} will be allowed to diffuse into the overlying water (Montimer 1941, 1942). This release of inorganic P from anaerobic systems was substantiated during investigations using ^{32}P (Li et al., 1972). The extent of exchange in the anaerobic system was greater from noncalcareous than from calcareous sediments, which suggests partial resorbtion by $CaCO_3$ (Williams et al., 1971b). Release was also a function of the total inorganic P content of the sediments (Li et al., 1972), and the concentration of dissolved inorganic P in the interstitial and lake waters (Latterell et al., 1971).

During anaerobic periods characterized by thermal stratification and quiescent conditions, the availability of solubilized inorganic sediment P to algae in the epilimnion is limited. However, during overturn and strong wind events, the solubilized material above the sediments will be circulated. Furthermore, for systems such as the western basin of Lake Erie (typical depth of 10 m), resuspension of sediment particles can be significant (Lam and Jaquet, 1976). Specifically, resuspension will depend on turbulent stress, water content of the sediments, composition of the sediments, activity of benthic organisms and bacteria, and the manner of deposition (Lee et al.,

1981).

When exposed to the aerobic lake waters, some of the solubilized P will precipitate with or adsorb to ferric oxyhydroxides as Fe^{+2} is oxidized to Fe^{+3} (Langmuir and Whittmore, 1971). Also, the resuspended bottom sediments will provide further adsorption or nucleation sites to bind the phosphorus when they are oxidized. However, this resorbed phosphorus should be relatively loosely bound and may have a relatively higher biological availability than the sediment bound P before deposition and anaerobic conditions. The availability of the phosphorus from these suspended sediments and the associated interstitial water must be known in order to determine their true impact on eutrophication in the Great Lakes.

CHAPTER 3

METHODS AND MATERIALS

3.1 General

In order to determine the effect of anoxic conditions on the bioavailable phosphorus from suspended sediments in Lake Erie tributaries, samples were deprived of atmospheric oxygen for a period of incubation and reaerated. This was to simulate the natural processes occurring due to sedimentation and resuspension. A bioassay procedure was used to measure the cumulative uptake of phosphorus by cultures of Selenastrum capricornutum according to the methods described by DePinto (1982). This release was then compared to the release from the same sediments that had not been exposed to anoxic conditions. The chemical forms of phosphorus associated with the sediments were evaluated by using a series of sequential chemical fractionations which have been employed for evaluation of particulate phosphorus availability. The chemical fractions were measured before any treatment, after the control bioassays, after the anoxic incubation, and after the post-anoxic bioassays.

3.2 Field Sampling

Grab samples were collected from mid-depth of the station near the mouths of the Cayahoga, Maumee, and Sandusky Rivers, and Honey Creek (a tributary of the Sandusky River) as shown in Figure 3.1. The samples were taken during April, May, and June of 1981 near high-flow runoff periods. This is when sediment-

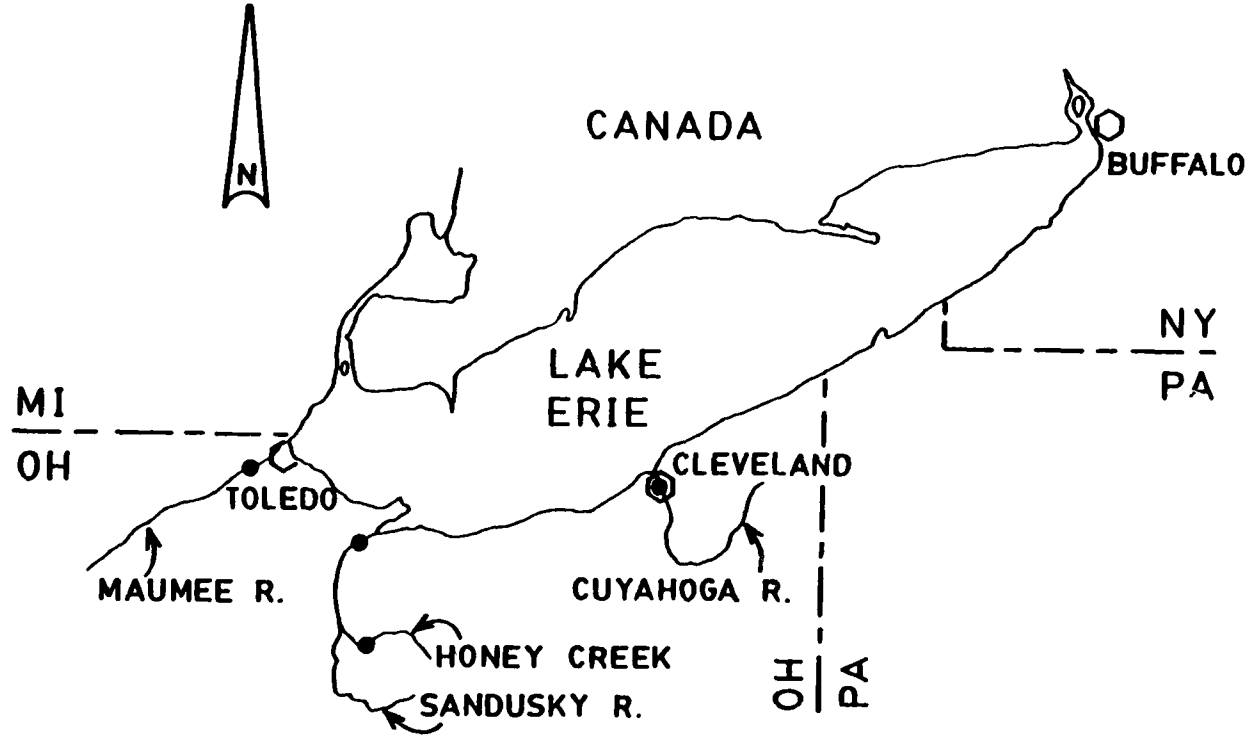


Figure 3.1 Locations of the four tributaries and sampling stations used for this study.

bound phosphorus concentrations should be the highest (Yaksich and Rumer, 1980).

After transfer into polyethylene cubitainers, the samples were cooled to 4°C and shipped to Clarkson College in insulated transportation coolers. The collection dates, flows at the time of sampling, and the suspended solids are shown in Table 3.1 for each sample used in this report.

3.3 Preparation for Anaerobic Incubations

Upon arrival at Clarkson, a portion of the sample was filtered through a 0.45 μm pore diameter membrane, and the collected solids were resuspended in a synthetic phosphorus-free medium containing $CaCl_2$, $MgSO_4$, and $NaHCO_3$ as specified in Table 3.2. This concentrate, stored at 4°C, was then used for an initial sequential fractionation and for the initial, or control, bioassays referred to in Procedures, I, II and III (Sections 3.3.1-3.3.3). The remainder of the samples were stored at 4°C as received to be used as described in Procedure III.

3.3.1 Procedure I: Anaerobic Incubation with Dextrose. For each sample, three bioassays were run for 28 days as part of a related research project, and the quantity and rate of phosphorus release from the sediments were measured. Upon termination of these three bioassays, the remaining sediment material was concentrated by centrifugation at 11,300 g for 30 minutes. The sediment material was then resuspended in the synthetic P-free medium, and the three replicates were composited to form a suspension of 3 to 4 mg of sediment·ml^{-1}.

Table 3.1 Samples Employed for Anaerobic Incubation Study

Sample	Date	Tributary	Flow ($\frac{m^3}{s}$)	SS ($\frac{mg}{L}$)
26	4/14/81	Sandusky River	237	520
28	4/15/81	Sandusky River	160	247
29	4/15/81	Cuyahoga River	-	206
32	4/14/81	Honey Creek	24	404
33	4/30/81	Honey Creek	14	220
41,42	5/5-11/81	Maumee River	~300	148
43	6/10/81	Honey Creek	53	815
45	6/10/81	Sandusky River	379	1,432
48	6/14/81	Honey Creek	111	2,130
49	6/14/81	Sandusky River	623	3,120
50	6/16/81	Maumee River	1857	918
51	6/15/81	Sandusky River	570	1,002
52	6/16/81	Sandusky River	516	838

Table 3.2 Composition and concentrations of nutrient media solutions

Stock Solutions	Media Concentrations ($mg \cdot L^{-1}$)	Synthetic P-free Medium	Algal Growth Medium	Sediment Dilution Medium*
1. $CaCl_2 \cdot 2H_2O$	36.755	x	x	
2. $MgSO_4 \cdot 7H_2O$	36.97	x	x	
3. $NaHCO_3$	12.60	x	x	
4. Na_2 EDTA	4.36		x	x
5. Trace Metals			x	x
$CuSO_4$	0.0064			
$ZnSO_4 \cdot 7H_2O$	0.023			
$CoCl_2 \cdot 6H_2O$	0.0119			
$Na_2MoO_4 \cdot 2H_2O$	0.0066			
$MnSO_4 \cdot H_2O$	0.152			
6. H_3BO_4	1.0		x	x
7. KNO_3	26.288		x	x
8. $Na_2PO_4 \cdot 12H_2O$	0.1875		x	
9. Iron Solution				
$FeCl_3 \cdot 6H_2O$	3.16			
Na_2EDTA	4.63			
10. Tri-vitamin Solution			x	
Biotin	0.05			
B_{12}	0.05			
Thiamine	0.10			

* Used in Procedure I and II to dilute concentrate before anoxic incubation, and also to dilute the sediments added to the DCDA regeneration vessels.

As outlined in Figure 3.2, after removal of sufficient sediment material for suspended solids, total phosphorus, and chemical fractionation measurements; equal amounts of concentrate, 45 to 60 mg of sediment, were allotted to each of three 250 ml Erlenmeyer flasks. The sediments were suspended in 150 ml of Lake Erie water that had been passed through a 0.2 μm pore diameter filter and spiked with 50 mg of dextrose$\cdot L^{-1}$, 3.64 mg NO_3-N$\cdot L^{-1}$, and trace elements as shown in Table 3.2 to ensure biological growth. The samples were purged with N_2 for an hour and immediately sealed securely with rubber stoppers having a light grease coating.

The incubation period consisted of 28 days in the dark at a constant 20°C, during which the samples were inspected and mixed daily. At termination, the rubber stoppers were removed, and pH and oxidation-reduction potential (ORP) measurements were taken. The samples were then aerated for two hours, and soluble reactive phosphorus, pH, and ORP measurements were made.

One of the three replicates was reserved for the post-incubation fractionation, and the other two were bioassayed a second time. The second bioassay was to determine the effects of the anaerobic incubation on algal available phosphorus in the sediments.

3.3.2 Procedure II: Anaerobic Incubation Without Dextrose. Procedure II follows the same steps as Procedure I for the preparation of the sediments and the anaerobic incubation (see Figure 3.2). However, no dextrose spike was added to the 150 ml of nutrient-spiked Lake Erie water in which the sediments were

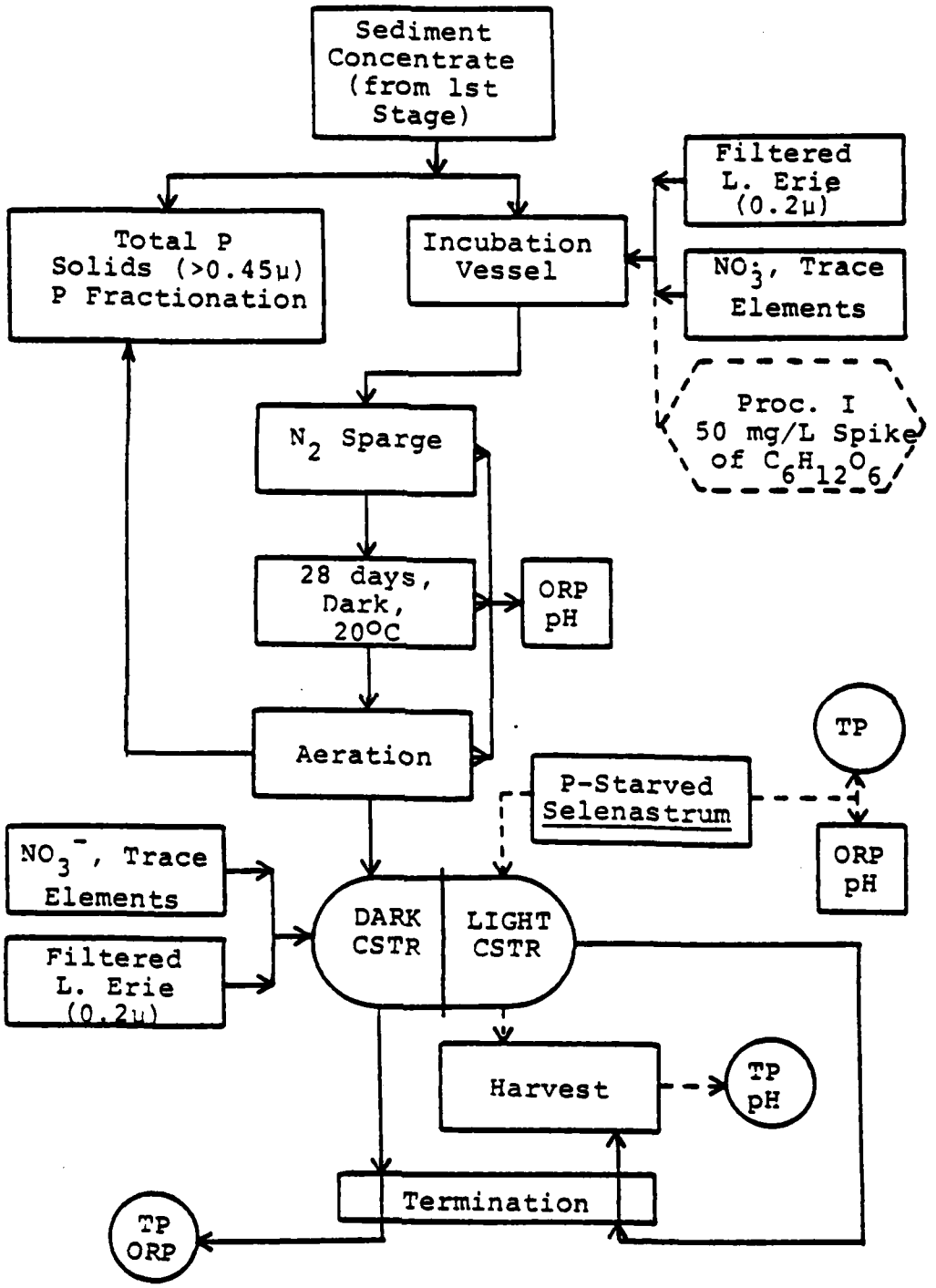


Figure 3.2 Analytical flowchart for Procedure I (glucose) and Procedure II (unspiked) for determination of available phosphorus release during second-stage bioassays

incubated. Also, the incubation period was extended to 31 days.

3.3.3 Procedure III: Anaerobic Incubation of Concentrated Sediments. Procedure III utilized the initial tributary samples directly, not the sediments from the initial bioassays. As shown in Figure 3.3, this procedure involved centrifugation of the initial tributary samples at 11,300 g for 30 minutes, and then resuspension in synthetic P-free medium to form a slurry of six to eleven percent solids. The slurry was added directly to 50 ml, screw top, culture tubes to a depth of about 50 mm. After the pH and ORP measurements were made, the sediment slurry was purged with N_2, and immediately the teflon-lined screw caps were fastened securely.

The slurry samples were incubated, undistrubed in the dark for 49 days at 20°C. Upon termination of the incubation, 10 ml of the supernate was removed to measure both total soluble and reactive soluble phosphorus. After ORP and pH measurements were taken on the slurry, it was diluted to 200 ml with synthetic P-free media and aerated for two hours. Suspended solids, ORP, pH, and total and reactive soluble phosphorus measurements were all made on the diluted slurry. To prepare the post-anoxic bioassay, the volume of diluted slurry required for 125 mg of sediment was pipetted into the regeneration vessel of the bioassay apparatus, and the remainder saved for the phosphorus fractionation scheme.

3.4 Bioassay Procedure

In order to measure the quantity of phosphorus that was bioavailable from the anaerobically incubated sediments, and its rate of release, the bioassay procedure given by DePinto (1982)

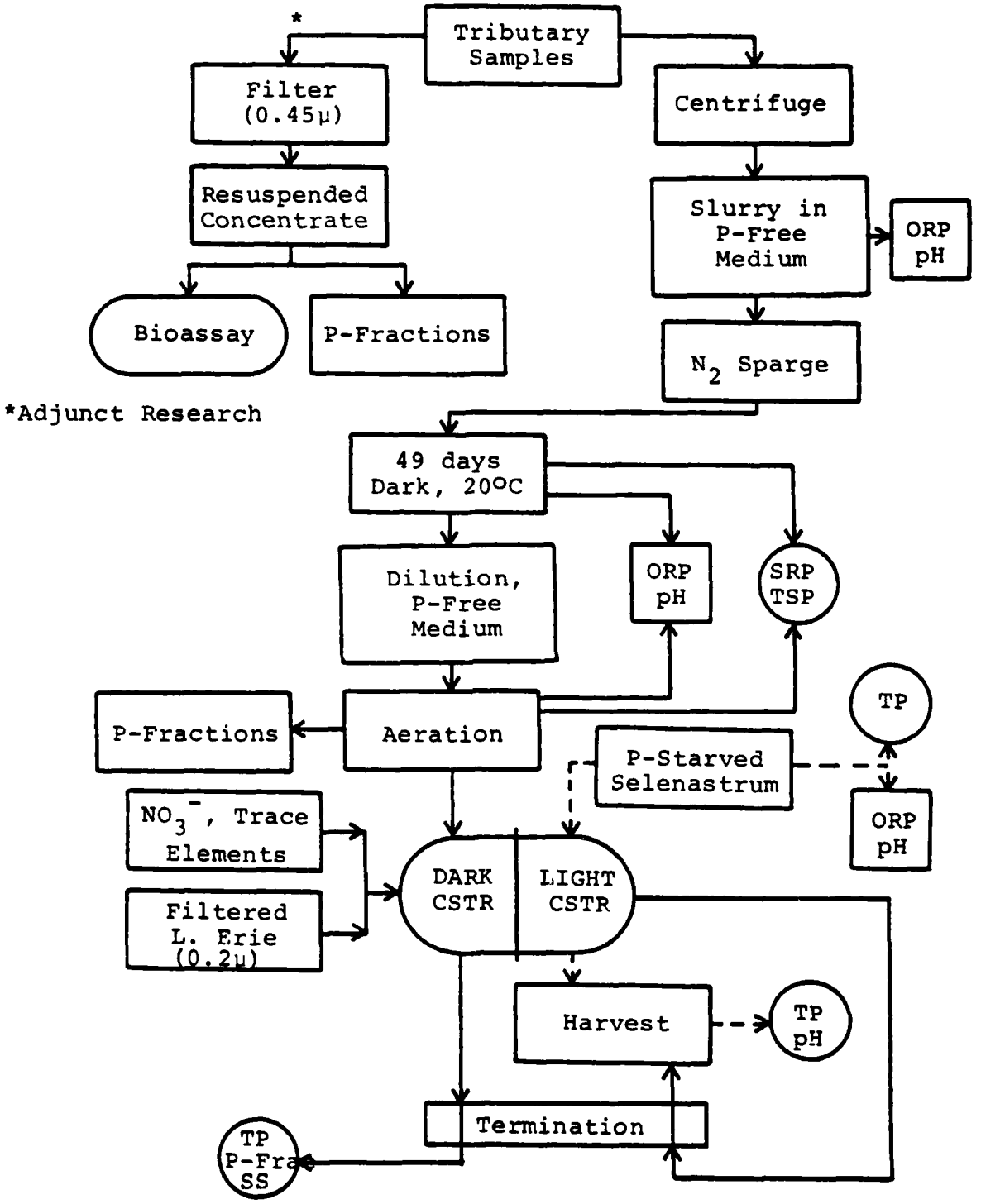


Figure 3.3 Analytical flowchart for Procedure III (thick slurry incubation) for determination of available phosphorus release on anaerobically incubated sediments by single-stage bioassay.

was used. Using the Dual Culture Diffusion Apparatus (DCDA) shown in Figure 3.4, the sediment samples were placed in the darkened, regeneration vessel while the algal culture was incubated in a separate, clear, assay vessel. The two vessels, approximately 400 ml each, were clamped together so that the algae and the sediments were separated only by a 0.4 μm pore diameter polycarbonate membrane. This membrane allows diffusion of soluble substances, such as phosphorus, from one vessel to the other, but it keeps the algae and sediments in their respective vessels. The rate of diffusion across the membrane was not a rate-limiting process, since it has been found to be large relative to typical phosphorus release rates (DePinto, 1982).

The algae placed in the 400 ml assay vessels were seven day old, phosphorus-starved, cultures of Selenastrum capricornutum. The cultures were incubated under flourescent lighting at 20°C in filtered Lake Erie water that was spiked with the essential nutrients listed in Table 3.2. So that the biological growth can be controlled, the Lake Erie water used here and throughout this investigation was pressure filtered through a 0.2 μm pore diameter membrane and stored at 4°C.

The sediments from Procedure I, II, and III were added to the regeneration vessel as previously indicated, and brought up to a total volume of 400 ml with nutrient spiked, filtered Lake Erie water (see Table 3.2). Both vessels were magnetically stirred to keep the contents uniform, and inverted periodically so that the stirbars would dislodge any solids accumulating at

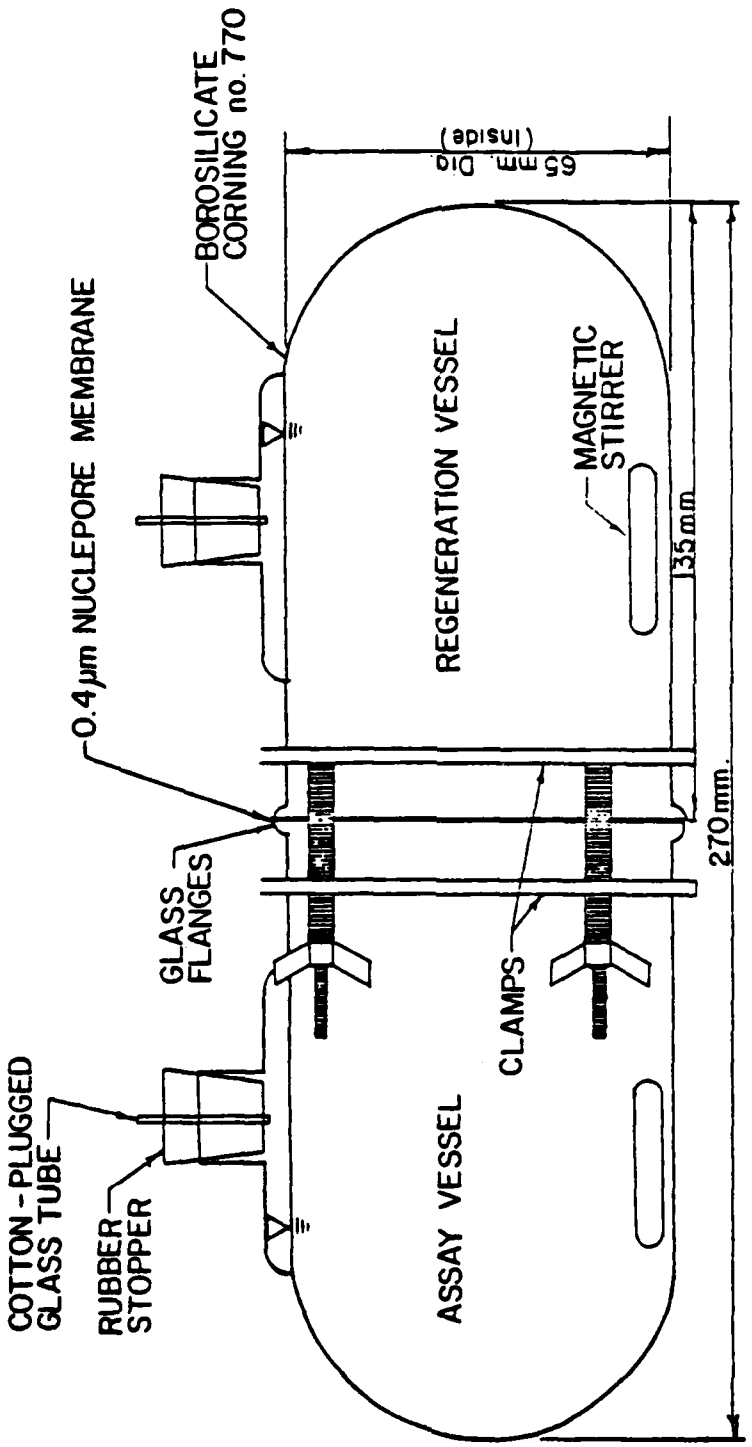


Figure 3.4 Dual culture diffusion apparatus for particulate phosphorus bioassay tests (DePinto, 1982).

the ends or sticking to the vessel walls. Finally, to keep the environmental conditions constant, the bioassays were continually exposed to flourescent light and kept in a temperature controlled room.

After the incubation period of three to ten days, the contents of the assay vessel were harvested and immediately replaced with another seven day old, phosphorus-starved, algal culture. Since the total phosphorus in the initial stock culture, typically around 30 μg $P \cdot L^{-1}$, was measured, the phosphorus added to the system was known. The uptake by the algae during a certain sampling period, therefore, was the difference between the total phosphorus of the harvested culture and the total phosphorus measurement of that culture initially. By keeping the mass-balance on the system over four or five sampling periods both the rate and extent of uptake can be calculated.

3.5 Chemical Fractionations

The chemical fractionation procedure used to characterize the particulate phosphorus followed that given by DePinto *et al.* (1981) as modified from Logan (1978). A flow chart is shown in Figure 3.5, and the procedure is described below.

An adequate volume of sediment concentrate was pipetted into a 40 ml polypropylene centrifuge tube, and centrifuged at 15,000 rpm's for 30 minutes. The supernatant was discarded and the pellet was resuspended in 37 ml of 0.1 N sodium hydroxide. After this suspension was mixed on a rotary shaker table at room temperature for 17 hours, it was centrifuged at 31,000 g for

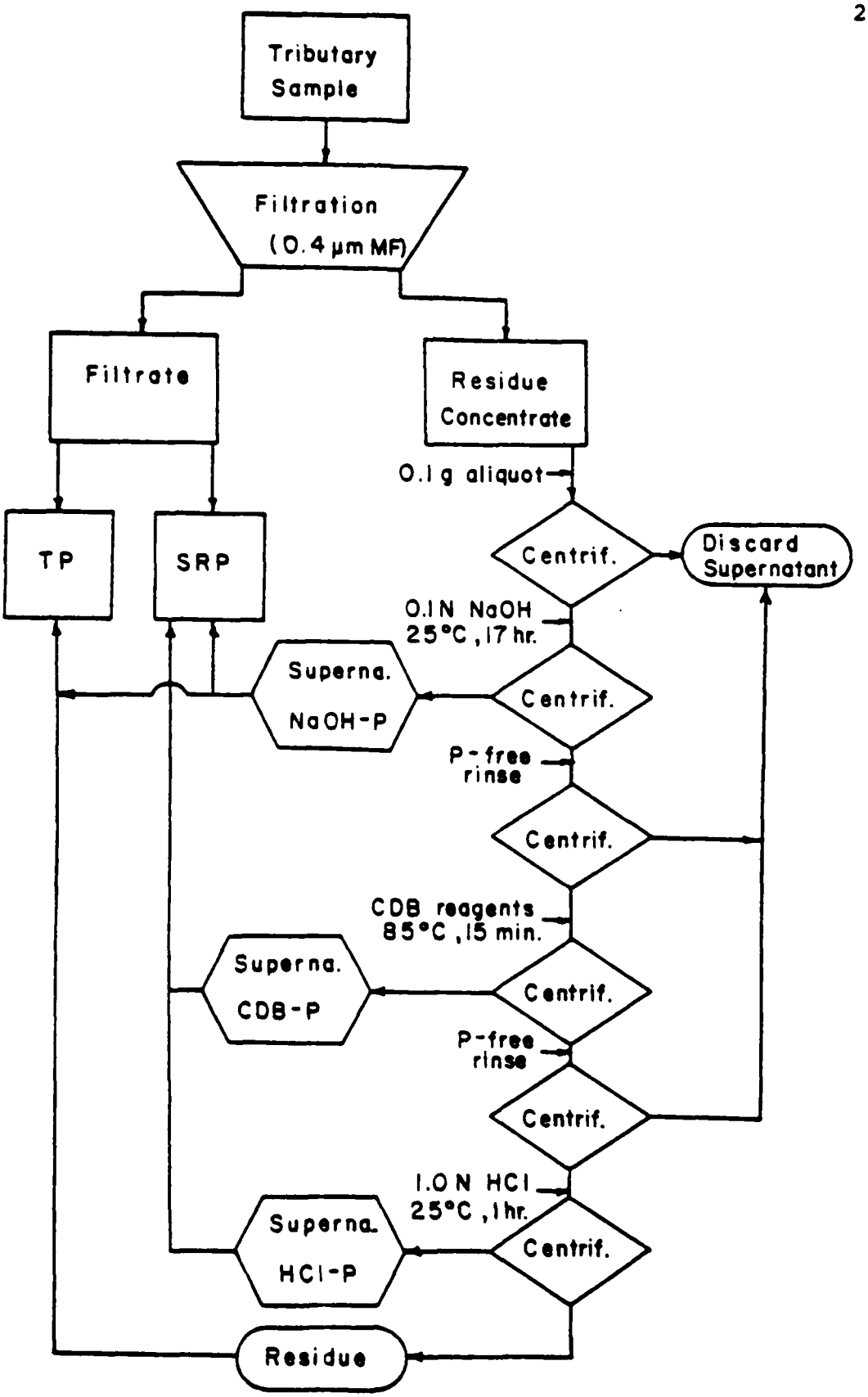


Figure 3.5 Flowchart of the sequential chemical fractionation (TP = Total P analysis, SRP = soluble reactive P analysis, CDB = Citrate-Dithionite-Bicarbonate, MF = membrane filter).

30 minutes. This sodium hydroxide extraction supernatant was decanted and saved for later reactive and total phosphorus analysis.

The sediments were again resuspended in synthetic P-free medium and centrifuged as described above. After the centrate was discarded, the pellet, still in the centrifuge tube, was resuspended with 32 ml of 0.25 M sodium citrate, 1.0 g of sodium dithionite, and 5 ml of 1.1 M sodium bicarbonate. The tubes were then placed in an 85°C water bath for 15 minutes with periodic mixing. This mixture was centrifuged after cooling and the CDB extraction supernatant was decanted. The decanted supernate was aerated for at least six hours to oxidize the remaining dithionite. Soluble reactive phosphorus was measured after excess ammonium molybdate was added to correct for citrate interference as directed by Weaver (1974).

For the HCl extraction, the sediments were again mixed with synthetic P-free medium, centrifuged, and the supernatant discarded. The residue was then resuspended with 1.0 N hydrochloric acid and placed on a shaker table for one hour. The suspension was centrifuged and the supernatant was stored until it was prepared by neutralization for soluble reactive phosphorus measurement.

The residue was resuspended with synthetic P-free medium, centrifuged, and the centrate discarded. The remaining material was resuspended in deionized water and analyzed for total residual phosphorus. Although the non-reactive phosphorus in the CDB and HCl extracts was not measured, the residual plus the sum

of the fractions can be compared against the initial total particulate phosphorus as an indication of the completeness of the procedure.

3.6 Analytical Measurements

Oxidation reduction potentials were measured electrometrically using a Pt-calomel combination electrode. The accuracy of the measurements were checked using Zobell's solution (Langmuir, 1971). A glass-calomel electrode, which was calibrated using standard buffers, was used for pH measurements.

Suspended solids samples were collected on pre-washed, tared, 0.4 μm membrane filters. Gravimetrical measurements were made on the non-filterable residue after drying for at least one hour at 104°C (Am Publ. Health Assn., 1980).

Phosphorus was measured colorimetrically (880 nm) using the ascorbic acid reduction method (Am. Publ. Health Assn., 1980). Reactive phosphorus was measured directly after dilution with deionized water and treatment for color development. However, total phosphorus measurements required acid-persulfate digestion to convert all of the phosphorus to orthophosphate form prior to neutralization and color development.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effects of Anoxia on Soluble Phosphorus

The effect of anoxic incubation and aeration on the oxidation reduction potential (ORP), pH, and soluble phosphorus concentrations of each sample is shown in Table 4.1. From the ORP values it is apparent that Procedure III developed more extensive reducing conditions than Procedures I or II.

4.1.1 Procedure III. The low oxidation reduction potentials developed by Procedure III were due to an approximately 250-fold higher sediment incubation concentration and a 60% longer incubation period. These values are at a level consistent with the reduction of Fe^{+3} to Fe^{+2} (ORP $\leq$ -200 to +200 mV calomel reference; Patrick, 1964). The reducing conditions should have allowed phosphorus that was bound in iron complexes to be released when the iron was solubilized as Fe^{+2}.

As expected, the data shown in Table 4.1 for Procedure III shows substantial increases during the incubation of both soluble reactive phosphorus (SRP) and total soluble phosphorus (TSP) in the undisturbed water overlying the sediments. For comparison, the pre-incubation SRP readings were less than 4 $\mu gP \cdot L^{-1}$ and the pre-incubation TSP measured less than 5 $\mu gP \cdot L^{-1}$.

When the sediments were diluted and thoroughly aerated, any phosphorus concentration gradient that developed through the sediments and overlying water column during incubation was equalized. Assuming any such gradient for SRP to be proportional

Table 4.1 Effect of anaerobic incubation and aeration on oxidation reduction potentials, pH, and soluble phosphorus concentrations

Tributary	Sample	Procedure	Initial		Post-Incubation				Post-Aeration			
			ORP* (mV)	pH	ORP* (mV)	pH	SRP (µgP/L)	TSP (µgP/L)	ORP* (mV)	pH	SRP (µgP/L)	TSP (µgP/L)
Sandusky River	26	I	-	-	123	6.7	-	-	168	8.0	3.8	7.4
Sandusky River	28	I	-	-	72	6.7	-	-	172	8.0	2.5	3.4
Cuyahoga River	29	I	-	-	145	6.7	-	-	174	8.2	2.8	4.3
Honey Creek	32	II	167	7.4	207	6.9	-	-	199	7.8	8.3	8.0
Honey Creek	33	II	183	7.5	198	7.2	-	-	176	7.9	10.1	19.2
Maumee River	41,42	II	205	7.5	191	7.5	-	-	144	7.8	6.9	11.7
Sandusky River	45	III	261	7.6	-130	7.1	135.6	351.4	214	7.5	50.3	284.1
Honey Creek	48	III	247	7.1	- 63	7.0	217.6	250.4	224	7.2	41.3	225.3
Sandusky River	49	III	271	7.4	- 85	7.1	127.6	256.8	225	7.3	36.8	236.4
Sandusky River	51	III	287	7.5	-115	7.1	241.7	417.1	218	7.4	36.5	265.0
Sandusky River	52	III	277	7.6	-110	7.2	217.6	460.4	216	7.5	38.4	325.5
Honey Creek	43	III	206	7.1	-116	7.1	240.3	324.1	223	7.3	24.6	231.6
Maumee River	50	III	255	7.7	-130	7.2	135.6	385.1	214	7.5	67.6	314.4

* E_H = ORP + 244 mV

to that of TSP, the ratio of SRP:TSP from any depth should be valid throughout the incubation tube. This assumption was used to compare the effect of aeration on the samples incubated by Procedure III.

The ratio of SRP:TSP decreased from an average value of 0.56 at the end of the anoxic incubation to 0.16 after dilution and aeration. The proportionate decrease in SRP with respect to TSP suggests a substantial uptake of SRP by the sediments when they were oxidized during aeration.

4.1.2 Procedure II. A small increase in SRP and TSP was measured in the water overlying the sediments incubated according to Procedure II. There are two probable causes for the soluble phosphorus concentrations measured after the Procedure II incubation being much lower than those measured after Procedure III. First, Procedure II used a significantly lower sediment incubation concentration, approximately 0.04% solids as compared with 10% solids used in Procedure III. Secondly, the oxidation reduction potentials, which were near 200 mV, may not have been sufficiently low to cause iron reduction and the corresponding phosphorus release.

4.1.3 Procedure I. Procedure I, which was identical to Procedure II except for a 50 $mg \cdot L^{-1}$ dextrose spike, did not result in a SRP or TSP increase. Although the solids concentration was again approximately 0.04%, the ORP was lower than Procedure II. Even with the lower ORP, the soluble phosphorus concentrations were lower after Procedure I than after Procedure II. This may be due to the phosphorus being assimilated by

microbial growth that was stimulated by the dextrose spike.

4.2 Effects of Anoxia on Chemical Fractionations

To understand the effects of anoxic conditions on particulate phosphorus, chemical extractions were run on the samples initially, before anaerobic incubation, and after the incubation and aeration. The initial fractionation results are presented in Table 4.2.

4.2.1 Fractionation before Anaerobic Incubation. For Procedures I and II the initial samples were bioassayed for available phosphorus prior to the anaerobic incubation (see Section 3.3.1). The fractionations after these bioassays, immediately prior to the incubation, are presented in Table 4.3.

By comparing the data from Tables 4.2 and 4.3, for the samples taken through Procedures I and II, a definite change in the fractions can be observed during these pre-incubation bioassays. The decreases in the non-apatite inorganic fractions (reactive NaOH-P and CDB-P) were a result of available phosphorus release, and can be correlated with the uptake by assay algae (DePinto et al., 1981). Although not experimentally substantiated, it is likely that the observed increase in residual phosphorus was due to bacterial uptake and incorporation as detrital organic phosphorus.

For Procedure III the original sediments were used for the anaerobic incubation, so the initial fractionations in Table 4.2 are the same as the pre-incubation fractionations in Table 4.3.

4.2.2 Fractionation after Incubation and Aeration. The fractionation data gathered after the samples were exposed to

Table 4.2 Initial fractionation of sediment phosphorus (µg P/g)

Tributary	Sample	TP	R-NaOH	NR-NaOH	CDB	HCl	Residual-P
Cuyahoga River	29	1426	568	109	230	180	102
Honey Creek	32	1346	426	162	201	76	307
	33	1367	423	162	262	85	305
	43	1054	322	127	152	37	263
	48	988	254	144	198	27	184
Maumee River	41,42	1231	313	119	208	159	276
	50	1149	289	117	252	87	240
Sandusky River	26	1299	379	100	262	138	297
	28	1366	389	128	270	118	312
	45	1018	277	116	180	57	295
	49	974	229	121	217	44	196
	51	1078	278	129	232	48	194
	52	1100	256	138	235	46	202

Table 4.3 Fractionation of sediment phosphorus before anaerobic incubation (µg P/g)

Tributary	Sample	Procedure	TP	R-NaOH	NR-NaOH	CDB	HCl	Residual-P
Sandusky River	26	I	1069	128	121	192	120	406
Sandusky River	28	I	1123	116	125	223	108	446
Cuyahoga River	29	I	1007	113	109	231	153	228
Honey Creek	32	II	901	118	135	127	68	288
Honey Creek	33	II	997	122	140	131	74	302
Maumee River	41,42	II	925	102	114	131	131	278
Sandusky River	45	III	1018	277	116	180	57	295
Sandusky River	49	III	974	229	121	217	44	196
Sandusky River	51	III	1078	278	129	232	48	194
Sandusky River	52	III	1100	256	138	235	46	202
Honey Creek	43	III	1054	322	127	152	37	263
Honey Creek	48	III	988	254	144	198	27	184
Maumee River	50	III	1149	289	117	252	87	240

anaerobic conditions and reaerated is given in Table 4.4. The changes in the fractionation values from before the incubation to after aeration are listed in Table 4.5, and averaged for each procedure in Table 4.6.

The data in Table 4.6 suggest that much of the change in the fractions during the incubation periods can be attributed to heterotrophic microbial activity. In Procedure I, as in each of the three procedures, the substantial loss from the residual fraction probably represents microbial mineralization of detrital organic phosphorus. Procedure I also exhibits a large increase in the NR-NaOH-P fraction which is probably due to the extraction by NaOH of phosphorylated organic molecules or polyphosphate from the bacteria that thrived due to the glucose spike.

Procedure II incubation and aeration resulted in a decrease in the NR-NaOH and residual phosphorus fractions along with an increase in the CDB fraction. Again the mineralization of organic detrital phosphorus by heterotrophic activity is suspected for causing the decreases. However, in this case endogenous decay of microbial cells probably followed due to an insufficient organic carbon supply. The thereby-liberated phosphorus would precipitate with iron after the cells underwent lysis or during the post-incubation aeration and be accounted for in the CDB fraction. Since conditions were not strongly reducing, the CDB extractable fraction probably accumulated before aeration due to precipitation as $FePO_4$ or as phosphorus occluded in hydrous oxides of iron. The later is more likely in natural waters, especially under neutral or alkaline conditions (Towe and

Table 4.4 Fractionation of sediment phosphorus after anaerobic incubation and aeration (μgP/g)

Tributary	Sample	Procedure	TP	R-NaOH	NR-NaOH	CDB	HCl	Residual-P
Sandusky River	26	I	1069	140	268	195	125	240
Sandusky River	28	I	1123	133	280	223	113	278
Cuyahoga River	29	I	1007	98	210	169	195	161
Honey Creek	32	II	901	118	111	228	62	218
Honey Creek	33	II	997	131	90	257	70	221
Maumee River	41,42	II	925	106	46	226	138	241
Sandusky River	45	III	969	274	114	211	49	151
Sandusky River	49	III	973	249	124	223	45	183
Sandusky River	51	III	1079	293	127	253	49	187
Sandusky River	52	III	1089	269	144	255	49	202
Honey Creek	43	III	1105	358	136	241	35	154
Honey Creek	48	III	905	223	112	196	28	179
Maumee River	50	III	1095	308	120	253	95	199

Table 4.5 Change in phosphorus fractionation due to anaerobic incubation and aeration (μgP/g)*

Tributary	Sample	Procedure	ΔR-NaOH	ΔNR-NaOH	ΔCDB	ΔHCl	ΔResidual-P
Sandusky River	26	I	12	147	3	5	-166
Sandusky River	28	I	17	145	0	5	-168
Cuyahoga River	29	I	-15	101	-62	42	-67
Honey Creek	32	II	0	-24	101	-6	-72
Honey Creek	33	II	9	-50	126	-4	-81
Maumee River	41,42	II	4	-68	95	7	-37
Sandusky River	45	III	11	4	42	-6	-136
Sandusky River	49	III	20	3	6	1	-13
Sandusky River	51	III	15	-2	21	1	-7
Sandusky River	52	III	15	7	23	4	2
Honey Creek	43	III	19	3	78	-4	-116
Honey Creek	48	III	-11	-22	16	4	11
Maumee River	50	III	34	9	13	13	-31

* Corrected to ΔTP = 0 to compensate for losses incurred during sample transfer and other analytical procedures. Range of recoveries: 91.6 to 104.8 percent, mean: 98.0 percent for TP in post-aeration analyses, Procedure III.

Table 4.6 Average change and percent change in sediment phosphorus fractionation due to anaerobic incubation and aeration (μgP/g)

Procedure	ΔR-NaOH	ΔNR-NaOH	ΔCDB	ΔHCl	ΔResidual
I	+5 (+2.0%)	+131 (+107.4%)	-20 (-9.3%)	+17 (+13.4%)	-134 (-37.2%)
II	+4 (+3.5%)	-47 (-36.2%)	+107 (+82.3%)	-1 (-1.1%)	-63 (-21.8%)
III	+15 (+5.5%)	0	+28 (+13.4%)	+2 (+4.1%)	-41 (-18.2%)

$$\% \text{ change} = \frac{\text{final} - \text{initial}}{\text{initial}} \times 100$$

Bradley, 1967; Syers et al., 1973).

Although conditions were significantly more reducing during Procedure III, there was less change in the fractions. The stability of the NR-NaOH fraction suggests that there was comparatively less microbial activity during Procedure III. The low rates of microbial activity could have been caused by an accumulation of inhibitory metabolic waste products, since the sediments were not mixed during incubation. Even so, restricted microbial activity is probably responsible for the loss from the residual fraction. When the incubation was terminated by aeration, most of the phosphorus released by the anoxic period appears to have precipitated as occluded (CDB-extractable) or surface adsorbed (R-NaOH-extractable) forms.

4.2.3 Fractionation Changes to Predict Availability. From the fractionation data, it is apparent that the anoxic incubations do affect the distribution of the sediment phosphorus fractions. Procedure I enhanced the NR-NaOH fraction which consists largely of particulate organic phosphorus (DePinto et al., 1981). However, the availability of this fraction is uncertain, and likely depends on endogenous metabolism and lysis of microbial heterotrophs before it will become soluble. Procedure II largely enhanced the CDB-extractable fraction, which may contribute to phosphorus availability, but only at a slow rate (Logan et al., 1979). Finally, Procedure III seems most likely to increase the sediment phosphorus availability by enhancing the available R-NaOH fraction and the potentially available CDB fraction (DePinto et al., 1981), and by releasing

inorganic soluble phosphorus during the incubation. In order to verify these predictions and better determine if anoxic conditions enhance particulate phosphorus availability, each sediment sample was bioassayed.

4.3 Effects of Anoxia on Particulate Phosphorus Bioavailability

The results of the bioassays performed on the sediments taken through the three procedures are shown in Table 4.7 and presented graphically in Figures 4.1 to 4.9. The results are mean values taken from duplicate bioassays for each sample, except Honey Creek (#32) where only one bioassay was used.

4.3.1 Procedure I. Figure 4.1 shows the release of available phosphorus through the two 28 day bioassay periods with the intermediate anoxic period established using Procedure I. When glucose was added during the incubation to stimulate heterotrophic activity, no net release of available phosphorus occurred during the second stage bioassay. In fact, a net loss of phosphorus from the Selenastrum cultures to the sediments occurred. This loss is most likely due to the sediment microbiota cultivated during the incubation period having a greater assimilative capacity than the phosphorus-starved algal culture (Wetzel, 1975).

The release seen during the final sampling period may be attributed to the endogenous decay of heterotrophic organisms and an accompanying release of cellular phosphorus. This upset could have been sparked by the unusually low phosphorus concentration in that set of algal cultures.

Table 4.7 Cumulative sediment release of available phosphorus over time after the anaerobic incubation, (µg P/g)*.

			Time of Sampling (d)				
Tributary	Sample	Procedure	3	7	14	21	28
Sandusky River	26	I	-20.6	-42.8	-68.4	-88.2	-80.8
Sandusky River	28	I	-19.6	-16.3	-33.6	-48.6	-2.3
Cuyahoga River	29	I	-20.3	-16.6	-38.3	-53.5	19.9
			3	10	20	30	
Honey Creek	32	II	63.8	110.9	122.4	129.5	
Honey Creek	33	II	12.0	12.8	11.5	19.3	
Maumee River	41,42	II	10.4	20.8	48.0	21.1	
			3	7	14	21	28
Sandusky River	45	III	86.8	132.8	151.1	160.9	173.8
Honey Creek	48	III	54.5	93.5	107.8	117.7	129.7
Sandusky River	49	III	68.0	84.8	87.8	91.6	108.1
Sandusky River	51	III	93.4	119.8	137.6	144.9	163.6
Sandusky River	52	III	91.9	110.4	136.5	145.0	156.1
Honey Creek	43	III	105.1	166.1	195.6	206.6	224.1
Maumee River	50	III	110.6	120.7	135.7	144.5	155.7

* All values are averages of two replicate bioassays, except Honey Creek (#32)

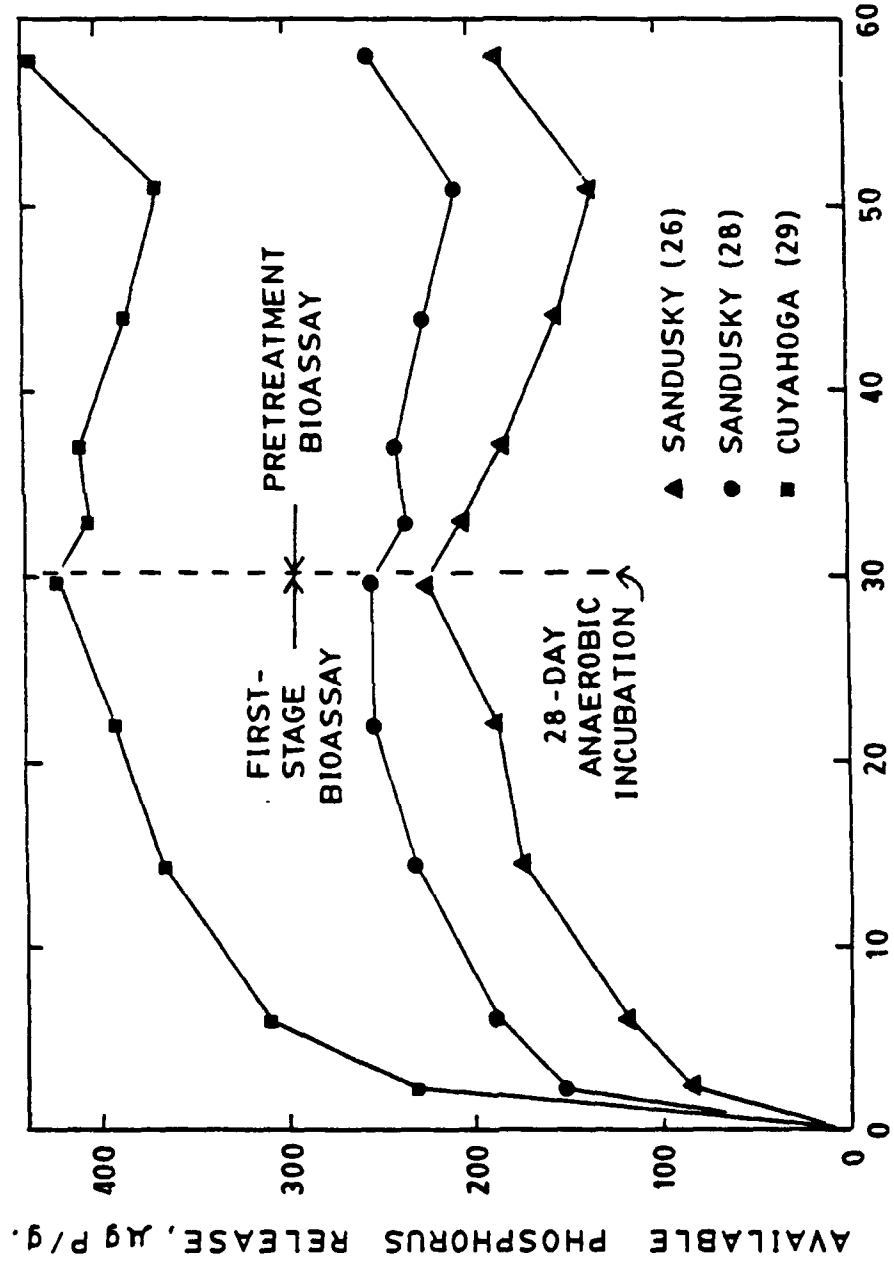


Figure 4.1 Release of available phosphorus from stream sediments before and after anaerobic incubation, Procedure I (50 mg/L spike of $C_6H_{12}O_6$).

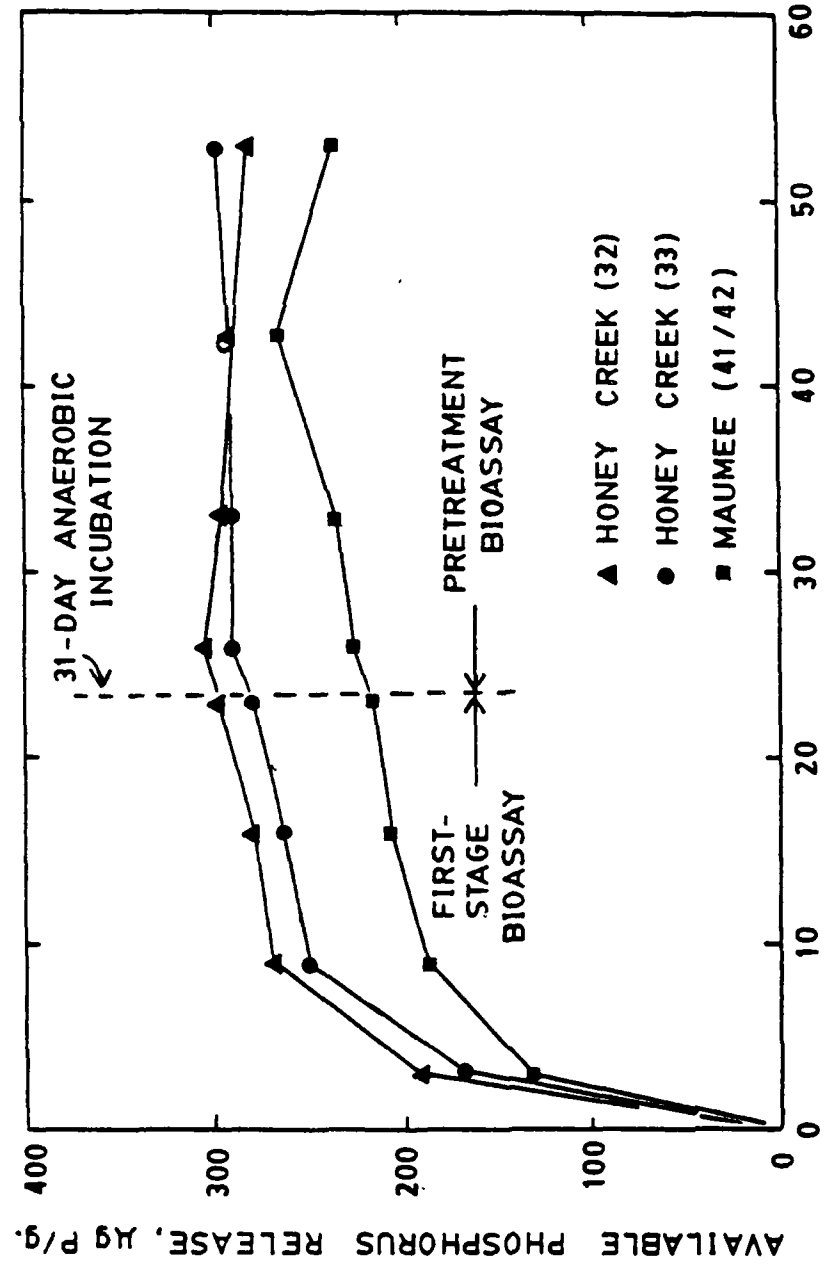


Figure 4.2 Release of available phosphorus from stream sediments before and after anaerobic incubation, Procedure II (no $C_6H_{12}O_6$ spike).

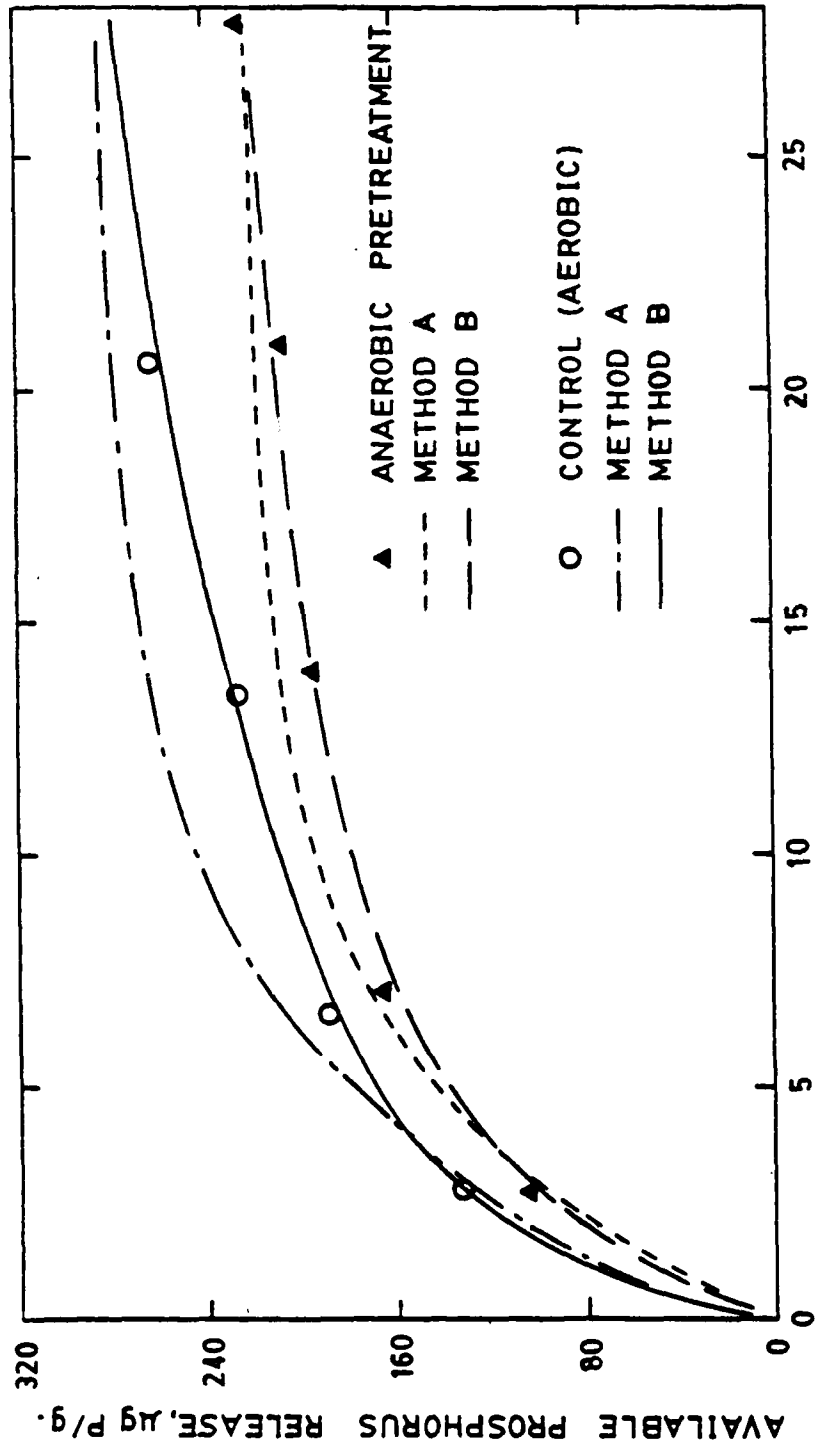


Figure 4.3 Honey Creek #43:Comparison of available phosphorus release from suspended sediments for control and anaerobically pretreated (Procedure III) bioassays.

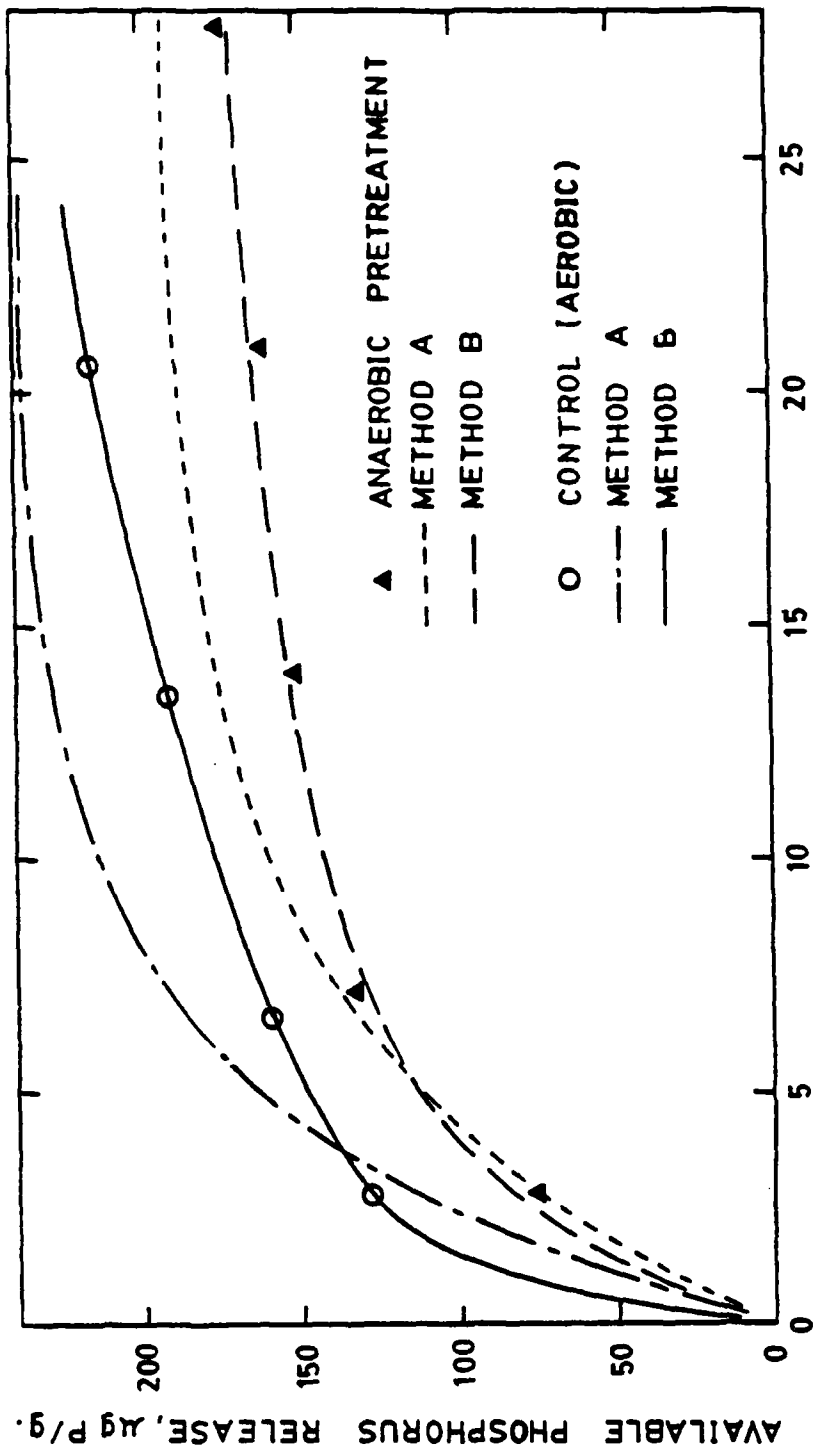


Figure 4.4 Sandusky River #45: Comparison of available phosphorus release from suspended sediments for control and anaerobically pretreated (Procedure III) bioassays.

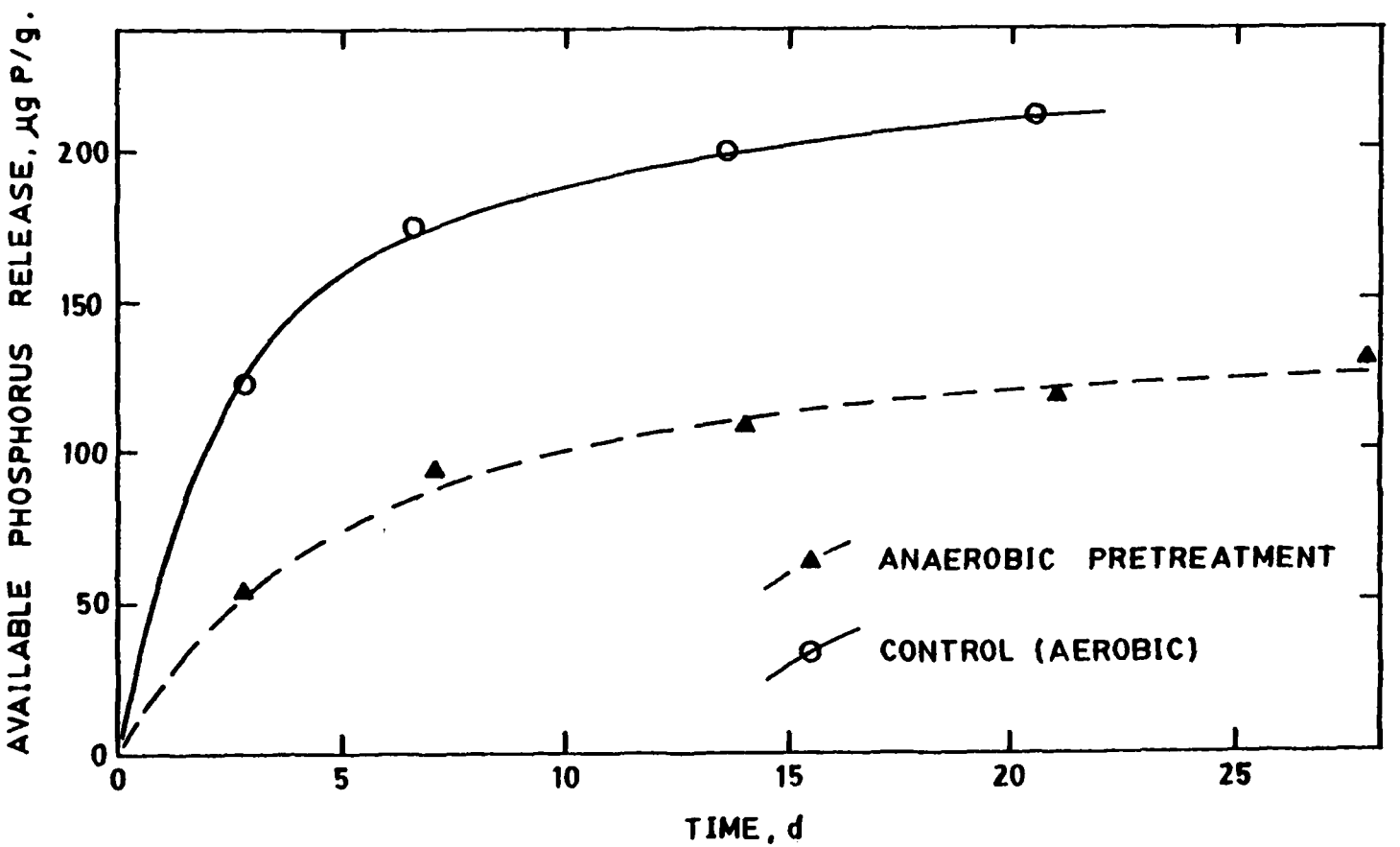


Figure 4.5 Sandusky River #48: Comparison of available phosphorus release from suspended sediments for control and anaerobically pretreated (Procedure III) bioassays (curves developed by Method B).

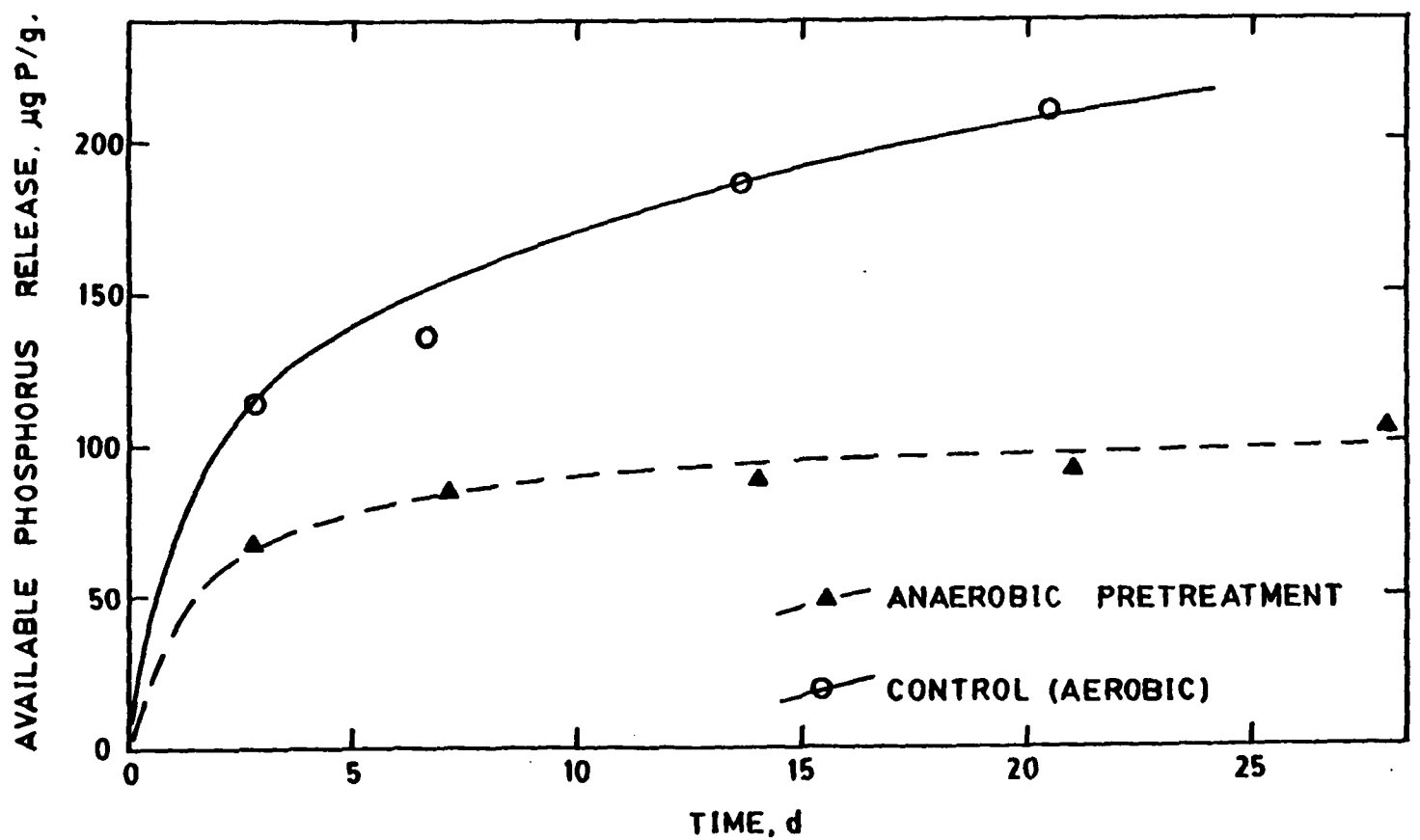


Figure 4.6 Sandusky River #49: Comparison of available phosphorus release from suspended sedments for control and anaerobically pretreated (Procedure III) bioassays (curves developed by Method B).

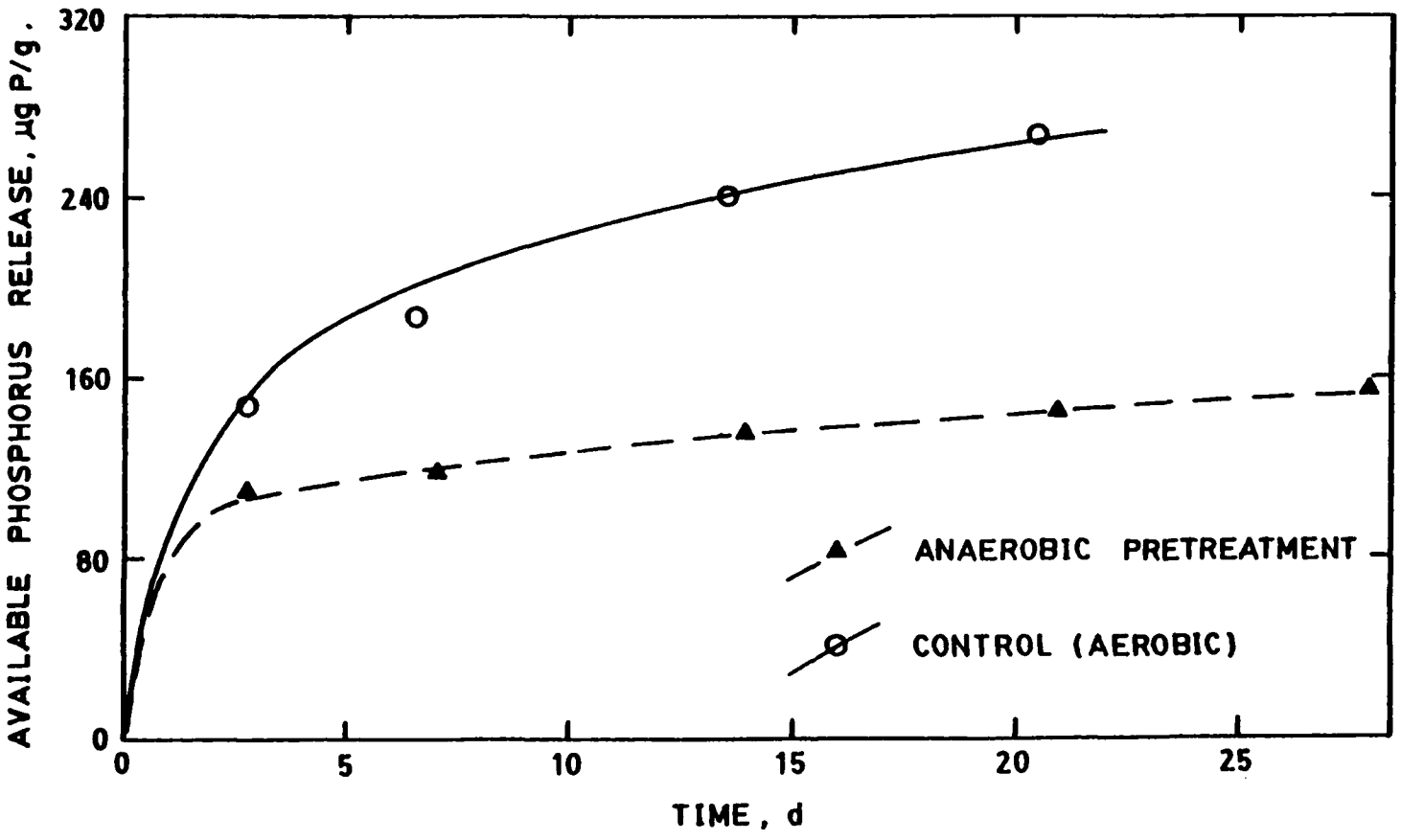


Figure 4.7 Maumee River #50: Comparison of available phosphorus release from suspended sediments for control and anaerobically pretreated (Procedure III) bioassays (curves developed by Method B).

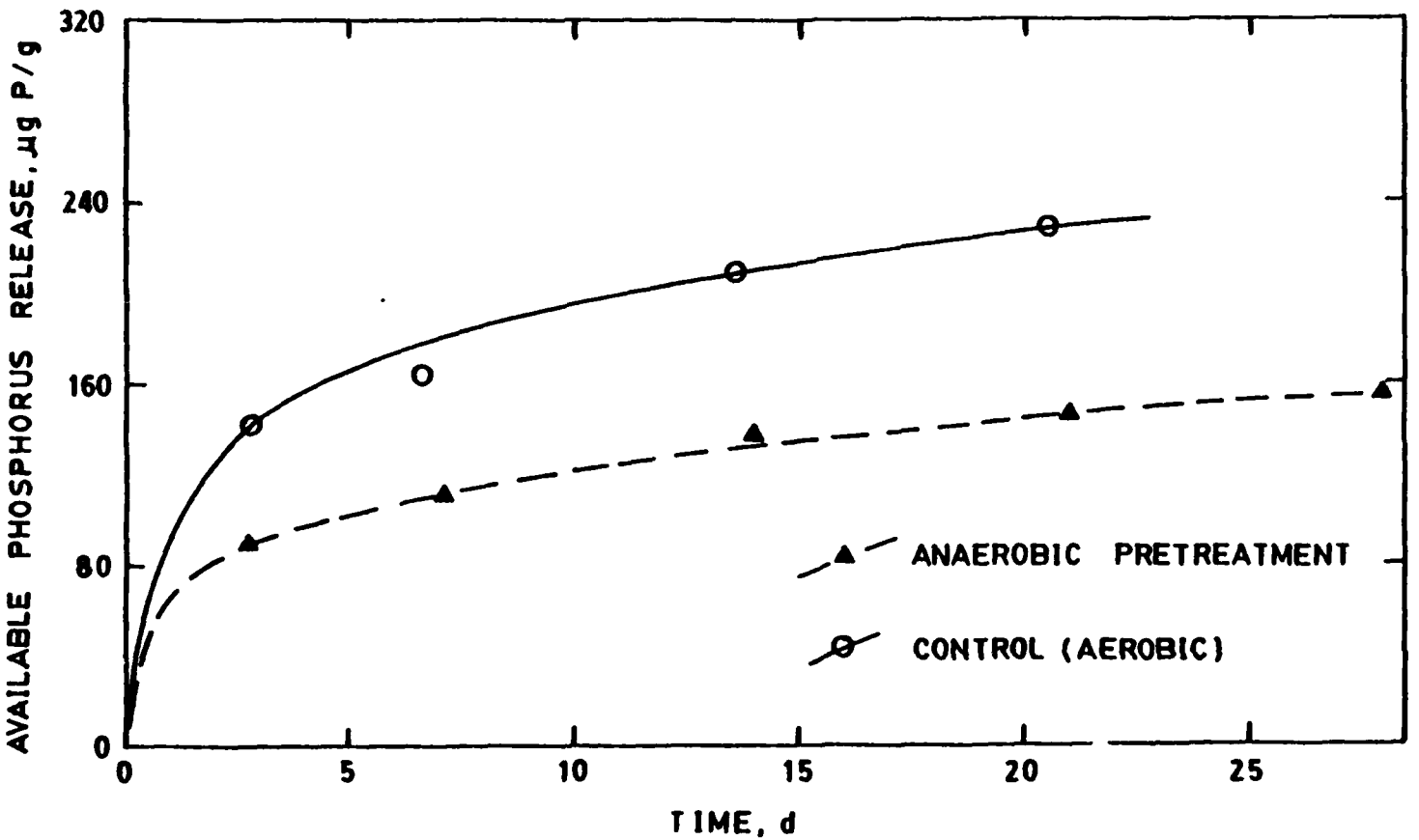


Figure 4.8 Sandusky #51: Comparison of available phosphorus release from suspended sediments for control and anaerobically pretreated (Procedure III) bioassays (curves developed by Method B).

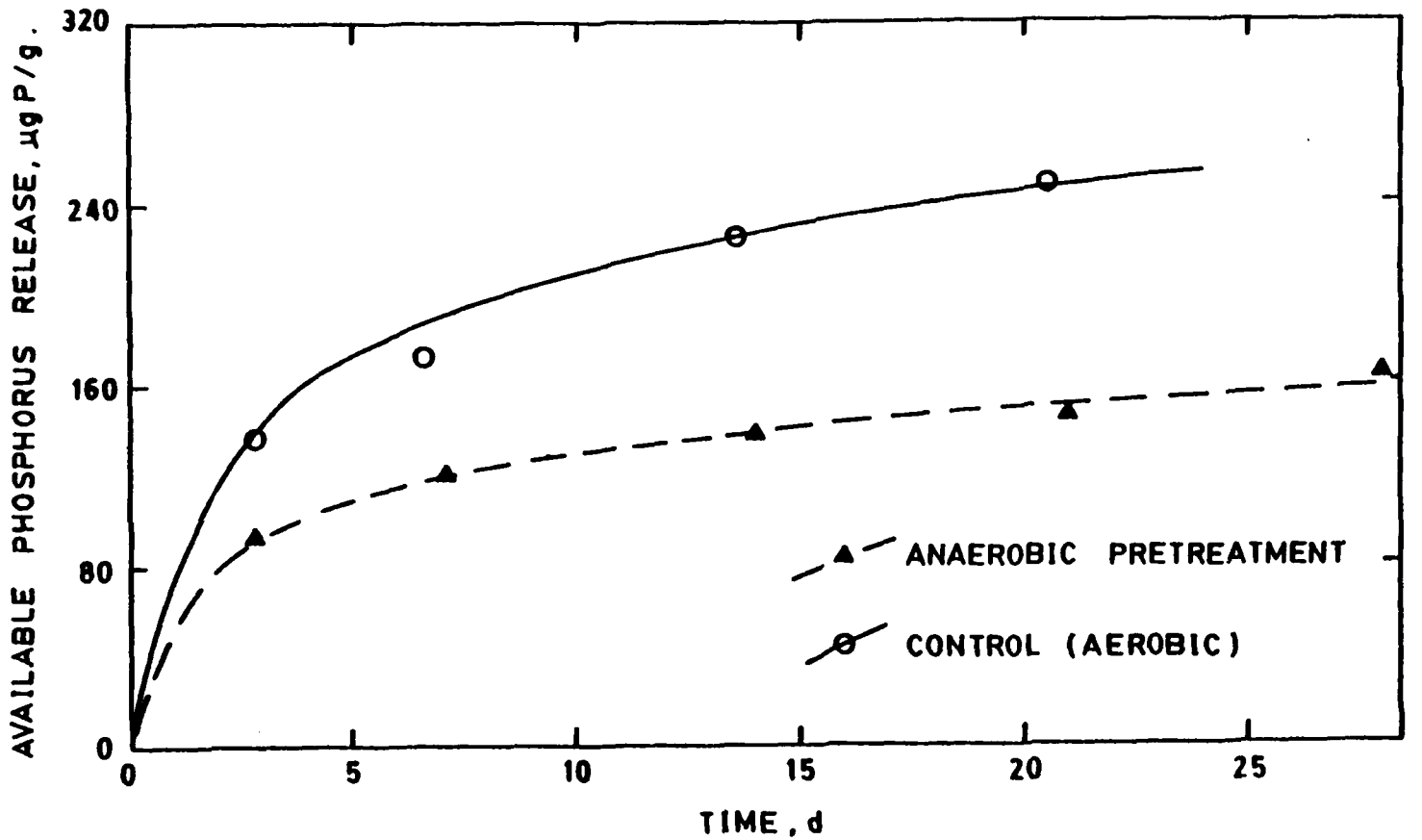


Figure 4.9 Sandusky River #52: Comparison of available phosphorus release from suspended sedments for control and anaerobically pretreated (Procedure III) bioassays (curves developed by Method B).

4.3.2 Procedure II. Illustrated in Figure 4.2 is the available phosphorus released during the first stage, 21 day bioassay and the second stage, 30 day bioassay. The intermediate anaerobic incubation was 31 days long. During the second stage bioassay only the Maumee sample (#41/42) showed any additional phosphorus release, and this release appeared to be a continuation of that observed during the first stage bioassay. Overall, the anoxic conditions imposed by Procedures I and II on the initially bioassayed sediments had no effect on increasing the phosphorus release from these sediments.

4.3.3 Procedure III. For Procedure III the initial sediment samples were exposed to anoxic conditions, aerated, and bioassayed. To determine the effect of the anoxic incubation, the mean of two Procedure III bioassays run on the uniform sediment-water mixture was compared against the mean of three control bioassays run on the original sediment concentrate. Since for both the Procedure III and control bioassays, all the phosphorus that was initially on the solids was bioassayed, the differences in the phosphorus that becomes available can be directly compared.

The data showing the available phosphorus release for the control and experimental bioassays over time is illustrated for each sample in Figures 4.3 through 4.9. The rate and ultimate release of available phosphorus from the sediments was determined by fitting the data to two separate mathematical models, termed A and B.

Method A used an equation suggested by DePinto (1982) which

assumes available phosphorus release is a first order function of the initial, ultimately releasable quantity, P_{ult}:

$$P(t) = P_{ult} [1 - \exp(-k_r t)] \quad (1)$$

where: $P(t)$ = available phosphorus released over time, t $\mu gP \cdot g^{-1}$;

P_{ult} = ultimately available phosphorus, $\mu gP \cdot g^{-1}$;

k_r = first order release coefficient, t^{-1}.

Method B was developed from the assumption that available phosphorus is released simultaneously from two particulate fractions at significantly different rates (Amer et al., 1955):

$$P(t) = P_{ult} [1 - p_1 \exp(-k_{r_1} t) - p_2 \exp(-k_{r_2} t))] \quad (2)$$

where: p_1, p_2 = fractions of P_{ult} which are released rapidly (p_1) and slowly (p_2) over time, t;

k_{r_1}, k_{r_2} = first order release coefficients, t^{-1}; and

$P(t), P_{ult}$ are defined as in Equation (1).

The slow release parameters p_2 and k_{r_2} were determined from the portion of the release curve where the rapid release has gone essentially to completion. The rapid release coefficients p_1 and k_{r_1} can then be estimated by the difference between the actual release data and the slow release values in the early part of the curve.

The parameters for Equations (1) and (2) are listed in Table 4.8 for both the anaerobically pretreated and control bioassays. The reliability of both methods for predicting the actual data is illustrated for comparison in Figures 4.3 and 4.4. To avoid

Table 4.8 Available phosphorus and release rates for treated and control bioassays, Procedure III

Sample	Method A		Method B				
	P_{ult} (µgP/g)	k_r (d^{-1})	P_{ult} (µgP/g)	p_1	p_2	k_{r_1} (d^{-1})	k_{r_2} (d^{-1})
TREATMENT BIOASSAYS							
Honey Creek(#43)	222	0.210	232	0.50	0.50	0.39	0.083
Sandusky River(#45)	195	0.174	178	0.52	0.48	0.43	0.090
Honey Creek(#48)	141	0.153	130	0.41	0.59	0.34	0.100
Sandusky River (#49)	120	0.201	100	0.55	0.45	1.00	0.140
Maumee River(#50)	182	0.208	170	0.60	0.40	1.40	0.050
Sandusky River(#51)	181	0.185	170	0.52	0.48	0.72	0.070
Sandusky River(#52)	176	0.183	170	0.44	0.56	1.50	0.066
CONTROL BIOASSAYS							
Honey Creek(#43)	282	0.199	330	0.41	0.59	0.57	0.049
Sandusky River(#45)	240	0.225	260	0.43	0.57	1.04	0.058
Sandusky River(#48)	241	0.223	230	0.62	0.38	0.52	0.074
Sandusky River(#49)	226	0.192	250	0.40	0.60	0.81	0.062
Maumee River(#50)	293	0.203	320	0.48	0.52	0.65	0.055
Sandusky River(#51)	271	0.200	290	0.49	0.51	0.60	0.061
Sandusky River(#52)	254	0.221	260	0.51	0.49	0.79	0.067

confusion Figures 4.5 to 4.9 show only the actual data points and the best fit of the data to Equation (2) (Method B) for the control and pretreated bioassays.

The data for every sample indicate that the release of available phosphorus from the control exceeds that released from the post-incubation bioassays. The extent of the decrease in the ultimately available phosphorus and the 21 day available phosphorus is shown in Table 4.9. On the average, anoxic incubation and reaeration showed about a 35% decrease in available phosphorus release.

4.4 Effects of Procedure III and Control Bioassays

In order to investigate the effect of the bioassays, fractionation measurements were made on the sediments from both the post-Procedure III bioassays and the control bioassays. The data are listed in Tables 4.10 and 4.11, respectively. For ease of comparison, the average and percent change from each fraction is shown for the post-incubation bioassays in Table 4.12 and for the control bioassays in Table 4.13. More importantly, Table 4.14 lists the changes in the fractionation from the beginning of the Procedure III incubation to the termination of the bioassays.

4.4.1 Effects of Anoxia and Bioassays on the Fractionations.

By comparing the average changes in total phosphorus from Tables 4.13 and 4.14, it is again apparent that the anoxic conditions did not enhance phosphorus release from the sediments. The comparison is also made in Figure 4.10 on a per sample basis by

Table 4.9 Extent of decrease in available phosphorus release with respect to control bioassays, %.

Sample	Method A		Method B		Actual Data*
	P_{ult}	21 day	P_{ult}	21 day	
Honey Creek(#43)	21.8	21.6	29.7	18.7	21.3
Sandusky River(#45)	18.8	20.1	31.5	23.6	25.5
Honey Creek(#48)	41.5	43.3	43.5	43.0	44.4
Sandusky River(#49)	46.9	46.7	60.0	53.6	56.2
Maumee River(#50)	37.9	37.8	46.9	45.5	46.0
Sandusky River(#51)	33.2	33.6	41.4	39.3	41.4
Sandusky River(#52)	30.7	31.5	43.6	36.2	36.3
Average	33.0	33.5	41.1	37.1	38.7

* Percent of decrease in available phosphorus at the actual 21 day data points.

Table 4.10 Fractionation of sediment phosphorus at termination of post-anaerobic bioassay, Procedure III; (µgP/g)

Tributary	No.	TP	R-NaOH	NR-NaOH	CDB	HCl	Residual	Available
Sandusky River	45	801	59	97	201	53	202	174
Sandusky River	49	819	62	107	203	41	212	108
Sandusky River	51	868	67	101	232	48	241	164
Sandusky River	52	896	65	115	224	46	237	156
Honey Creek	43	831	75	112	220	45	187	224
Honey Creek	48	773	64	124	168	28	203	129
Maumee River	50	901	75	97	210	89	241	156

Table 4.11 Fractionation of sediment phosphorus at termination of control bioassays, Procedure III; (µgP/g)

Tributary	No.	TP	R-NaOH	NR-NaOH	CDB	HCl	Residual	Algal Avail
Sandusky River	45	814	57	99	216	46	196	216
Sandusky River	49	832	76	124	259	43	176	209
Sandusky River	51	894	85	133	240	44	177	247
Sandusky River	52	901	87	117	245	45	185	228
Honey Creek	43	792	100	104	223	34	205	263
Honey Creek	48	787	86	118	180	27	159	211
Maumee River	50	912	85	108	219	84	198	268

Table 4.12 Average change and percent change in sediment phosphorus fractionation during post-anaerobic bioassays, Procedure III (µgP/g)

ΔTP	ΔR-NaOH	ΔNR-NaOH	ΔCDB	ΔHCl	ΔResidual	Algal-P
-189 (-18.3%)	-215 (-76.2%)	-18 (-14.1%)	-25 (-10.6%)	0 (0%)	+38 (+21.4%)	+159 (15.1%)*

* Average percent of initial TP which was algal-available during the bioassay (28 days).

Table 4.13 Average change and percent change in sediment phosphorus fractionation during standard-control bioassays (µgP/g)

ΔTP	ΔR-NaOH	ΔNR-NaOH	ΔCDB	ΔHCl	ΔResidual	Algal-P
-204 (-19.4%)	-191 (-69.9%)	-13 (-10.2%)	+16 (+7.6%)	-3 (-6.1%)	-40 (-17.8%)	+235 (+22.3%)

Table 4.14 Average change and percent changes in sediment phosphorus from before the anaerobic incubation to termination of the Procedure III bioassays (µgP/g)

ΔTP	ΔR-NaOH	ΔNR-NaOH	ΔCDB	ΔHCl	ΔResidual	Algal-P
-211 (-20.0%)	-207 (-75.6%)	-20 (-15.5%)	-1 (0.5%)	+1 (+1.2%)	-7 (-3.2%)	+159 (15.1%)

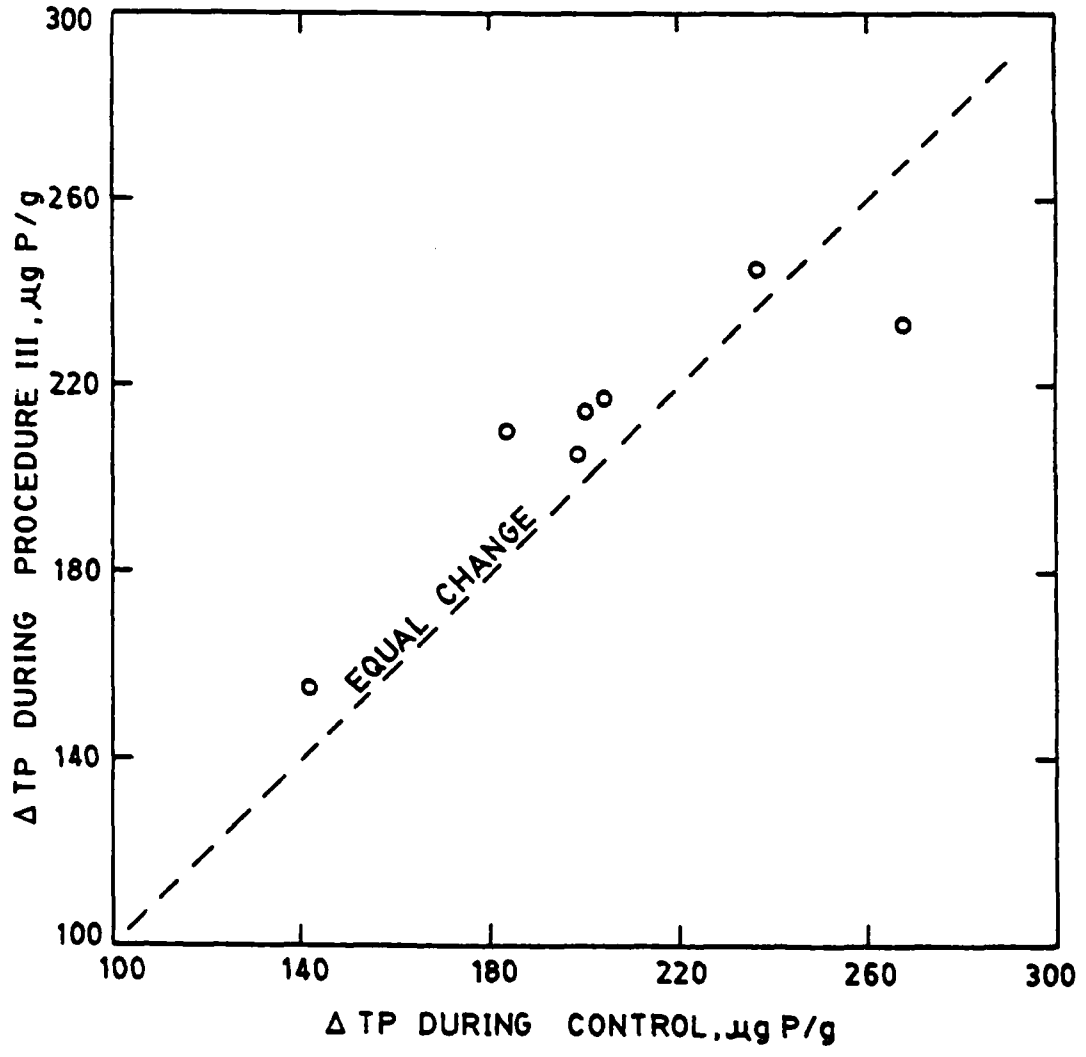


Figure 4.10 Total phosphorus lost during Procedure III (anaerobic incubation, aeration, and bioassay) compared with that lost during the controls (bioassay only).

plotting the change in total initial sediment phosphorus due to Procedure III against the change due to the controls. Since the points are scattered around the equal loss line, loss in total phosphorus due to Procedure III was similar to the loss in total phosphorus due to the control bioassays.

The average changes in the fractions considered potentially available (R-NaOH and CDB) suggest that the anoxic conditions cause a slightly greater decrease in the R-NaOH fraction and a slightly smaller increase in the CDB fraction. These changes also hold true on a per sample basis as seen in Figure 4.11 and 4.12, but the difference in the changes is not large. Since the changes in the R-NaOH and CDB fractions during Procedure III are slightly greater than those during the control bioassays, while the changes in total phosphorus remain similar, it would seem that other fractions must be showing smaller losses during Procedure III. This is seen to be true by comparing the average changes in the residual and other fractions in Tables 4.13 and 4.14.

These changes in the sediment fractionations seem to suggest that certain mechanisms during the anoxic period, probably microbial activity, cause the available phosphorus to be rearranged among the fractions. However, the anoxic conditions do not enhance the overall phosphorus release.

4.4.2 Procedure III and Control Bioavailability. Since changes in the R-NaOH fractions have been determined to correlate well with the available phosphorus released during similar bioassay studies (Beckwith, 1982), the initial R-NaOH fraction may be useful in predicting the amount of particulate phosphorus that

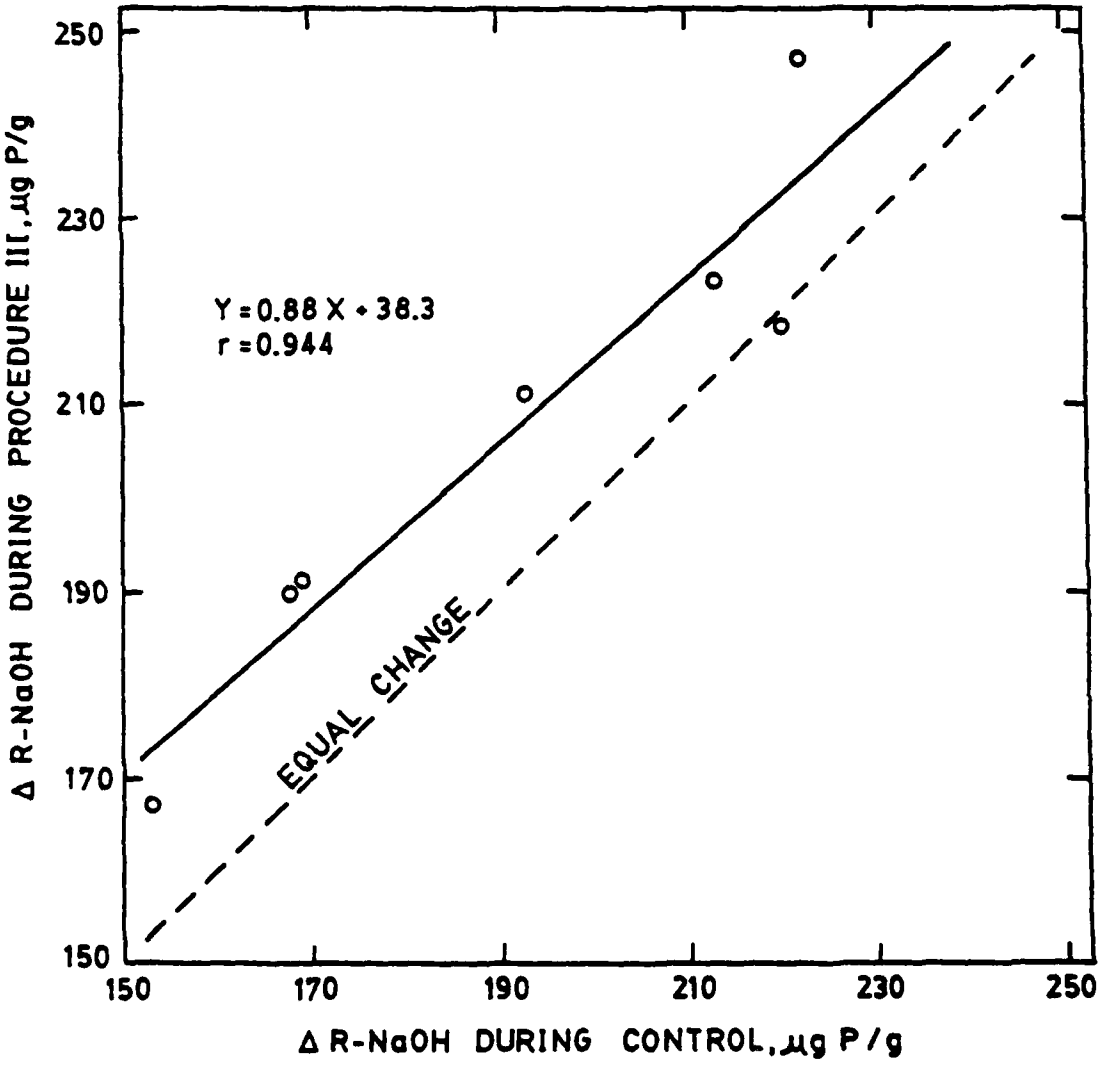


Figure 4.11 Reactive-NaOH-extractable phosphorus lost during Procedure III (anaerobic incubation, aeration, and bioassay) as compared with that lost during the controls (bioassay only).

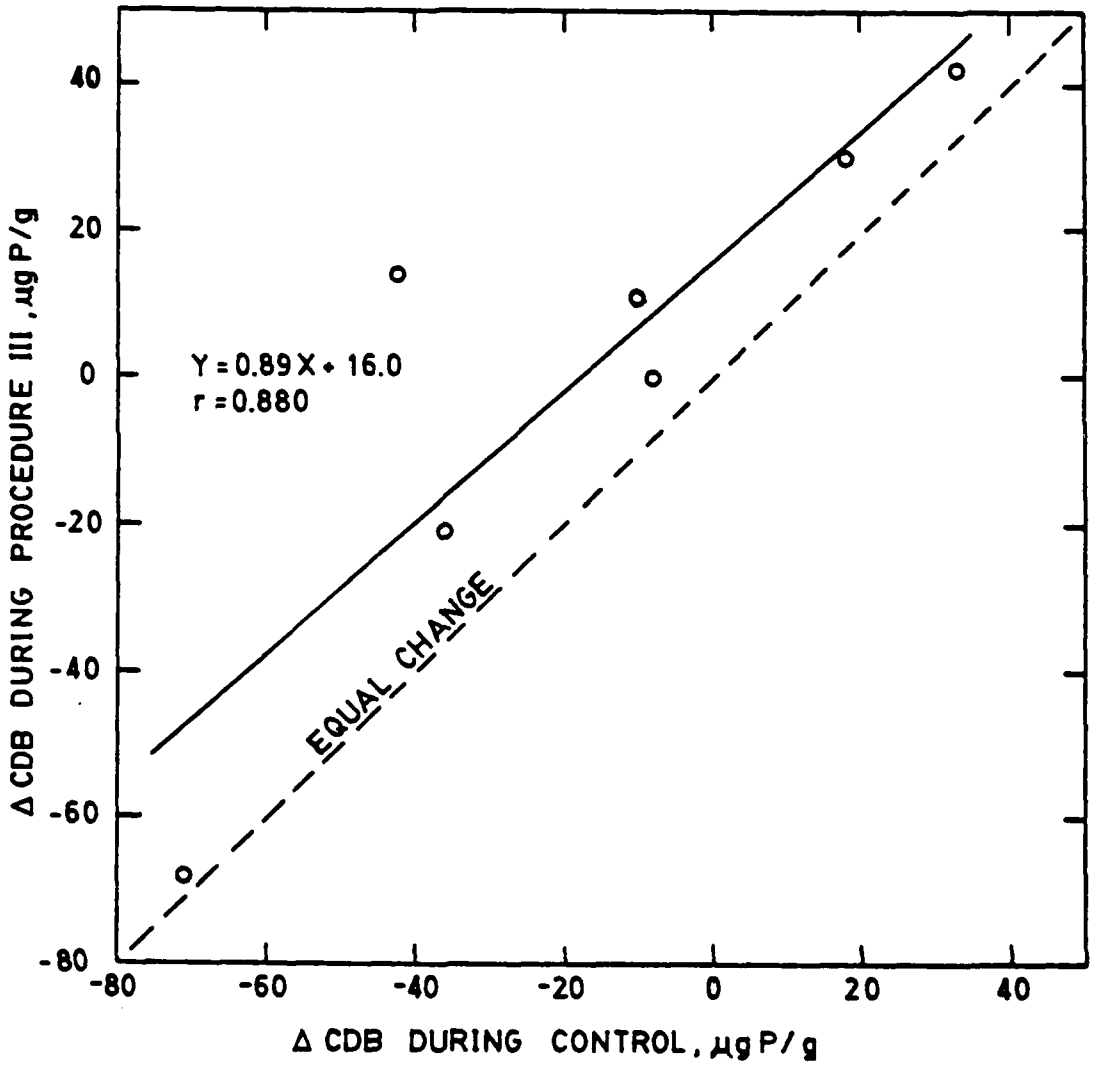


Figure 4.12 CDB-extractable phosphorus lost during Procedure III (anaerobic incubation, aeration, and bioassay) compared with that lost during the control (bioassay only) (Note: when $\Delta CDB < 0$, a gain occurred).

is ultimately available. The ultimately available phosphorus is shown as a function of the initial R-NaOH fraction for both the control bioassays and Procedure III in Figure 4.13. Since the same samples were run through the Procedure III and control bioassays, the initial R-NaOH was the same, and the larger ultimately available phosphorus release seen during the control bioassays is again apparent. Although the control bioassays showed an average 35% greater phosphorus release, the increases in available phosphorus with increases in initial R-NaOH are similar.

4.4.3 The Bioassays in Perspective. It is possible that the differences between the available phosphorus released from the Procedure III and control bioassays is the result of experimental variability and not as a result of varying phosphorus availability. Comparisons of the average changes in TP and algal-P in Tables 4.13 and 4.14 suggests that the control bioassays overestimated the algal-P and the Procedure III bioassays underestimated it. Also, the relationship between ultimately-available phosphorus release and initial R-NaOH found by Beckwith (1982) on a larger set of samples from the Cuyahoga, Sandusky, and Maumee Rivers and Honey Creek predicts the release to be between that seen by the control and Procedure III bioassays.

Overall, the bioassay and fractionation data shows that tributary sediments that are deposited, exposed to anaerobic conditions, and resuspended will release no more phosphorus than tributary sediments not deposited. Again, this data pertains

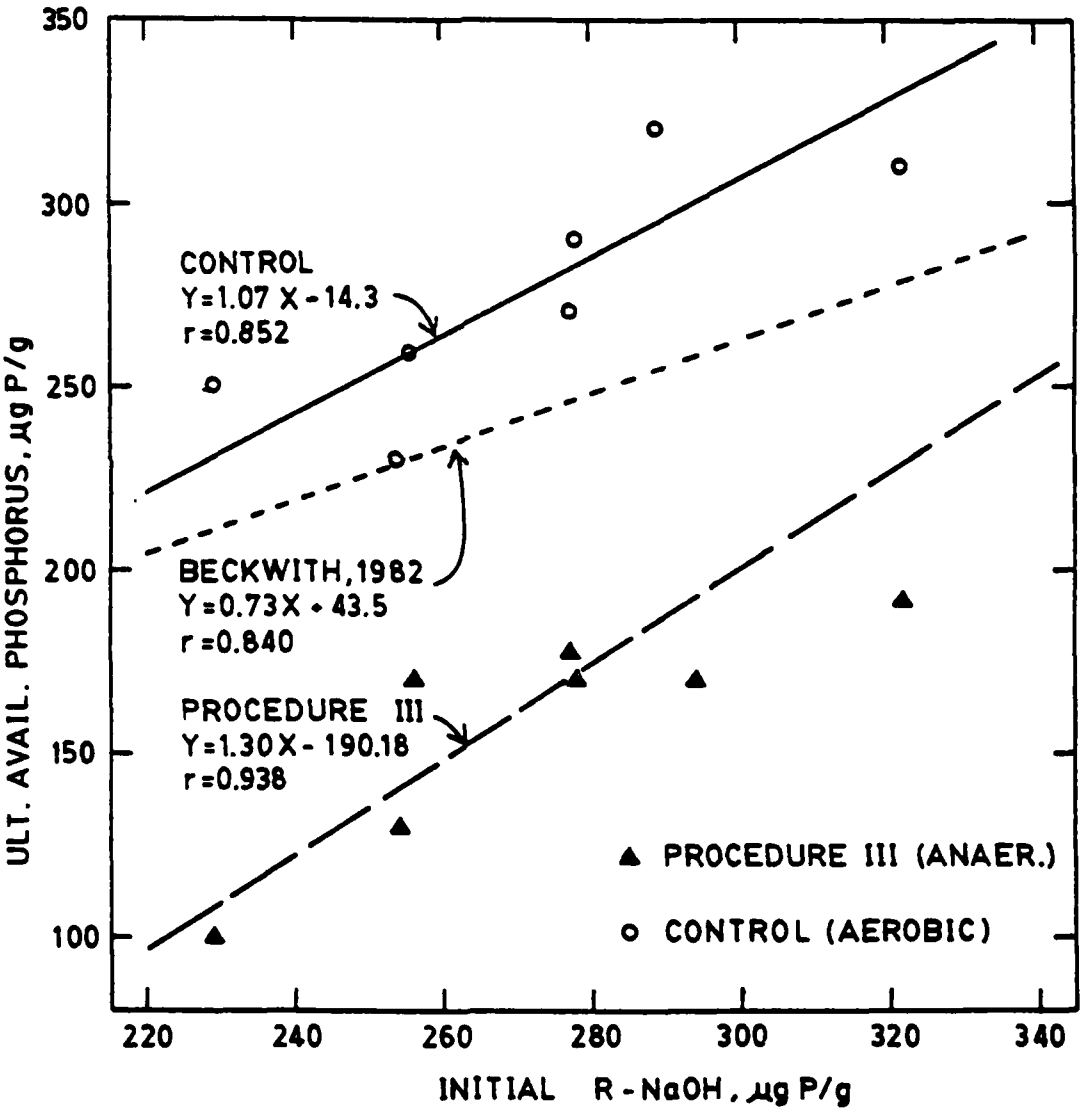


Figure 4.13 The ultimately available phosphorus release as a function of the initial-reactive-NaOH fraction for Procedure III, the controls, and a larger set of bioassays (n=38) similar to the control (Beckwith, 1982).

to particulate phosphorus associated with suspended tributary sediments from the Cuyahoga, Maumee, and Sandusky Rivers, and Honey Creek; and may not apply to organic phosphorus formed in the water column. Also, in lakes where the sediments are not resuspended, it is possible that small amounts of phosphorus, released during the reduction of iron oxides, may slowly diffuse into the water column during anoxic periods. However, when sediment particles are resuspended into the water column, as is often the case in the western basin of Lake Erie, the phosphorus release from these particles will not have been increased by exposure to anoxic conditions.

CHAPTER 5

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

After suspended tributary sediments are deposited in lake bottoms, they are often exposed to periods of low oxygen concentration. These anoxic conditions will result in the solubilization of some of the sediment-bound inorganic phosphorus. Upon circulation and exposure to aerobic conditions, this soluble phosphorus will be resorbed and may have a different degree of availability.

In order to investigate the effect of anoxic conditions on the bioavailability of sediment phosphorus, thirteen samples from western Lake Erie tributaries were exposed to a period of anoxia, reaerated, and bioassayed. The phosphorus released during these treated-sediment bioassays was compared to the release during bioassays on the same samples that had not been exposed to the anoxic period. Sequential chemical fractionations were also used to identify the change in particulate phosphorus fractions that may be considered available.

The information gathered in this study is summarized as follows:

- The anaerobic incubation, using a concentrated sediment slurry, caused low enough oxidation reduction potentials to solubilize inorganic phosphorus. When the concentrated slurry incubation lowered the ORP to between -60 and -130 mV, phosphorus concentrations in the overlying water increased from near zero to around 0.2 mg SRP/L and 0.4 mg TSP/L.

- The aeration step reprecipitated a major portion of the soluble reactive phosphorus. The average SRP:TSP ratio dropped from 0.56 after the concentrated slurry anaerobic incubation to 0.16 after aeration.
- The chemical fractionations changed during the anaerobic period, probably due to microbial activity. Procedure I, with a dextrose spike, caused a loss in the residual fraction, probably due to microbial mineralization of detrital organic phosphorus, and an increase in the NR-NaOH fraction, probably due to extraction of the increased microbial phosphorus. Procedure II, without dextrose, caused a loss in the residual and NR-NaOH fractions and an increase in the CDB fraction, which is probably the result of microbial mineralization followed by endogenous decay and precipitation into the CDB fraction. Procedure III, with higher solids concentrations, caused a loss from the residual fraction and a small gain in the R-NaOH and CDB fractions. This trend can probably be associated with limited microbial activity and effective reducing conditions.
- The anaerobic incubations did not increase the bio-availability of the sediment-bound phosphorus. In fact, the post-incubation bioassays showed consistently less available P release than the control bioassays, about 35% on the average. However, the post-incubation bioassays did, generally, release this smaller amount of available phosphorus at a rate faster than the control bioassays.

- The changes in total sediment phosphorus during the bioassays indicate that the release from the anaerobically-incubated sediments was nearly identical to the release from the control sediments. This suggests that the changes seen in the fractionations during the anaerobic incubations were due to rearrangement of the available phosphorus among the fractions.

Overall, the bioassay and fractionation data gathered in this study indicates that after tributary sediments are deposited, exposed to anaerobic conditions, and resuspended, they will release no more phosphorus than if they had remained suspended. Therefore, when considering resuspension of tributary sediments, mathematical submodels of sediment phosphorus availability should not predict release greater than that expected before deposition.

To better understand the mineralization and release of phosphorus occurring in sediments, it is recommended that efforts be made to characterize the indigenous microbial populations active in the sediments. Also, the principles used in this study should be extended to investigate the availability of phosphorus from sediments containing a combination of tributary particles and organics from the water column.

LITERATURE CITED

Amer, F., D.R. Boulin, C.A. Black, and F.R. Luke, 1955, "Characterization of soil phosphorus by anion exchange resin adsorption and ^{32}P equilibrium," Plant Soil, 6:391-408.

Am. Publ. Health Assn., 1980, Standard Methods, 15th edition, American Publich Health Association, Washington, D.C.

Beckwith, W.R., "Chemical fractionations as an indicator of phosphorus bioavailability in suspended solids from lower Great Lakes tributaries," Masters Thesis, Clarkson College, Potsdam, N.Y., 1982.

Chang, S.C. and M.L. Jackson, 1957, "Fractionation of soil phosphorus," Soil Science, 84:133-144.

Chapra, S.C. and W.C. Sonzogni, 1979, "Great Lakes total phosphorus budget for the mid 1970's," J. Water Polluction Control, 5(10):209-233.

DePinto, J.V., 1982, "An experimental apparatus for evaluating biochemical process kinetics of aquatic systems," Water Res., 16 (in press).

DePinto, J.V., T.C. Young, and S.C. Martin, 1981, "Algal-available phosphorus in suspended sediments of lower Great Lakes tributaries," J. Great Lakes Res., 7:311-325.

Heiltjes, A.H.M., and L. Lijklema, 1980, "Fractionation of inorganic phosphate in calcareous sediments," J. Environ. Qual., 9:405-407.

Howler, R.H. and D.R. Bouldin, 1971, "The diffusion and consumption of oxygen in submerged soils," Soil Sci. Soc. Amer. Proc., 35:202-208.

Langmuir, D. and D.O. Whittemore, 1971, "Variations in the stability of precipitated ferric oxyhydroxides," Adv. Chem. Ser., No. 106:209-233.

Langmuir, D., 1971, "E_H-pH determinations," In: Procedures in Sedimentary Petrology; R.E. Carver, 597-635, Wiley Interscience, New York.

Latterel, J.J., R.F. Holt, D.R. Tommons, 1971, "Phosphate availability in lake sediments," J. of Soil and Water Conservation, Jan.-Feb., 21-24.

Lee, D.Y., W. Lick, and S.W. Kang, 1981, "The entrainment and deposition of fine grained sediments in Lake Erie," J. Great Lakes Res., 7:224-233.

Lee, G.F., 1970, "Factors affecting the transfer of materials between water and sediments," Eutrophication Information Program, Univ. of Wisconsin-Madison.

Li, W.C., D.E. Armstrong, J.D.H. Williams, R.F. Harris and J.K. Syers, 1972, "Rate and extent of inorganic phosphate exchange in lake sediments," Soil Sci. Soc. Amer. Proc., 36:279-285.

Logan, T.J., 1978, "Chemical extraction as an index of bioavailability of phosphate in Lake Erie basin suspended sediments,"Lake Erie Wastewater Management Study, U.S. Army Corps of Engineers, Buffalo, N.Y.

Logan, T.J., F.H. Verhoff, and J.V. DePinto, 1979, "Biological availability of total phosphorus," Lake Erie Wastewater Management Study, U.S. Army Corps of Engineers, Buffalo, N.Y.

Montimer, C.H., 1941, 1942, "The exchange of dissolved substances between mud and water in lakes," J. Ecology, 29:280-329, 30:147-201.

Patrick, W.H., Jr., 1964, "Extractable iron and phosphorus in a submerged soil at controlled redox potentials," 8th Intern. Congress of Soil Sci., Vol. 4:605-608.

Patrick, W.H., Jr. and R.A. Khalid, 1974, "Phosphate release and sorption by soils and sediments: effect of aerobic and anaerobic conditions," Science, 186:53-55.

Patrick, W.H., Jr., S. Gotoh, and B.G. Williams, 1973, "Strengite dissolution in flooded soils and sediments," Science, 179:564-565.

Sagher, A., 1967, "Availability of soil runoff phosphorus to algae," Ph.D. Dissertation, University of Wisconsin-Madison.

Shulka, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong, and R.F. Harris, 1971, "Sorption of inorganic phosphate by lake sediments," Limnol. Oceanogr., 15:301-304.

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. Oceanogr., 15:301-304.

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.

Stumm, W. and J.J. Morgan, 1981, Aquatic Chemistry, Wiley Interscience, N.Y., pp. 282-285, 562-590.

Syers, J.K., R.F. Harris, and D.E. Armstrong, 1973, "Phosphate chemistry in lake waters," J. Environ. Quality, 2:1-14.

Towe, K.M. and W.F. Bradley, 1967, "Mineralogical constitution of colloidal 'hydrous ferric oxide'," J. Coll. Interface Science, 24:384-392.

Verhoff, F.H., M. Heffner, and W.A. Sack, 1978, "Measurement of availability rate for total phosphorus from river waters," Unpublished report from West Virginia Univ., Dept. of Chemical Eng.

Wetzel, R.G., 1975, Linmology, W.B. Saunders Co., Philadelphia, PA, pp. 215-245.

Weaver, R.M., 1974, "A simplified determination of reductant soluble phosphate in soil phosphate fractionation schemes," Soil Sci. Soc. Amer. Proc, 38:153,154.

Williams, J.D.H., H. Shear, and R.L. Thomas, 1980, "Availability to Scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes," Limnol. Oceanog., 25:1-11.

Williams, J.D.H., J.K. Syers, D.E. Armstrong, and R.F. Harris, 1971a, "Characterication of inorganic phosphate in noncalcareous lake sediments," Soil Sci. Soc. Amer. Proc., 35:556-561.

Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris, and D.E. Armstrong, 1971b, "Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters," Environ. Sci. Technol., 5:1113-1120.

Yaksich, S.M. and R. Rumer, 1980, "Phosphorus management in the Lake Erie basin," LWEMS Report, U.S. Army Corps of Engineers, Buffalo, N.Y.

Young, T.C., J.V. DePinto, D.J. Kwolek, and A.M. Victore, 1982, "Particle size and settling velocity distributions of suspended solids in tributaries of Lakes Erie and Ontario," Presented at the 25th Great Lakes Research Conference, Sault Ste. Marie, Ontario.