Please Return to:
6/02

DEP - DWM
627 MAIN ST 2ND FL
WORCESTER MA
01608

✓

September 1976 1
Report No. Env. E. 54-76-3

Mathematical Modeling of Phosphorus Exchange Between Sediments And Overlying Water In Shallow Eutrophic Lakes

Phillip D. Snow
Francis A. DiGiano

Report to the Division of Water Pollution Control
Massachusetts Water Resources Commission
Department of Environmental Quality Engineering
Contract Number 76-10 (3)

ENVIRONMENTAL ENGINEERING PROGRAM
DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF MASSACHUSETTS
AMHERST, MASSACHUSETTS 01003

MATHEMATICAL MODELING OF PHOSPHORUS EXCHANGE BETWEEN SEDIMENTS AND OVERLYING WATER IN SHALLOW EUTROPHIC LAKES

By

Dr. Phillip D. Snow
Assistant Professor of Civil Engineering
Union College, Schenectady, New York

Dr. Francis A. DiGiano
Associate Professor of Civil Engineering
University of Massachusetts/Amherst

Division of Water Pollution Control
Massachusetts Water Resources Commission
Contract Number MDWPC 76-10 (3)

Environmental Engineering Program
Department of Civil Engineering
University of Massachusetts
Amherst, Massachusetts 01002

September 1976

Preface

Since 1970, the Massachusetts Division of Water Pollution Control has sponsored research work at the University of Massachusetts dealing with the phosphorus exchange process between sediments and overlying water. Previous technical reports generated by this research have covered (1) a limnological survey of nine Massachusetts lakes with emphasis on measurement of the distribution of phosphorus between sediment and overlying water (Report No. EVE 32-73-2) and (2) a detailed laboratory study of the effect of oxidation-reduction potential, temperature and sediment chemistry with interpretation of the equilibrium distribution of phosphorus by an adsorption model (Report No. EVE 45-75-1).

This report concerns the development and field testing of a mathematical model to predict the role of sediments as a source of phosphorus once phosphorus loading to a lake has been reduced. Lake Warner in Hadley, Massachusetts served as the field study site for application of the model. A methodology for general use of the model is also presented. The research was conducted by Dr. Phillip D. Snow, then a doctoral candidate and now Assistant Professor of Civil Engineering at Union College in Schenectady, New York.

The following faculty members contributed generously by their valuable advice: Dr. Tsuan H. Feng, Professor of Civil Engineering; Dr. Gerald W. Foess, formerly Assistant Professor of Civil Engineering; and Dr. Oliver T. Zajicek, Associate Professor of Chemistry. In addition, special thanks are extended to William H. Frye, Dr. Thomas Sanders, C. James Martel, Robert Pariseau and Arnold Glazier.

Dr. Francis A. DiGiano
Associate Professor
of Civil Engineering &
Principal Investigator

ABSTRACT

The eutrophic state of a lake can be controlled by adjusting the concentration of phosphate, especially orthophosphate, in the lake water. In order to alter the trophic state of a lake, the restoration program should include the reduction of influent loading as well as the control of release of phosphate from the sediment. A phosphorus exchange model between sediment and overlying water is proposed to predict the time dependent response of lake phosphorus concentration as a result of these restoration techniques.

Both release and sedimentation of phosphate were considered. Release was shown to be proportional to the concentration gradient of total phosphate between lake water and sediment interstitial water. The rate of sedimentation was shown to be first order with respect to total phosphate in the lake water. A relationship was derived to relate total phosphorus to exchangeable phosphate and to interstitial water phosphate within the sediment.

The steady-state solution of this model is used to develop a nomograph which interrelates influent phosphate loading, lake water phosphate and interstitial phosphate in the sediment. The non-steady state solution of the proposed model is used to determine the transient response of a lake to changes in either input phosphate loading or interstitial exchangeable phosphorus retained in the sediment. Further, the interstitial phosphate concentration can be adjusted to account for the effects of the addition of alum and kaolinite on the release of phosphate from the sediment. Using a caisson emplaced in Lake Warner, Hadley, Massachusetts the rates of sedimentation and release of phosphate were determined in-situ.

The steady and non-steady state phosphate exchange models were then tested on Lake Warner. The model predicted the response of lake phosphate to input of excess phosphate due to agricultural and urban drainage as well as to bypassing of wastewater. Model results agreed closely with historic and field data. Because of release of stored phosphate available in the sediment, the model predicts that 8-10 years will be required to substantially lower lake phosphate after reducing input phosphate loading. The model also showed that suppression of interstitial phosphate by addition of alum and kaolinite dramatically reduces the time to lower the level of phosphate in the lake. Finally, the model predicted that decreasing input phosphate loading and adding alum and/or kaolinite to a shallow eutrophic lake will rapidly decrease the lake water phosphate. These restoration measures should therefore result in the lowering of the trophic state of a lake.

TABLE OF CONTENTS

CHAPTER

---

*Appendices B through E are not included in this report but can be found in the Ph.D. Dissertation of the same title by Phillip D. Snow, University of Massachusetts/Amherst (July 1976).

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Symbol	Definition and Dimensions in Mass (M), Length (L), and Time (T).
A_z	Cross Sectional Area (L^2)
A	Area of Lake (L^2)
Dr	Reactive Depth of Sediment (L)
K	Vollenweider (1969) Sedimentation Coefficent (T^{-1})
K_1	Release Rate Coefficent (L/T)
K_2	Sedimentation Rate Coefficent (T^{-1})
K_s^*	Lorenzen (1973) Sedimentation Coefficent (M/T)
K_R^*	Lorenzen (1973) Release Coefficent (M/T)
N	Flux of Phosphate into the Sediment (M/L^2T)
N_p	Flux of Phosphate from the Sediment (M/L^2T)
P_i, P_i^*	Interstitial Water Total Phosphate (M/L^3)
P_L	Lake Water Total Phosphate (M/L^3)
P_{Leq}	Equilibrium Lake Water Total Phosphate (M/L^3)
P_o	Influent Total Phosphate (M/L^3)
P_s	Exchangeable Total Phosphate in Sediment (M/L^3)
P_T	Total Phosphorus in Sediment (M/M)
Pz	Lake Water Total Phosphate at Distance z from Inlet (M/L^3)
Q_o	Flowrate (L^3/T)
R_r	Rate of Release of Phosphate (M/L^3T)
R_{sed}	Rate of Sedimentation of Phosphate (M/L^3)
r	Piontelli (1964) Sedimentation Coefficent (dimensionless)

$\overline{T}$	Detention time (T)
t	Time (T)
V	Volume of Lake Water (L^3)
V_s	Volume of Sediment (L^3)
v	Velocity (L/T)
Z	Lake Depth (L)
z	Distance (L)
ε	Porosity (dimensionless)
Δt	Finite Time Difference (T)
Δz	Finite Distance Difference (L)

CHAPTER I

INTRODUCTION

Eutrophication in lakes, caused by either natural aging or man-induced additions of algal nutrients has been the topic of extensive research for the past 20 years. In the progression of eutrophication, lakes have been observed to be classified into one of three broad categories. Oligotrophic lakes have very low concentrations of algae due to limited amounts of phosphate and nitrate in the water. Dissolved oxygen is high at all depths and light penetration is evident to depths of 40 feet. Increases in the concentrations of nitrate and phosphate will cause larger growths of algae. In a mesotrophic lake, algal concentrations are higher than in an oligotrophic lake and a subsequent decrease in light penetration and dissolved oxygen is evident. The entire biomass is greater than in an oligotrophic lake and a greater diversity of species are present.

When either natural or man-induced additions of nitrates and, especially phosphate, cause the lake water concentrations of these nutrients to reach a critical level, the lake will shift to the eutrophic state. Here, bloom proportions of algae, mainly the blue-green species, are found throughout much of the year. As a result, dissolved oxygen in the water will be absent at certain times of the year or at certain depths in the lake. Light penetration is low and a low diversity of species can be expected.

Most researchers in the last 20 years have attributed the changes from oligotrophic and mestrophic to eutrophic conditions to have been mainly caused by increases in the concentration of phosphate in the lake water. Thus, the most straightforward approach to reversing this trend is to reduce the loading of phosphate to the lake. However, recent research has shown that phosphate already in the sediment of a eutrophic lake can be released back into the lake water. Sullivan (1967) and Harriss (1967) both indicated that chemical and biological reactions between interstitial water and the solid fraction in the sediment will allow nutrients, especially phosphate, to migrate back into the lake water. The sediment can, therefore, have a strong influence on the overlying water chemistry. In order to reverse the current eutrophic state of a lake, Broecker (1973) recommends that no change in the current loading be undertaken until the effect of the sediment on the overlying water is known. Latterell (1971) states:

> "It seems likely that sediments act as a buffer, removing phosphorus and nitrogen from lake water when the concentration is high and releasing nutrients when the concentration is low."

The concept of the sediment acting as a nutrient sink to remove phosphate from the lake water has been generally recognized to apply to most lakes which are oligotrophic or mesotrophic. For the eutrophic lake in which reductions of the influent loading of phosphate are planned, the sediment can act as a source of phosphate:

> "The entire nutrient equilibrium may shift in the direction of the water in lakes in which external nutrient sources have been reduced or eliminated, thereby delaying the recovery period for a long time" (Frink, 1967).

The basic questions generated by current research in reversing the eutrophic state of a lake are:

(1) How great is the effect of the sediment on the phosphorus budget in a lake?

(2) What is the magnitude of release from the sediment and how can it be controlled?

(3) How much time is needed after a decrease in loading to achieve a lower phosphate concentration in a lake, with and without controls on the sediment?

In order to predict changes in phosphate concentrations in a lake and the subsequent change in algal concentrations and eutrophic state, a mathematical model is proposed in this research. The model will account for the effects of phosphate loading, flux of phosphate from the sediment, and sedimentation of phosphate onto the sediment. All three parameters interrelate to determine the concentration of phosphate in the lake water. With the use of this model, the percent reduction of loading to affect a desired concentration of phosphate in a lake can be predicted. Moreover, the model can be used to predict the time required to reach this concentration with and without the addition of chemicals to suppress phosphate release from the sediment.

The application of the proposed model will be a great aid to those involved in lake renovation and in the planning of loading reductions to reverse the eutrophic state of a lake. The results of the model can also be used to determine what effects the addition or removal of wastewater discharges will have on the eutrophic state of a lake.

To obtain the necessary kinetic and equilibrium constants needed in the model and to apply the results to an actual eutrophic lake, Lake Warner in Hadley, Massachusetts was chosen. Eutrophication of this lake has been accelerated in the last ten years by the bypassing of primary treated wastewater from the Town of Amherst into the Mill River, the main tributary into Lake Warner (Stein, 1968; Gagnon, 1972; Snow, 1973). Bypassing occurs when the Amherst Waste Treatment Plant is hydraulically overloaded due to excessive infiltration during storm events and spring thaws. In 1975, greater pumping capacity should make bypassing unnecessary and cause a decrease in the loading of phosphate to the lake. For Lake Warner and many other small, eutrophic lakes, many researchers and officials are interested in the impact of reduced loadings. This impact can be measured by the time needed at this reduced loading to affect a lower concentration of phosphate in a lake and the attainable new value thereof.

The proposed research will, therefore, be to:

1. derive a specific mathematical model to describe the concentration of phosphate in a lake as a function of loading, release, and sedimentation of phosphate.
2. obtain specific data needed for the model with reference to Lake Warner.
3. determine kinetic and equilibrium constants that are needed to apply the model.
4. test the model on Lake Warner and predict the effect of a decrease in loading on the future status of the lake.
5. determine the effect of suppressants on the flux of phosphate from the sediment.
6. generalize the application of the proposed model to other small, eutrophic lakes.

CHAPTER II

CAUSES OF EUTROPHICATION AND CONTROLS OF PHOSPHORUS IN LAKES

General Overview

Eutrophication of a lake is generally defined as increased fertility due to inputs of the nutrients phosphorus and nitrogen which cause large algal blooms. Associated with these blooms are distinct changes in temperature, dissolved oxygen, pH, and Eh of the lake.

Phosphorus as PO_4^{-3} is usually considered the limiting and most controllable nutrient in regulating algal blooms. Its deposition onto the bottom of a lake is mainly due to algal uptake and subsequent settling as well as adsorption onto either iron or aluminum complexes or surface exchange on clay minerals. Subsequent to sedimentation, the phosphate can be released back into the lake water, especially if the concentration of phosphate in the sediment is high.

One method of reversing eutrophication in lakes, has been to reduce the loading or influent concentration of phosphate. Along with this, various methods have been tried to reduce the amount of phosphate released from the sediment back into the lake water. To reverse the process of eutrophication, the limit of phosphate loading must first be decided. Subsequently, the method (if any) needed to suppress the release of phosphate from the bottom sediment can be established. The selection of method must be accompanied by a prediction of the time needed to affect the desired results.

Algal Nutrients and their Effect on Lakes

The basic nutrients which are necessary for algal growth are HCO_3^- or CO_2, NO_3^-, and PO_4^{-3}. Many other trace nutrients are needed for algal growth but their nature or concentrations are such that they cannot be easily controlled or removed by man. Temperature and light, which also affect algal growth, cannot be easily controlled.

Carbon Dioxide. Carbon, usually as CO_2,(H_2CO_3), or HCO_3^- is currently not considered to be a limiting or controllable nutrient except in special cases where nitrate and phosphate are in extreme excess (Goldman, 1971). The partial pressure of CO_2 and rate at which equilibrium is attained in rivers and in the upper regions of the epilimnion of a lake are much greater than algal uptake of carbon (Park, 1969). Schindler (1972) has measured the flux rate of CO_2 at .2gm/m^2/day for partially saturated lake water which is much higher than the uptake rate of prokaryotic (blue-green) algae. Also, in shallow lakes and rivers, CO_2 generated from the breakdown or organics in the benthic sediments adds to the atmospheric derived CO_2 (Goldman, 1971).

In the succession of a lake from oligotrophic to eutrophic, the eukaryotic (green) algae are replaced by prokaryotic (blue-green) algae. This transition is accompanied by: (1) an increase in the pH which decreases the amount of CO_2(H_2CO_3) in solution and (2) a gradual rise in water temperature which also decreases the solubility of CO_2. Recent studies (Goldman, 1971; Brock, 1973; and Shapiro, 1973) have indicated that the blue-green algae are biochemically more successful in extracting low levels of CO_2 (at high pH levels) from water than are the green algae. Below pH 6, the green algae are dominant, but as a bloom of algae occurs in a lake, more CO_2 is extracted from the water, the pH rises, and the blue-green algae with their associated mats and smells, become dominant. The blue-green algae will continue to bloom because: (1) CO_2 influx is still occurring; (2) HCO_3^- and CO_3^- can be converted to CO_2 by blue-green algae (green algae cannot, Brock, 1973); (3) uptake of phosphate by blue-green algae is more efficient than by green algae (Shapiro, 1973); (4) some of the blue-green algae can convert N_2 to nitrate (Shapiro, 1973); and (5) the breakdown of dead algal cells by bacteria liberates CO_2 back into the water (Brock, 1973). All of the above factors indicate that efforts to limit carbon as an algal nutrient would be ineffective in controlling eutrophication in lakes.

Nitrogen. Nitrogen, usually in the form of nitrate, NO_3^{-1}, is also a algal nutrient which, if limited, has, in some cases, reduced algal populations. Usually, it has been found that natural levels of nitrate in most watersheds are high enough to sustain algal blooms and the reduction of man-derived nitrates alone is not enough to decrease algal populations (Schindler, 1974). Since nitrate is very weakly bound to soil particles (due to surface adsorption) it tends to pass through the soil and into the groundwater (Ponnamperuma, in press). This is especially true in farming areas where nitrate fertilizers are used (Kohl, 1971). Along with surface and groundwater inputs of nitrates, which are not easily controlled, is the ability of prokaryotic algae to convert N_2 gas to nitrates. Horne (1974) has estimated that one-half of yearly nitrogen budget in an eutrophic lake was derived from N_2 fixation by the blue-green algae.

It would appear that limiting the nitrates only from man-derived sources would not necessarily limit or control eutrophication in lakes. This is especially true for shallow lakes where dead algae settle to the bottom to undergo breakdown by bacteria. Up to one-half of the nitrogen in algal tissue is derived from N_2. Because nitrate is so weakly bound to sediment particles, release back into the water will enable algae to continue their growth (Stumm, 1973).

Oxygen. Although oxygen is not a nutrient for algae (except for evening uptake when photosynthesis stops), the concentration of oxygen in lakes is directly affected by algae. The natural by-product of active photosynthesis is O_2 and during the daylight hours a lake with an algal bloom can reach 180-200 percent saturation with respect to O_2. During the evening hours, much of this O_2 can be taken up by algae and bacteria in the water thus causing a diurnal fluctuation of dissolved oxygen in the lake water. During a bloom of algae, the dead algae on the bottom exert a high BOD due to bacterial decomposition. The peak O_2 demand occurs at the peak of the bloom (Welch, 1969). This oxygen demand is actually due to bacterial decomposition of organic matter at the mud-water interface (Ogunrombi, 1970) as well as oxygen used to oxidize anaerobic end products eminating from within the sediment (Martin, 1971; Ogunrombi, 1970). The breakdown of organic matter due to algal cells is 80 percent complete within 220 days with the greatest demand obviously occurring during the peak of the bloom (Skopintsev, 1964). A shallow lake with a large bloom of algae will therefore experience tremendous fluctuations, both vertically and diurnally, in dissolved oxygen. Anaerobic conditions at or near the sediment-water interface are therefore usually encountered in eutrophic lakes (Snow, 1973).

Phosphate. Phosphate, usually as HPO_4^{-2} or $H_2PO_4^{-1}$, is currently the algal nutrient which can be most easily limited to reduce eutrophication in lakes. As it is used in algal photosynthesis, phosphate is incorporated into plant tissue as shown by following equation (Stumm, 1973)

$$106CO_2 + 16NO_3^- + HPO_4^{-2} + 81\ H_2O + 18H^+ + \text{trace elements} + \text{light} \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftarrows}} C_{106}H_{181}O_{45}N_{16}P + 150\ O_2 \qquad (1)$$

Actually, when phosphate is available in a bloom, luxury uptake by algae will occur such that up to 60 percent more phosphate will be accumulated in the cells than is needed for growth (Shapiro, 1967). This phosphorus is weakly bound as inositol polyphosphate within the cell but, as orthophosphate concentrations in the lake decrease, 90 percent of the polyphosphates are enzymatically released back into the water within 24 hours (Herbes, 1975; Lean, 1973). Release of luxury phosphate also occurs when conditions become anaerobic, with 60 percent of the orthophosphate being released in 3 hours (Shapiro, 1967). Diurnal exchange of phosphate between dead algae at the bottom (low O_2) and blooming algae (luxury uptake) therefore may take place in shallow lakes. Minear (1972) has noted that the breakdown of algal cells yields DNA molecules which constitute 30 to 60 percent of the organic P fragments in lake water during a bloom. Bacterial action in the water column and at the sediment-water interface breakdown organically bound phosphate which can then be recycled back to algal growth in shallow, mixed lakes. The dynamics of the cycling of phosphate in lakes is therefore very dependent on algal growth and death, especially during a bloom. Large numbers of algae tend to accumulate phosphate rapidly. With large amounts of organic matter present, the combination of bacterial degradation and algal excretion tend to recycle phosphate back into the system to sustain an algal bloom.

Of concern to most researchers is the concentration of phosphate (or phosphorus) which will cause and sustain algal growth. The lower limit at which growth is limited, presuming all other factors are favorable, is usually set between 10 to 20 μg/l of phosphorus (Welch, in press). As phosphorus levels are increased, the number of algae, usually measured as chlorophyll a, will also increase (Welch, in press; Malueg, 1973; Dillon, 1975). This is usually a log-log relationship based on either phosphorus concentration in lake or on phosphorus loading (ie. gm $P/m^2/yr$). This direct and highly correlated dependence of algal populations and phosphorus levels has led most recent researchers in the field (Schindler, 1974; Goldman, 1971; Stumm, 1973; Horne, 1974) to conclude that by controlling the loading or concentration of phosphorus in a lake, eutrophication can be controlled. Control of carbon and nitrogen compounds is deemed secondary in comparison to phosphorus.

Phosphorus Cycling Between Sediments and Water

The fate of phosphorus in water is usually considered to consist of: (1) chemical, physical, or biological removal of the ionic form into a particle; (2) sedimentation of this particle to the bottom; (3) partial breakdown in the sediment; and (4) the release of some of the ionic phosphorus back into the lake water if conditions are favorable. Depending on the chemistry of influent water, the chemical removal of ionic phosphorus in river and lake water is by either: 1) calcium phosphate-apatite (Stumm, 1970a), 2) aluminum and iron phosphates (Hsu, 1964; Hutchinson, 1957), or 3) phosphorus being incorporated into amorphous hydrated oxides of iron and aluminum (Wentz, 1969; Ku, 1975; Shukla, 1971; Williams, 1971; Stumm, 1970a). Surface adsorption of ionic phosphorus onto the hydrated oxides of iron and aluminum and into positive charged sites of organic particles and clay minerals also removes phosphorus from the water (Stumm, 1970a; Ponnamperuma, in press). Finally, biological uptake, especially by algae, also removes phosphorus from the water.

Almost all of the original phosphorus particles coming into a lake and those that are formed in the lake itself settle to the bottom. Obviously, the larger or heavier particles settle faster and greater removal is affected by longer detention times in a lake.

Although the sediment is usually considered a sink with respect to phosphorus, the amount of phosphorus, both total and exchangeable, in the sediment can affect the concentration of phosphorus in the lake water (Feng, 1967). Equilibria studies (Ku, 1975; Lotse, 1973) with phosphorus and lake sediments all indicate an equilibrium relationship between total phosphorus in the sediment and the phosphorus in the interstitial water. The amount of phosphorus adsorbed and desorbed from the sediment as well as the concentration of phosphorus in the lake water as compared to that in the sediment vary with different chemical, biological, and physical conditions. The observed ratios of orthophosphate in the overlying water and interstitial water of anaerobic sediment cores in six Western Massachusetts lakes are tabulated in Table 1.

Lake Quinsigamond in Central Massachusetts exhibited a similar ratio, .1, (25/250) for an analysis that was not allowed to go anaerobic. And Sutherland (1966) has shown a ratio in Lake Ontario of .16 (15/90). The overall average of these ratios is approximately .1 (.1056) which indicates a strong correlation between the amount of orthophosphate in the interstitial water and the amount of orthophosphate in

TABLE 1

RATIOS OF ORTHOPHOSPHATE CONCENTRATIONS IN LAKE AND INTERSTITIAL WATER

(MODIFIED FROM SNOW, 1973)

Lake	$\frac{\mu g/l \text{ lake water}}{\mu g/l \text{ interstitial water}}$	
Laurel	.1	(4/40)
Warner	.15	(70/464)
Wyola	.1	(18/179)
Mattawa	.11	(7/64)
Norwich	.08	(13/160)
Aldrich	.135	(55/410)

the lake water itself.

There are various mechanisms which control the adsorption and release of phosphorus in the lake sediment. The redox potential or Eh of the sediment has been recognized as a major controller of adsorption-desorption in the sediment. High amounts of orthophosphate are adsorbed with aerobic (high Eh) conditions and desorbed under anaerobic conditions (Ku, 1975; Fink, 1970). The amount desorbed generally increases with a decrease in the redox potential (Ku, 1975; Patrick, 1964). With greater concentration of biodegradable organic matter in the sediment, the benthic bacteria will decrease the redox potential proportionately (McKee, 1970). Anoxic conditions at the sediment-water interface have caused from 7 to 10 times as much phosphorus to be liberated into the overlying water as compared to aerobic conditions (Ku, 1975; Mortimer, 1941).

The pH of the sediment is also critical to the degree of adsorption of phosphorus. At a pH near 5.5, many researchers have noted a maximum in the adsorption of phosphorus (McKee, 1970; Ku, 1975). This is usually attributed to aluminum and iron phosphates which have a minimum solubility near this pH (Ku, 1975). The adsorption of phosphate decreases as the pH is increased and phosphate that may have been originally adsorbed is released from the solid phase in the sediment (Macpherson, 1958; Bailer, 1968). The pH rise and subsequent release of phosphate can be caused by algal blooms, temperature increases, and changes in the redox potential (Ku, 1975; Morgan, 1964).

Finally, temperature has a marked effect on both the rate of adsorption of phosphorus and the equilibria existing between sediment and interstitial water. Ku (1975) noted the rate of adsorption to decrease with increasing temperatures while Fanning (1971) observed a four-fold increase in phosphate in the interstitial water of marine sediments when temperatures increased from 3°C to 25°C. The cause for a shift in equilibria can be related to the chemical equilibrium existing between the solid and dissolved phases of aluminum and iron phosphates (Stumm, 1970a). This yields more phosphate in solution. Also, the rate of bacterial metabolism increases as temperature is increased, tending to lower the redox potential and release more phosphate.

Within a shallow eutrophic lake, the sediment acts as a sink during the colder winter months and adsorbs or retains phosphorus. As temperatures increase during the summer, the pH increases near the sediment-water interface and the Eh decreases. All three factors allow phosphate to be released back into the interstitial water where it can then be transported back into the overlying water.

Adsorption and Release of Phosphorus

Along with the previously mentioned controls on adsorption and release is the actual adsorption capacity of the sediment itself. Most studies have shown that the adsorption of phosphate occurs on the fine grained clays, on aluminum and iron hydroxometal complexes, and on some organic compounds (Ku, 1975); Tofflemire, 1973; Shukla, 1971; Williams, 1971). With a constant pH, Eh, and temperature, adsorption appears to follow Langmuir's monolayer adsorption isotherm (Ku, 1975; Tofflemire, 1973; Woodruff, 1965).

The capacity of each soil and lake sediment is different mainly due to the amount of amorphous Al and Fe, the amount and type of fine grained clays, and time of exposure to phosphate. *Soils range in adsorption capacity* from .017 to 17 mg P/gm soil (Tofflemire, 1973), while lake sediments have a range of .1 to 9 mg/gm dry sediment (Ku, 1975; Shukla, 1971; Williams, 1971). The adsorption capacity in most soils and sediments is rarely reached and, if left for six months, will again possess about the same adsorption capacity they originally had due to mineralization of the phosphate (Tofflemire, 1973).

The rate at which the fine grained sediments adsorb phosphate is initially rapid (3-14 days), followed by a slower rate (Ku, 1975; Tofflemire, 1973; Woodruff, 1965). Ionic phosphate in the interstitial water is initially rapidly adsorbed onto positively charged sites on the surface of clays or aluminum-iron complexes. The slower step involves diffusion into the complex, mineralization of the aluminum-iron complexes into $AlPO_4$ or $FePO_4$, and substitution of PO_4 for Al or Si in the clay minerals (Ku, 1975; Stumm, 1970a).

Release of phosphate from the sediment is usually attributed to the high PO_4^{-3} concentration in the interstitial water. Due to biochemical breakdown or organic -P compounds, temperature increases, pH changes, lowering redox potentials, and increased ionic strength, some of the PO_4^{-3} that was attached to organic and inorganic particles is desorbed or released into the interstitial water. Gahler (1969) and Feng (unpublished paper) indicate that mixing or agitation of the sediment due to wind action will cause the interstitial PO_4^{-3} near the sediment-water interface to be released into the lake water. This is especially true in shallow lakes. The compaction of the sediment under loading of overlying sediments will decrease the porosity of the sediment and may also force some of the interstitial water out of the sediment and into the lake water (Moore, 1973). Most researchers believe that flux of PO_4^{-3} out of the sediment due to the concentration gradient between lake water and interstitial water is the main mechanism for release.

Studies of desorption of phosphate by soils and sediment all indicate a certain percentage of the originally adsorbed phosphate can be released. Aerobic samples having low temperature and pH desorbed the least phosphate (3 to 10 percent), while aerobic samples of high temperatures and pH all desorbed much more phosphate (20 to 80 percent) (Tofflemire, 1973; Ku, 1975; McKee, 1970). About 80-90 percent of the extractable phosphorus was orthophosphate (Ku, 1975) and most(67 percent) of this was released from the iron and aluminum complexes in the sediment (Shukla, 1971; Williams, 1971; Ku, 1975).

A more in-depth examination of the release of phosphate from lake sediments will follow in Chapter III. However, the discussion thus far established that phosphate is incorporated into the sediment and can subsequently be released back into the lake water.

In order to understand and possibly control the recycling of phosphate, it is necessary to examine the chemistry of the sediment, with respect to phosphate.

Chemistry of Phosphate in Sediments

As previously mentioned, the major controls on the adsorption of phosphate are iron and aluminum hydroxometal gels, $AlPO_4$ and $FePO_4$, calcium phosphates, and clay minerals. The amounts of phosphate adsorbed or desorbed are governed by the pH, Eh, temperature, degree of mixing, biological activity, and the amounts of phosphate in the water and on the sediment. Mineral control by calcium phosphates, specifically hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, has been eliminated from this study since Lake Warner is undersaturated with respect to hydroxyapatite (Snow, 1973). Only in lakes with a high pH and much higher calcium concentrations could hydroxyapatite be considered a possible control of phosphate (Ponnamperuma, in press; Kramer, 1967). Even with the correct chemical environment, the rate at which hydroxyapatite forms is so slow that any major control of phosphate is unlikely (Snow, 1973; Sutherland, 1966). The only place where hydroxyapatite may control phosphate adsorption-desorption is in ocean sediments (Stumm, 1973). Statistically, phosphates in sediments is also not associated with Mn, Mg, or Na (Delfino, 1969). The mineral controls that will be looked at in more depth are therefore those of iron, aluminum, and clay.

Iron System. Numerous researchers have associated iron and phosphate together in sediments and attributed the adsorption and desorption of phosphate to the iron system (Delfino, 1969; Stumm, 1973; Allen, 1970; Williams, 1971; Upchurch, 1974; Ku, 1975; Wentz, 1969; Hsu, 1964). The concentration of free ferric iron in solution is governed by the pH and Eh of the system. Previous work (Schindler, 1967;

Snow, 1973) has shown that the concentration of free ferric iron is relatively small in lake water and will usually occur as FeOOH, $Fe(OH)_3$ or a hydrated complex of iron (Garrels, 1965; Stumm, 1970a). Ferrous iron may also be present in equilibrium with ferric iron at pH-Eh ranges normally found near the sediment-water interface (Sillen, 1967; Bostrom, 1967; Garrels, 1965; Stumm, 1970a). Dissolved oxygen and bacterial metabolism are usually the mediators of the redox potential which governs which iron species is present. Dissolved oxygen in surface waters tends to keep the Eh above 250 mv. (pH7). When the Eh drops below 240 mv., or when the dissolved oxygen is below 2 mg/l (at pH7), ferrous iron becomes predominant. As the amount of dissolved oxygen is increased, ferrous iron is oxidized to ferric iron. According to Stumm and Lee, (1962) the following kinetic expression describes the rate of oxidation of ferrous to ferric iron:

$$\frac{-d\ [Fe^{+2}]}{dt} = K\ [Fe^{+2}]\ [O_2]\ [OH]^2 \qquad (2)$$

The constant varies with redox potential and temperature. At pH7, a temperature of 25°C, and O_2 of 2 mg/l, the half-time of this reaction is 16 minutes (Stumm, 1970a). One can, therefore, assume that iron in the lake system will be either in a ferric iron complex or as ferrous iron depending on the pH and Eh of the specific level. Also, fairly rapid conversion from one species to another will occur if the pH-Eh balance is altered.

The direct precipitation of iron and phosphate is usually not considered to be a mechanism whereby phosphate is removed from lake water. Previous workers (Hutchison, 1957; Fair, 1968; Harter, 1968) have suggested a form of $FePO_4$, usually strengite ($FePO_4 \cdot 2H_2O$), which precipitates from water and settles to the bottom. Strengite is stable in oxidizing environments (Harter, 1968), but will dissolve in the sediment which has a low redox potential and/or a low pH , according to the following reaction (Patrick, 1973):

$$FePO_4 \cdot 2H_2O + 2H^+ + \bar{e} \rightleftarrows Fe^{+2} + H_2PO_4^{-1} + 2H_2O \qquad (3)$$

Marked dissolution of strengite occurred when the Eh was less than -100 mv. and pH was less than 6.5. Biological (bacterial) action appeared to speed up dissolution (Patrick, 1973). Therefore, unless the sediment is well oxygenated, phosphate will not be controlled by strengite. This is especially true in eutrophic lakes where the sediment Eh is well below -100 mv. and pH of the water rises due to algal blooming.

Within the sediment, other researchers have considered vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, to control the concentration of phosphorus (Patrick, 1973; Morris, 1967). Singer (1972) has shown that vivianite would not form at pH7, unless the Fe^{+2} was equal to 11 mg/l and PO_4 was equal to 20 mg/l. Both concentrations are much higher than normally occurring even in eutrophic sediments; hence, crystal formation of vivianite is eliminated from consideration (Stumm, 1970a).

The mechanism whereby iron and phosphate combine is currently believed to be surface adsorption onto hydroxide gels of iron. Sorption could occur onto FeO (OH) gels in aerobic environments and onto $Fe(OH)_2$ gels in anaerobic environment (Patrick, 1973). Formation of the iron gels can occur chemically through the formation of $Fe(OH)_3 \cdot nH_2O$ or biologically by iron depositing bacteria and actinomycetes (Shapiro, 1971). Equations 4, 5, and 6 have been proposed by Williams (1971), Allen (1970), and Stumm (1970a) respectively to account for the adsorption of phosphate onto anionic exchange sites of iron hydroxide gels:

$$\mathrm{Fe\ (OH)_3 \cdot nH_2O^{+}PO_4^{-3} \longrightarrow Fe(OH)_2\ PO_4} \tag{4}$$

$$\mathrm{Fe\ (OH)_n + H_2PO_4^{-1} \longrightarrow Fe(H_2PO_4)_n(OH)_{3-n}} \tag{5}$$

$$\mathrm{Fe\ (OH)_n + PO_4^{-3} \longrightarrow Fe(OH)_x(PO_4)_1{-x/3}} \tag{6}$$

Exchange of OH^{-1} or H_2O for PO_4^{-3} in the amorphous hydrated oxides of iron is favored over coprecipitation of $FePO_4$ within the iron gel (Ponnamperuma, in press; Ku, 1975; Shukla, 1971; Stumm, 1970a). Also, the ferric iron amorphous hydrated gel usually has 5 to 10 atoms of iron associates with 1 atom of phosphate (Williams, 1971). Therefore, in aerobic environments, the amorphous iron hydroxide gels can adsorb phosphate from the water. This may be the most dominant, non-biological mechanism for the binding up of phosphate and its deposition onto the bottom sediment.

Phosphate associated with ferric iron will be released when this particle is in an environment where the redox potential is below 200 mv. and the ferric iron is reduced to ferrous iron (Gahler, 1969; Allen, 1970). The breakdown of the ferric hydroxometal complex releases PO_4^{-3} back into the interstitial water (Williams, 1971). Formation of a ferrous hydroxometal gel would involve much higher concentrations of iron that are encountered in interstitial water (Singer, 1972). Along with a decrease in the redox potential, the breakdown of ferric iron complexes can be mediated by benthic bacteria. These bacteria can biochemically reduce $FePO_4$ which releases the PO_4^{-3} (Wood, 1965). Along with this reaction, H_2S is also generated in the anaerobic sediment. According to Equation 7, ferrous iron sulfide, FeS, which removes iron from solution, is the final end product (McKee, 1970; Gahler, 1969).

$$FePO_4 + H_2S \rightarrow FeS + H_2PO_4^{-1} \qquad (7)$$

This iron therefore cannot recombine with PO_4^{-3}. Along with changes in the redox potential are changes in the pH and ionic strength which occur in the sediment. Upchurch (1974) has noted desorption of PO_4^{-3} from Fe^{+3}- PO_4 complexes as ionic strength was increased. Interstitial water in the sediment has a much higher concentration of ions than the overlying water. Chloride and sulfate ions would displace PO_4^{-3} on the ferric iron complexes and release PO_4^{-3} back into the water. Also, as the pH gradually rises in the water due to algal blooming, ferric phosphate, which may still be present at the surface of the sediment (not reduced to Fe^{+2}), tends to dissolve. At pH5, $FePO_4$ will be in equilibrium with .1 mg/l of PO_4^{-3}, while at pH6, $FePO_4$ will be in equilibrium with 1 mg/l of PO_4^{-3} (Stumm, 1970a; Fair, 1968; Snow, 1973). An increase in pH also decreases the surface charge on the iron hydroxometal complex, thus causing a release of PO_4^{-3} (Ponnamperuma, in press). Hence, desorption of PO_4^{-3} from ferric iron hydroxometal complexes increases as pH increases, as Eh decreases, and as temperature increases (Ku, 1975; Morgan, 1974). Adsorption of PO_4^{-3} by ferric iron will, therefore, usually occur in the winter and spring and cause the PO_4^{-3} to be incorporated into the sediment. All of the conditions for desorption occur from the late spring to early fall in an eutrophic lake. Release of PO_4^{-3} back into the lake water is most likely to occur when algal blooms are in progress.

Aluminum System. Aluminum phosphate, $AlPO_4$, and its amorphous hydrated complexes act in a way similar to iron in adsorbing and reacting with PO_4^{-3}. Direct formation of $AlPO_4 \cdot 2H_2O$ (variscite) is usually not considered to occur in lake water (Stumm, 1970a). Rather, phosphate is attracted and adsorbed to aluminum polymers which exist in water below pH7. Al^{+3} ions exhibit OH^{-1} bridging and are coordinated with water molecules to form $Al(H_2O)_6^{+3}$ and $Al_2(OH)_2(H_2O)_8^{+4}$. The positive charge attracts PO_4^{-3} and PO_4^{-3} is adsorbed to complex (Hem, 1968; Hsu, 1968). The complex later tends to exchange

OH^- ions for PO_4^{-3} and form either vascarite,aluminum hydroxite-phosphate, $Al(OH)_x(PO_4)_{1-x/3}$ (Stumm, 1970a), or hydrated amorphous aluminum phosphate (Williams, 1971; Shukla, 1971; Ku, 1975). The latter form exhibits dissolution properties similar to $AlPO_4$ (Ku, 1975). At pH6, $AlPO_4$ is in equilibrium with 10 µg/l PO_4^{-3}-P, which is 100 times lower than the equilibrium level with respect to $FePO_4$. The equilibrium concentration of PO_4^{-3} increases with pH but the level of PO_4^{-3} in solution is still much lower: e.g., at pH7, the PO_4^{-3} concentration is 0.3mg/l (Stumm, 1970a).

The hydrated amorphous aluminum phosphate or aluminum hydroxide-phosphate is therefore considered to be one of the dominant adsorbers of phosphate in anaerobic, slightly acidic sediments (Ponnamperuma, in press; Hem, 1968; Shukla, 1971; Williams, 1971; Ku, 1975). Unlike ferric phosphate complexes, the aluminum complexes do not become reduced in the sediment (Ku, 1975). Phosphate that is released from the breakdown of ferric phosphate can be adsorbed by aluminum phosphate complexes and thus reduce the amount of free PO_4^{-3} which could diffuse back into the lake water.

Clay System. Small, colloidal clay minerals, especially kaolinite, have been also found to adsorb PO_4^{-3}. Kaolinite, $Al_4(Si_4O_{11})(OH)_8$, contains two layers of silica tetrahedra and two layers aluminum octahedra (Stumm, 1970a). At the edges of the lattice, kaolinite possesses positive charges which will attract PO_4^{-3} (Hemwall, 1957; Stumm, 1970a). Also, exchange of OH^- for PO_4^{-3} occurs at the edges (Ponnamperuma, in press; Stumm, 1970a). Aluminum hydroxy complexes are also found attached to kaolinite; phosphate will be adsorbed to the surface or exchanged for H_2O or OH^- in the aluminum complex (Lotse, 1973). Adsorption of PO_4^{-3} by kaolinite has been shown to follow the Langmuir isotherm with equilibrium established within 24 hours (Lotse, 1973). The maximum adsorption capacity was observed to be about 0.2mg P/mg sediment.

As with aluminum phosphate complexes, lowering the redox potential does not alter the adsorption capacity of kaolinite. However, an increase in pH will cause desorption (Kafkafi, 1967). In general, desorption occurs as either pH or ionic strength is increased (Lotse, 1973; Edzwald, 1974). In experiments by Lotse (1973), only about 16 to 24 percent of the total PO_4^{-3} adsorbed was desorbed. This would indicate that PO_4^{-3} was bound to the clay or had formed an aluminum-phosphate complex (Edzwald, 1974; Stumm, 1970a).

Adsorption to form $Al_4(Si_4O_{10})(OH)_8.PO_4$ can occur in rivers where fine grained sediments come in contact with PO_4^{-3}. This is especially true during the spring runoff when bank erosion and bottom scour increase the clay and phosphate concentration in the streams (Cahill, 1974; Carritt, 1954). Clays entering a lake tend to settle to the bottom, thus removing PO_4^{-3} from the lake water and increasing the PO_4^{-3}

stored in the sediment (Carritt, 1954). Release of some of the PO_4^{-3} will occur in the summer when the pH rises and ionic strength in the interstitial water increases. The ability of kaolinite to retain PO_4^{-3} is definitely enhanced in eutrophic lakes of soft water regions where pH within the sediment will probably be kept below 7 due to the low Eh and buffering capacity.

Methods to Control Phosphorus in Lakes

A wide assortment of methods have been employed to reverse eutrophication in lakes and many of them have been directed to controls of the concentration of phosphorus. There are three basic approaches: (1) decrease of the influent loading of phosphorus; (2) removal of phosphate-rich sediment, water, or plant matter in the lake; and (3) addition of suppressants to control the release of phosphate from the sediment. The various methods employed to decrease influent loading are: (1) elimination of phosphate-based detergents; (2) controlled use of phosphate fertilizer and better land use in the watershed; (3) removal of phosphate from the wastewater discharges; (4) diversion of wastewater away from a lake; (5) in-stream treatment to remove phosphate; and (6) dilution of high phosphate influent water with "clean" water.

Control methods tried within the lake itself are: (1) dredging and removal of the sediment; (2) harvesting of attached plants and algae; (3) drying and dessication of the sediment; (4) selective discharge of hypolimnic water; (5) mixing of the hypolimnion and epilimnion,usually with oxygen bubbled in the water; and (6) addition of suppressants to cover the sediment and retard release of phosphorus. With regard to the last method, physical sealers such as sand and polyethylene as well as chemical adsorbers such as fly ash, iron, aluminum and clays have been tried (Dunst, 1974).

In order to decrease the influent loading of phosphorus, many states have limited or eliminated the sale of phosphorus detergents. Grundy (1951) has estimated that 30 to 40 percent of phosphorus in waste water is derived from detergents. Tofflemire (1973) and Dillon (1975) have shown little phosphorus removal in sandy soils around lakes which receive septic tank effluent. Although some authors (Mitchell, 1971) do not believe that detergent control alone will significantly decrease phosphorus loading, it is generally accepted that limiting phosphate-based detergents near lakes is an inexpensive, first step method to lowering eutrophication within a lake's watershed (Dunst, 1974).

Better land management in the watershed of the lake can also lower the phosphate loading. These include controlled use of phosphate-based fertilizers, control of bank erosion, restrictive zoning of lake shore property and special vegetative covers to adsorb phosphate.

In many areas, significant reduction in loading has been achieved by improved waste water treatment including specific processes for the removal of phosphorus. Phosphate loading to the Great Lakes, especially Lake Michigan and Lake Erie, has been reduced by the compulsory addition of secondary sewage treatment. However, increased removals are being sought with tertiary treatment in the hopes of lowering the eutrophic state of the lakes (Lee, 1967, 1972). Phosphate loading is also being decreased in Lake Leman between Switzerland and France, through better wastewater treatment, as are many other smaller lakes in the United States and Europe (Dunst, 1974). The well documented Shagawa Lake project (Malueg, 1973; Brice, 1969; Larsen, unpublished paper) has shown that secondary treatment of wastewater will not significantly reduce the algal blooms. However, tertiary treatment, using lime for phosphorus removal as well as ion exchange and activated carbon, will reduce the loading and lake phosphorus to the point where algal blooms will be minimal, if not eliminated.

Diversion of phosphate laden water from a lake offers another possible means of control. Edmonson (1970) has documented the decrease in algal blooms due to diversion of waste water from Lake Washington. Similar diversions have been reasonably successful for Kegonsa and Waubesa lakes in Wisconsin (Dunst, 1974). However, Lake Sammamish in Washington has not shown significant lowering of algal populations or phosphorus even though waste water discharges have been decreased. Release of phosphorus from the sediment is indicated as the source of phosphorus in the lake water (Dunst, 1974). Diversion of natural streams with high amounts of phosphorus has also been suggested. For example, Greeson (1972) recommends diversion of four small streams which flow into Lake Oneida, New York. Although this would cut the flow by 28 percent, it would reduce the phosphorus loading by 58 percent. Diversion, by itself, is not apt to result in rapid or extensive recovery of eutrophic lakes due to the release of phosphorus from the bottom sediments (Welch, 1969). Other methods must also be employed to suppress sediment release.

Two other methods have also been suggested to lower the loading. One method involves in-stream treatment, using aluminum, iron, calcium ions or clay, zeolites, or fly ash to precipitate or adsorb phosphate from the river water. This could possibly be done for streams where there is no point source of phosphate. Alternatively, dilution or flushing of the lake with "clean" water has been suggested. Here, the disadvantage is that a lower concentration of phosphate in the lake water may cause more release of phosphate from the sediment (Dunst, 1974). Both of the above methods would require a long time period for significant improvements to be noted.

The most common method of controlling phosphate within a lake is dredging. One technique involves draining, drying and finally bulldozing to remove the sediment at a cost of \$.70 to \$.90 per cubic yard (D.N.R., 1970). In another dredging technique, a cutterhead dredge is used to hydraulically remove the sediment as a slurry. Costs for this method average \$1.25 per cubic yard, excluding the cost of disposal of the slurry (D.N.R., 1970). The slurry may be disposed of by using a separate settling pond and treating the water with alum to reduce the phosphate content of the returning water (Bengtsson, 1971).

To illustrate the costs of dredging, removal of three feet of sediment from Warner Lake would cost about \$375,000. Even with sediment removal, it may still be possible for the deeper sediment to release significant amounts of phosphate into the lake water.

Instead of removing the sediment, it has been suggested that draining the lake and drying of sediment would eliminate release. Exposure and desiccation would oxidize the sediment, fixing phosphate to iron and thus reduce the available phosphorus in the sediment (Syers,1973). However, the later reduction of Fe^{+3} to Fe^{+2} and release of the fixed phosphate still remains a problem.

The removal of attached plants and algae has also been tried as a method to lower lake and sediment phosphate levels. Biotic harvesting of attached plants (macrophytes) does remove phosphate from the system but the process is costly, slow, and must be repeated a number of times (Dunst, 1974). Filtration or skimming of algae has been suggested along with removal of trash fish but the efficiency is low and the economics of these methods are prohibitive.

Other methods of in-lake treatment are concerned with lowering hypolimnetic phosphorus. Mixing hypolimnetic water (high in PO_4^{-3}, low in O_2) with the epilimnion has been tried, usually by bubbling air into the lake near the bottom. This method tends to oxidize ferrous iron which can then adsorb phosphate. It also can keep the sediment-water interface oxidizing, thereby lowering the release of phosphate. This method was used in Beloye Lake in U.S.S.R. (Dunst, 1974). Another way to reduce the high phosphate and low dissolved oxygen concentration in the hypolimnion is to selectively discharge the lower waters in a lake (Dunst, 1974). This could most easily be done in a man-made lake where different depths could be tapped at the dam.

The method which appears to be the least costly and perhaps the most effective for in-lake treatment is the addition of physical or chemical suppressants or barriers at the sediment-water interface to reduce or eliminate phosphorus release from the sediment. Lining of the bottom of small ponds has been tried, using polyethylene and plastic; thick layers of sand over the bottom have also been used to seal the phosphate into the sediment (Hynes, 1967, 1970). The costs of such methods have restricted their use to only the smallest lakes.

A number of unusual adsorbers of phosphate have been added to lakes to suppress release. Fly ash has been tried with varying degrees of success in some lakes (Anon, 1972). Other methods which have been suggested are anionic exchange resins, polyelectrolytes (added as Purifloc C-31 to two ponds in Indiana), zeolites, powdered cement, slag and peat ash (U.S.S.R.) and zyrconyl chloride (Dunst, 1974; Gahler, in press). All of the above should remove phosphate from lake water and may adsorb phosphate as it is released from the sediment. Treatment with lime is usually excluded because the calcium phosphate thus formed will subsequently dissolve at the pH usually encountered in lakes. Lime treatment was tried in Pas du Riot, France. While algae and taste problems were reduced, the pH of the lake was elevated to 10 (Dunst, 1974).

Most of the phosphate suppression work has been directed toward the use of iron, aluminum or clay. In direct field application, the addition of aluminum, mainly as alum, has been the most common phosphate adsorber. The addition of clay, as bentonite and/or kaolinite, has been added to the Grebiner See in Germany and a few lakes in Sweden (Dunst, 1974). Success with clay addition was enhanced by simultaneous addition of alum. The addition of iron, as $FeCl_3$, has been tried in one lake in the United States, in the Reither See, Austria, and in the Wahnbach Reservoir, Germany (Dunst, 1974). Phosphate release was not substantially reduced in the summer bloom period.

Aluminum could be added as activated alumina (Neufield, 1969) and as sodium aluminate. The Twin Lakes, Ohio and Long Lake, in Wisconsin had a combination of alum and sodium aluminate added to suppress phosphate release (Dunst, 1974). In Cline's Pond, Oregon, sodium aluminate and zirconyl chloride were added (Gahler, in press). The aluminate appeared to reduce phosphate release about as well as alum, without reducing the pH and alkalinity, as is common with the addition of alum.

Additions of alum have been tried on Lake of the Four Seasons, Indiana; Powder Horn Lake, Minnesota; and Horseshoe, Pickerel, and Snake Lakes in Wisconsin (Dunst, 1974). Browman (1973), Peterson (1972), and Wildung and Schmidt have all shown that adsorption of phosphate can be achieved by alum additions; however, the layer formed is susceptible to scour and resuspension. The dosage and application rates varied between 7 to 20 milligrams of alum to a liter of lake water and coverage of the sediment ranged from 20 to 100 mg/m^2 of alum. Tests have also been done in other countries on the Langsjon and Sodra Horken in Sweden, the Uttersler Mose in Denmark, the Mytajarvi in Finland, and a part of the Welland Canal in Canada. All but one of the above lakes showed marked (60 to 90 percent) reduction in phosphate release (Dunst, 1974).

SUMMARY

The preceding review of the literature on lake eutrophication has been concerned with controlling phos*phorus and thereby controlling nuisance algal blooms and* the other problems associated with eutrophication. Phosphorus, usually as phosphate, is considered to be the limiting nutrient and its control in lakes will subsequently control algal blooms. The mechanisms which lower the concentration of phosphate in lakes are: (1) a decrease in the influent concentration of PO_4^{-3}; (2) the adsorption and retention of PO_4^{-3} onto iron and aluminum amorphous hydroxide complexes; (3) the adsorption of PO_4^{-3} onto clay minerals; and (4) the uptake of PO_4^{-3} by algae. Increases in the PO_4^{-3} concentration in lakes are governed by: (1) an increase in the influent concentration, and (2) release of interstitial PO_4^{-3} back into the lake water due to pH, Eh, and temperature changes in the sediment, bacterial decomposition of algae, breakdown of ferric iron complexes, and desorption of some PO_4^{-3} from aluminum complexes and clay.

CHAPTER III

MATHEMATICAL MODELS APPLIED TO LAKE EUTROPHICATION

Introduction

There are numerous citations to mathematical models describing the eutrophication process with particular emphasis on the phosphorus budget. These models range from strictly empirical equations relating phosphate loading to algal growth to the more sophisticated descriptions of reaction rates in control volumes. To determine the model best describing the fate of phosphorus in a lake system, it is necessary to account for: (1) influent loading of phosphorus; (2) phosphorus removed to the bottom due to sedimentation; (3) phosphorus released from the sediment; and (4) phosphorus remaining in the lake water. Also to be included in the modeling process are the volume of the lake, area of the sediment surface and the hydraulic detention time.

The objective of modeling is often to predict the time required for a specific lake to reach a desired concentration of phosphorus, given specific parameters of influent loading, detention time and rates of release and sedimentation. In other models the objective is limited to determining the results of a specific loading on the algal population.

Sedimentation Models

The degree of sophistication of models proposed for predicting the phosphate level in lakes depends upon the configuration of the reactor selected and the extent of accountability for phosphate reactions within the lake. Biffi (1963) assumed a constant input of a nutrient with no chemical or physical reactions in a completely mixed system as given by Equation 8:

$$V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L \tag{8}$$

or

$$P_{L_t} = P_o - (P_o - P_{L_o}) e^{-t/\bar{T}}$$

where:

V = Volume of lake (L^3)

Q_o = Flow in and out of lake (L^3T^{-1})

P_o = Concentration of PO_4^{-3} -P into lake (ML^{-3})

P_L = Concentration of PO_4^{-3} -P leaving lake (ML^{-3})

P_{L_t} = Concentration of PO_4^{-3} -P at time = t (ML^{-3})

P_{L_o} = Initial PO_4^{-3}-P concentration in lake at t = 0 (ML^{-3})

t = Time (T)

$\bar{T}$ = Detention time = V/Q_o (T)

Biffi's model is then used to find the half-life or time it would take for a lake to reach $P_L = 1/2\ P_{L_o}$, if $P_o = 0$ at $t = 0$. Thus:

$$P_{L_t} = P_{L_o}\ e^{-t/\bar{T}} \tag{9}$$

This model is only applicable to dilution of a non-reactive substance and therefore cannot be applied to a phosphorus budget. The same basic model was used by Sonzogni (1974) to predict the decrease in phosphorus levels in Lake Kegonsa after wastewater diversion. As a result, poor correlation was obtained between the model and field results in which a phosphate decrease was observed with time.

Piontelli (1964) proposed the following lake model which assumed a constant fraction of the influent P (P_o) to be removed (sedimented) in a completely mixed system:

$$V\ \frac{dP_L}{dt} = Q_o\ P_o - r\ Q_o\ P_o - Q_o\ P_L \tag{10}$$

At steady state, Equation 10 reduces to:

$$P_L = (1-r)\ P_o \tag{11}$$

Where:

r = sedimentation coefficient

According to this model, the fraction of incoming phosphate undergoing sedimentation (r) is constant and thus independent of the concentration (P_L) in the lake water itself. The unsteady state model describing the response of a step change in P_O resembles that obtained by Biffi and is given here as Equation 12.

$$P_{L_t} = P_o \ (1-r) \ (1-e^{-t/\bar{T}}) + P_{L_o} \ e^{-t/\bar{T}} \tag{12}$$

This model was used to predict the time it would take to decrease the phosphate level in a lake (P_L) if low phosphate water (P_o) was introduced.

Vollenweider (1968, 1969, 1974) has proposed numerous models of varying complexity. The simplest model, given in Equation 13, assumes that removal (sedimentation) of a nutrient is a function of the lake water concentration.

$$V \frac{dP_L}{dt} = Q_o \ P_o - Q_o \ P_L - KP_L \ V \tag{13}$$

or, at steady state:

$$P_L = \frac{Po}{1 + K \ \bar{T}} \tag{14}$$

The constant K is a sedimentation rate for a first order reaction in a completely mixed system. At steady state, the value of K can be found from:

$$K = \frac{P_O - P_L}{\bar{T}\ P_L} \qquad (15)$$

Once K is determined, the steady state model to predict the response of lake phosphate concentrations to changes in influent (P_O) concentrations is found by integrating Equation 13 between P_{L_O} at t = 0 and P_L at t = t:

$$P_L = \frac{P_O}{1+K\bar{T}} \left[1 - e^{-(t/\bar{T}) + Kt} \right] + P_{L_O}\ e^{-\left[(t/\bar{T})+Kt\right]} \qquad (16)$$

This model, as well as Piontelli's, does not attempt to include any flux (N, in units of $ML^{-2}\ T^{-1}$) of phosphate <u>from</u> the sediment to the lake water when the equilibrium condition is changed. The flux of phosphate <u>into</u> the sediment can be derived from Equation 13 at steady state:

$$P_L = \frac{\frac{Qo}{A}\ P_O}{KZ+\frac{Qo}{A}} = \frac{N}{KZ + \frac{Qo}{A}} \qquad (17)$$

Where A is the area of the lake (L^2), Z is depth (L), and A Z is equal to the volume (V) of the lake. The flux (N) is, in actuality, a surface loading parameter. The constant K is really an apparent sedimentation coefficient since it includes sedimented phosphate less phosphate released from the sediment.

The models derived by Vollenweider (1968, 1969, 1974) have been modified by Welch (1973), Lorenzen (1973), and Emery (1973) to account for incomplete mixing of stratified lakes with an emphasis on surface or influent loading of phosphorus as related to eutrophic state. Emery (1973) has tried to model Lake Sammamish, Washington using Equation 13 proposed by Vollenweider. While phosphorus loading was reduced by 40 per cent, no substantial recovery has been observed in four years. However, Vollenweider's model predicted approach to near equilibrium conditions in 3.3 years. Release from the sediment was considered to be responsible for the large discrepancy. Larsen (unpublished paper) has also tried to use Vollenweider's model to predict the decrease in phosphorus level in Shagawa Lake, Minnesota. After initiating tertiary treatment (to decrease phosphorus loading), the model predicted near equilibrium conditions should be reached in two years. However, after treatment was installed, the output loading of phosphate from the lake was observed to be higher than the input loading and phosphate concentrations in the lake increased from 30μg/l to 80μg/l (total P). Here, again, release from the sediment was indicated as the source of the phosphate in the lake water.

Similar work of Larsen (unpublished paper) and Malueg (unpublished paper) has relied on the empirical model of Vollenweider (1974) which relates phosphorus loading to the mean depth divided by hydraulic residence time as shown in Figure 1. Diagonal lines on the graph separate oligotrophic

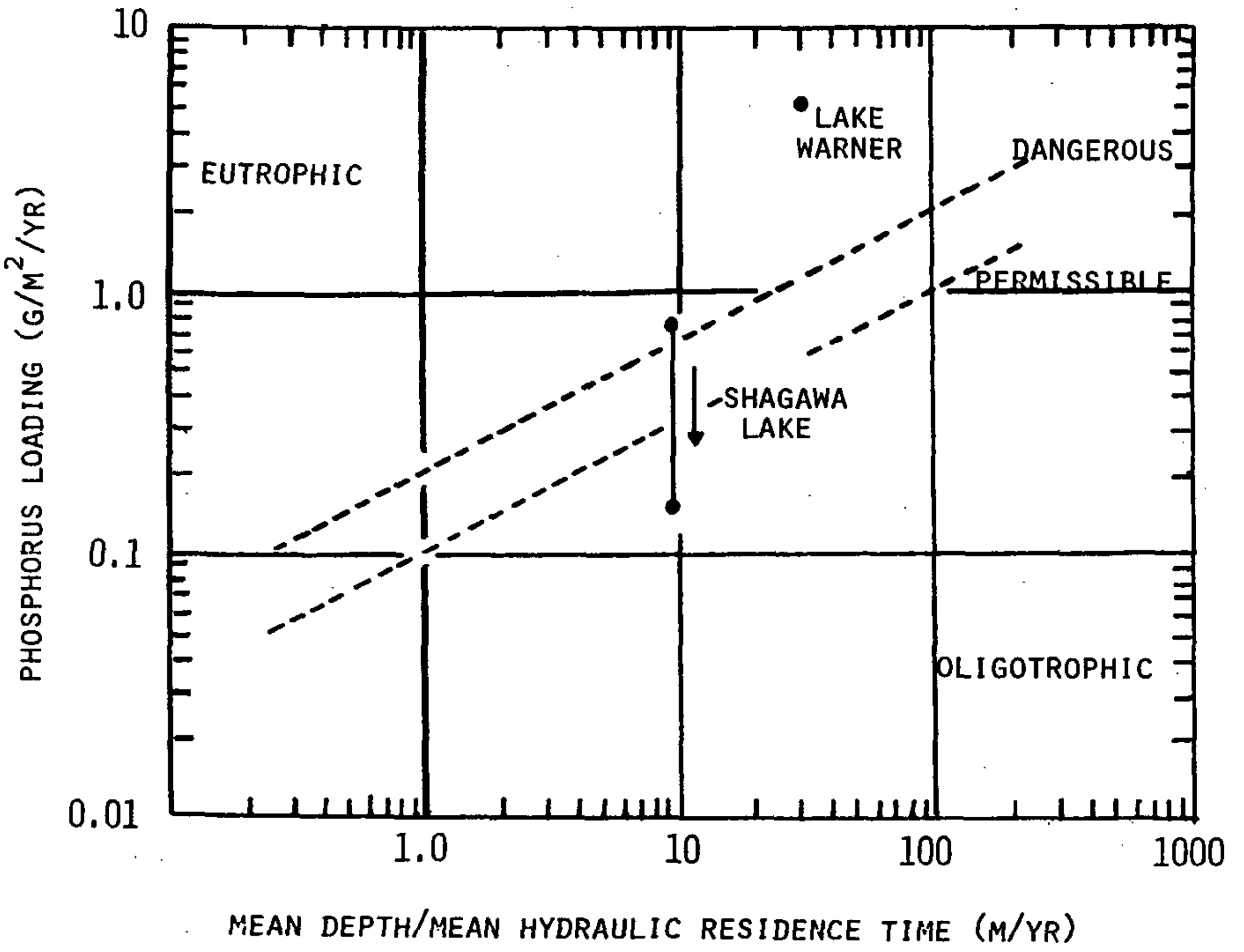

Figure 1. Phosphorus loading and depth/detention time as related to eutrophic state. (Vollenweider, 1974)

loadings and eutrophic loadings. The lines are approximate and based on the conditions of a number of lakes as determined by Vollenweider (1974). The inference given is that the eutrophic state obtainable in a lake can be predicted by knowledge of the phosphorus loading. Unfortunately, the time required to change the eutrophic state is not given by this relationship. Nevertheless, the relationships given by Figure 1 indicate the importance of influent loading on the eutrophic state of a lake. Low loadings will normally insure oligotrophic conditions while critically high loadings will cause eutrophic conditions to prevail. In this research, data for Lake Warner (see Chapters 4 and 5) indicates an approximate loading of 5.3 gm/m^2/year. With average depth equal to 1.6 meters and hydraulic detention time about .055 years, the ordinant value of Figure 1 is 29. This currently places Lake Warner far above the "Dangerous" level and in the eutrophic zone.

In order to estimate current and future loading parameters more carefully, Dillon (1975), Shannon (1972), and Hetling (1974) have outlined all of the pertinent sources of phosphorus within the watershed of a lake. While these authors rely heavily on loading estimates, a fairly reasonable value for overall loading can be obtained using their methods. After loading values are obtained, the relationship given by Vollenweider in Figure 1 can be used to determine the current state of the lake and future reductions in loading required to obtain a less eutrophic lake.

The direct implication of the loading factor is that for a specific lake there will eventually be a specific equilibrium concentration of phosphorus within the lake water itself. The work of Bartsch (1975) has related the concentration of phosphorus in a lake to the algal population (measured as chlorophyll a) and to the turbidity (measured by Secchi disc readings). As shown in Table 2, his work placed limits on the total phosphorus in lake water based upon the lake's eutrophic state. A similar approach was used by Shannon (1972) to determine a Trophic State Index. Statistical analysis showed a strong correlation between loading of phosphorus and the basic eutrophic parameters of productivity (including algae) and turbidity. Shannon's results are also summarized in Table 2.

The work of both Shannon (1972) and Bartsch (1975) strongly support the premise that lake phosphorus levels relate to algal concentrations and eutrophic state; these, in turn, are related to the influent P loading. However, neither approach provides a means of determining the time required to achieve a lower eutrophic state upon reduction of influent loadings. The lower eutrophic state will, in most cases, be monitored by the amount of algae present.

Sedimentation and Release Model

All of the models presented thus far have included a

TABLE 2

RELATIONSHIPS OF TROPHIC PARAMETERS WITH TROPHIC STATE

Bartsch's Trophic State

Trophic State	Chlorophyll a ug/l	Total P ug/l	Secchi depth - ft.
Oligotrophic	7	10	12
Mesotrophic	12	20	6
Eutrophic	3-200	10-150	6

Shannon's Trophic State Index

Trophic State	Trophic State Index	Loading gm $P/_{M}3$/year
Oligotrophic	1 - 2.5	.02 - .06
Mesotrophic	2.5 - 4	.06 - .10
Eutrophic	4 - 16	.09 - .28

single rate constant to describe a loss of phosphorus to the sediment rather than two independent constants describing both sedimentation and release. Lorenzen (1973) has extended the mass balance proposed by Vollenweider (in Equation 13) to include both the sedimentation and release rates. Equation 18 is the general mass balance proposed and Equation 19 is the integrated solution.

$$V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L - K_S^* A P_L + K_R^* A P_S \tag{18}$$

$$P_{L_t} = \frac{Q_o P_o + K_R^* A P_S}{K_S^* A + Q_o} \left[1 - e^{-(Q_o + K_S^* A/V)t} \right] + P_o e^{-\left[(Q_o + K_S^* A/V)\, t\right]} \tag{19}$$

Where: K_R^* = release coefficient

K_S^* = sedimentation coefficient

P_S = total phosphorus in sediment

The sedimentation rate is considered first order with respect to the concentration of P in the lake water. The release rate of P is also first order but with respect to the concentration of P in the sediment (P_S). The release rate ($K_R^* P_S$) is independent of the concentration of P in the lake water (P_L). There is neither provision for a mechanism to slow this release as P_S decreases nor to allow a fraction of the P_S to remain (non-reactive) in the sediment. According to Lorenzen's model, all of the P in the sediment would eventually be released irregardless of the level of P in the lake water (P_L). It may also be noted that because the release rate remains constant, the only rate constant affecting the non-steady state behavior of Equation 19 is K_S^*.

Lorenzen (1973) attempted to predict how P_S would change over time by matrix analysis of a coupled set of equations involving both P_L and P_S. For P_S, the following mass balance was applied to the volume of sediment, V_S:

$$V_S \frac{dP_S}{dt} = K_S^* P_L A - K_R^* P_S A \tag{20}$$

Integrating Equation 20 from $P_S = P_{S_o}$ at $t = 0$ to $P_S = P_S$ at $t = t$ yields:

$$P_{S_t} = \frac{K_S^* P_L}{K_R^*} \left[1 - e^{-(K_R^* A/V_S)t} \right] + P_{S_o} e^{-(K_R^* A/V_S)t} \tag{21}$$

From Equation 21, it can be seen that at equilibrium:

$$P_S = \frac{K_S^* P_L}{K_R^*} \tag{22}$$

or

$$K_R^* P_S = K_S^* P_L \tag{23}$$

This indicates that the rate of sedimentation becomes equal to the rate of release at equilibrium. Returning to Equation 19 proposed by Lorenzen, at steady-state with the rate of sedimentation equal to the rate of release, it follows that:

$$Q_o P_o = Q_o P_L \qquad (24)$$

or

$$P_o = P_L \qquad (25)$$

That is, at equilibrium, the influent P to the lake is the same as the concentration of P in the lake. It should also be noted that the mass release rate, $K_R^* AP_S$, is assumed to take place throughout the sediment volume and that interstitial phosphorus can immediately diffuse into the lake water irregardless of the phosphorus concentration in the lake water.

Proposed Model

The mass balance equation used by Lorenzen (1973) was also used in this research in an attempt to quantify all of the major inputs and outputs of phosphorus in a lake system. Equation 26 describes the most general form of a mass balance for lake phosphorus.

$$V \frac{dP_L}{dt} = Q_o\ P_o - Q_o\ P_L \pm \text{ Rates of Reaction} \cdot V \qquad (26)$$

The reactions within the system are determined by biological, chemical, and physical phenomena which are responsible for:

(1) release of phosphorus from the sediment by diffusion from interstitial water

(2) removal of phosphorus from the lake water by sedimentation

and

(3) retainment of phosphorus in the sediment by adsorption.

The sum total effect of these phosphorus exchange mechanisms is to govern the concentration of phosphorus in the lake water for any given input of phosphorus.

Release of Phosphorus. The majority (65-90 percent) of the released phosphorus is in the form of PO_4^{-3}. Of this fraction, 65 to 85 percent originates from the aluminum and iron complexes in the sediment (Wildung; 1973; Ku, 1975; Shukla, 1971; Williams, 1970, 1971); The remainder probably originates from bacterial decomposition of organically bound phosphorus and desorption from clay minerals (Chen, 1973; Lotse, 1973). Released inorganic phosphorus is mainly responsible for the seasonal changes of phosphate in eutrophic lakes (Wildung, 1973; Welch, 1973).

In Chapter II it was shown that the amount released from the solid phase into the interstitial water is governed by temperature, pH, Eh, and amount of phosphorus in the solid phase. An approximate equilibrium (~10:1) between the interstitial ortho phosphate concentration and the orthophosphate in the lake water has been observed (Snow, 1973). Some researchers (Welch, 1973; Lorenzen, 1973) have interpreted the release of P to be first-order with respect to the concentration of total phosphorus in the solid phase. However, other researchers have observed that release from the sediment is governed by the concentration gradient that exists between the phosphate in the interstitial water and that in the lake water above the sediment (Wildung, 1973; Kamp-Nielsen, 1974; Shih, 1969; Chen, 1973). Hence, the flux of phosphate out of the sediment depends directly on the concentration gradient (Wildung, 1973).

Mass transfer of phosphorus from the sediment interstitial water to the overlying water could be controlled by diffusion either within the interstitial water or across the water-sediment boundary (DiGiano, 1971). In the proposed model, the latter controlling mechanism is assumed such that:

$$N_P = K_1 \ (P_i - P_L) \tag{27}$$

where:

N_P = flux of P from the sediment $(M/T\ L^2)$

K_1 = mass transfer release coefficient (L/T)

P_i = interstitial P concentration (M/L^3)

P_L = lake P concentration (M/L^3)

The rate of release of phosphorus (R_r) into the lake water is therefore:

$$R_r = \frac{\varepsilon A}{V} \ K_1 (P_i - P_L) \tag{28}$$

where:

ε = porosity of the sediment

A = area of the sediment

V = volume of the lake

The interstitial phosphate concentration, P_i, is dependent upon the distribution of phosphorus between the sediment solid phase and the adjacent liquid phase. This equilibrium distribution represents a dynamic state of phosphate exchange. To determine P_i, the exchange zone within the sediment must be established.

Sedimentation of Phosphorus. The sedimentation of ionic and organically bound phosphorus has been shown in Chapter II to be controlled mainly by algal uptake, adsorption onto clays, and adsorption onto aluminum and iron hydroxometal complexes. The rate at which algae remove phosphate increases with increasing phosphate concentrations (Bartsch, 1975; Shannon, 1972). In addition, the adsorption of phosphate onto clays (Lotse, 1973), and aluminum and iron hydroxometal complexes increases with increasing phosphate concentrations (Ku, 1975). Sedimentation due to clays (Lotse, 1973) and the combined effects of algae and metal complexes (Vollenweider, 1968; Lorenzen, 1973; Welch, 1973; Chen, 1973) can be modeled by assuming a pseudo,first-order expression with respect to lake P concentrations, P_L.

Thus,

$$R_{sed} = K_2 P_L \tag{29}$$

where K_2 is a composite sedimentation constant representing a combination of physical, chemical, and biological effects. The constant K_2 will be assumed to remain the same throughout the year. This assumption can be justified by recognizing the dominance of algal removal during the warmer months with minor removal by the ferrous-ferric hydroxide system and of adsorption and exchange onto hydroxometal complexes and clay minerals during winter and spring when the larger inflows are accompanied by inorganic sediments.

Evaluation of Rate Constants. Evaluation of K_1 and K_2 would be impossible in an actual lake since both release and sedimentation are on-going simultaneous processes. However, by isolating a small volume of the lake and removing phosphorus from the overlying water, the release of phosphorus from the sediment will initially dominate over sedimentation thus enabling estimation of K_1. As phosphorus is released, the increased concentration of phosphorus in the overlying water will cause sedimentation to subsequently decrease the overlying P concentration. Eventually, an equilibrium should be attained such that the amount of phosphorus released is equal to the amount of phosphorus sedimented.

Isolation of a lake volume, V, provides for modeling of a completely mixed batch reactor as given by Equation 30.

$$V \frac{dP_L}{dt} = \text{Rate of release} \cdot V - \text{Rate of Sedimentation} \cdot V \tag{30}$$

or, substituting the appropriate rate terms already derived yields

$$V \frac{dP_L}{dt} = \frac{\varepsilon A}{V} K_1 (P_i - P_L) V - K_2 P_L V \tag{31}$$

For release of phosphorus from a heavily laden sediment to a fixed volume of overlying water, it is reasonable to assume that P_i remains relatively constant. Thus, Equation 31 can be integrated to provide a mathematical model for P_L as a function of time. More specifically, assuming the overlying water to contain a low concentration of phosphorus, P_{L_o} at t = 0 and reaching a concentration P_L at t = t yields

$$P_L = \frac{\frac{\varepsilon A}{V} K_1 P_i}{\frac{\varepsilon A}{V} K_1 + K_2} \left[1 - e^{-\left((\varepsilon A/V)\ K_1 + K_2 \right) t} \right]$$

$$+ P_{L_o} e^{-\left[(\varepsilon A/V)\ K_1 + K_2 \right] t} \qquad (32)$$

As $t \rightarrow \infty$, the equilibrium value of P_L is shown to be

$$P_L \text{ (equilibrium)} = \frac{\frac{\varepsilon A}{V} K_1 P_i}{\frac{\varepsilon A}{V} K_1 + K_2} \qquad (33)$$

To approximate K_1, it may be assumed that sedimentation can be neglected at low concentrations of phosphorus in the overlying water. Thus, for initial time t,

$$\frac{dP_L}{dt} = \frac{\varepsilon A}{V} K_1 (P_i - P_L) \qquad (34)$$

or

$$P_{L_t} = P_i - (P_i - P_{L_o})\, e^{-\left[\frac{\varepsilon A}{V} K_1\right] t} \qquad (35)$$

Knowing the physical constants for the system, namely ε, A, V and assuming P_i to remain constant, measurements of P_L as a function of time permits calculation of K_1. The value of K_2 can then be calculated from the equilibrium expression given by Equation 33.

Application of Model to Lake Systems. The rate constants, K_1 and K_2, which can be derived from the complete mix batch model can then be applied to either complete mix or plug flow reactors describing a continuous flow lake system. The lake models proposed are applicable to only shallow lakes which are not thermally stratified since vertical mixing is assumed. Secondly, all streams entering the lake must be monitored to determine flow rates and respective concentrations of phosphorus. The proposed lake models could not easily be applied to lakes with no influent streams (water table lakes) unless the flow and concentration of influent springs and ground water could be approximated.

For non-steady conditions, the following mass balance may be written for a complete-mix reactor having an inflow Q_o containing P_o concentration of phosphorus and in which both phosphorus release and sedimentation are significant:

$$V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L + \frac{\varepsilon A}{V} K_1 (P_i - P_L) V - K_2 P_L V \tag{36}$$

At this point it is important to note that the term P_i cannot be considered constant in a continuous flow system. Instead, as phosphorus is released from the interstitial water of the sediment, more phosphorus is released from the solid phase of the sediment to maintain chemical equilibrium. Necessarily then, the equilibrium relationship between the interstitial (P_i) and solid phase (P_S) phosphorus as given by

$$P_i = f \quad (P_S) \tag{37}$$

must be used simultaneously with Equation 36 to obtain a valid mathematical solution. The exact expression will require experimental data in order to determine the functional relationship of P_i with respect to P_S.

For short time periods with sediments of high phosphorus exchange capacity, the value of P_i will remain relatively constant. Under these conditions, Equation 36 can be easily used to show a pseudo-equilibrium value of lake phosphorus concentration (P_L) and the non-steady state approach to this value. Thus, setting

$$V \frac{dP_L}{dt} = 0 \tag{38}$$

in Equation 36 yields:

$$P_L \text{ (equilibrium)} = \frac{P_o + \frac{\varepsilon A}{V} K_1 P_i \bar{T}}{1 + \frac{\varepsilon A}{V} K_1 \bar{T} + K_2 \bar{T}} \tag{39}$$

Thus, with the assumption of P_i constant, the pseudo-equilibrium value of P_L should be dependent on the influent phosphorus concentration (P_o), the rates of sedimentation and release, the ratio of the interstitial area (εA) to the lake volume (V), and the hydraulic detention time. The rate of approach of the lake P concentration to this pseudo-equilibrium value is useful in prediction of the time required to lower the lake P concentration if either the influent concentration, P_o, or the phosphorus in the interstitial water, P_i, is reduced (with all other parameters assumed constant). Integration of Equation 36 from $P_L = P_{L_o}$ at $t = 0$ (when either P_o or P_i is reduced) to $P_L = P_L$ at $t = t$ yields

$$P_L = \frac{P_o + \frac{\varepsilon A}{V} K_1 P_i \bar{T}}{1 + \frac{\varepsilon A}{V} K_1 \bar{T} + K_2 \bar{T}} \left[1 - e^{-\left(\frac{1}{\bar{T}} + \frac{\varepsilon A}{V} K_1 + K_2\right) t} \right] + P_{L_o} e^{-\left(\frac{1}{\bar{T}} + \frac{\varepsilon A}{V} K_1 + K_2\right) t} \tag{40}$$

The value P_o could be lowered in many eutrophic lakes by providing phosphorus removal at wastewater treatment plants discharging to the lake and control of stormdrain inputs or surface runoff from residential and farming areas. Having defined the fixed parameters of Equation 40 for a given lake, the response of the lake as measured by a reduction in P_L can be predicted as a function of time.

In order to artificially reduce the interstitial concentration of phosphorus and thereby lower the driving force for the flux of phosphorus across the interface, it may be possible to "seal" the sediment by chemical additives. One such possibility is the use of kaolinite mixed with alum. The added aluminum will form hydrated hydroxometal complexes which, as previously mentioned, will adsorb phosphate released from the sediment. Kaolinite, with a lesser adsorption capacity, will also adsorb released phosphate. Kaolinite will, in addition, enable the aluminum floc to settle rapidly and remain on the bottom since the specific gravity of kaolinite is 2.6 and alum floc is only about 1.1 (Fair, 1968). In turn, the floc formed will entrain colloidal kaolinite causing more rapid settling. The presence of both the kaolinite and the aluminum complex at the interface has already been shown to adsorb appreciable amounts of sediment released phosphate. The net result will be a lower apparent value for the interstitial concentration and a resulting lower flux of phosphate from the sediment.

A similar modeling approach can be used for a plug flow lake system. Here, the mass balance becomes

$$V \frac{\partial P_Z}{\partial t} = Q_o P \Big|_{Z} - Q_o P \Big|_{Z+\Delta Z} + \frac{\varepsilon A}{V} K_1 \, (P_i - P_Z) \, A_Z \Delta Z - K_2 \, P_Z A_Z \Delta Z \tag{41}$$

where:

P_Z = P concentration at distance Z measured from inlet (ML^{-3})

$P_Z + \Delta Z$ = P concentration at distance $Z + \Delta Z$ measured from inlet (ML^{-3})

ΔZ = incremental distance between two points (L)

A_z = cross section area perpendicular to flow (L^2)

At steady state and rearranging terms, Equation 41 may be written as

$$\frac{dP_Z}{dZ} = \frac{1}{v} \left[\frac{\varepsilon A}{V} K_1 \left(P_i - P_Z \right) - K_2 \, P_Z \right] \tag{42}$$

where:

v = Velocity in the Z direction (Qo/A_z)

Again, the value of P_i will necessarily decrease over a long period of time. However, for a short time period with sediments having a high phosphorus binding capacity, Equation

42 may be integrated between $P_Z = P_O$ at $Z = 0$ (Z being distance downstream from influent) to $P_Z = P_Z$ when $Z = Z$ to yield a steady state expression for the plug flow lake system. Thus,

$$P_Z = \frac{\frac{\varepsilon A}{V} K_1 \; P_i}{\frac{\varepsilon A}{V} K_1 + K_2} \left[1 - e^{\frac{-Z}{v} \left(\frac{\varepsilon A}{V} K_1 + K_2 \right)} \right] + P_O e^{\frac{-Z}{v} \left(\frac{\varepsilon A}{V} K_1 + K_2 \right)} \tag{43}$$

Summary. The objective of modeling the lake water phosphorus concentration is to predict the time required for lake recovery. The application of the proposed model is restricted to shallow, unstratified lakes which currently receive a high phosphorus loading and are considered eutrophic. The physical and chemical characteristics required in modeling are flow (Q_O), influent concentration (P_O), lake bottom area (A), lake volume (V), porosity (ε) of the sediment, lake phosphorus concentration (P_{L_O}), interstitial phosphorus concentration (P_i), the sediment phosphorus concentration (P_S), and flow regime (complete mix or plug flow). These characteristics can be obtained from a lake survey. Experimentation is required to determine: (1) the release rate coefficient, K_1; (2) the sedimentation rate coefficient, K_2; (3) the equilibrium relationship between P_i and P_S; and (4) the effective interstitial concentration (P_i) resulting from chemical suppression of sediment phosphorus. The methodologies used in this research to determine the physical and chemical characteristics of Lake Warner and

CHAPTER IV

LIMNOLOGICAL SURVEY OF LAKE WARNER

Analytical Techniques

Physical. The physical parameters needed for this study are lake detention time (derived from lake depth, average and peak flows), rainfall, sediment porosity and specific gravity. Depth configuration of the lake was determined using a Heathkit Depth Meter. Determination of lake volume was then derived from the depth contour map using a Polar Planimeter. Measurements of flow through the lake, from which detention time could be calculated, were made at the dam. The dam is constructed of concrete and is straight crested. A stage recorder was used to determine the height of water flowing over the dam. Flow was determined using the equation,

$$Q = KBH^{3/2} \tag{44}$$

where: Q = flow (cfs)

B = width of dam (ft.)

H = height of flow over dam (ft.)

$K = 3.1$ (constant approximated by Higgins, personal communication)

Lake volume and average flow data were used to determine the hydraulic detention time of the lake.

Rainfall duration and intensity were also measured at the dam using a recording tipping-bucket rain gage. Correlation of rainfall and flow were used to determine the change in lake detention time during extreme rainfalls.

Sediment sampled for porosity (ε) and specific gravity were gathered using either an Eckman Dredge or a modified Type 217 Gravity Corer made by Benthos, Inc. The corer was operated using a davit and winch mounted in an 18 foot aluminum boat. Porosity was determined on an undisturbed core sample. Volume of the sample was determined by measuring the plastic core barrel width and depth. The sample was then weighed and air dried. The loss in weight was used to determine the volume of water in the pores of the sediment sample. This volume of water divided by the total volume (water plus sediment) is the porosity. Specific gravity was calculated using the weight and volume of the wet sediment sample as compared to the weight of an equal volume of water.

Chemical. Sample collection for chemical analysis of the sediment are described above. Water samples were collected in 300 ml glass bottles for surface samples and by use of a Kemmerer Water Sampler for subsurface samples. Samples taken for iron and total phosphate determination were acidified in the field.

Separation of interstitial water from the sediment was accomplished by centrifuging the sample for 30 minutes at 10,000 rpm in 250 ml polycarbonate bottles in a refrigerated centrifuge. Care was taken not to introduce air into the sample. This only separated the free, interstitial water from the sediment. Water bound to the sediment particles was not removed (Gaines, 1973). The supernatant was then analyzed for ortho and total phosphate as well as iron.

The following parameters were, in most cases, measured *in situ*:

1) pH
2) Redox Potential (Eh)
3) Dissolved Oxygen
4) Temperature

In order to obtain these measurements on lake water, a flow-through, Plexiglas sampling cell was constructed such that probes for each parameter could be inserted. A submersible, 12 volt D.C. pump was used to pass samples of water from different depths into this sampling cell for analysis. The entire unit, cell and instrumentation, was quite portable, thereby enabling convenient use in a boat. The pH and Eh (Redox Potential) of water and sediment samples were determined using an Orion Model 407 portable pH meter. The pH was determined using a Corning combination electrode while the Eh was determined using a one centimeter square platinum electrode and reference electrode. Dissolved oxygen and temperature of the water were analyzed using a YSI Portable Dissolved Oxygen meter.

Orthophosphate, measured as µg/l PO_4^{-3} -P, was determined using an ammonium molybdate and ascorbic acid complex and extracted with isobutanol (Snow, 1973; Sutherland, 1966). The exact procedure is given in Appendix A. Total phosphate samples were first digested in H_2SO_4 with potassium persulfate and then analyzed using the same procedure as ortho phosphate. This method was used on water as well as sediment samples (EPA, 1971). Values for sediment analysis are expressed in milligrams of phosphorus per gram of oven dried sediment. Total iron analyses were performed using a Perkin-Elmer Atomic Absorption Spectrometer on the acid (HNO_3) fixed samples (EPA, 1971).

Biological. Two methods were employed to approximate algal productivity. A Turner Model 111 Fluorometer was used to measure *in vivo* chlorophyll by fluorescence (EPA, 1971; Strickland, 1968; Lorenzen, 1966). Data gathered by Kuzminski and Fredette (1974) was used to relate fluorescence units to cells of *Anabaena sp*. per milliliter. The other method used was the determination of the total organic carbon in mg C/l. This was measured on a Model 915 Beckman Total Organic Carbon Analyzer. The determination of algal types was ascertained by microscopic identification.

Lake Description

<u>Physical Features</u>. Lake Warner (North Hadley Pond) is located in the Village of North Hadley, in Western Massachusetts. Construction of a dam at the western end in the early 1800's limnologically classifies this lake as a man-made river lake. The major tributary to Lake Warner is the Mill River which enters at the eastern end and drains 32.1 square miles (8313.8 hectares) (Jubinville, 1973). More than one-half of the drainage basin is located in undeveloped woodlands, while the rest is situated in suburban and agricultural lands in Amherst and North Hadley. The only other pertinent source of flow originates at the Amherst Primary Wastewater Treatment Plant during periods of bypassing.

The depth and configuration of Lake Warner is described in detail in Figure 2. Depth contours are based on 110 high frequency sonar soundings. The area, volume, and depth of the lake were determined to be 68 acres (27.5 ha), 352 acre-feet (4.35×10^5 m^3), and 5.15 ft (1.58 m) respectively. The maximum depths occur in the main channel of the old river which is located along the southern shore of the lake. Flow and rainfall measurements were taken at the dam (see Figure 2). Water quality and sediment characteristics were examined throughout the lake beginning at the entrance to the lake given by point C in Figure 2.

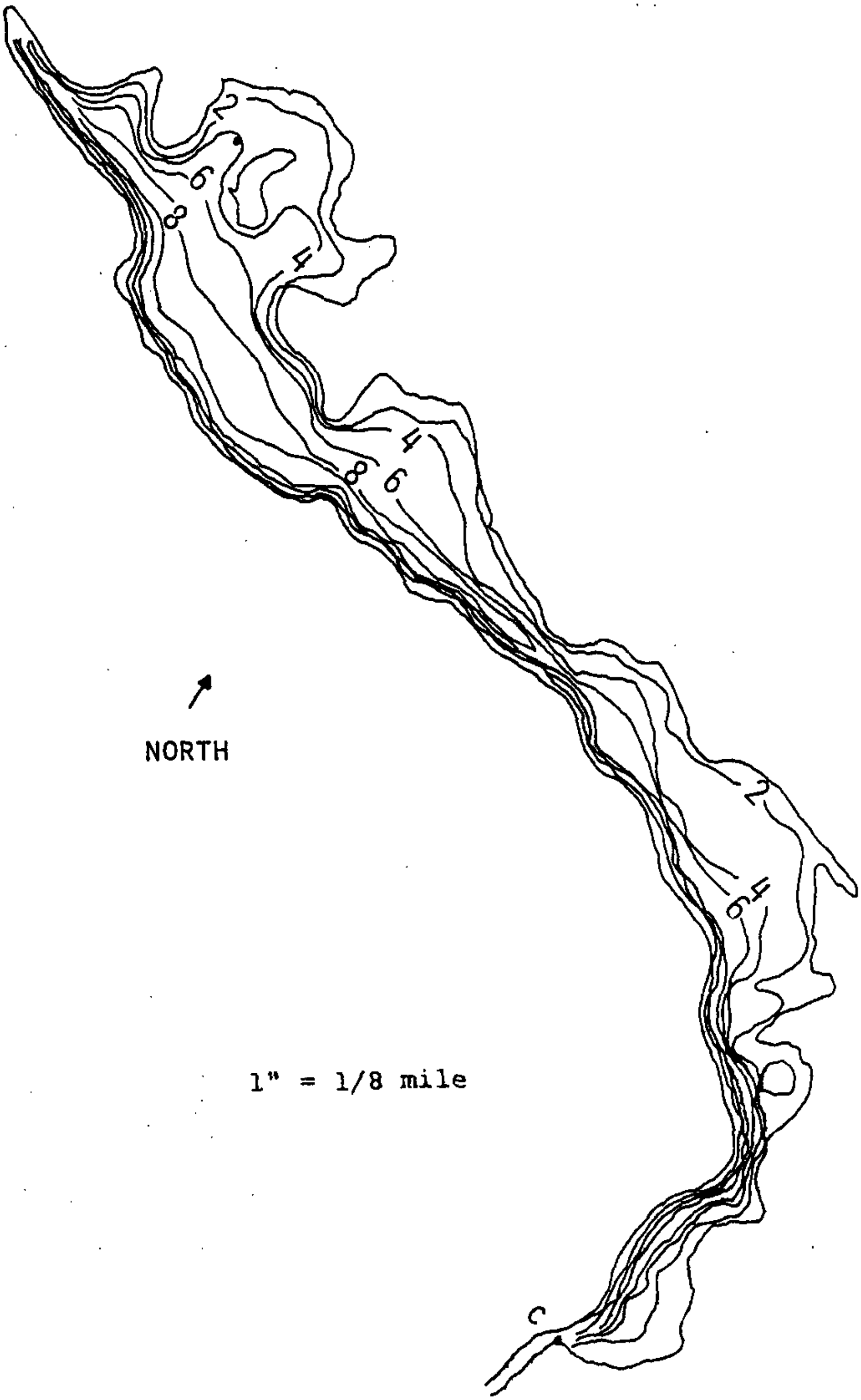

Figure 2. Depth (in feet) Contour Map of Lake Warner.

Lake Detention Time. Hydraulic detention time ($\bar{T}$) was determined using the lake volume and the derived flow rate (Q). Figure 3 shows the variation of flow and rainfall in Lake Warner during July and August, 1973. Base flow is estimated at 13 million gallons per day (50 x 10^6 l/day) with peak (24 hour average) flow being 50 million gallons per day (190 x 10^6 l/day). The detention time of water in the lake at normal flow is about 9 days and drops to about 2.25 days at the average peak flow. Significant changes in flow through the lake occurred when rainfall intensity was greater than 0.5 inches (1.25 cm) per day. The geomorphic shape and the detention time of ten days indicated this lake to be best described as a completely mixed reactor.

A more detailed comparison of rainfall versus flow is shown in Figure 4 for the period of August 2-4, 1973. Rainfall duration was approximately 12 hours and totaled 2.29 inches (5.8 cm). The time to reach the maximum outflow of the lake was approximately 15 hours. About 72 hours after the peak flow, the outflow from the lake was back to normal. Flow rates of 100 million gallons per day (378 x 10^6 l/day) or greater, effectively reduce the detention time of the lake to one day or less. The overall effect of this sporadic high flow is to wash out bloom proportions of algae and give the lake a relatively

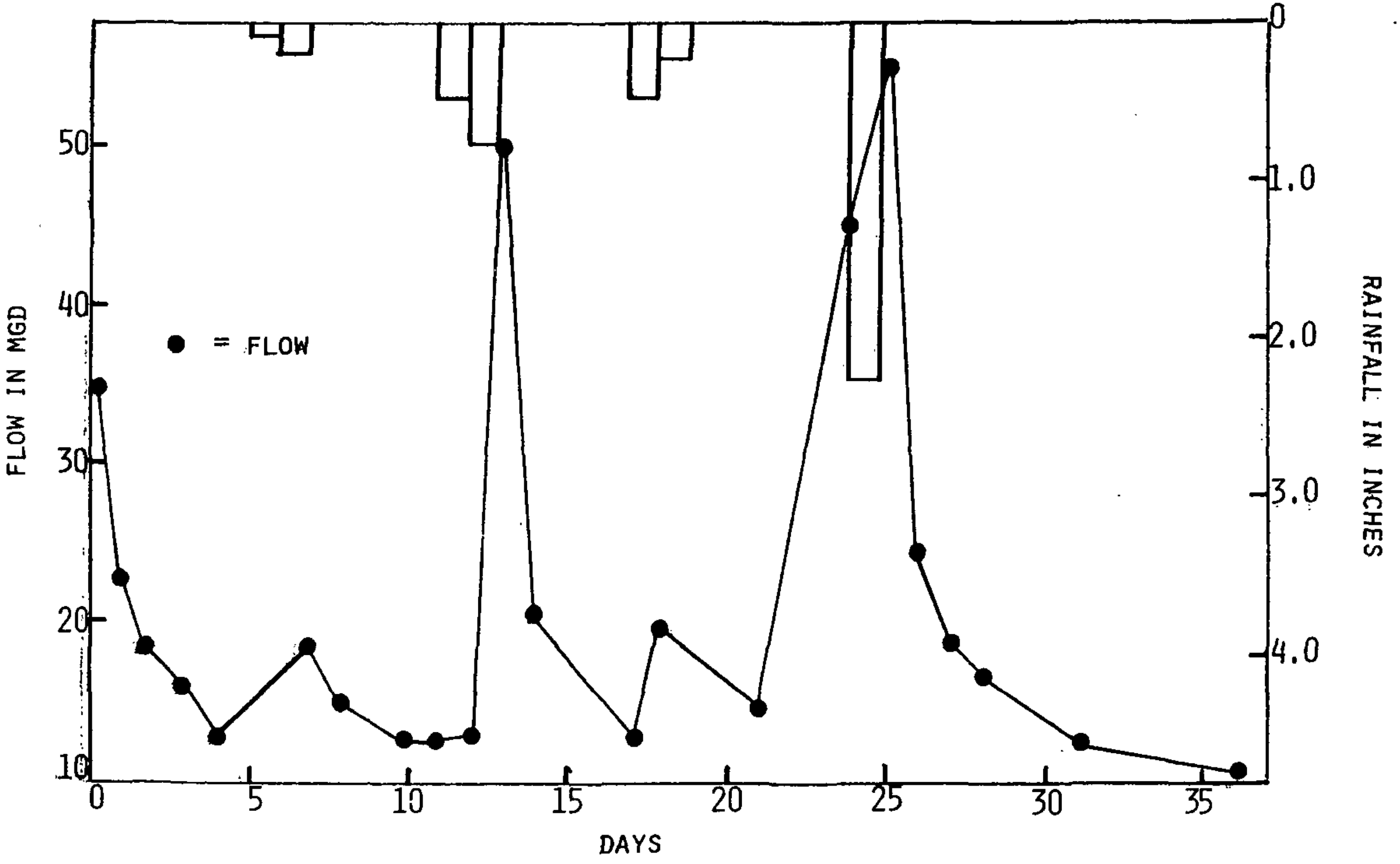

Figure 3. Temporal variation of rainfall versus flow in lake, July 9 to August 14, 1973.

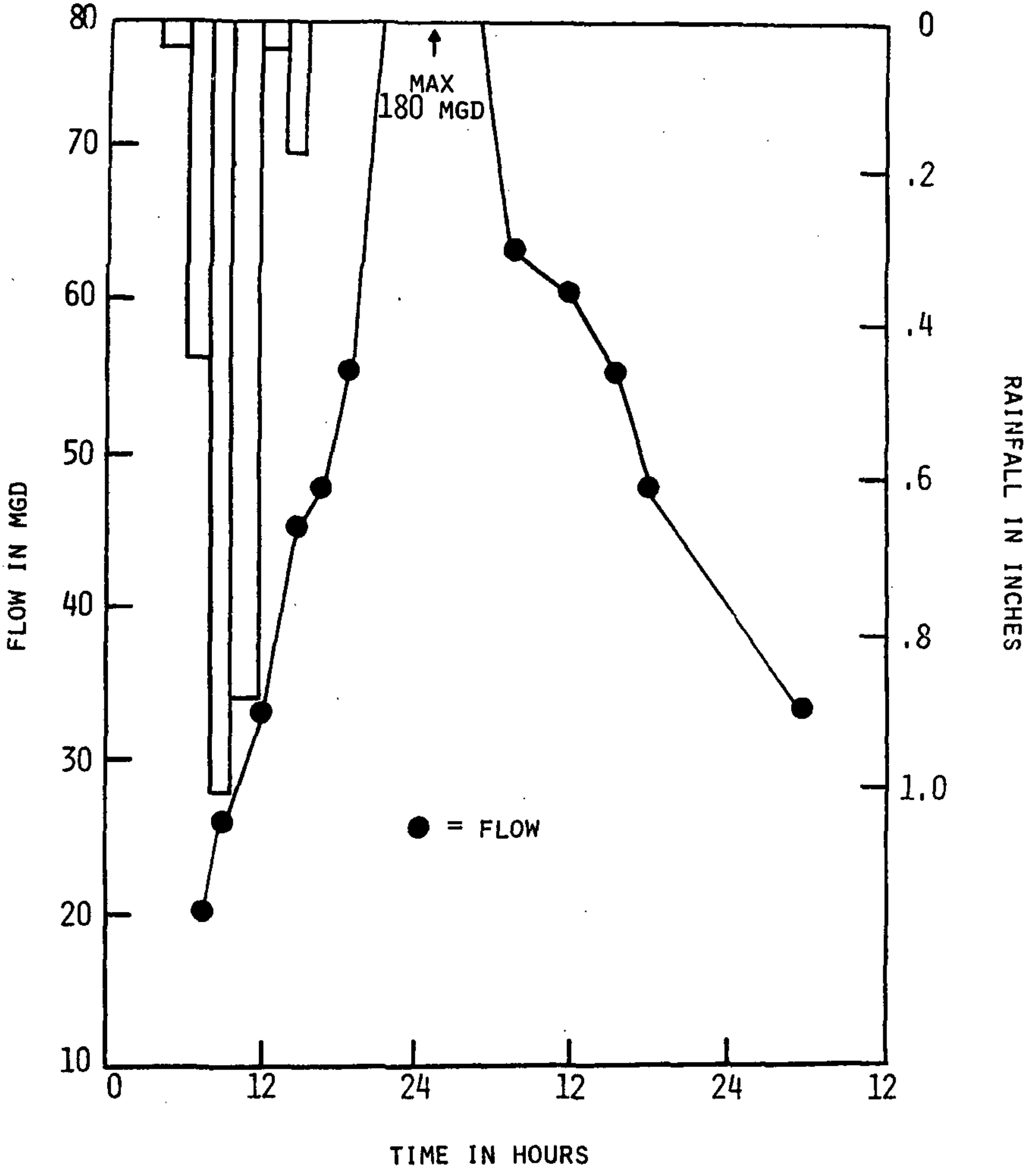

Figure 4. Rainfall and flow for flood flow, August 2 to 4, 1973.

"clean" appearance until such time as the flow again reaches 26 million gallons per day (100 x 10^6 l/day) and the detention time of 5 days. At this flow rate, the algal population appears to have sufficient time to reach bloom proportions during the summer months.

Sediment Characteristics. Physical properties of the lake sediments which are pertinent to this study are porosity and density. Figure 5 shows the longitudinal variation of porosity and density for Lake Warner in June 1974. The high density of the sediment at the inlet of the lake is caused by a high concentration of fairly coarse sand which is deposited in the deltaic area due to the drop in velocity of the in-coming water. The higher density at the outlet is also caused by a higher concentration of sand in the sediment. This area is quite deep and narrow which causes a higher velocity of water. Finer organic particles are probably scoured from this area leaving behind the denser, larger particles.

The gradual increase in porosity from inlet to outlet is caused by an increase in the concentration of finer clay-like particles and the increase in flocculent organic particles. Samples for both porosity and density were taken in the top 5 cm (2 inches) of sediment. Obviously, as depth increases into the sediment, the porosity should decrease and the density should increase

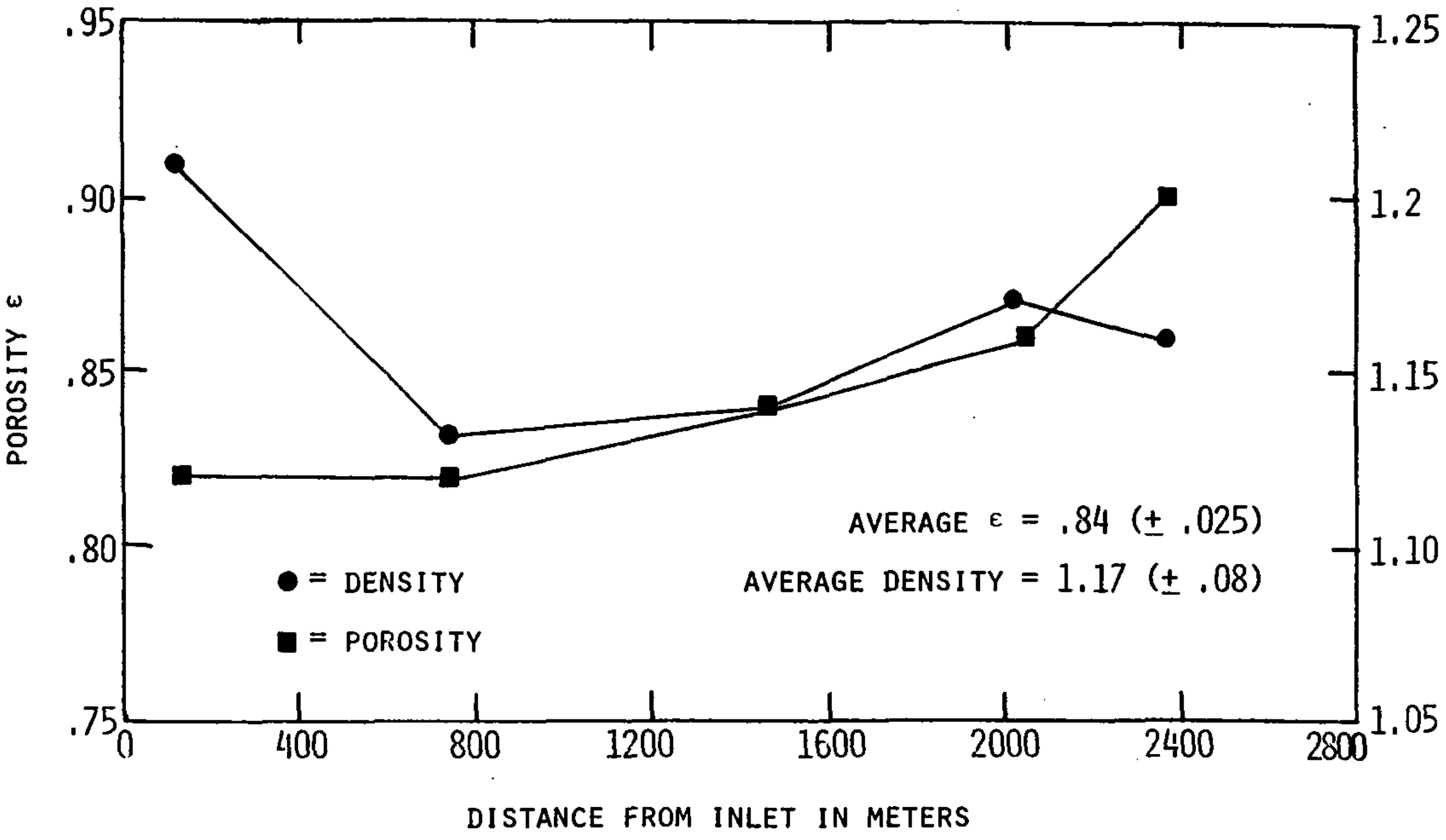

Figure 5. Spatial variation of sediment porosity and density, June,1974.

due to compaction and realignment of platy clay minerals. The value for porosity ($\varepsilon = .84$) will be used in the subsequent mathematical model of the lake and is considered to be the porosity of the sediment at the sediment-water interface where transport of phosphorus is occurring.

Typical Temperature and Dissolved Oxygen Profiles. Variations in water temperature during July and August, 1973 are shown in Figure 6. Significant here is the rapid changes (up to 8°C in 4 days) in water temperature of the lake which can be attributed to solar heating and cooling, influent water temperature, and varying inflows. The difference in temperature between surface and bottom water is attributed to the algal concentration near the surface. The lake had bloom proportions of algae which would tend to adsorb sunlight. Although the temperature at the very bottom of the lake is 2 - 3°C cooler than the surface, the lake itself is not thermally stratified. There is a vertical gradation in temperature within the lake which is attributed to incomplete mixing and the time of day in which the temperatures were recorded. Diurnal studies were not undertaken to determine if the vertical temperature differences created during the day disappeared during the evening due to mixing.

The vertical variation in dissolved oxygen for two summer days in July 1973 is illustrated in Figure 7. The

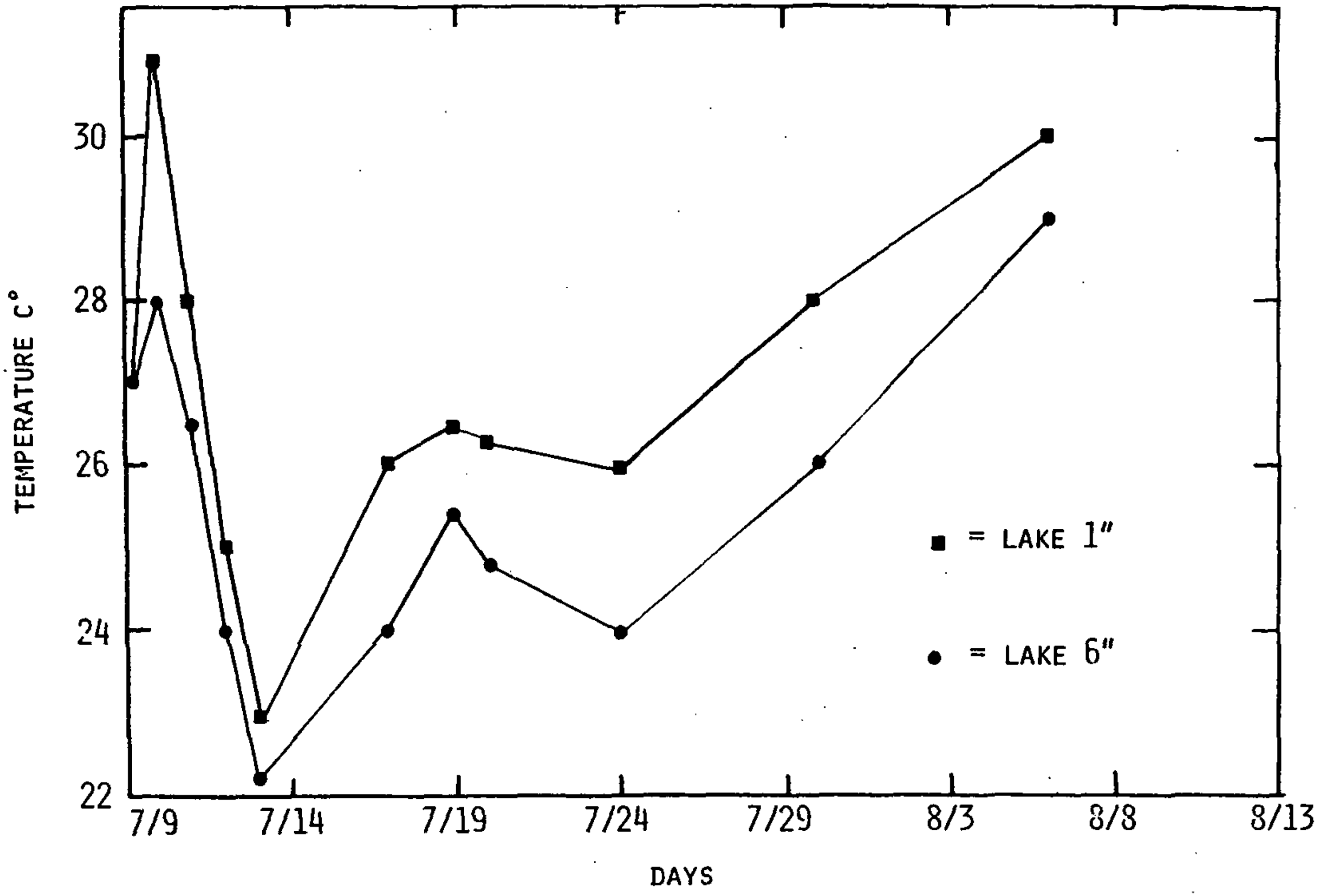

Figure 6. Temporal variation of lake water temperature, July 9 to August 13, 1973.

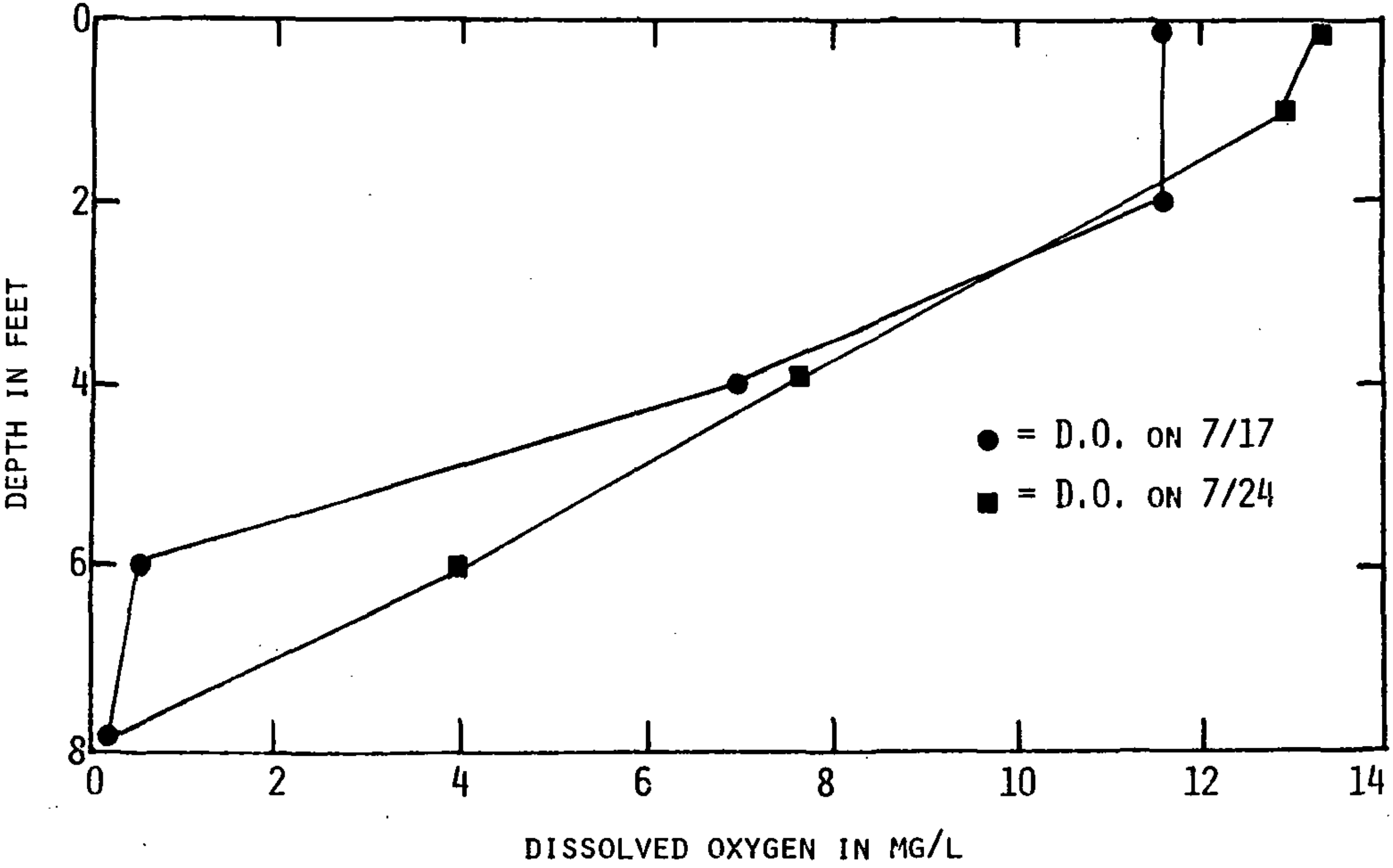

Figure 7. Vertical variation of dissolved oxygen, July 17 and July 24, 1973.

two most significant facts shown are: (1) the supersaturation of dissolved oxygen at the surface of the lake and (2) the extreme oxygen gradient from surface to bottom in the lake. The supersaturation at the surface (140-160 percent) is due to algal photosynthesis present near the surface. Both measurements were taken in the early afternoon and reflect the influence of bloom proportions of algae on the amount of dissolved oxygen present near the surface during the day.

The extreme gradient of dissolved oxygen from the surface to the bottom (a change of 11.5 mg/l dissolved oxygen in 8 feet) is mainly due to the high demand for dissolved oxygen by benthic bacteria in their breakdown of dead algal cells. As with temperature, diurnal studies were not conducted to observe the change in this gradient during the evening due to mixing and the absence of photosynthetic activity. A rapid change is predicted since bacterial uptake of oxygen would be enhanced by algal uptake during the evening.

As shown in Figure 8, the dissolved oxygen profiles for December 4 and 12, 1973 are quite different when compared to the July data. This difference is attributed to the high flow rate (100×10^6 l/day) through the lake and colder temperatures. The incoming water to the lake would be nearly saturated with dissolved oxygen which would keep the entire lake well oxygenated. Also, both algal photosynthesis

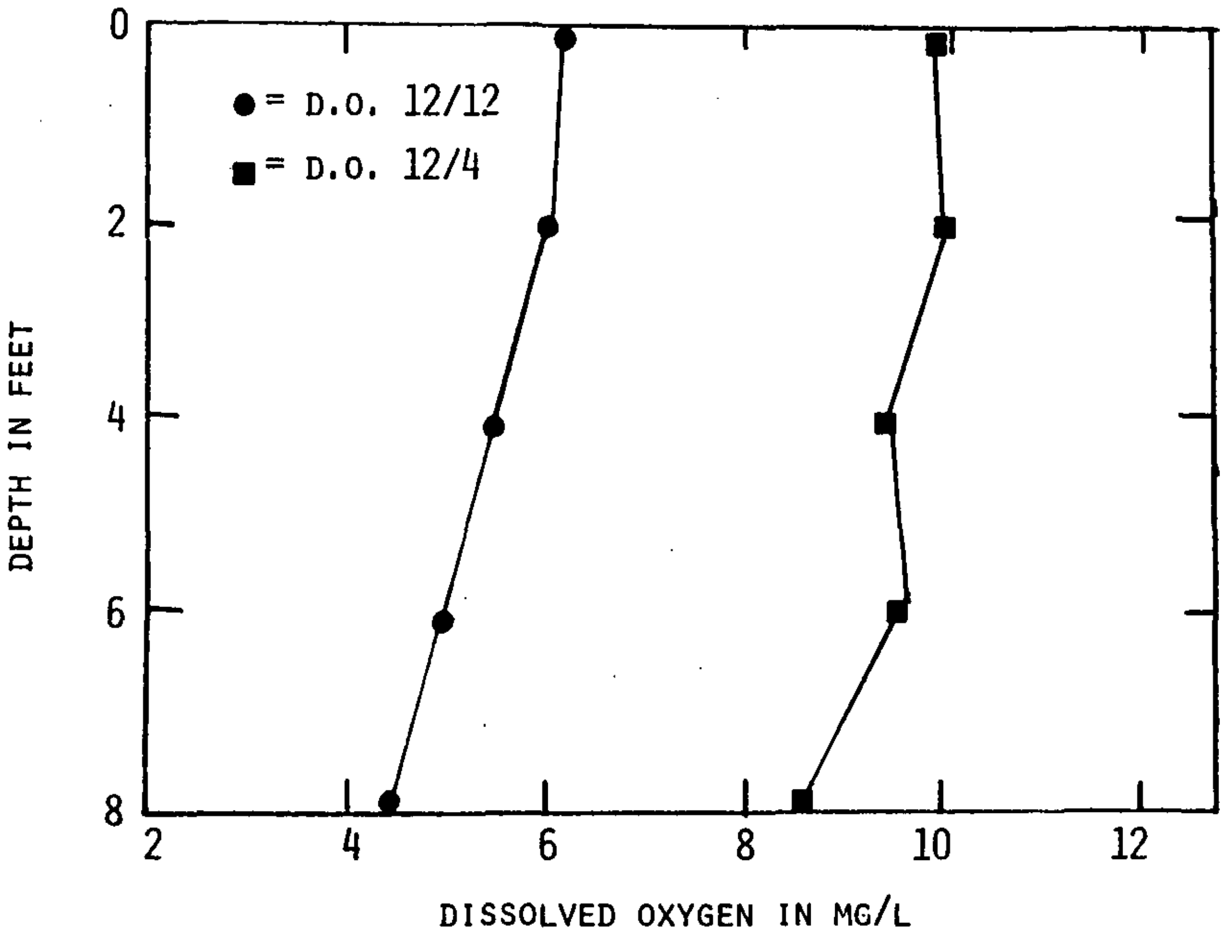

Figure 8. Vertical variation of dissolved oxygen, December 4 and December 12, 1973.

and benthic bacterial demands for oxygen would be low due to the low temperature.

The oxygen and temperature data gathered in the summer support the premise that algal blooms and benthic bacteria play a dominant role in regulating the dissolved oxygen concentrations in this eutrophic lake. Only during the winter months, when both biological systems are operating at a minimum, will the influent flow rate and temperature be the controlling factors influencing the dissolved oxygen concentrations.

The summer dissolved oxygen profiles also support the premise that at the sediment-water interface, the redox potential (Eh) should be low enough to have reducing conditions. With reducing conditions, more phosphorus is available for transfer to the water due to the breakdown of ferric phosphate complexes at the interface.

The interrelationship, therefore, between the summer biological community (blue - green algae and benthic bacteria) and the dissolved oxygen profiles has a direct bearing on the availability of phosphorus. As more algae are produced, more die and settle to the bottom. Benthic bacteria utilize more of the oxygen produced in photosynthesis until there is no more dissolved oxygen at the sediment-water interface. This condition probably occurs most commonly during the evening when no photosynthetic oxygen is being generated. With anaerobic conditions, complexing of phosphorus by ferric hydroxide gels no longer occurs and more phosphorus will be released from the sediment.

Algal Types and Concentrations. The lake appeared to be completely dominated by the blue - green variety of algae. During both the summer of 1973 and 1974, large floating mats of Oscillatoria princeps were observed. Many of the bays were entirely covered by this blue - green algae and the decaying odor was similar to corn silk. In the summer of 1973, the other algal types were the blue - green genera; Anabaena sp. (70 percent) and Anacystis sp. (30 percent). During the early parts of the summer of 1974, the blue - green genera were; Anabaena sp. (50 percent), Anacystis sp. (30 percent), and Volvox sp. (20 percent). No green algal genera were observed and zooplankton were not considered in microscopic observation since they lack chlorophyll.

The concentration of algae in the lake has a direct relationship to the amount of phosphate in the lake water. Figure 9 presents the relationship of TOC and fluorescence versus time during July and part of August 1973. At peak bloom periods during the summer, the cell count approached 1×10^9 per liter in the lake. This usually occurred about 5 days after a high flow period when the previously established bloom has been washed out and new nutrients had been introduced. Fluorescence derived values of cell

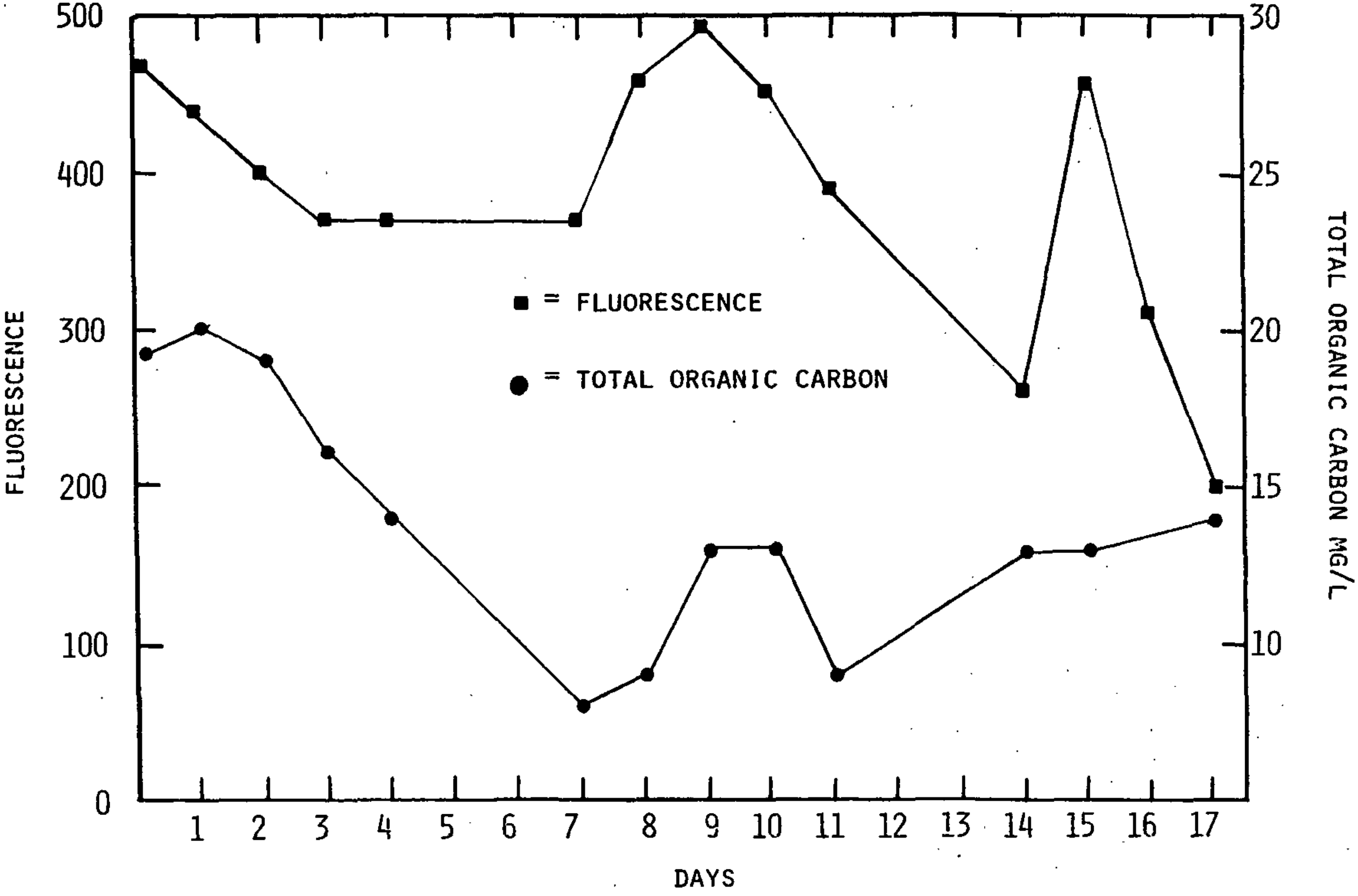

Figure 9. Temporal variation of fluorescence and total organic carbon, July 9 to July 27, 1973.

numbers are based on the correlation of the amount of chlorophyll in a known number of *Anabaena* sp. to the actual induced fluorescence. Since *Anabaena* sp. is the dominant algal type in Lake Warner, the use of TOC values to indicate lake productivity is considered less accurate than those obtained by fluorescence.

The estimated number of algal cells present in Lake Warner during the summer are indicative of a highly productive eutrophic lake. The number of algae are probably the maximum amount that can bloom and are limited, not by nutrients, but by the absence of light penetration and the washout rate.

The by-products of photosynthesis and bacterial breakdown of these blue - green algal cells cause the taste and odor problems which are associated with this type of lake. Also, bloom proportions of blue - green algae cause extreme gradients in the dissolved oxygen profile of the lake which directly affect higher forms of aquatic life. The main objective, therefore, of this research is to limit the numbers of blue - green algae in the lake by limiting and/or controlling the amount of phosphorus in the water.

Lake and Water Chemistry

Spatial Variations in Lake Water P. The variations of total and ortho phosphate from the inlet to the outlet were measured in December 1973 and June 1974. Figure 10 shows the variation of both phosphorus parameters from inlet to outlet for various depths in the lake in December 1973. Higher levels of orthophosphate (50-65μg/l) at the inlet end decreased to a fairly constant level of about 55μg/l within a relatively short distance. Phosphate was always higher near the bottom of the water column. Inlet concentrations of total phosphate were low (70-85μg/l), but reached an apparent equilibrium value of about 87μg/l near the surface in a short reach from the inlet. Here again, the water closer to the sediment had much higher concentrations of phosphorus (about 93μg/l).

Data taken during June 1974 indicated a somewhat similar pattern for the spatial distribution of both ortho and total phosphate as observed in December 1973. Orthophosphate at the surface (Figure 11) increased rapidly with distance from the outlet (from 17 to 36μg/l) and then decreased again to about 10μg/l. Concentrations near the bottom increased from 30μg/l at the inlet to 57μg/l within 100 meters and then decreased to approximately 40μg/l. Although not as pronounced, the concentration of total phosphate follow the same pattern; surface values varied

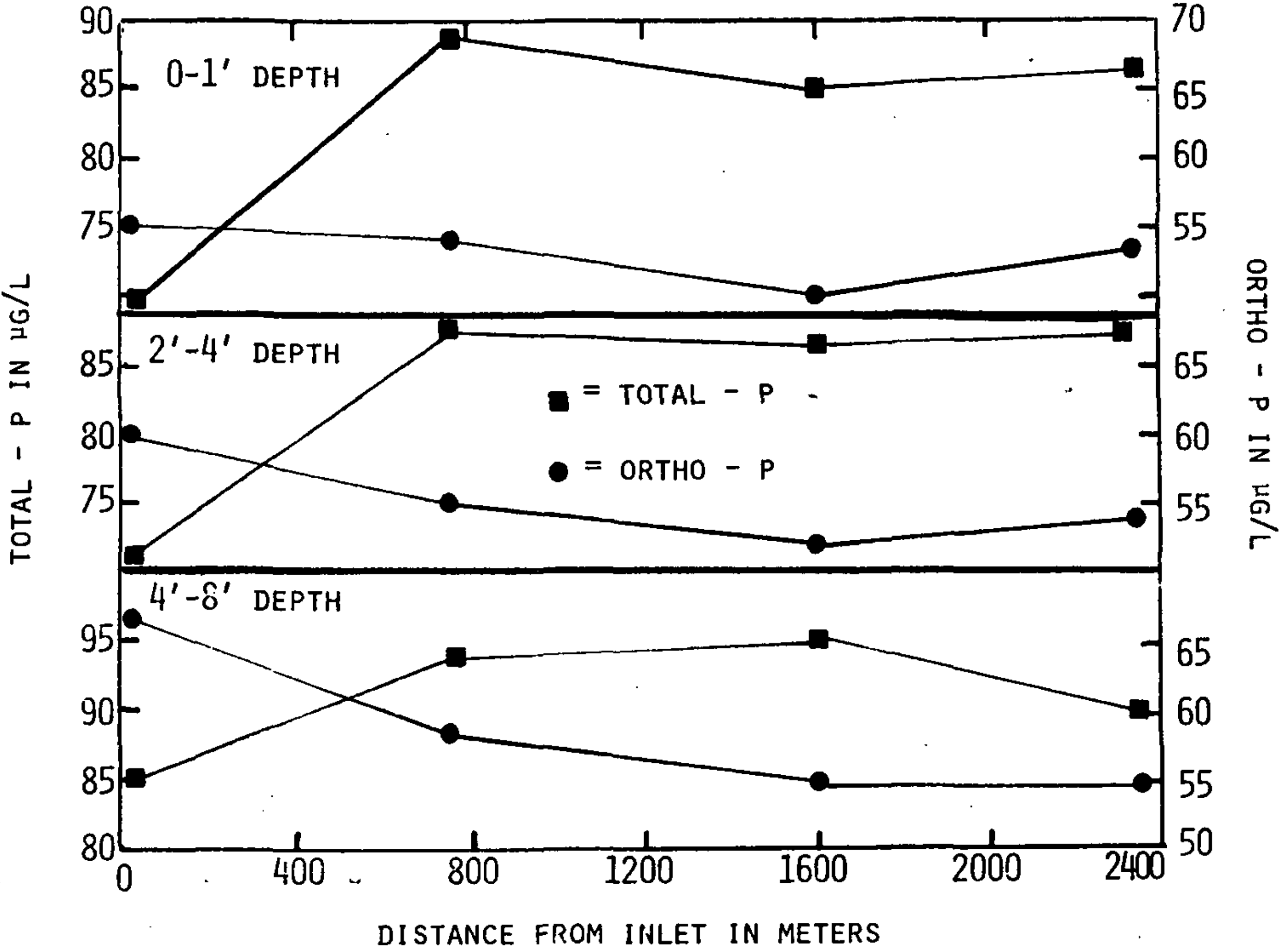

Figure 10. Spatial variation of total and orthophosphate in lake water at various depths, December, 1973.

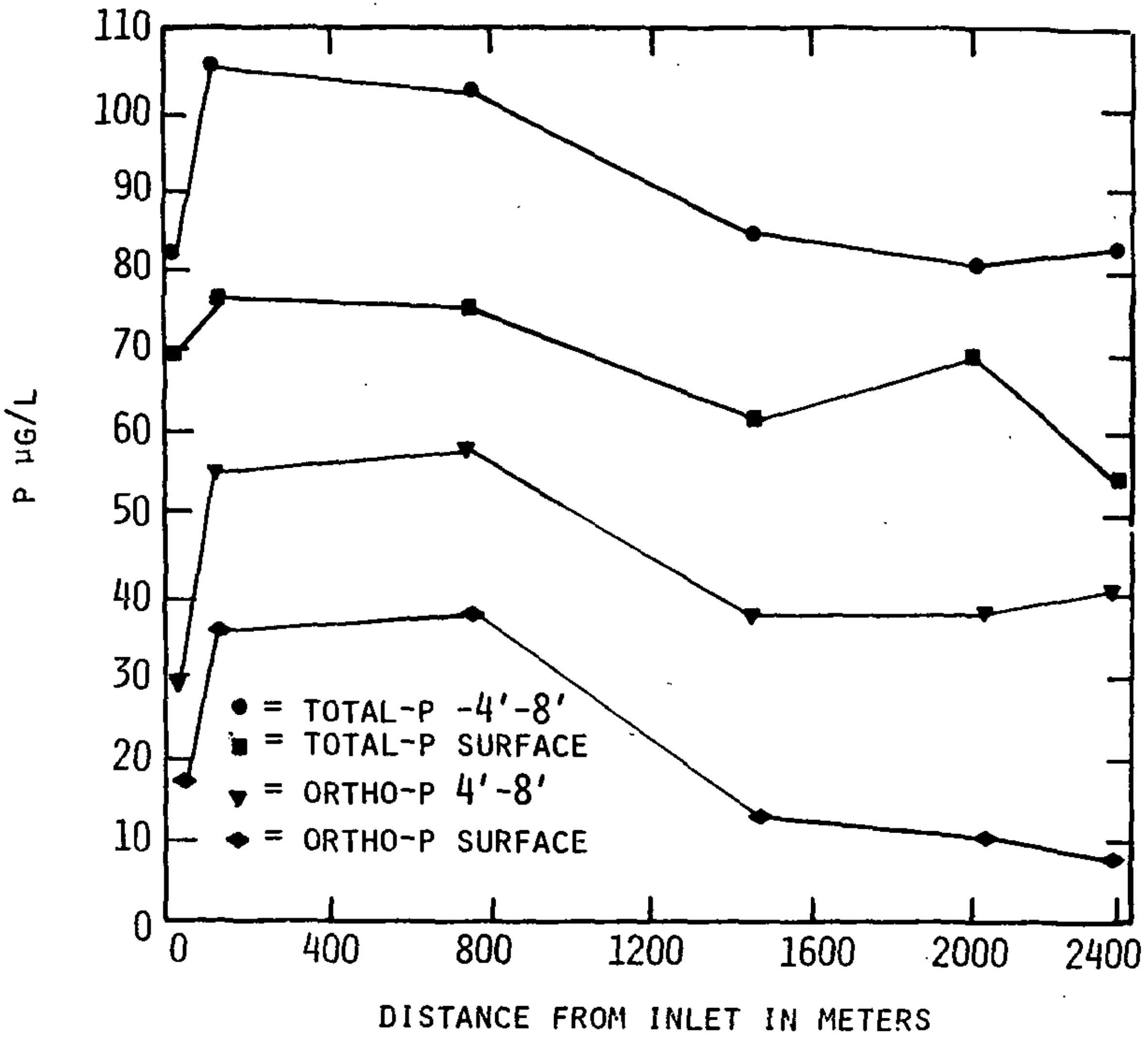

Figure 11. Spatial variation of total and orthophosphate in Lake Warner at various depths, June, 1974.

between 60 and 75μg/l and near-bottom samples increased from 80μg/l at the inlet to 105μg/l in a short distance and then decreased to about 84μg/l.

These measurements of spatial distribution of phosphorus indicated that modeling the lake as a completely mixed reactor appears to be reasonable since fairly constant values of total phosphate were present in most stretches of the lake. During the winter, the initial decrease in orthophosphate with respect to distance from the inlet was probably due to ferric ion adsorption in the water column. The contrasting increase from the inlet and equilibration of total phosphate was probably due to release of sediment orthophosphate followed again by sedimentation. However, summer sampling showed more dramatically the release of sediment orthophosphate with respect to distance from the inlet. Orthophosphate concentrations near the bottom increased from a value of 30μg/l at the inlet to 55μg/l in approximately 100 meters. The increase (25μg/l) accounts for almost all of the increase in total phosphate (83 to 106μg/l or 23μg/l) which supports the premise that orthophosphate is the main form of sediment released phosphorus. Higher values of orthophosphate (about 55μg/l) in the lake in the winter than in the summer are probably due to the high influent loadings caused by higher flows, more sediment erosion, and occasional by-passing of wastewater. A fraction of this loading is sedimented to the bottom during the winter. During the summer, when temperature increases (about 20°C at the bottom), pH increases (up to 9.4), and the redox potential drops to +50mv. in the overlying water, release of the orthophosphate from the sediment will occur at a greater rate. Flux of sediment orthophosphate in this eutrophic lake is therefore seen as a major source of phosphorus in the summer bloom period. An apparent equilibrium in the concentration of phosphorus in the lake water is evident in most stretches of the lake which supports the premise of combined release and sedimentation reactions acting together to regulate phosphorus in the lake water. Fluctuations of lake phosphate concentrations are mainly due to varying influent flow and concentrations.

Temporal Variations in Lake Water P. Concentrations of ortho and total phosphate were monitored in the lake between July 1973 and December 1973. Figure 12 shows the variation in ortho and total phosphate from July 9 to August 14, 1973. The larger variations in concentration occurring during the first two weeks of monitoring were probably caused by fluctuating inflows, while the low concentrations in the latter two weeks were more related to uptake of phosphate by algae.

Comparison of algal numbers and total phosphate concentrations are shown in Figure 13. An increase (up to

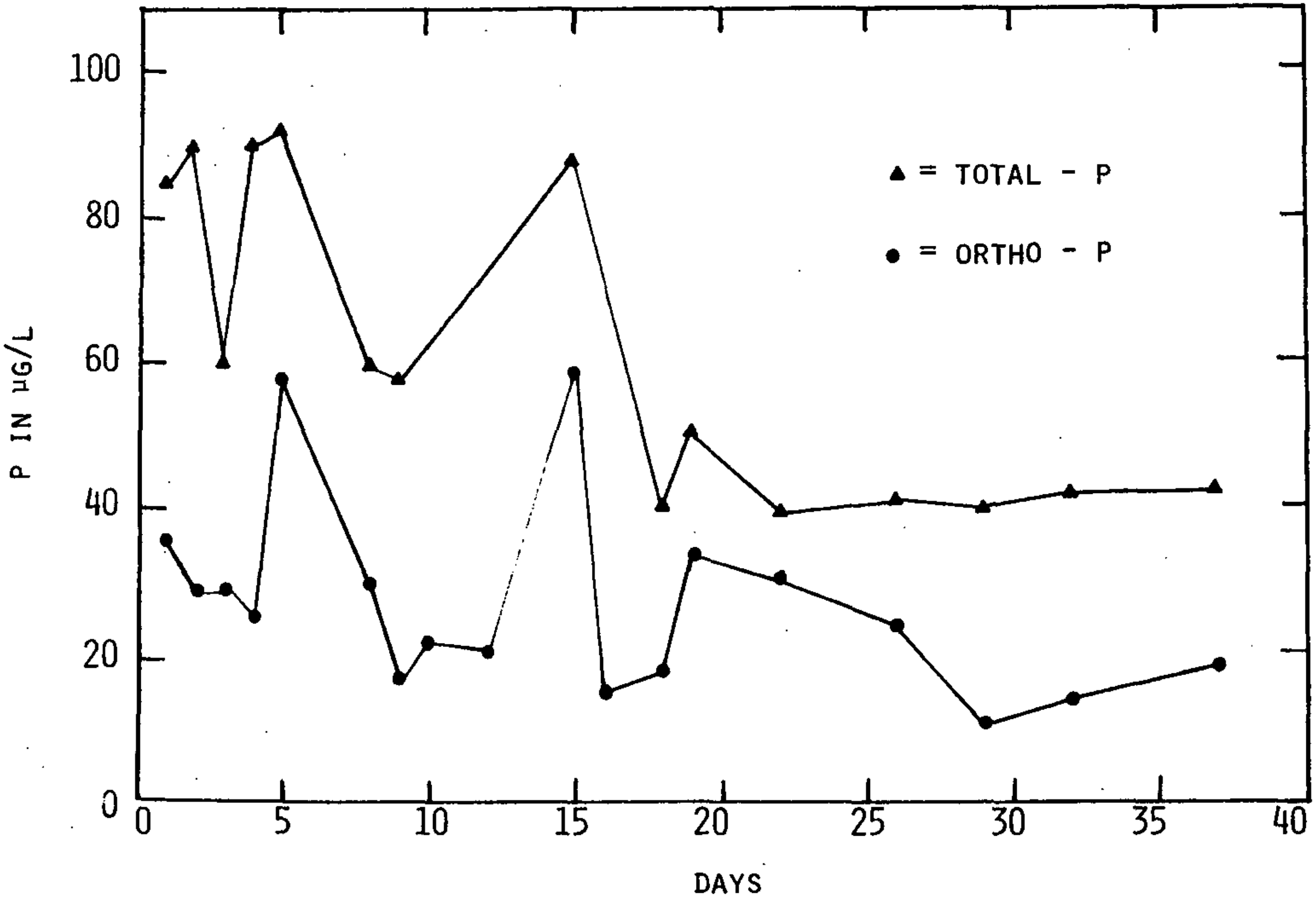

Figure 12. Temporal variation in total and orthophosphate in lake water, July 9 to August 14, 1973.

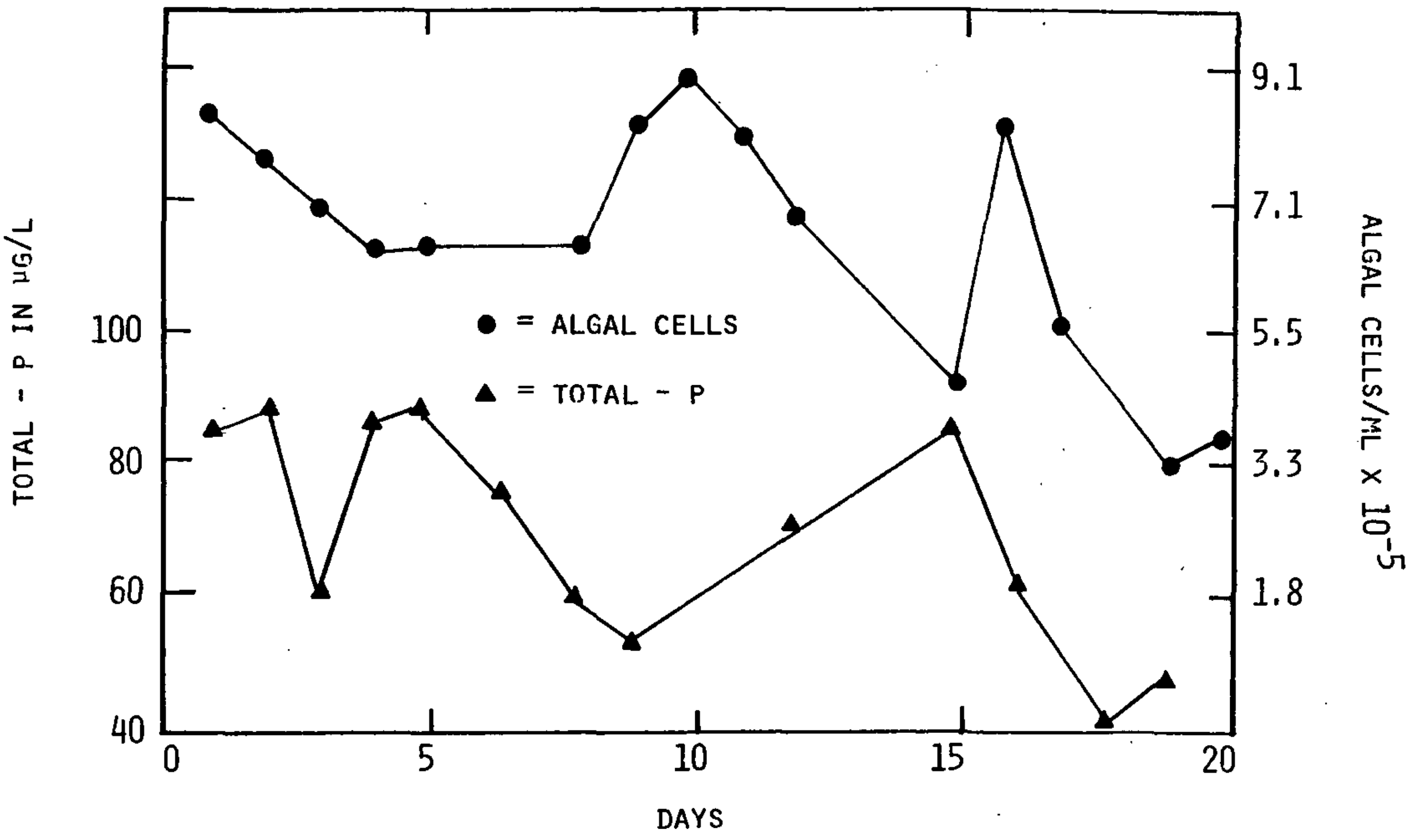

Figure 13. Temporal variation of total phosphate and algal cells, July 9 to July 30, 1973.

90μg/l) in the concentration of total phosphate was usuall·· followed by an increase in algal numbers, although bloom proportions (3 to 5 x 10^5 cells/ml) were evident in the lake even when total phosphate concentrations were near 40μg/l. Thus, algal growth in Lake Warner is dependent on the phosphate concentration; however, low concentrations (40μg/l) do not limit the bloom proportions of algae.

Figure 14 depicts ortho and total phosphate data gathered between September 27 and December 20, 1973. A gradual increase in total phosphate, from 60μg/l to approximately 100μg/l, and an increase in orthophosphate from 25μg/l to 55μg/l were evident as algal blooms diminished. This trend is probably due to the decrease in algal uptake and higher release from the sediment due to bacterial breakdown of the dead algal cells. The general decreases in ortho and total phosphate during the latter period (December 4-20, 1973) of this study may be attributed to a decrease in bacterial activity with colder temperatures which in turn reduces the release of phosphate from the sediment.

<u>pH and Redox Potential</u>. Samples were taken in the Mill River above and below the wastewater treatment plant during June 1974 when no bypassing of wastewater was occurring. As shown in Figure 15, the pH remained almost constant at 7.0 and the redox potential fluctuated between + 180 to + 195mv. At this pH and Eh, the river system would be considered as an oxidizing environment.

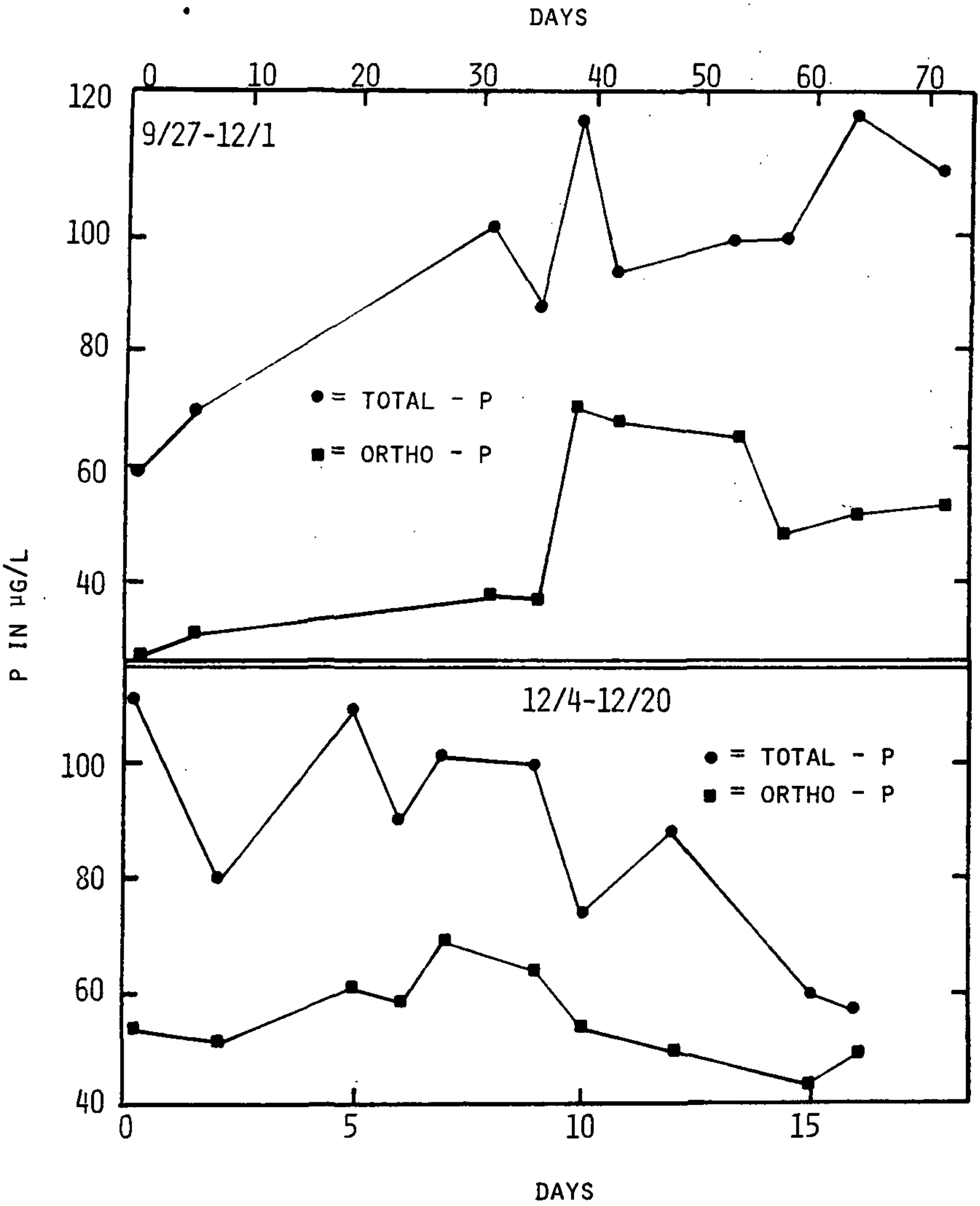

Figure 14. Temporal variation of total and orthophosphate in lake water for September to December 1, 1973 (top) and December 4 to December 20, 1973 (bottom).

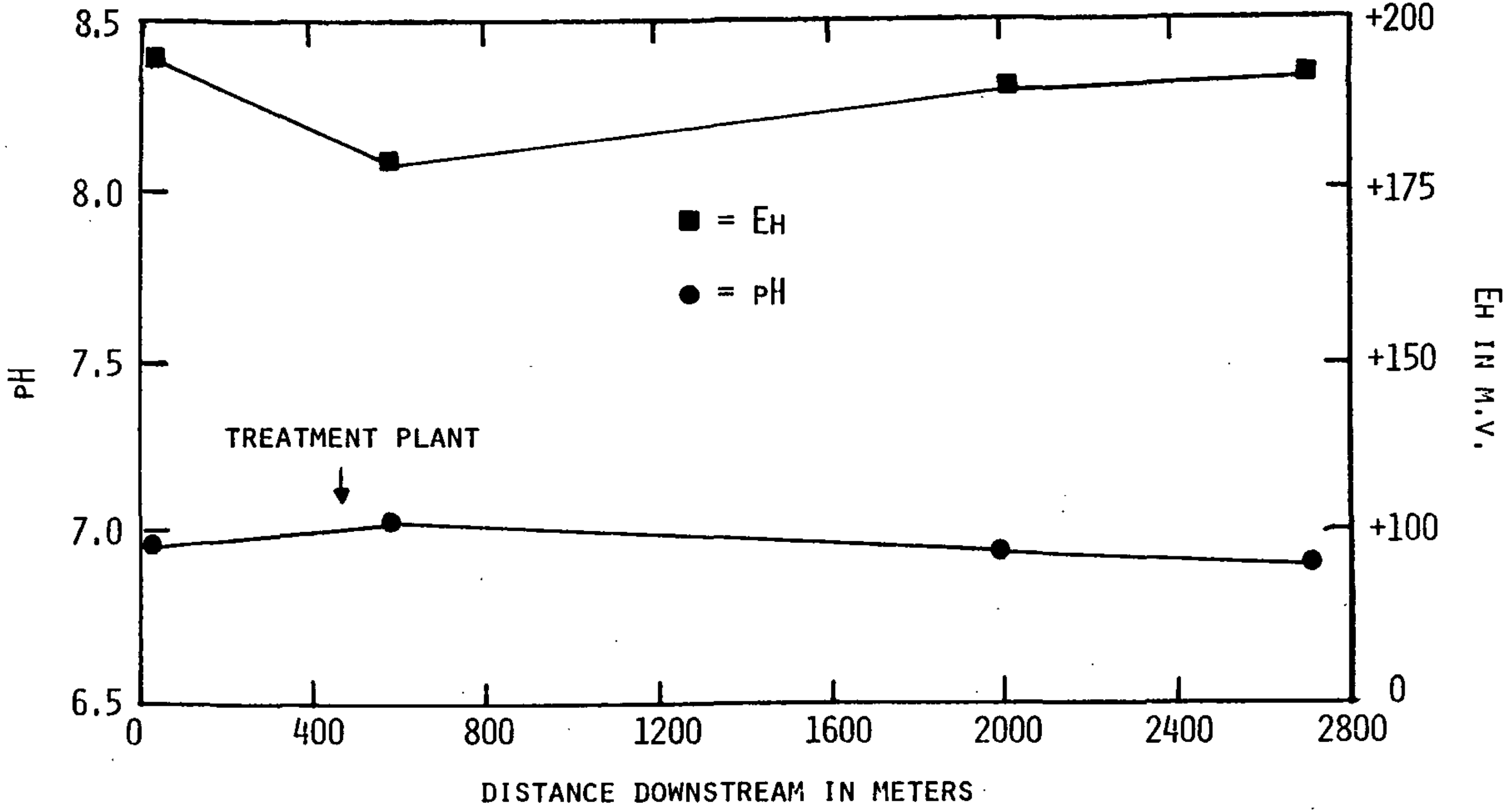

Figure 15. Spatial variation of Eh and pH in Mill River, arrow indicates location of Amherst Wastewater Treatment Plant, June, 1974.

Longitudinal profiles of pH and redox potential for the lake during June 1974 are shown in Figure 16. One point of special interest is the first half-mile of the lake. Here the pH still remained near 7.0 but the redox potential had dropped from about + 185mv to an average of only + 90mv. This drop is attributed to the uptake of dissolved oxygen by the sediment bacterial population and the lack of photosynthetic oxygen in this part of the lake.

The rapid drop in Eh and the concomitant rise in pH throughout the rest of the lake is mainly attributed to algal activity. Algae remove all available carbon dioxide according to Equation 1 (see Chapter II). Photosynthesis, especially in the upper layers of the lake, tends therefore to increase the pH by removing CO_2 (carbonic acid) and hydrogen ions. In the presence of dissolved oxygen, this increase in pH will decrease the Eh as given by Garrels and Christ(1965):

$$Eh = 1.23 + \frac{.059}{4} \log \bar{p}O_2 - .059pH \qquad (45)$$

Numerically, the change in O_2 concentration has only a slight effect on the Eh as compared to the change in pH.

If the above equation is used to define the Eh in terms of the pH and $\bar{p}O_2$ (pH 7.0, $\bar{p}O_2$ .21), then the Eh has a value close to + 800mv. The lake water exhibited an average Eh value of only + 90mv. This discrepancy is

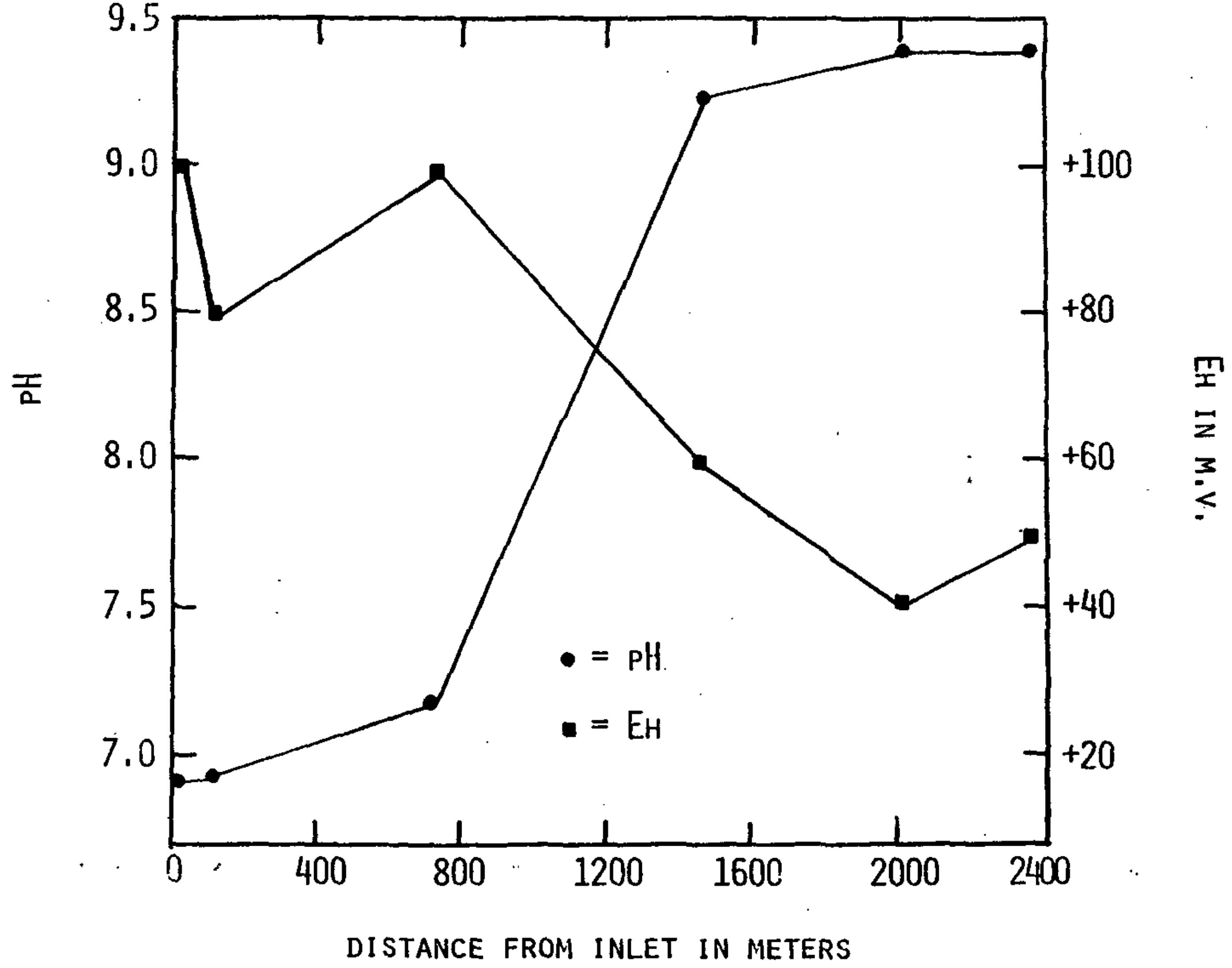

Figure 16. Spatial variation of Eh and pH of lake water, June, 1974.

attributed to photosynthesis as well as microbial uptake of oxygen. Photosynthesis produces localized centers of reducing conditions (around - 400mv) which will influence the Eh of the water (Welch, 1969). Bacteria in the water column are also utilizing O_2 in their breakdown of dead algal cells which tends to shift the Eh to a lower value. Another factor which may also play a role in lowering the Eh of the lake is the oxidation of organic and inorganic compounds mediated by dissolved oxygen, other by-products of photosynthesis or bacterial metabolism.

These findings confirm that intensive algal activity caused by the presence of excess phosphorus leads to extremely high pH and a subsequent lowering of the Eh in a lake water. In fact, the spatial distribution of pH and Eh given in Figure 16 indicates that photosynthesis was most prevalent in the latter half of the lake's reach.

Iron. The spatial distribution in total iron concentration in the lake is shown in Figure 17 for December 1974. The high inlet value (1.05 mg/l) near the lake bottom decreased with distance, while near surface iron concentrations increased and then decreased. The pattern can be explained by release of iron and orthophosphate from the deltaic sediments at the inlet (see Figure 10). Mixing of bottom and surface waters in the first 800 meters probably caused the surface iron increase. The apparent equilibrium Fe concentration within the lake

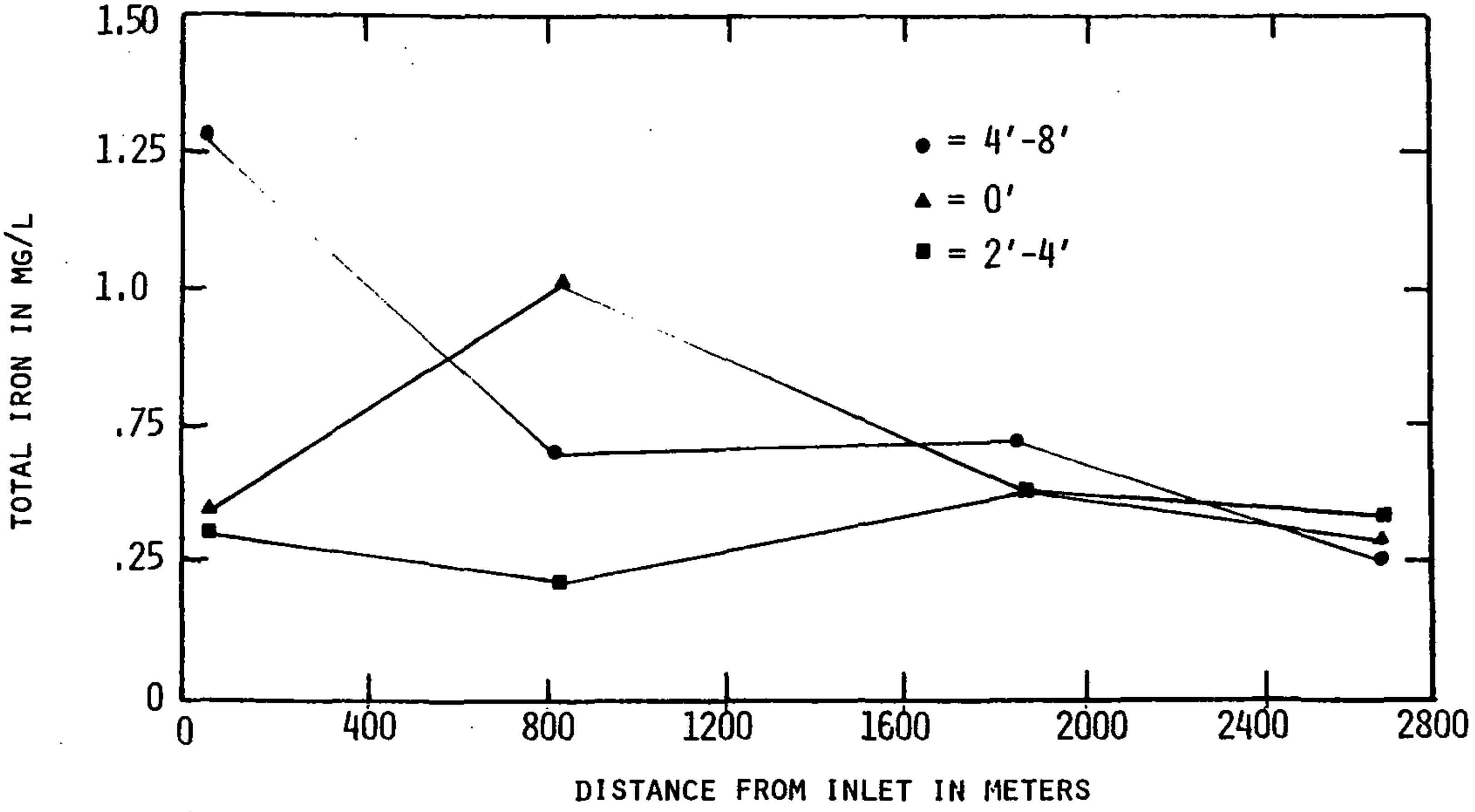

Figure 17. Spatial variation of total iron in lake water, December 16, 1973.

was between 0.3 and 0.4 mg/l.

The temporal variation in total iron is depicted in Figure 18 for both a summer and winter period. Considerable variation was noted in both periods with values ranging from a high of 1.25 mg/l to a low of 0.25 mg/l. Lower values may be related to adsorption of phosphate onto iron complexes. However, attempts to correlate iron and phosphate concentrations for either spatial or temporal distributions proved unsuccessful.

Sediment Phosphorus

Sediment studies were conducted to related interstitial phosphate to the total phosphorus within the sediment for later use in the proposed lake model. Figure 19 shows the spatial variation from the inlet to the outlet of Lake Warner for interstitial phosphorus within the sediment in June 1974. These variations will be shown to correspond to changes in Eh and total sediment phosphorus. Figure 20 depicts the spatial variation of total phosphorus (mg/gm) in the sediment from inlet to outlet during the same time period. Comparison of Figures 19 and 20 show similar trends, with high interstitial values being associated with high concentrations of total phosphorus in the sediment. This result should be expected because an equilibrium exists between total sediment phosphorus (P_T) and the related interstitial concentration (P_i) (see Equation 36). This relationship of interstitial

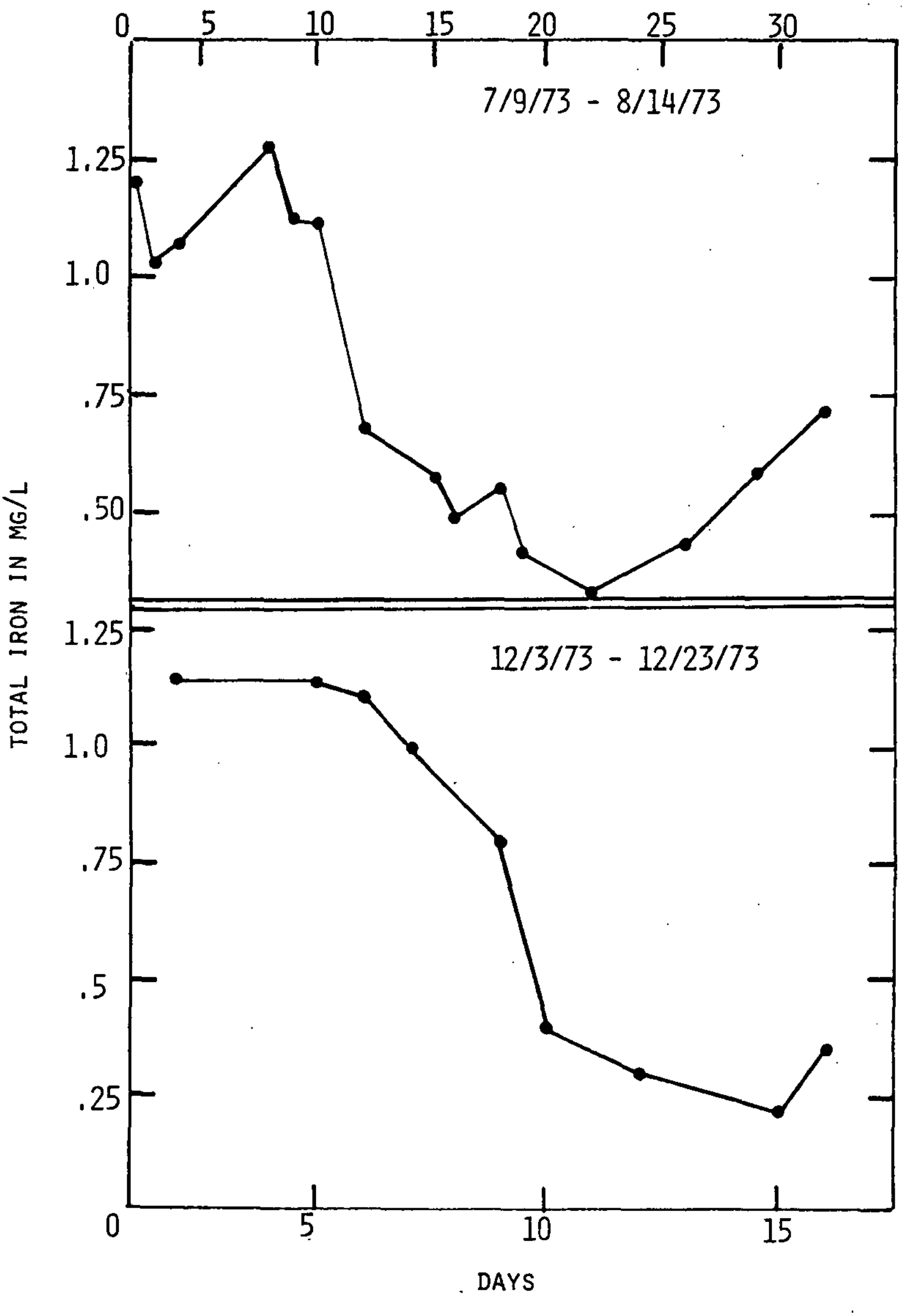

Figure 18. Temporal variation in total iron in lake water, July-August and December, 1973.

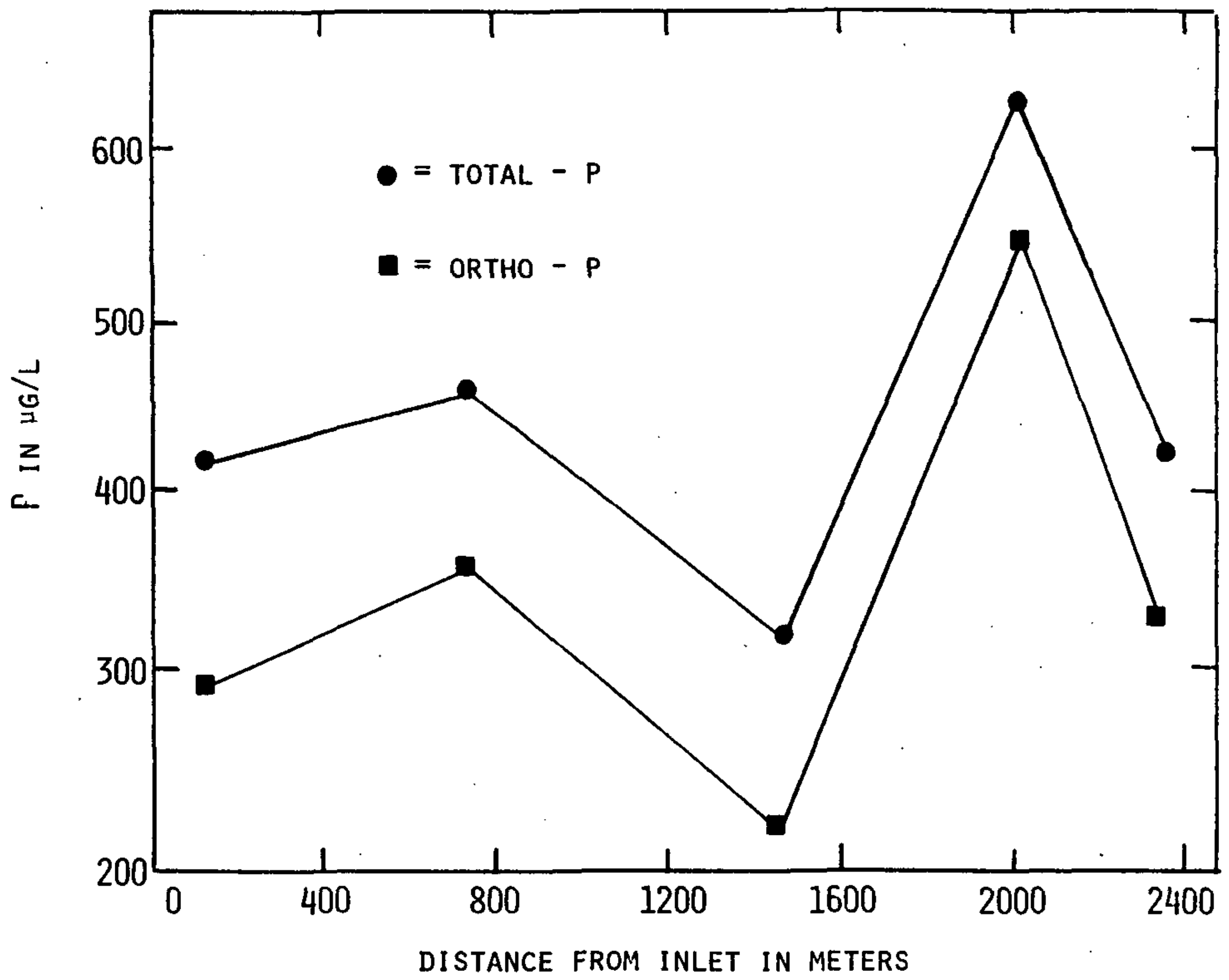

Figure 19. Spatial variation of total and orthophosphate in interstitial water, June, 1974.

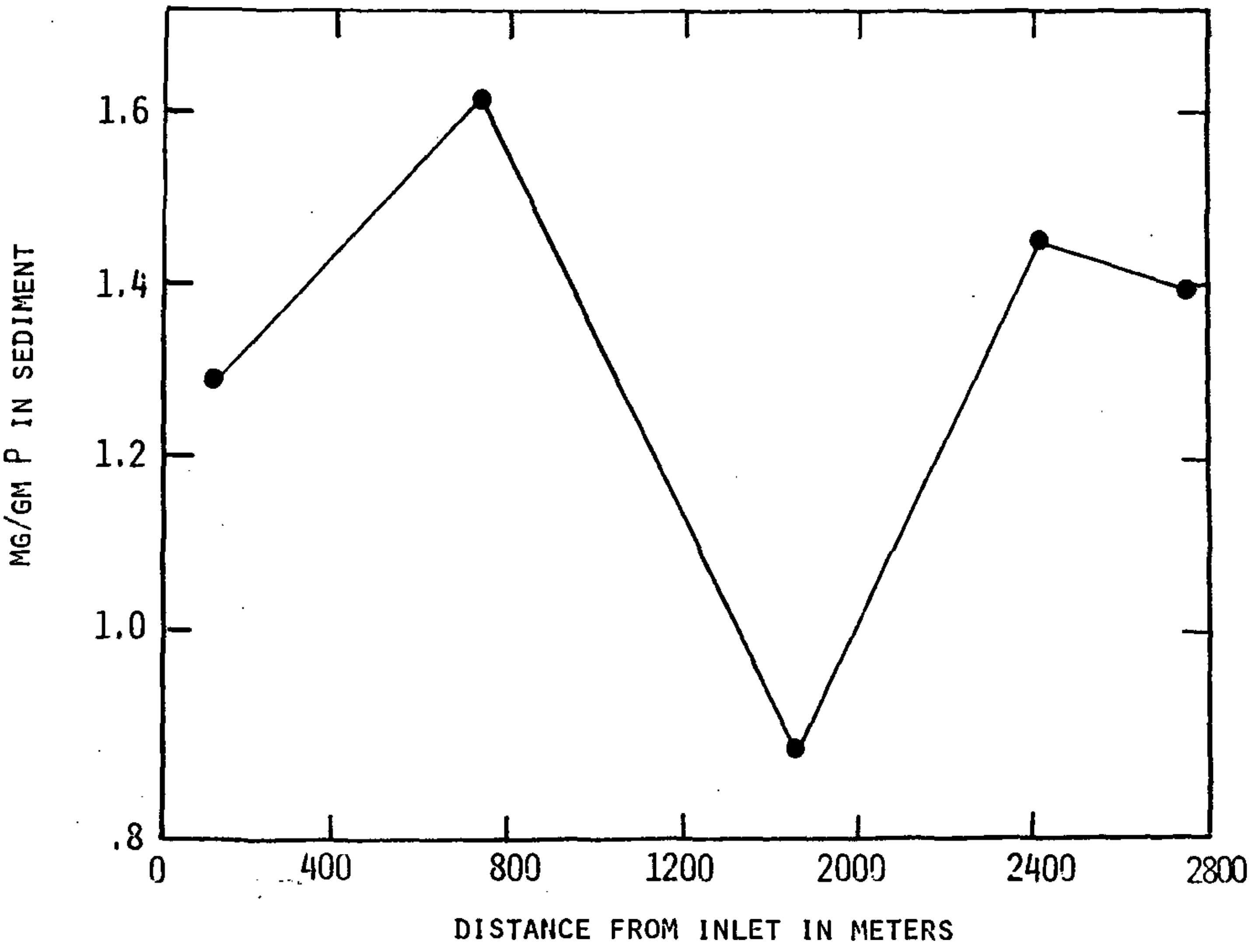

Figure 20. Spatial variation of total phosphorus in sediment June, 1974.

and sediment phosphorus is perhaps better shown in Figures 21 and 22. In Figure 21, visual inspection reveals that about 80 percent of the total interstitial phosphorus is orthophosphate. Also, as shown in Figure 22, an increase in the total sediment phosphorus is paralleled by an increase in the interstitial phosphate concentration.

The relationship between total sediment phosphorus and interstitial phosphorus for use within the model (Equation 36) requires further analysis of data presented in Figure 22; the raw data shows 1.5 mgP/gm dry sediment is associated with an approximate interstitial phosphate concentration of 450μg/l. It is then necessary to relate the dry sediment weight to the volume of the actual "wet" sediment (84 percent by volume being water and 16 percent being the solid fraction). Thus, the interstitial phosphorus may be expressed as 3.78×10^{-4} mg P/cm^3 and the sediment phosphorus as 0.6 mg P/cm^3, both in terms of "wet" sediment volume. Assuming from the discussion in Chapter II that 25 percent of the total dry sediment phosphorus is exchangeable, a volume of 1 cm^3 of the "wet" sediment would, therefore, contain about .15 mg of exchangeable phosphorus (P_s) and be associated with 3.78×10^{-4} mg of phosphate in the interstitial water. Expressed on a cubic meter basis, the total amount of exchangeable phosphate available for this sample calculation would be 1.5×10^{5} mgP

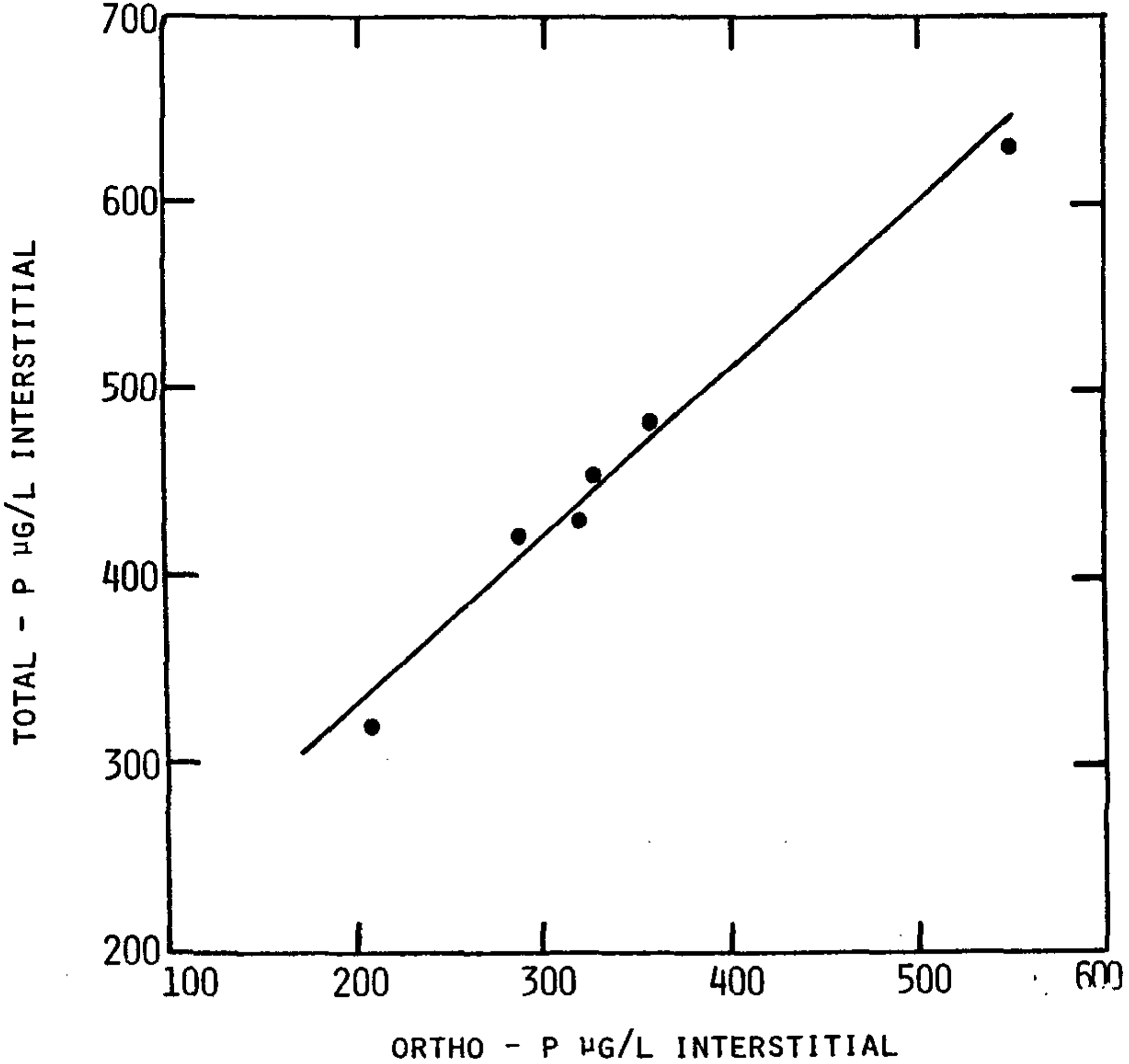

Figure 21. Correlation of orthophosphate and total phosphate in interstitial water.

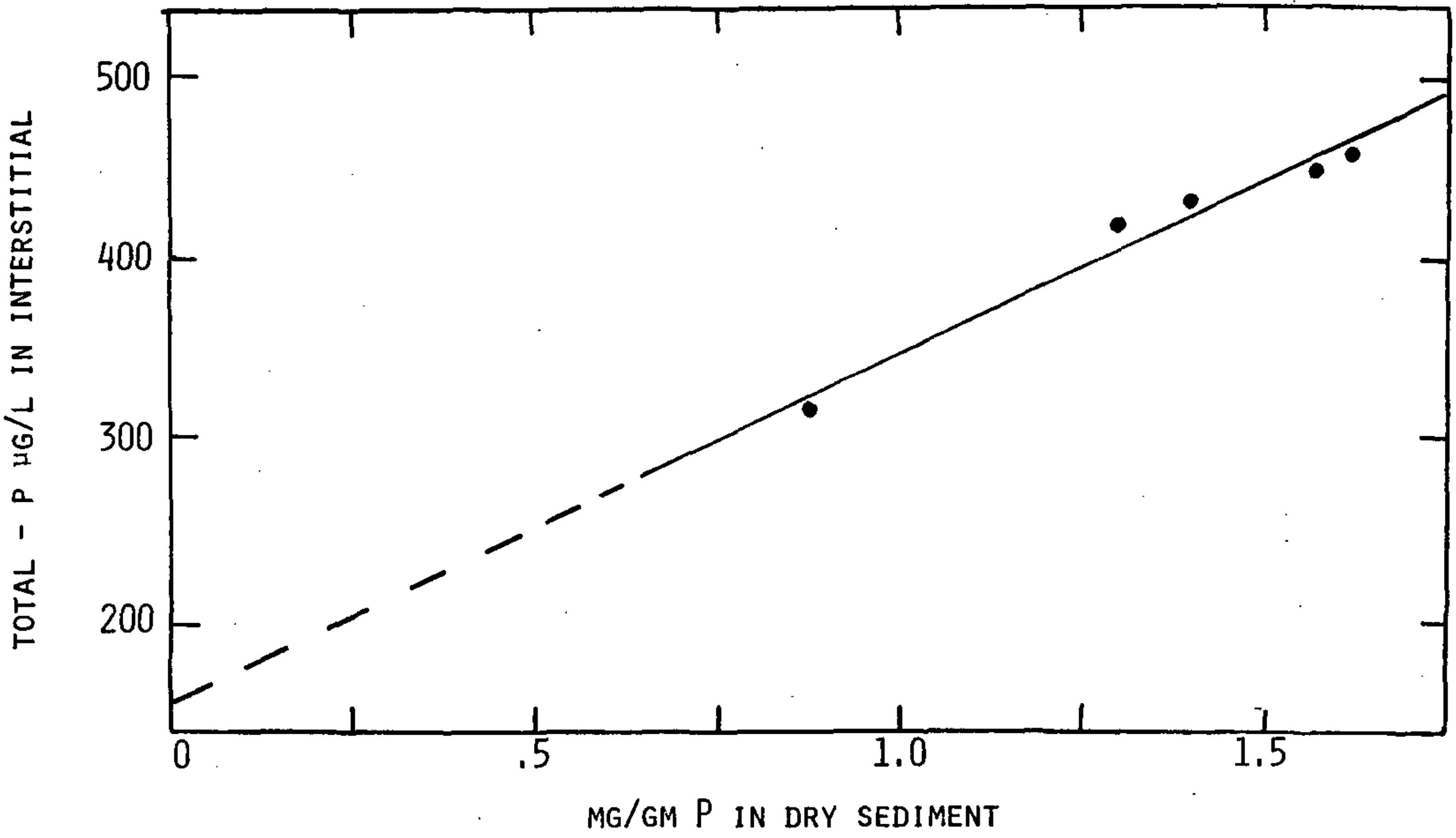

Figure 22. Correlation of total phosphate in interstitial water and total phosphorus in sediment, June, 1974.

and the total interstitial phosphate available would be 378 mg P. All of the data from Figure 22 were converted in this manner and plotted in Figure 23 to provide a correlation between total exchangeable phosphorus in the "wet" sediment and the interstitial phosphate concentration. Using a linear regression analysis of data, a correlation coefficient of 0.985 was obtained for the following equation:

$$P_i = (2.196 \times 10^{-3})\ P_s + 41.87 \qquad (46)$$

This relationship of total sediment phosphorus (P_T), exchangeable sediment phosphorus ($P_s = .25\ P_T$), and interstitial phosphorus (P_i) will be used in the proposed predictive model. The phosphate that is released from the sediment to the interstitial water and finally transported to the overlying water decreases the amount of exchangeable phosphate within the sediment. From the above equation, the new value of interstitial phosphate concentration can be predicted after a determined amount of exchangeable sediment phosphate is lost due to transport across the sediment-water interface. The application of this equation rests on the premise (discussed in Chapter II) that, within the physical, chemical and biological limits found in lake sediments, adsorption and desorption of exchangeable phosphate between interstitial water and the solid fraction should be a linear relationship (Ku, 1975). Also, within the "wet" sediment, an equilibrium exists between the amount of exchangeable phosphate on the solid fraction and the phosphate

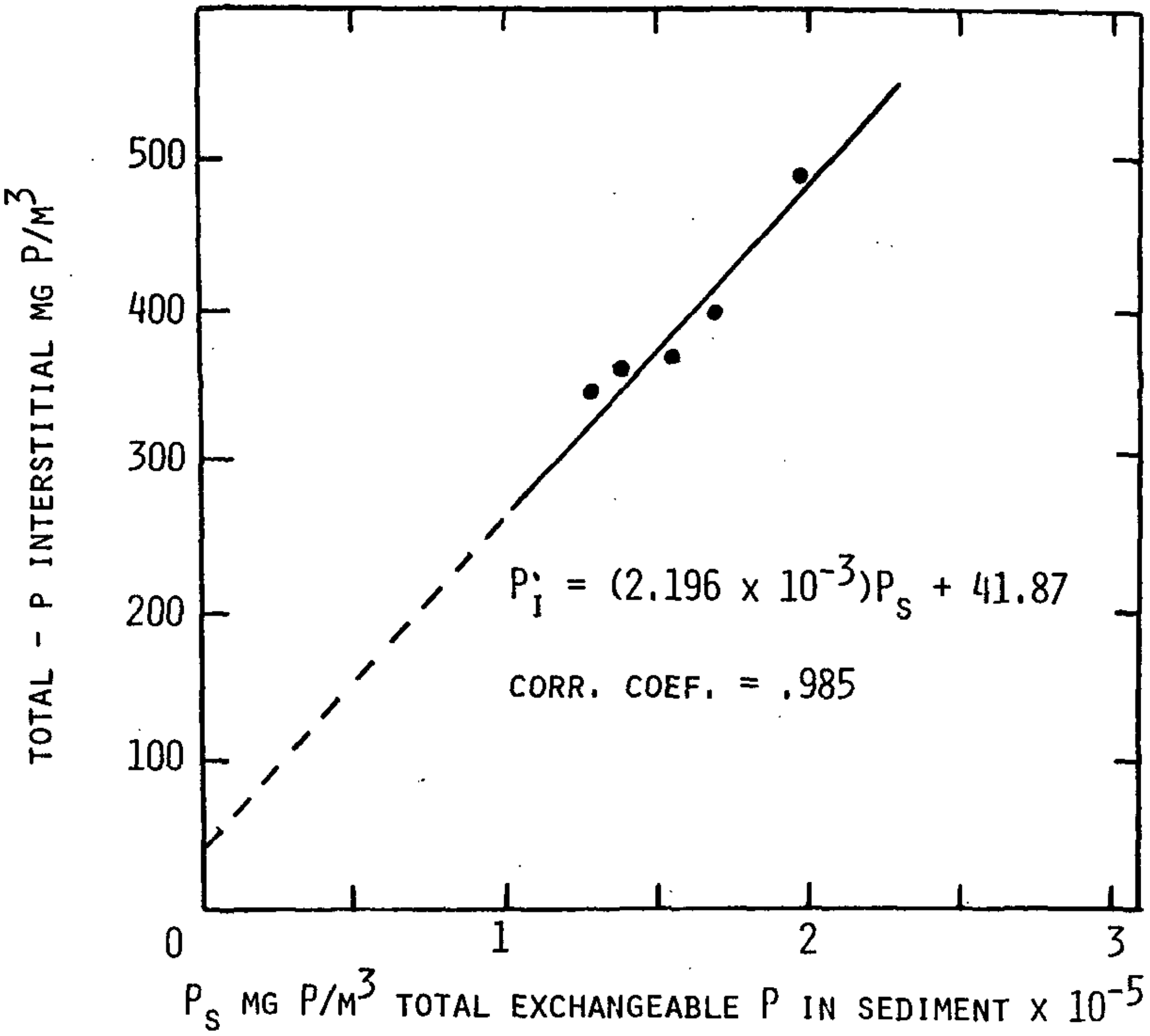

Figure 23. Equation for correlation of P_s, total exchangeable phosphorus ($.25P_t$) in sediment and total phosphate in interstitial water (P_i).

concentration in the interstitial water.

The influence of the pH and Eh on the amount of interstitial phosphate can be seen by comparing Figure 19 with Figure 24. More reducing environments (larger negative values of Eh) were found in lake areas with greater amounts of sediment phosphorus. This may have been caused by more deposition of dead algal cells. Figure 25 depicts the correlation of Eh with interstitial phosphorus. The trend noted by Ku (1975) is also shown here, with larger concentrations of interstitial phosphorus being associated with more reducing conditions. This observation can be explained by the greater extent of desorption associated with more reducing conditions.

Summary

The results of the limnological study indicate Lake Warner to be highly eutrophic with extreme bloom proportions of blue-green algae. The profile of dissolved oxygen, from supersaturation at the surface to near zero at the bottom, caused by the algal population resulted in an extremely high pH and low Eh during the summer months. These factors, along with warm temperatures, all enhance the release of phosphate from the bottom sediment (see Chapter II). With the extreme bloom proportions of blue-green algae, high phosphate concentrations in the lake water were taken up by the algae and deposited on

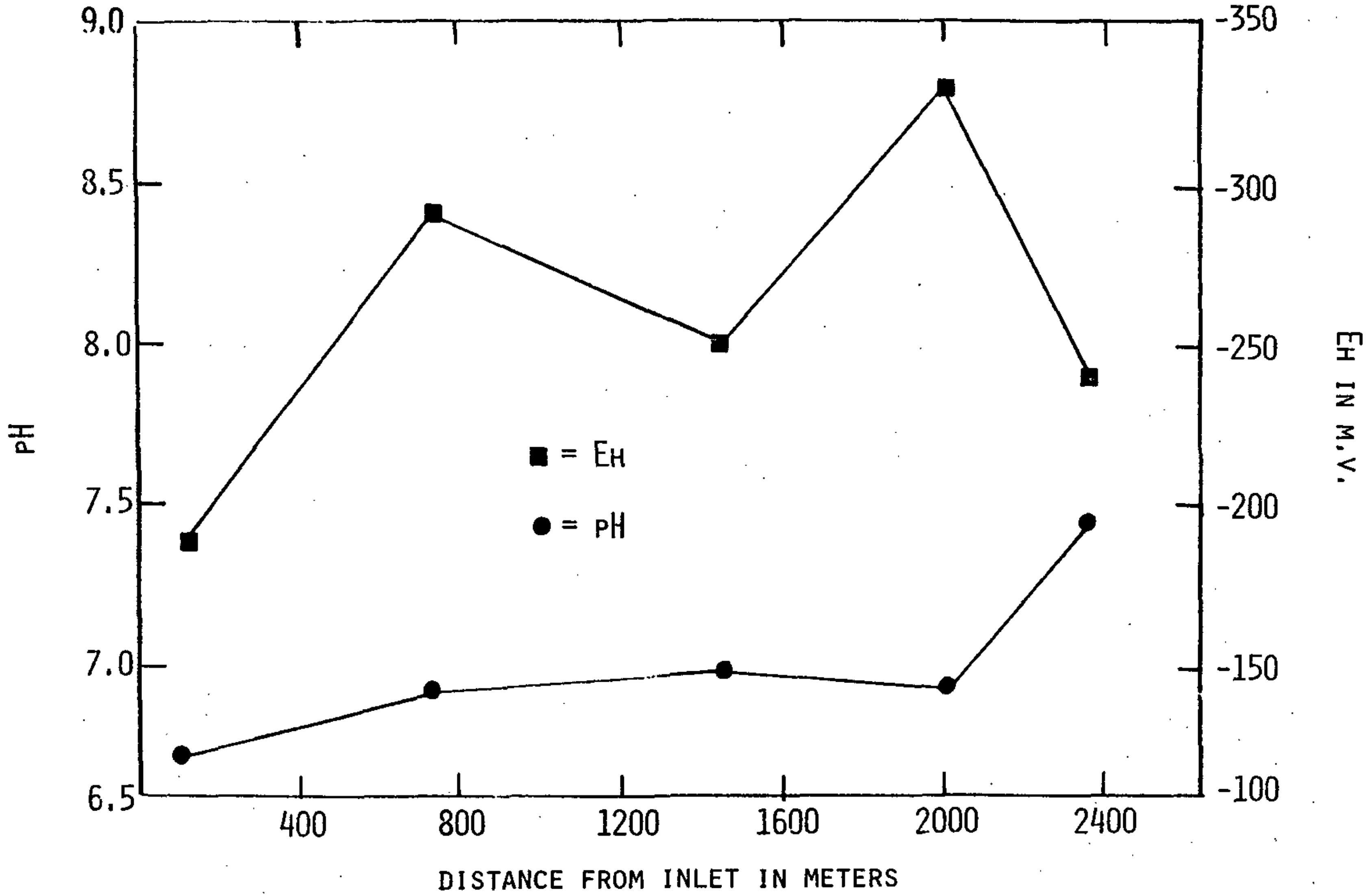

Figure 24. Spatial variation of pH and Eh in sediment, June, 1974.

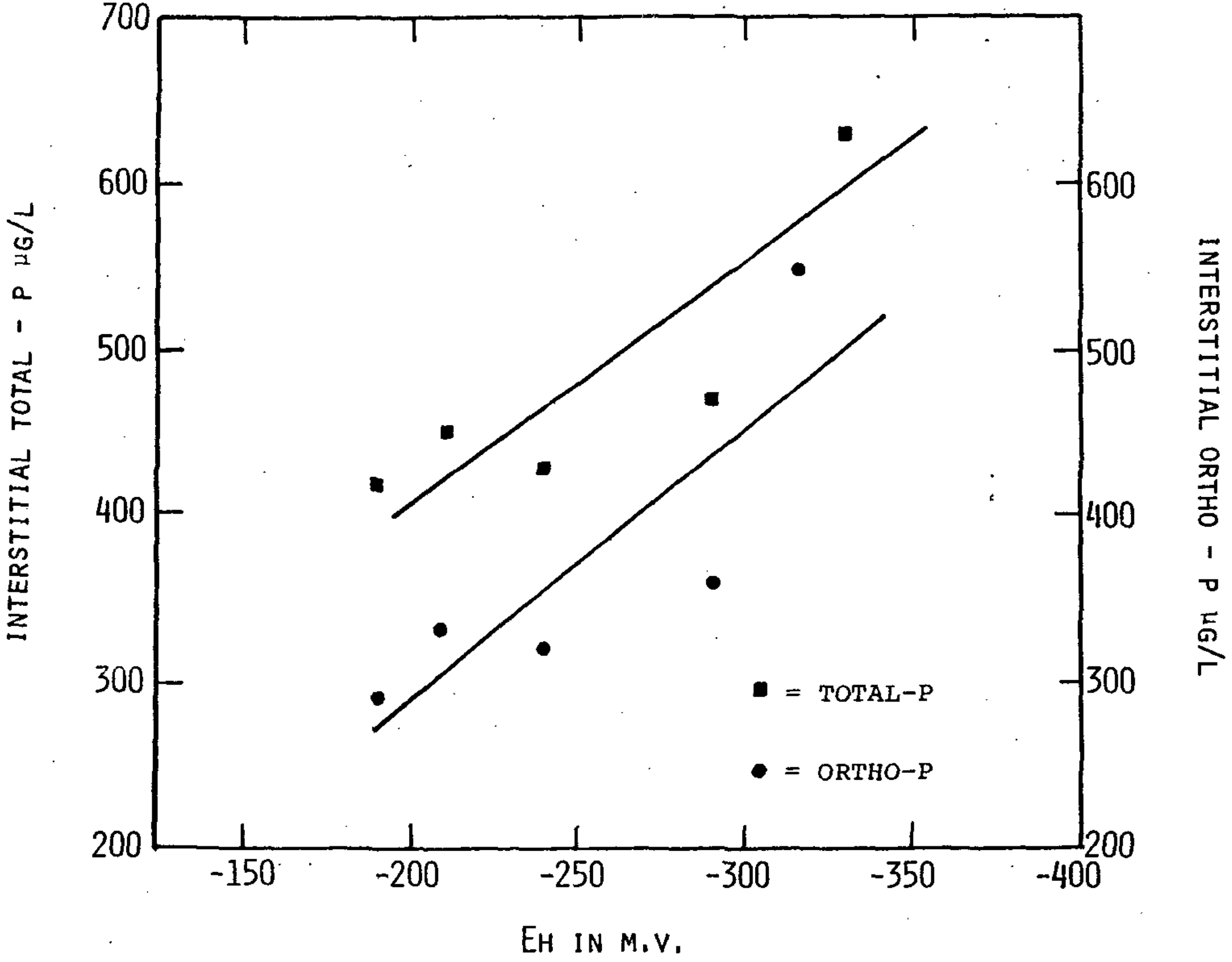

Figure 25. Parameter correlation of Eh and total and orthophosphate in interstitial water.

the bottom where decomposition occurred by the action of benthic bacteria.

Major observations drawn from the preceding data are:

(1) Daily and weekly fluctuations in the total phosphate concentration in the lake are probably due to varying influent flows and loading.

(2) Initial spring concentrations average between 70 and 90µg/l of total phosphate as P.

(3) A decrease to 40 to 60µg/l total phosphate as P occurs in the algal bloom period.

(4) An increase up to about 100µg/l total phosphate as P and then a slow decrease is apparent during the early winter as algal activity decreases.

(5) High pH and low Eh values are associated with high concentrations of phosphorus in the interstitial water.

(6) Hydraulically, the lake may be assumed to be closer to a completely mixed reactor rather than a plug flow reactor.

Obviously, interchange of phosphate between the sediment and the overlying water will be affected by seasonal variations in pH, Eh, and temperature. This was evident from the predominance of algal sedimentation during the summer and precipitation by ferric and aluminum interactions as well as adsorption onto clay particles during the winter. Similarly, release of phosphate is probably faster in the summer because of higher temperature, higher pH, and lower redox potential. Release may still occur, however, in early winter and in late spring due to bacterial decomposition of accumulated dead algal cells and desorption from clay, aluminum and iron particles. These variations in transport rates will undoubtedly affect the magnitude of the rate constants used in a descriptive lake model.

Also to be used in the predictive model is the relationship between exchangeable phosphate (P_s) and interstitial phosphate (P_i) in the sediment. Derived from experimental data taken on Lake Warner, this relationship was shown to be a linear function with dependency on Eh.

CHAPTER V

EVALUATION OF PHOSPHORUS EXCHANGE AND SUPPRESSION PROCESSES

Experimental Approach

Although laboratory studies of phosphorus exchange between sediments and overlying water are more convenient, extrapolation of results to field conditions is always suspect. Thus, in this research, the rate constants K_1 and K_2, which are most important parameters on the proposed predictive model, were determined from in-situ measurements within the lake. This was accomplished by isolating a volume of the lake to serve as a batch reactor in which overlying phosphorus was chemically removed by ion exchange to induce further release from the sediment. Thus, K_1 and K_2 could then be evaluated by application of the appropriate model and shown again here:

$$P_L = \frac{\frac{\varepsilon A}{V} K_1 P_i}{\frac{\varepsilon A}{V} K_1 + K_2} \left[1 - e^{-(\frac{\varepsilon A}{V} K_1 + K_2)t} \right] + P_{L_o} e^{-(\frac{\varepsilon A}{V} K_1 + K_2)t} \qquad (32)$$

The batch reactor consisted of a fiberglass caisson placed into the lake as schematically shown in Figure 26.

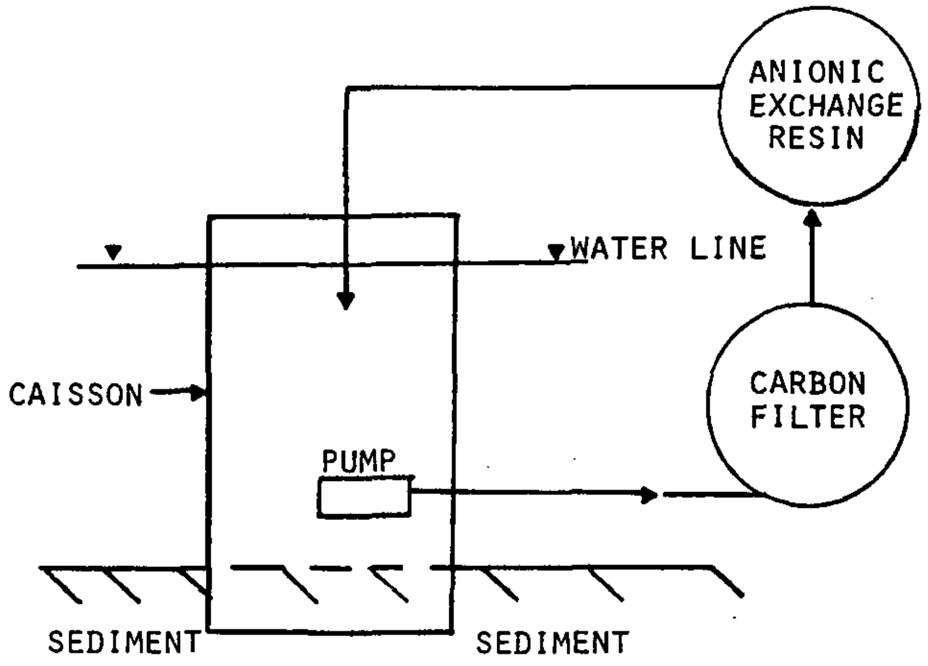

Figure 26. Schematic of caisson in lake with carbon filter and anion exchange resin.

Phosphate in the caisson water was removed using an activated carbon filter and an anionic exchanger column. Laboratory analysis was necessary to determine the proper design of both the activated carbon and anionic exchanger columns.

The objective of operating the anionic exchanger was to reduce phosphate to the lowest practical concentration. At this point, the exchange process was discontinued and the subsequent increase with respect to time was monitored. Results of this study were used to approximate the value of the release rate constant, K_1, using Equation 34. With this approximation for K_1 a gradient search technique was used to determine the value of K_2 from Equation 32.

Evaluation of the addition of kaolinite and alum as suppressants was also determined in six, smaller batch reactors imbedded in the lake. Different dosages of suppressants were added to each reactor and the equilibrium level of phosphate in the overlying water monitored. The resulting data was used to evaluate the effectiveness of these suppressants in reducing the apparent interstitial concentration of phosphate (P_i) and the subsequent reduction of the release of phosphate from the sediment (Equation 33).

Methodology for Design and Construction of Cassion, Exchange System and Suppression Tubes

Caisson. Feng (1971) has suggested the basic technique of using a caisson with the bottom protruding into the sediment. This caisson should simulate a lake volume with bottom sediments exposed to the overlying water and also be hydraulically separate from the lake. The caisson then can be modeled as a batch reactor.

A modified caisson design to that suggested by Feng (1971) was used in this study primarily for ease of transport and imbedding in the lake. The caisson shown in Figure 27, was built of No. 600, ice clear, corrugated fiberglass bolted to a aluminum frame. A plywood platform was built and positioned such that the lower 1.5 ft. of the caisson would sink into the sediment. Additional concrete anchors were also installed to prevent [illegible] caisson from overturning. The final caisson measured [illegible] height and 6' x 6' in cross section. Having a [illegible] of only 350 pounds, the unit was easily [illegible] by trailer and floated on pontoons to the site. [illegible] Because of its transparency, light penetration [illegible] during early morning and late afternoon, [illegible] overhead. This insured [illegible] changes in the

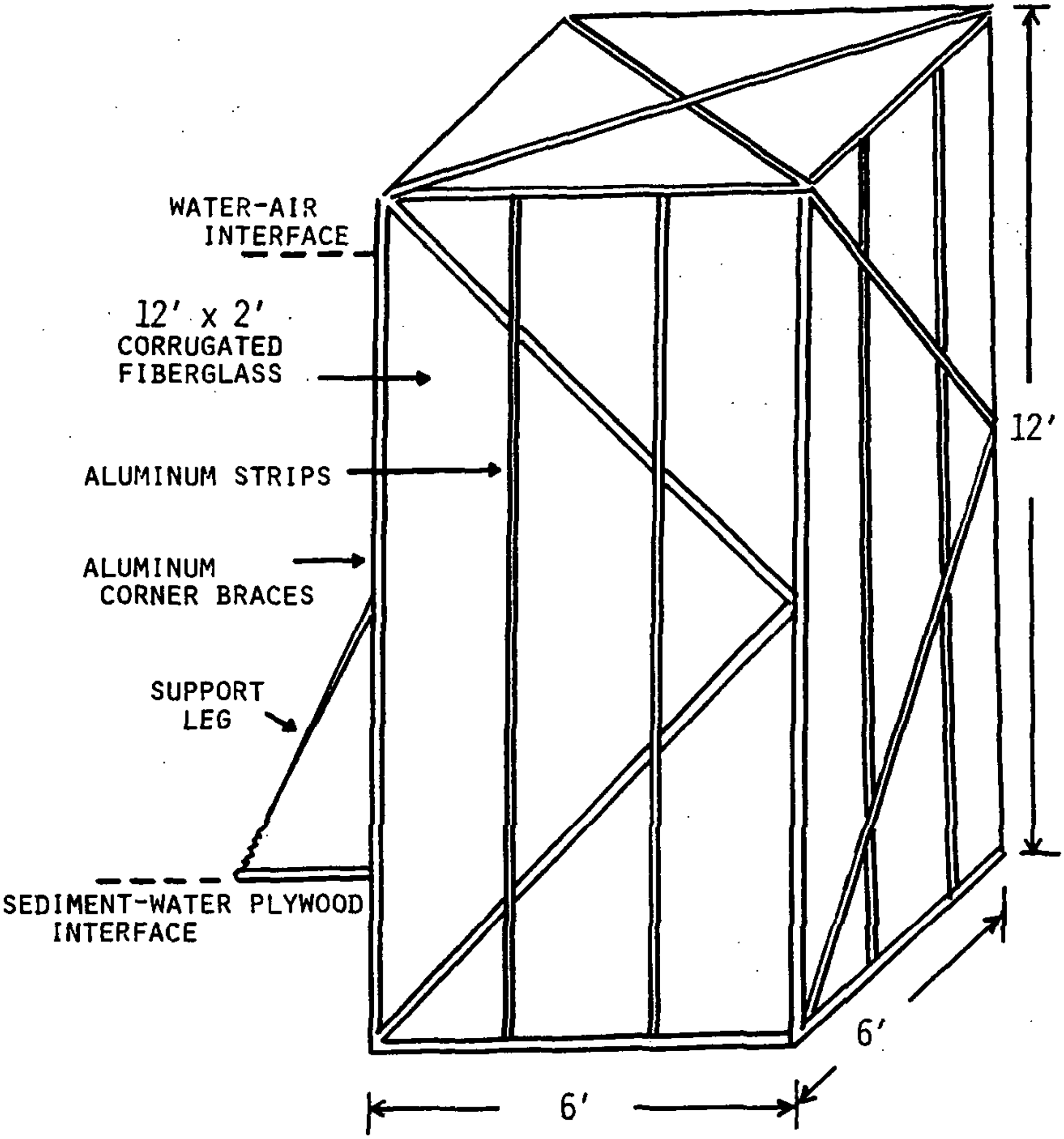

Figure 27. Caisson construction and placement.

lake were easily transmitted through the 0.032 in. fiberglass wall of the caisson. Although fiberglass itself is fairly non-reactive to phosphate all exposed aluminum parts on the inside of the caisson were coated with a non-reactive epoxy to eliminate any aluminum-phosphate reactions. The volume of water contained by the caisson was 8155 l. with the exposed sediment area being 3.34 m^2.

After the caisson was imbedded in a small cove in Lake Warner, a siphon was established between the inside of the caisson and the surrounding lake water. By changing the water level in the caisson, lake water was observed on numerous occasions to flow through the siphon. This indicated that the caisson walls, as well as the seal at the bottom of the tank, prevented water from entering. The tank was therefore considered hydraulically separate from the lake and could be used as a batch reactor.

The effect of diffusion of phosphate from the lake water through a small hole (1 cm^2) in the caisson wall was considered. Using the Wilke-Chang equation (Crank, 1956; Bird, 1960) to determine a diffusion coefficient, the theoretical flux that would occur if the lake concentration was 50 μg/l and the caisson concentration was 0 μg/l would be only 21.7×10^{-14} moles/day-cm^2. This would increase the cassion concentration by only 6.8×10^{-6} μg-P/day.

Therefore, the presence of small cracks in the walls would not cause any detectable changes during the tests for phosphate release.

This caisson arrangement provided not only the necessary batch reactor for evaluation of K_1 and K_2 but important characteristics of the surrounding lake water:

1) natural benthic, swimming, and floating organisms,
2) similar sunlight, temperature, and chemical properties,
3) the same sediment exposed to overlying water,
4) and the same phosphate interchange reactions between the sediment and the water.

Ion Exchange System. In order to study the release of phosphate from the sediment within the caisson, it was first necessary to reduce the concentration of phosphate in the overlying water. Thus, with a low value of P_{L_o} in the caisson, phosphate should release from the sediment, permitting evaluation of the release rate constant, K_1. As release proceeds, sedimentation will increase until near equilibrium conditions again prevail within the cassion. At equilibrium, K_2 can be calculated from knowledge of K_1 and the equilibrium phosphate concentration, P_{Leq} (see Equation 33).

The use of an anionic exchange resin has been suggested as a means of removing phosphate from lake water (Zajicek, 1970). Exchange of ionic phosphate at the low levels encountered in lake water can be successful in the presence of chloride, sulfate, and low bicarbonate ions present in Lake Warner (Zajicek, 1970). This method would also have minimal effects on the other chemical parameters thus simulating, as closely as possible, a natural change in P_L and promoting a natural release of phosphate from the sediment.

The initial packed bed column design was a single unit with a prefilter followed by a 1 ft. depth of Bio-Rad AG1-X4 resin. This resin consists of quaternary ammonium groups on a styrenedivinylbenzene polymer and operates with chloride ions on the exchange sites (Bio-Rad, 1971). The resin possesses an anionic exchange capacity of 3.2 meq./gm (Bio-Rad, 1971) and a 20 x 50 U.S. standard sieve fraction of resin was used.

The caisson water was passed through the ion exchanger by a submersible, 12 volt D.C. pump. Problems of clogging the pre-filter were encountered using cloth, sand, glass wool, and granular activated carbon. Activated carbon was finally selected because of ease in backwashing and cleaning. In addition, activated carbon was shown in subsequent laboratory studies to remove dissolved organic phosphate.

The amount of ion exchange resin initially proposed has sufficient exchange sites to remove all of the ionic phosphate in the caisson water. However, preliminary studies indicated that the contact time was too short and the application rate too high to provide satisfactory removals. Only about 20 percent of the phosphate and 30 percent of the total carbon was removed.

A bench-scale study was therefore conducted to determine the amount of ion exchange resin and activated carbon needed for more effective removal and the proper application rate. A 20 l. tank was filled with a distilled water solution containing 50 μg/l of PO_4^{-3}-P in order to model conditions to be expected in the caisson. A variable speed pump was used to deliver water from the tank to the ion exchange column. The effluent from the column was immediately reintroduced into the 20 l. tank thus simulating operation of the caisson. Various depths and application rates were tried.

Figure 28 shows the removal of orthophosphate from the tank as a function of time. In a similar bench-scale study, water from Lake Warner was applied to the pre-filter ion exchanger system. Figure 29 shows that much better removals of phosphate were obtained by using the activated carbon pre-filter. This suggested that organically bound phosphate was adsorbed by the carbon while algae and other particulate matter were removed by filtration.

Bench-scale study of the proposed ion exchange system indicated that:

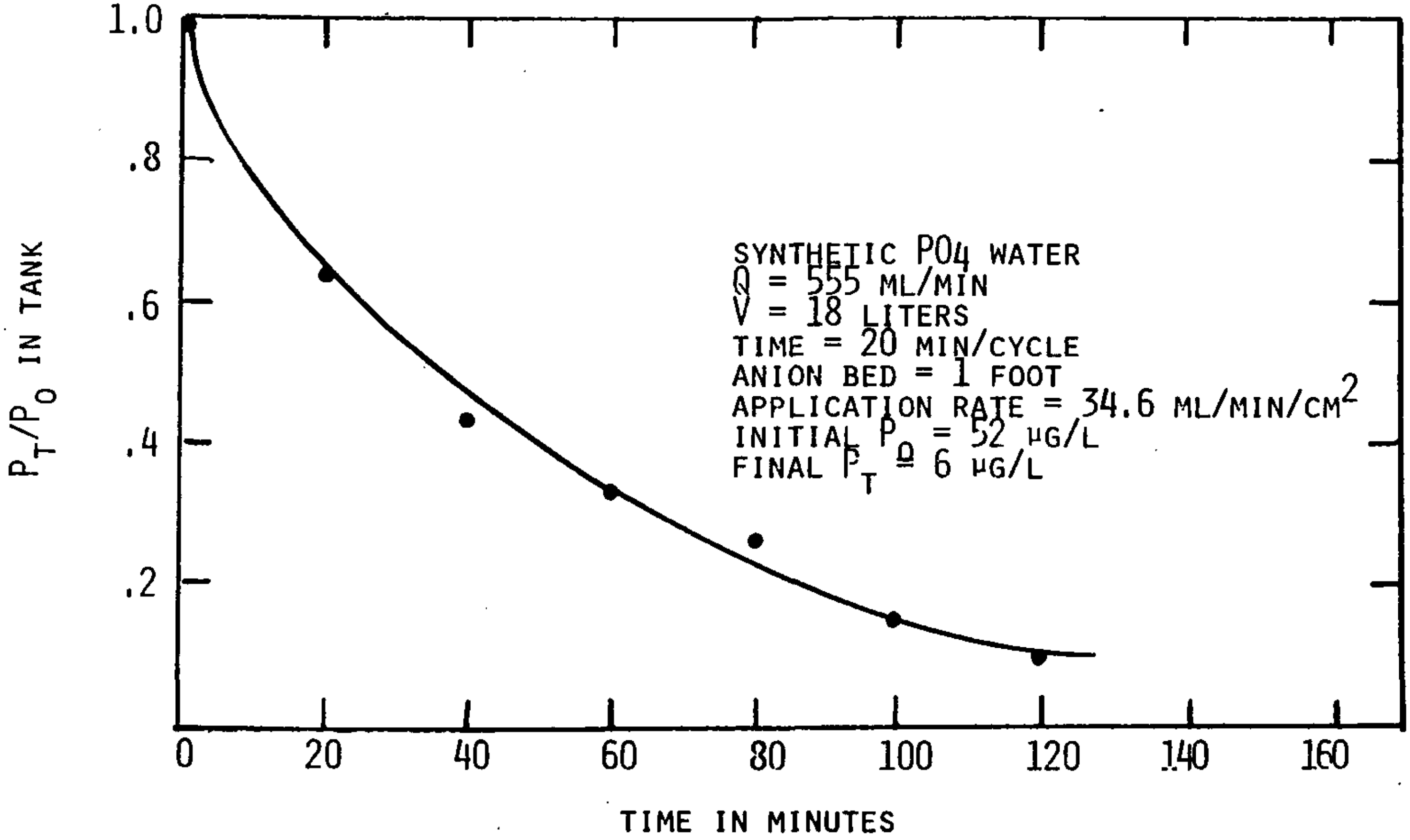

Figure 28. Orthophosphate removal without activated carbon in pilot study.

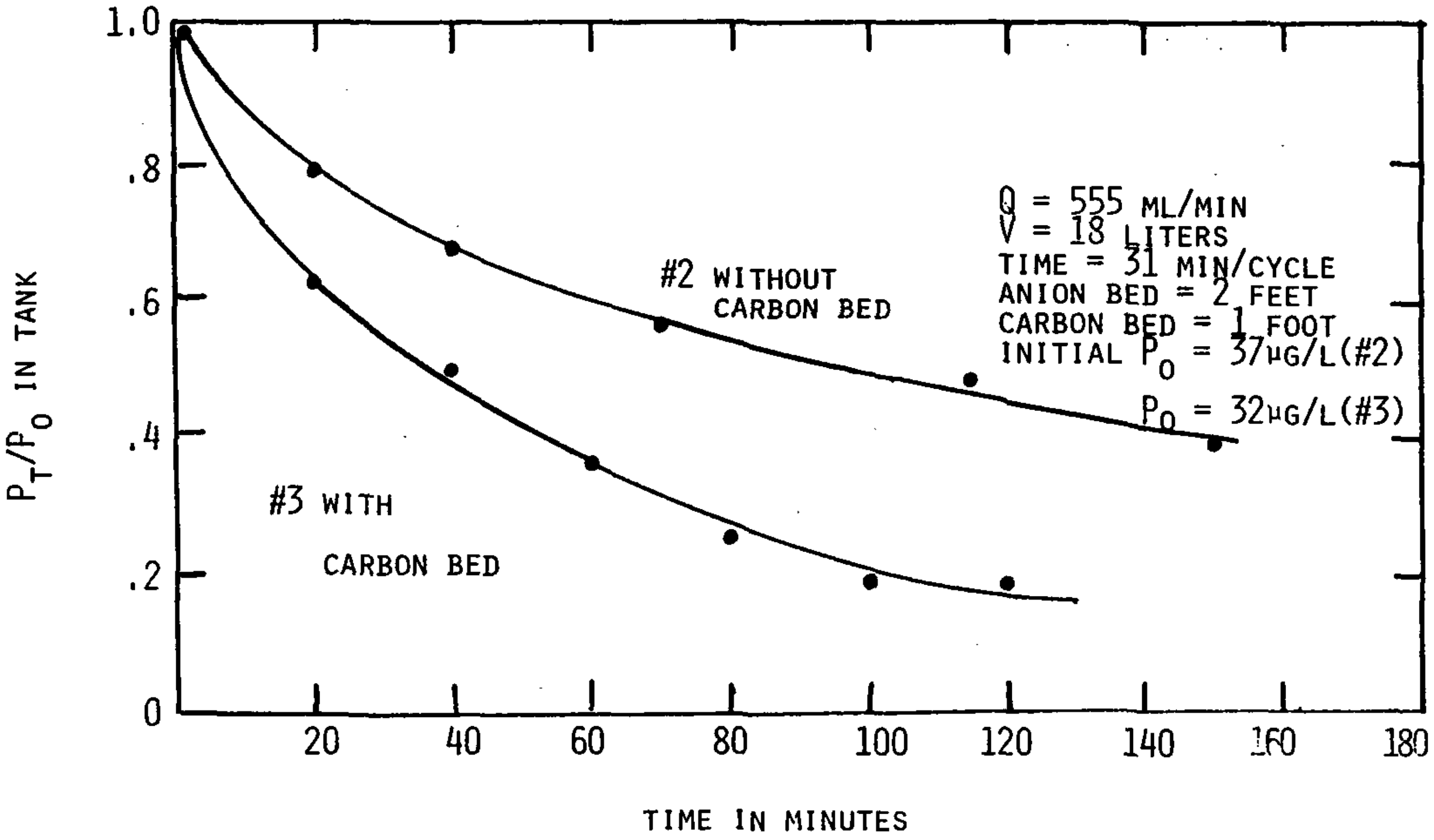

Figure 29. Orthophosphate removal from lake water with and without activated carbon in pilot study.

(1) Cycling of three caisson volumes (8155 liters) through the proposed system would be sufficient to remove approximately 80 percent of the phosphate. The time required for displacement of one caisson volume would be 23 hours.

(2) Using 1 ft. of activated carbon as a pre-filter and 3 ft. of resin for exchange would be sufficient to remove 80 percent of the phosphate.

(3) Application rate approximately 2 gpm/ft^2 would give sufficient contact time for the desired removal.

(4) A pressurized system would be needed to maintain this flow rate.

(5) Valving to allow backwashing to remove algae and sediment would be required.

(6) A coarse screen pre-filter should be placed around the pump to remove large algae clumps before they clog the activated carbon.

Suppression Study. To determine the effectiveness of kaolinite and alum in suppressing release of phosphate, six small batch reactors were constructed. These units were cylindrical in shape, having a height of 6 ft. and internal diameter of 11.5 in. The construction material was galvanized sheet metal, soldered together and tested to be watertight. The inside was coated with a non-reactive, epoxy spray paint (4 layers) to prevent any zinc or iron reactions with release phosphate. The six tubes were held in position by a plywood platform, and protruded a distance of 1 ft. into the sediment. Field tests using a siphon indicated that all tubes were hydraulically separate from the lake. The contained sediment area was 0.0729 m^2 (.785 $ft.^2$) with an overlying water volume of 88.9 l. (3.14 $ft.^3$).

The amounts of each suppressant added were first approximated using exchange capacities of about 1 meq/gm for alum and .25 meq/gm for kaolinite. If the assumed depth of active sediment exchange of phosphate is 10 cm then the potential release of phosphate into each tube is between 600 and 900 mg. This could be adsorbed by 32 gm of alum. Lesser estimates of required dosage can be arrived at from available literature values. Dosage of alum in other lakes varied from 20 to 100 gm/m^2 giving a required dosage in the suppression tubes of between 2 and 7 grams.

Table 3 lists the dosage of alum and/or kaolinite finally selected for addition to each suppression tube. These values fell within those reported in the literature and that calculated from exchange capacity of the sediment. The suppressants were mixed into each tube and agitation was continued to induce good floc formation. In tubes 1-5, all of the suppressants settled onto the bottom after 1 day. Tube N. 6 served as a control with no chemical addition. In these studies, adsorption of released sediment phosphate, as discussed in Chapter II, would most likely occur at

Table 3. Alum and Kaolinite Dosages

Tube Number	Alum Added grams	Kaolinite Added grams
1	4	0
2	1	0
3	1	8
4	.25	2
5	4	16
6	0	0

anionic exchange sites of aluminum, $Al(OH)_x(PO_4)_{1-x/3}$, and kaolinite, $Si_2O_5Al_2(OH)_4 \cdot PO_4$.

Evaluation of Release and Sedimentation Rate Constants

Three separate tests of phosphate release were conducted in the caisson. In each case, the procedure was as follows:

(1) install the ion exchanger column, activated carbon column, battery, pump, and hoses on platform within the caisson; (2) operate the system continuously to remove phosphate from the caisson water with daily backwashing;
(3) monitor the decrease in concentration of orthophosphate until a value of about 10 μg/l was reached; and
(4) discontinue operation of the ion exchanger - carbon system and monitor the increase in concentration of phosphate at various levels in the caisson until an equilibrium concentration is reached. In the first two tests, mixing was only provided during the operation of the exchanger. However, in the third test, mixing was provided following exchange of phosphate in order to provide a better approximation to a completely mixed reactor. The subsequent release of phosphate from the sediment can be used to determine the rate constant, K_1. The initial caisson test, was conducted from July 9 to August 14, 1973. Figure 30 shows that a reduction in orthophosphate of 78 percent was

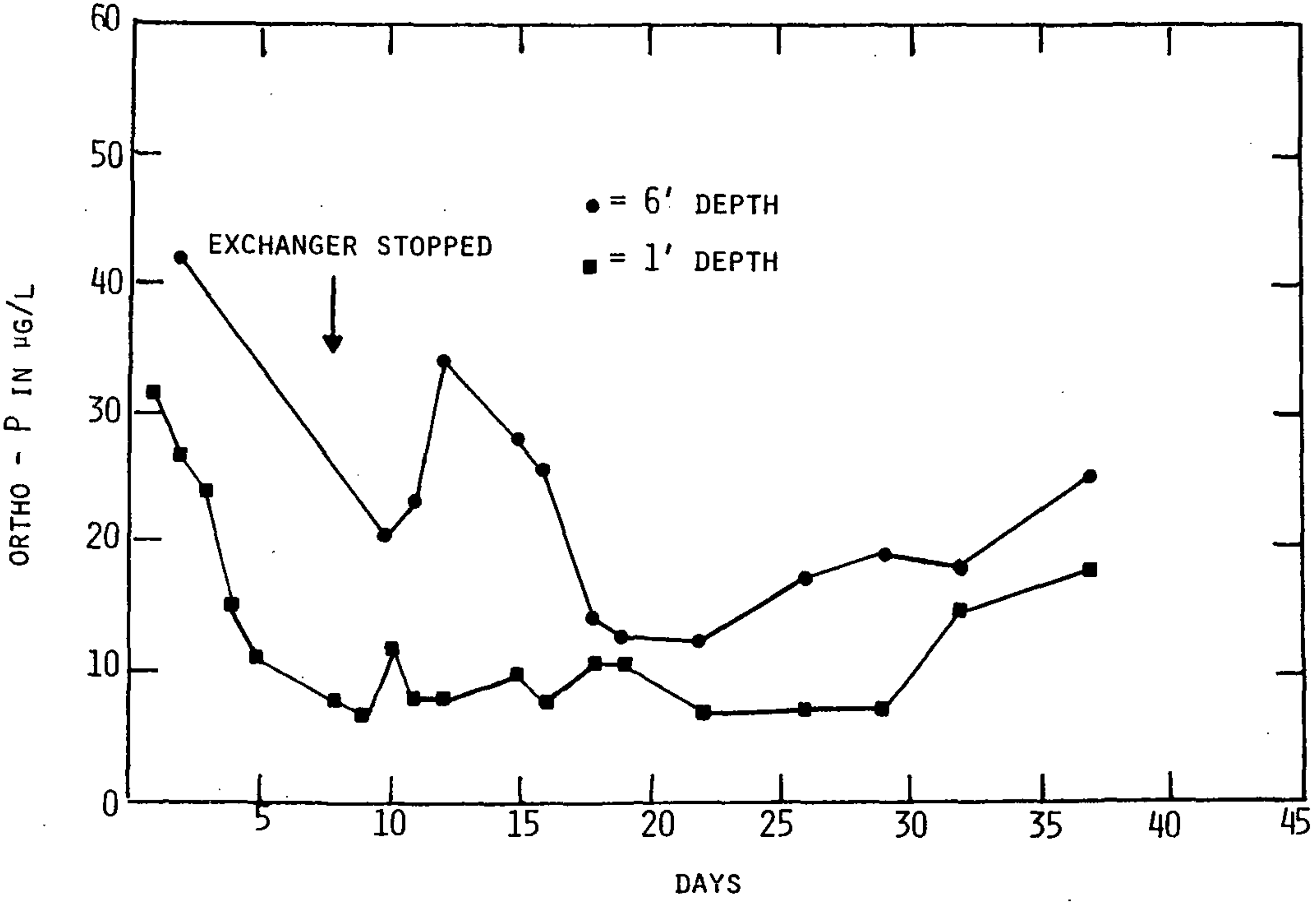

Figure 30. Temporal variation of orthophosphate in caisson during and after exchange, July 9 to August 14, 1973

achieved at 1 ft. and 52 percent at 6 ft. below the water surface (depth to sediment was 7.5 ft.). This reduction was accomplished by circulating the caisson water through the ion exchanger-carbon columns for 9 days. After the exchange process was stopped, the orthophosphate at the 6 ft. depth increased from 20 to 34 μg/l and then abruptly decreased. Removal by iron adsorption is believed to have caused this decrease. A gradual increase at both levels occurred for the next 20 days. Algal uptake of orthophosphate and conversion to organic phosphate may explain this rather slow increase in orthophosphate concentrations.

Figure 31 indicates that changes of total phosphate followed a more predictable pattern than orthophosphate. Here, a rapid and fairly uniform increase in concentration can be seen after the ion exchanger was stopped. Because mixing was discontinued at this time, the concentration was considerably greater at the bottom than at the surface. Thermal and wind induced mixing was the only mechanism to circulate the released phosphate.

In the second caisson test, (from September 27 to December 1, 1973), the ion exchanger system was operated for 17 days. Figure 32 indicates that orthophosphate initially decreased but then increased and remained near 25 μg/l for 8 days of exchanger operation. Similar results are shown in Figure 33 for total phosphate.

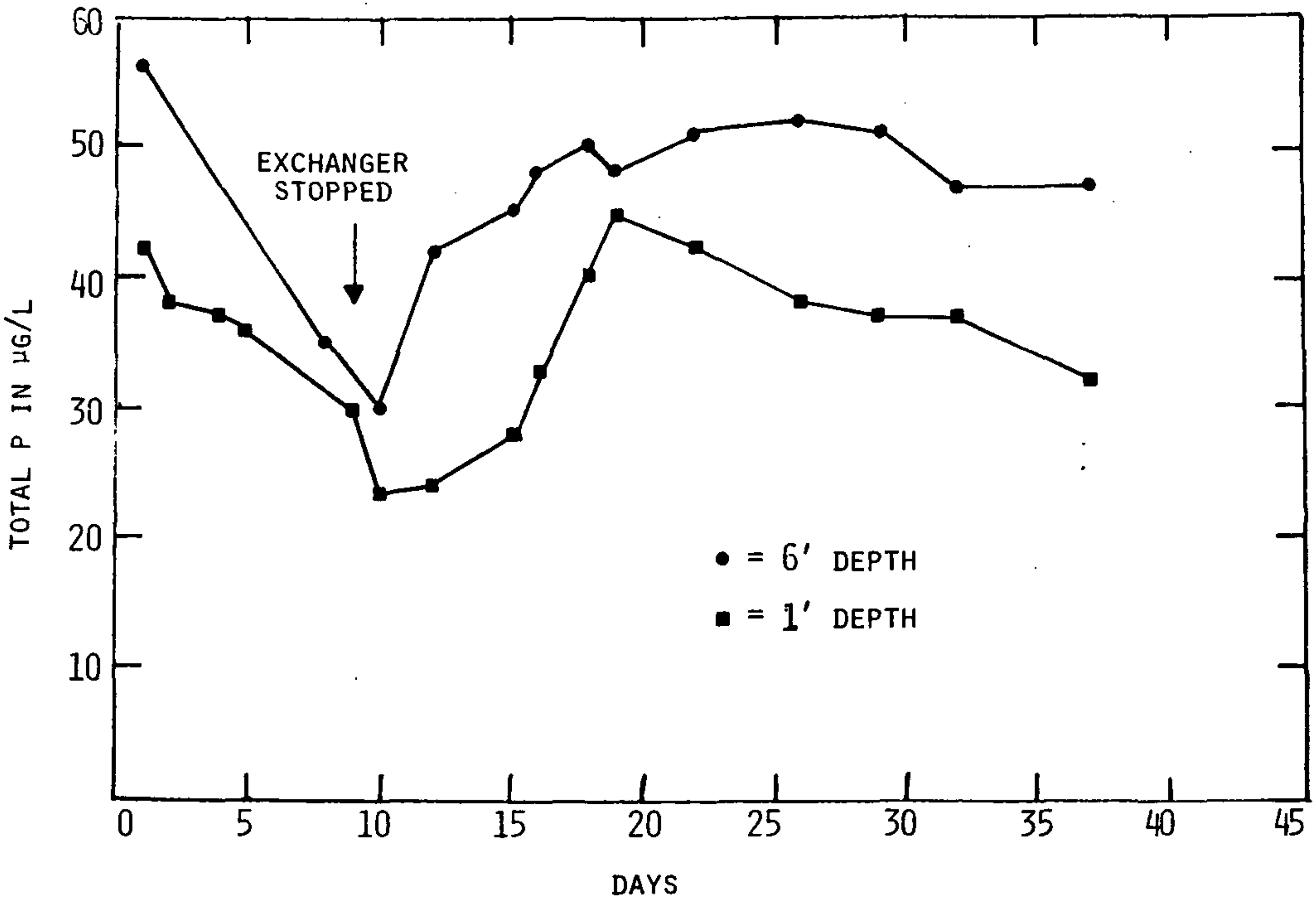

Figure 31. Temporal variation of total phosphate in caisson during and after exchange, July 9 to August, 1973.

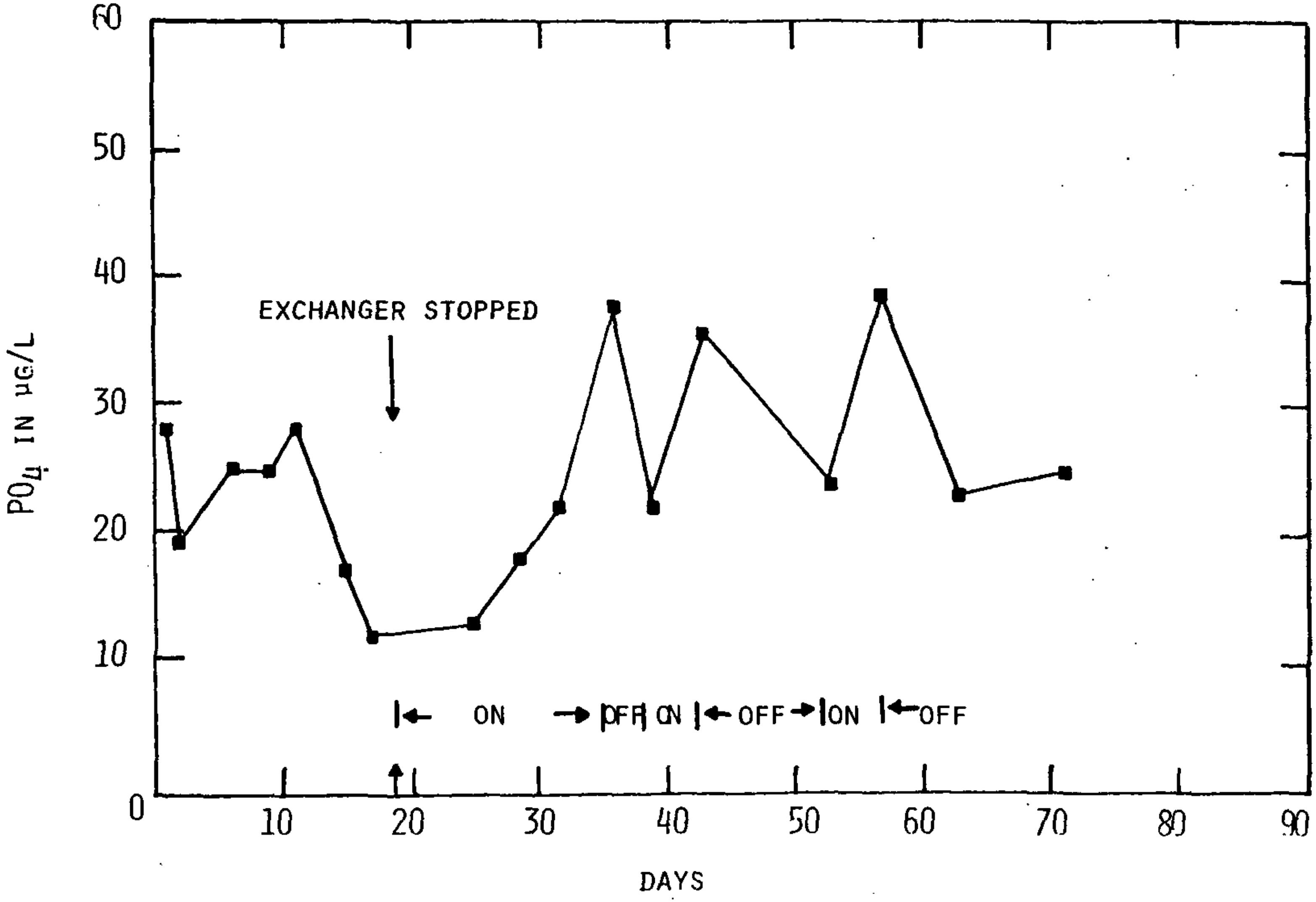

Figure 32. Temporal variation of orthophosphate in caisson during and after exchange, September 27 to December 1, 1973. On and off refer to time periods when mixing pump was operational.

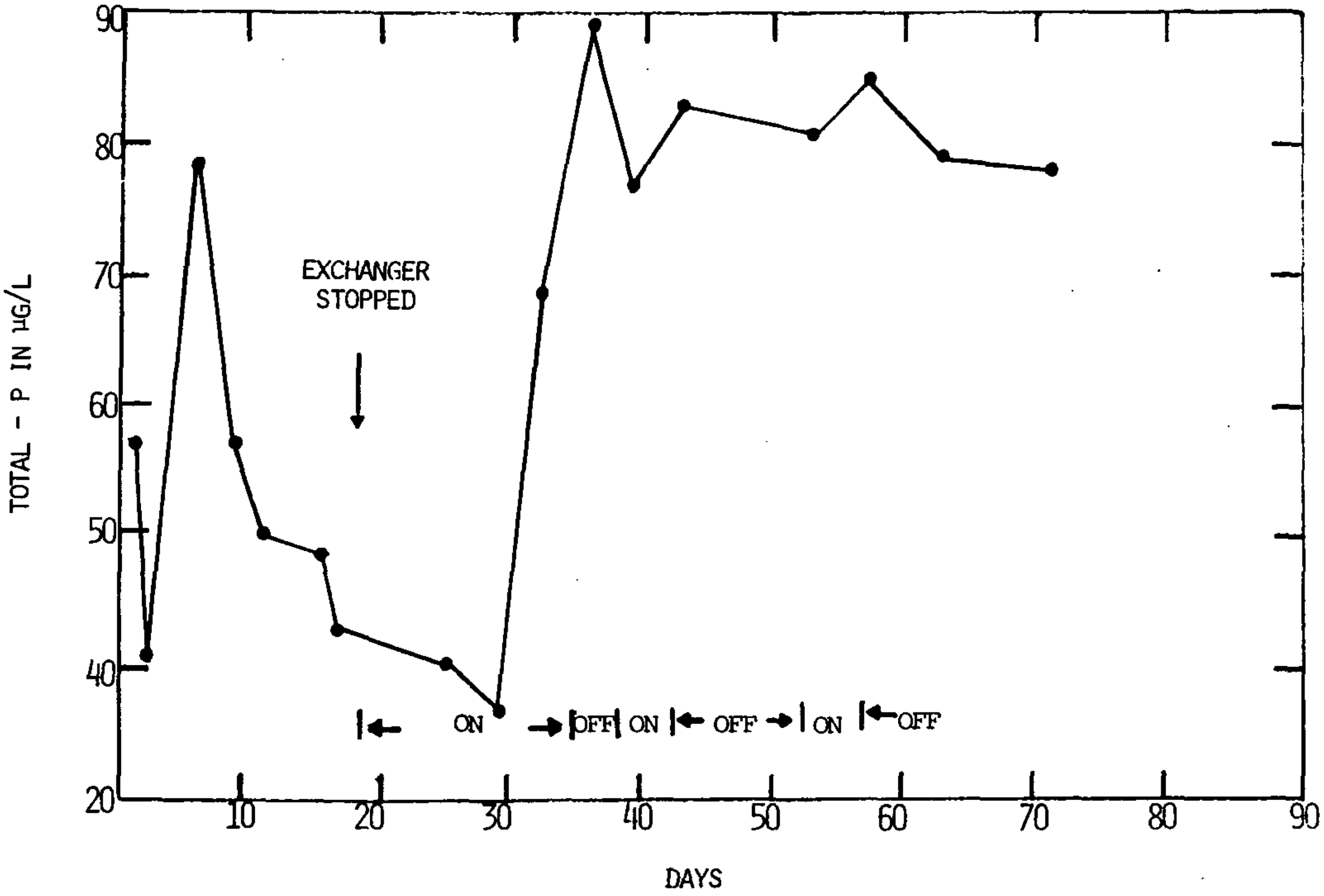

Figure 33. Temporal variation of phosphate in caisson during and after exchange, September 27 to December 1, 1973. On and off refer to time periods when mixing pump was operational.

Failure to reduce phosphate levels was caused by positioning of the submersible intake pump too close to the bottom from day 2 to 9 of ion exchanger operation. This allowed sediment and interstitial water to mix with the caisson water. After discontinuing the ion exchanger operation, mixing was attempted by using a submersible pump to bring water from the 6 ft. depth to the surface.

During mixing, higher levels of orthophosphate were observed; however algal uptake and conversion to organic -P reduced the concentration at the surface when the mixing process was stopped. This was due to lack of renewal of phosphate from the bottom. Total phosphate concentration was less affected by mixing (Figure 33) because both dissolved and suspended (including algae) phosphate were included. Problems with pump and battery operations produced interruptions in the mixing process as shown in Figures 32 and 33. Hence, although a definite release of phosphate was observed, the release rate was difficult to measure.

From the results of the first two caisson tests, a third test was needed in which gentle mixing was continuous and concentrations were determined at various depths in the tank.

The final caisson test was conducted from December 6 to December 27, 1973 with concentrations of total and orthophosphate being monitored at depths of 1, 3, and 7 ft.

In this test, the mixing pump remained in continuous operation after phosphate removal by the ion exchanger system. As shown in Figure 34, orthophosphate concentration was reduced from about 34 μg/l to 14 μg/l in 9 days. After ion exchange was stopped, release from the sediment increased the orthophosphate concentration by 29 μg/l (from 14 μg/l to 44 μg/l) at the 7 ft. depth. Despite continuous mixing, orthphosphate at the 1 and 3 ft. depths only increased by 18 μg/l (from 14 to 32 μg/l). While algae were not numerous, their presence at the surface may account for a lower concentration of phosphate. The removal and release of phosphate measured as total phosphate is shown in Figure 35. The depth averaged decrease in total phosphate was from 63 to 34 μg/l. Because both organically bound and orthophosphate are removed by the ion exchanger system, the increase in total phosphate after discontinuation of the ion exchanger, was 30 μg/l (from 36 to 66 μg/l) at the 4 ft. depth or about equal to the increase in orthophosphate (29 μg/l). Thus, release of orthophosphate from the sediment is definitely indicated as the source of increase in total phosphate in the caisson water.

Mixing appeared to keep the concentrations fairly uniform a short distance above the sediment. However, larger concentrations were still apparent near the sediment, probably as a result of the concentration driving force across the sediment-water interface.

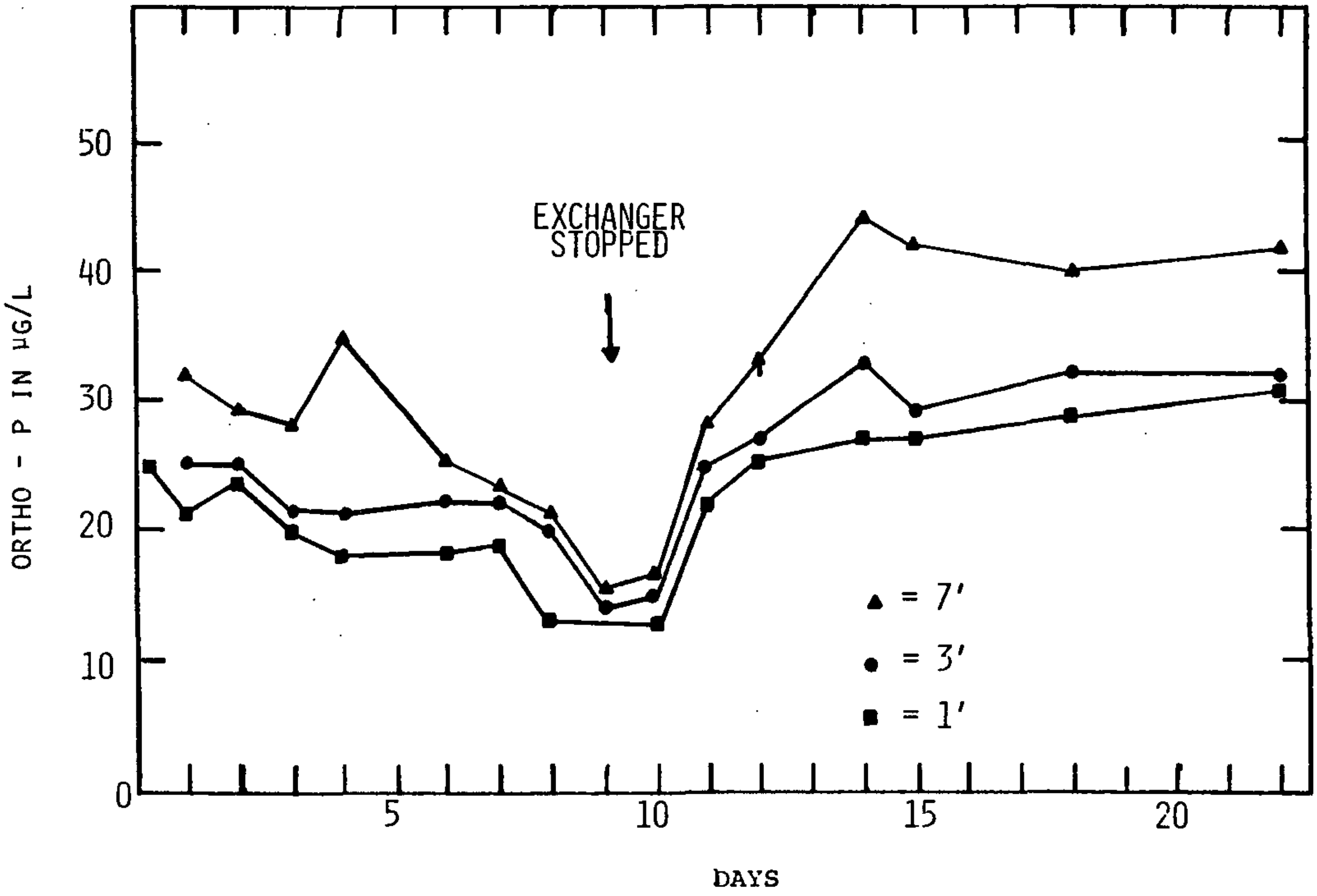

Figure 34. Temporal variation of orthophosphate in caisson during and after exchange, December 6 to 27, 1973.

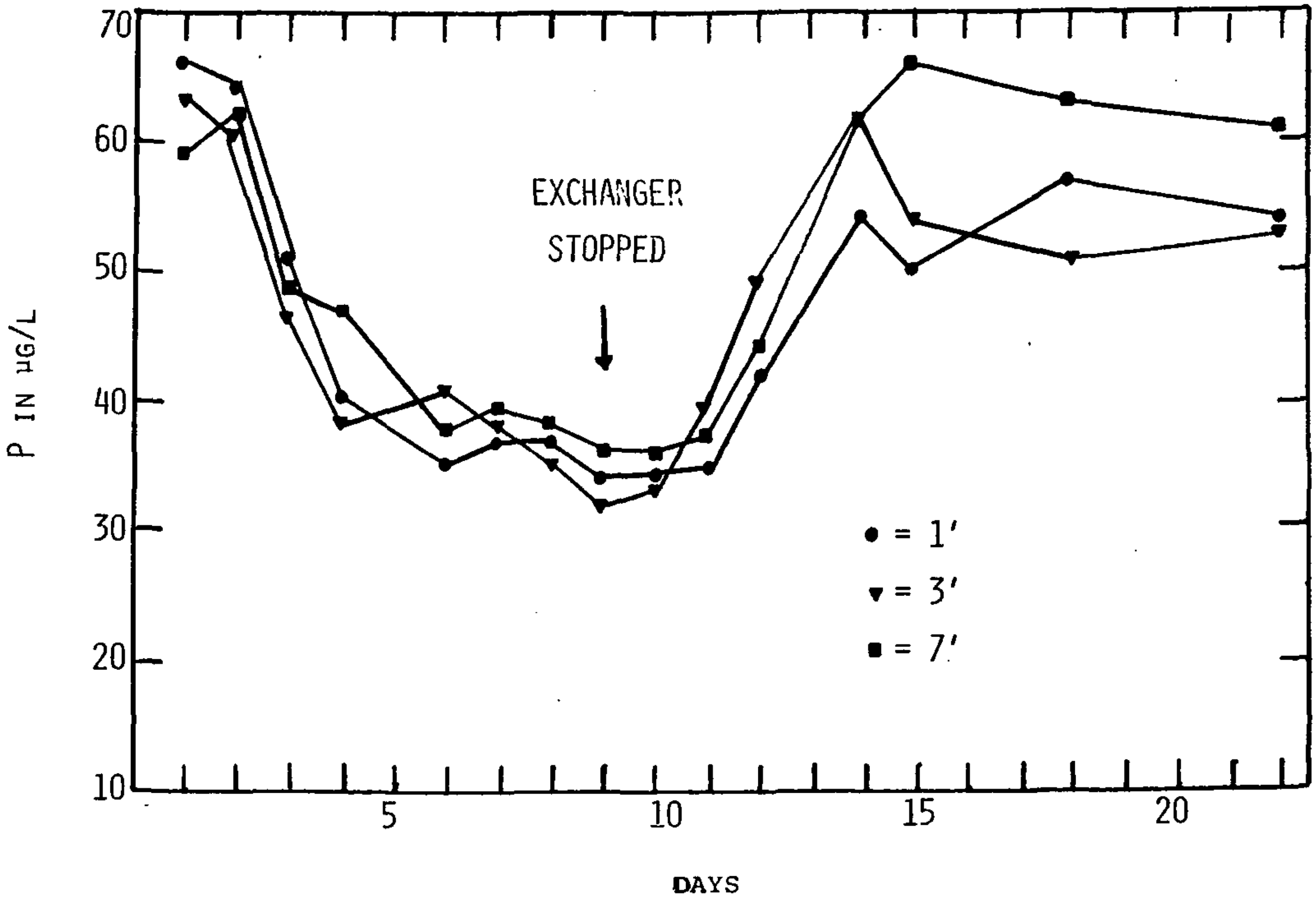

Figure 35. Temporal variation of total phosphate in caisson during and after exchange, December 6 to 27, 1973.

Of particular note in Figure 35 is the tendency towards an equilibrium concentration of total phosphate in the caisson after about 5 days. This is also apparent in the previous figures for total phosphate. Equilibrium is established when the rate of phosphate release from the sediment becomes equal to the rate of phosphate sedimentation. The initial increase in concentration after exchange had been terminated was due to release of orthophosphate from the sediment. The rate was initially high because the concentration gradient between interstitial (P_i) and caisson (P_L) water had been increased by reducing the concentration, P_L. Sedimentation of phosphate by algae and adsorption onto hydroxometal complexes was insignificant during this period. However, as the concentration of phosphate in the caisson increased, the rate of sedimentation also increased. An attempt was made to correlate total iron with phosphate in the caisson studies. A general trend was noted in the first two tests, with high concentrations of iron being associated with high phosphate concentrations (see Appendix C). However, correlation coefficients were less than 0.35. Release from the sediment under low redox potential can still be partially attributed to the breakdown of ferric iron complexes. The reduced ferrous iron may be re-precipitated as FeS or $Fe(OH)_2$ after the phosphate is released from the ferric complex. Analytical errors and instrumentation accuracy may also have contributed to the difficulty in correlating iron and phosphate data.

Determination of Rate Constants

According to the model derived in Chapter III, the release of phosphate from the sediment in a batch reactor can be described as:

$$P_L = \frac{\frac{\varepsilon A}{V} K_1 P_i}{\frac{\varepsilon A}{V} K_1 + K_2} \left[1 - e^{-(\frac{\varepsilon A}{V} K_1 + K_2)t} \right] + P_{L_o} \, e^{-(\frac{\varepsilon A}{V} K_1 + K_2)t} \qquad (32)$$

An estimate of K_1 can be obtained from the initial release data if sedimentation is considered negligible.

Thus, from Equation 31:

$$V \frac{dP_L}{dt} = \frac{\varepsilon A}{V} K_1 \; (P_i - P_L)V \qquad (47)$$

Using the data collected in the December 1973 study, which was considered the most representative, the initial rate of change of concentration, dP_L/dt, was 10 μg/l/day, or $V \frac{dP_L}{dt}$ equal to 82 mg/day.

The additional data required for substitution into Equation 47 is:

ε = porosity = .84

A = sediment area = 3.5m^2

V = tank volume = 8.155m^3

P_i = measured interstitial P conc. = 410 μg/l total P

P_L = average tank water P. conc. (0<t<5 days) = 53 μg/l. total P.

Solving for K_1 yields 0.078 m/day. The steady-state phosphate concentration, P_{Leq}, attained in the batch reactor was shown by letting $t \to \infty$ in Equation 32 such that,

$$P_{Leq} = \frac{\frac{\varepsilon A}{V} K_1 P_i}{\frac{\varepsilon A}{V} K_1 + K_2} \qquad (33)$$

An approximate value of K_2 was determined as .15/day by substituting known values of ε, A, V and estimates of P_i, K_1 and P_{Leq} into Equation 33.

Values of K_1 and K_2 thus obtained from initial rate and equilibrium data, value of P_i (interstitial phosphate concentration), were then refined using gradient search technique modified from Sanders (1974). This technique involves calculation of P_L in the unsteady-state batch reactor model describing the caisson system (Equation 32) over the experimental time period between discontinuation of ion exchanger operation and attainment of approximate equilibrium. Initial estimates of K_1, K_2 and P_i were used in the model to obtain calculated P_L values which were then compared to experimental values over the observation period. Each of the three constants K_1, K_2 and P_i was then incremented by a small value and a new set of values for P_L compared to the experimental data. This computational scheme was repeated until a minimum sum of the squared differences between the calculated and experimental values was obtained. The values of K_1 and K_2 derived using the gradient search technique are deemed more accurate than the estimates based on initial rate and final equilibrium data. The required computer program is found in Appendix D along with the results.

Figure 36 shows a comparison between the experimental and predicted results from the first test of the caisson. The experimental values were of total phosphate concentrations at a depth of 6 ft. The rate constants obtained from the gradient search technique were slightly higher than those approximated (0.087 m/day versus 0.078 m/day and 0.183/day versus 0.15/day for K_1 and K_2, respectively). However, a correlation coefficient value of 0.93 indicated a good fit between actual and calculated concentrations in the caisson.

Comparison of experimental and predicted total phosphate-time data for the second caisson test is given in Figure 37; a correlation coefficient of 0.89 was obtained. In this test, the calculated value of P_i of 460 μg/l was considerably higher than the observed of 425 μg/l. This discrepancy is probably due to samples being taken only at the surface and the lack of complete mixing during the entire sampling period. It should also be noted that a lower correlation coefficient of .81 was found for the first caisson test using only data obtained from surface samples.

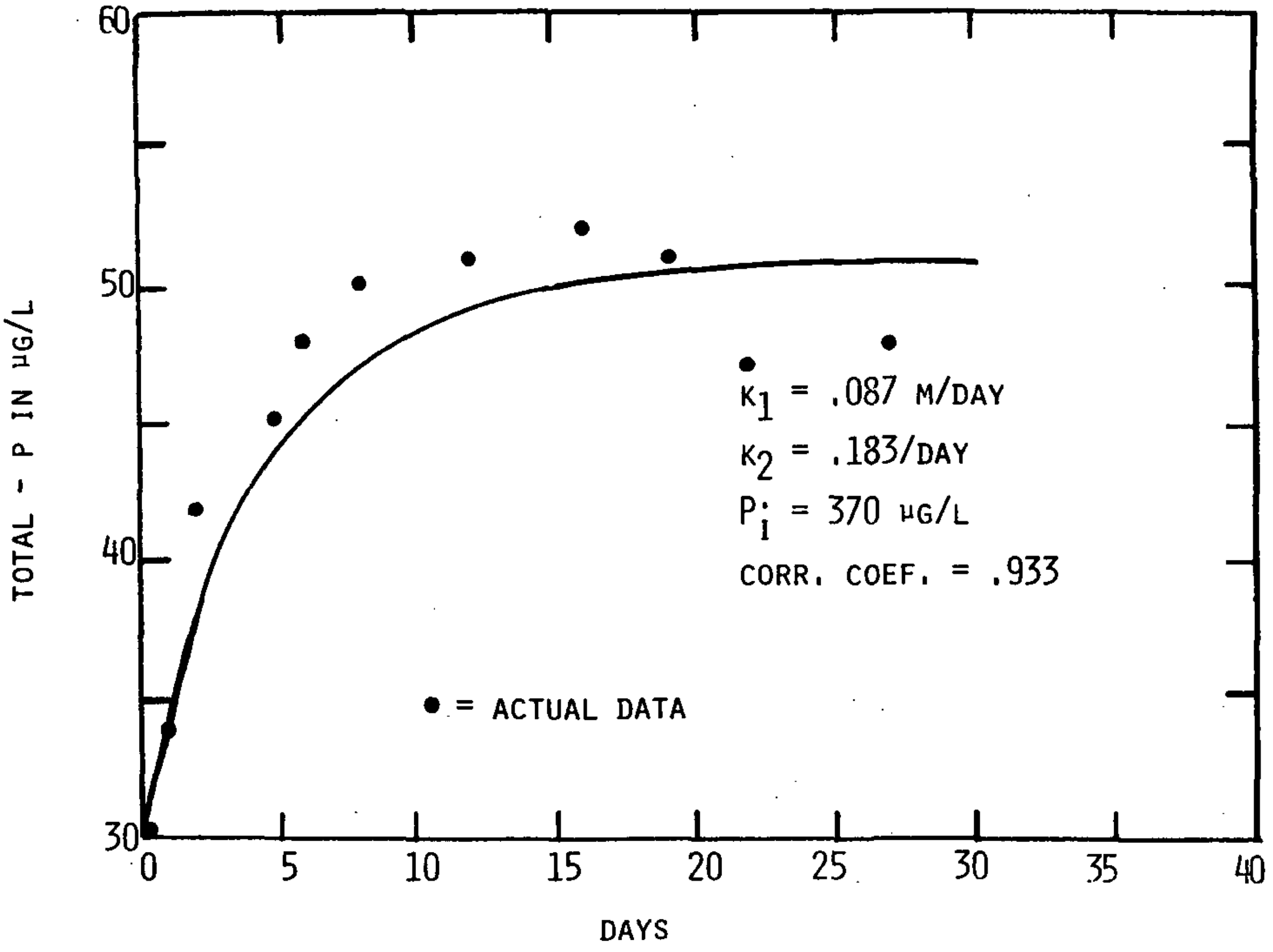

Figure 36. Batch model prediction versus caisson release data for total phosphate, July 9 to August 14, 1973.

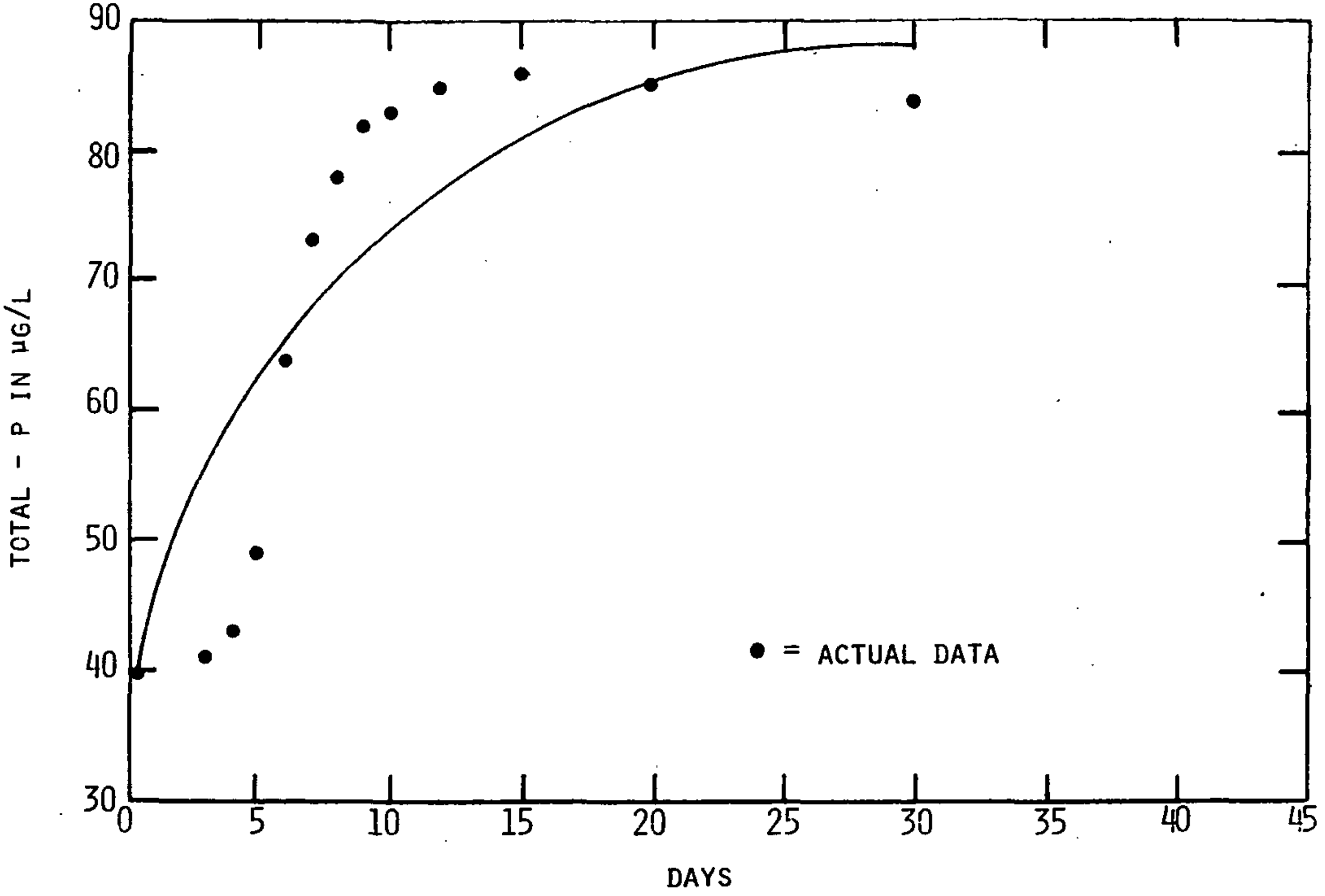

Figure 37. Batch model prediction versus caisson release data for total phosphate, September 27 to December 1, 1973.

Figure 38 depicts the experimental and predicted results of total phosphate versus time in the third caisson test, conducted in December 1973. Here, experimental data from the 1, 3, and 7 ft. depths were averaged together to obtain a value representative of a completely mixed, batch reactor. A best fit of the data by the gradient search technique yielded a correlation coefficient of 0.96. This was far superior to results from the first two caisson tests. The calculated best fit constants were thus:

K_1 = .091 m/day

K_2 = .176/day

P_i = 430 μg/l

Because greatest care was taken to insure proper mixing and measurement of phosphate, in this third caisson test, the values obtained for K_1 and K_2 are considered more reliable than in the two previous tests. In addition, the measured (410 μg/l) and predicted values (430 μg/l) of P_i were quite close.

Suppression Study Results

<u>Field Observations</u>. Phosphate suppression studies were conducted from October to December 1973 For comparative purposes, the resulting orthophosphate-time profiles observed in each of five suppression tubes are grouped in Figure 39-41. Also included are concentration-time profiles in the adjacent

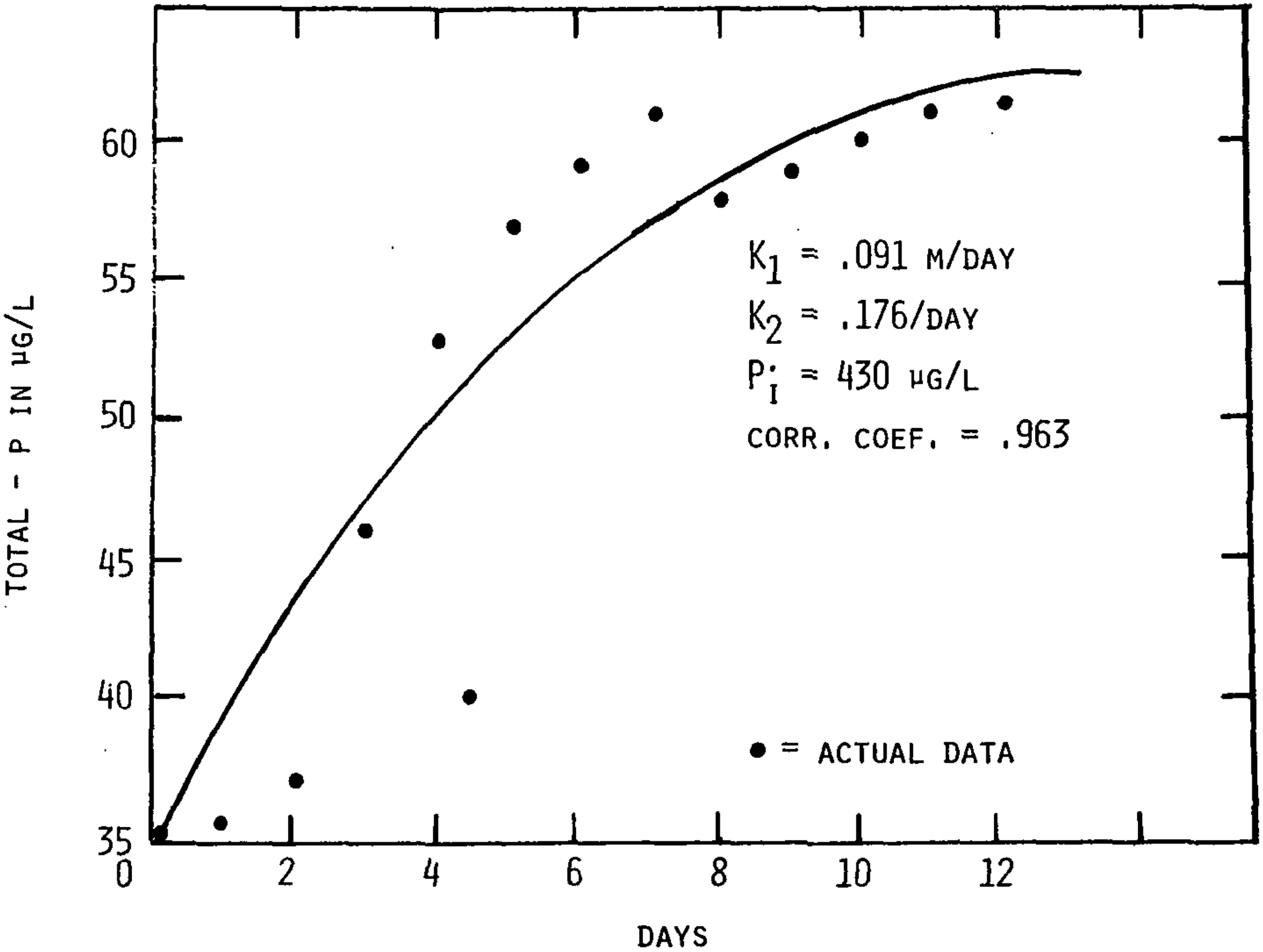

Figure 38. Batch model prediction versus caisson release data for total phosphate, December, 1973.

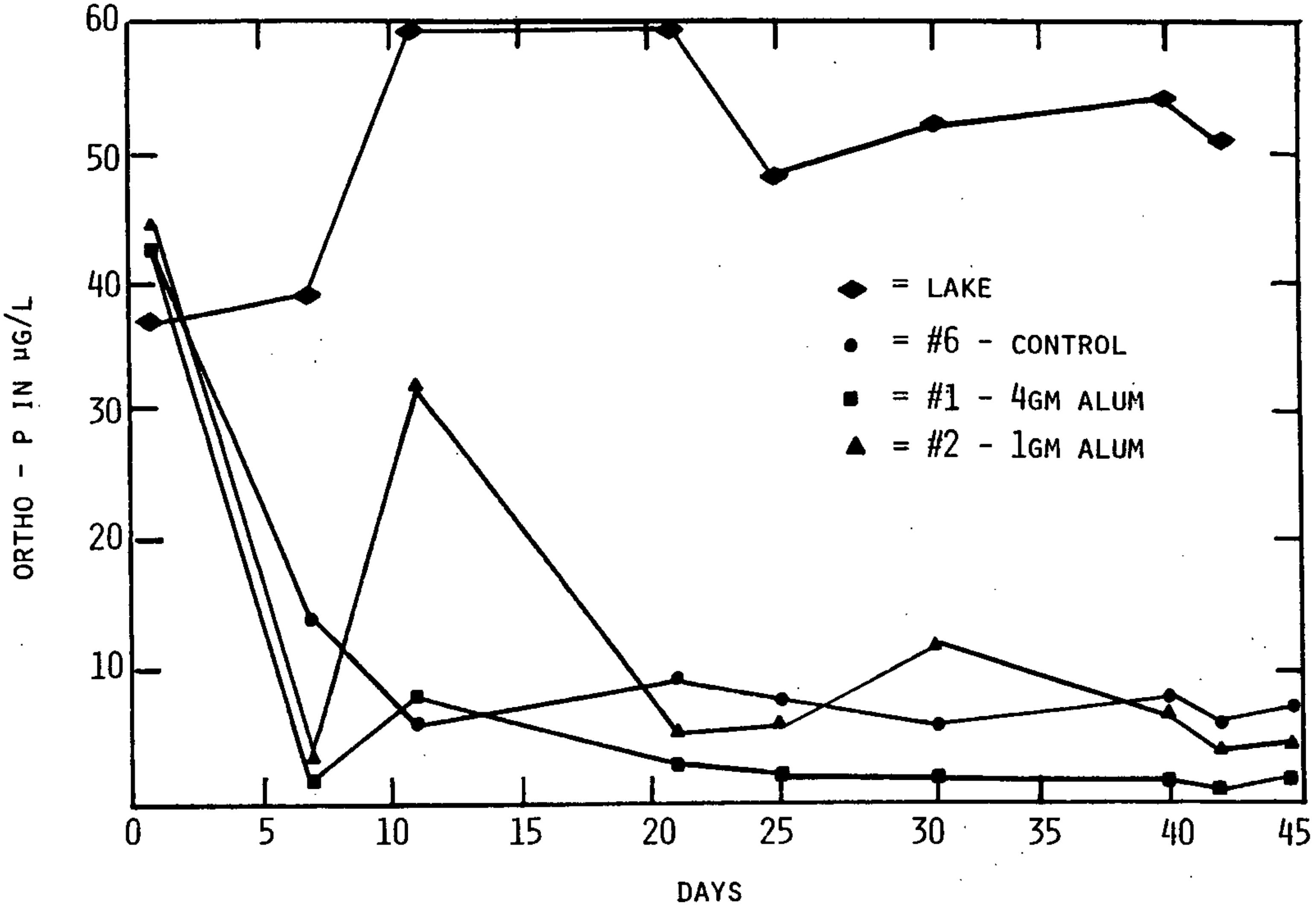

Figure 39. Temporal variation of orthophosphate in suppression tubes (1,2,6) and in lake water, October 26 to December 13, 1973.

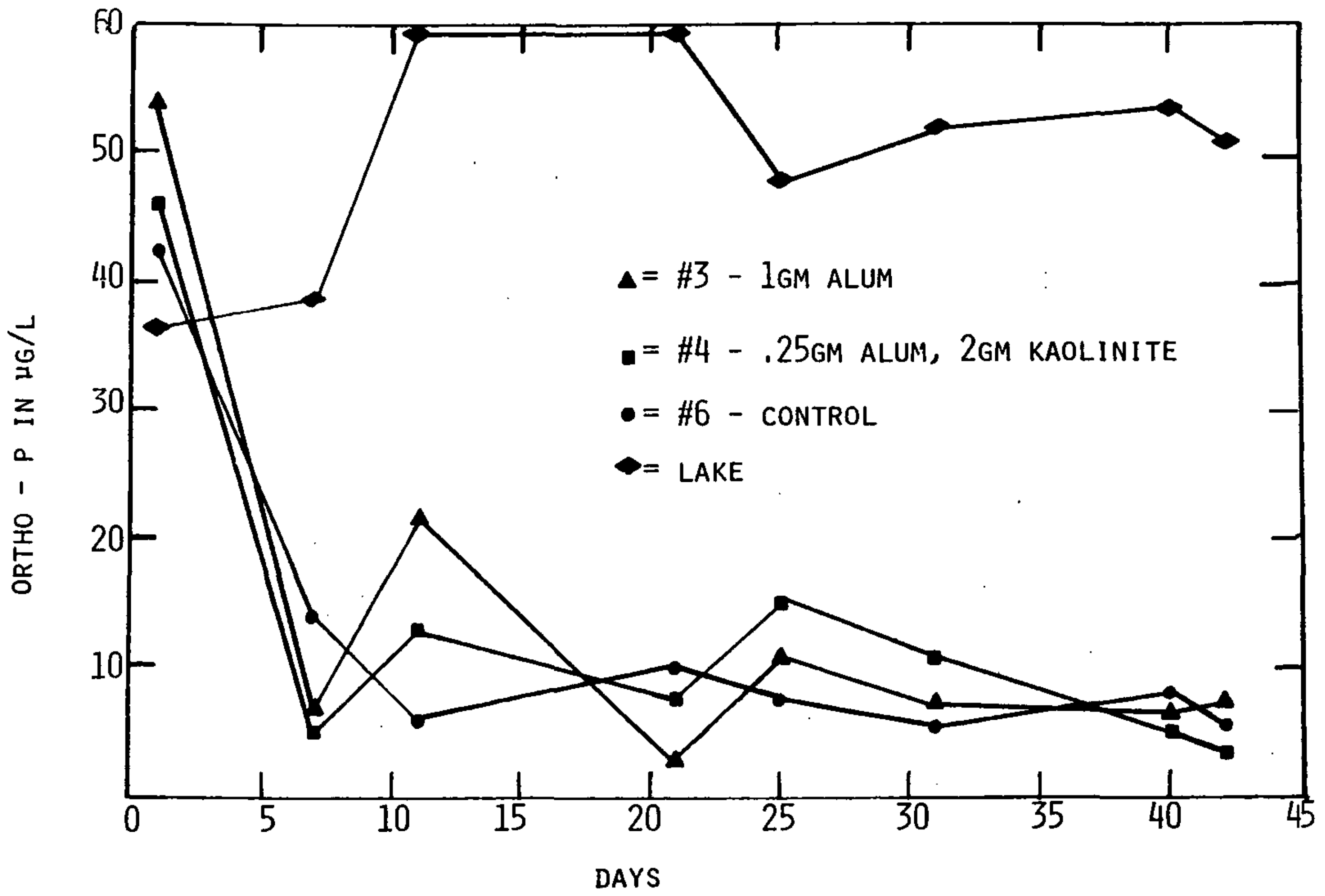

Figure 40. Temporal variation of orthophosphate in suppression tubes (3,4,6) and in lake water, October 26 to December 13, 1973.

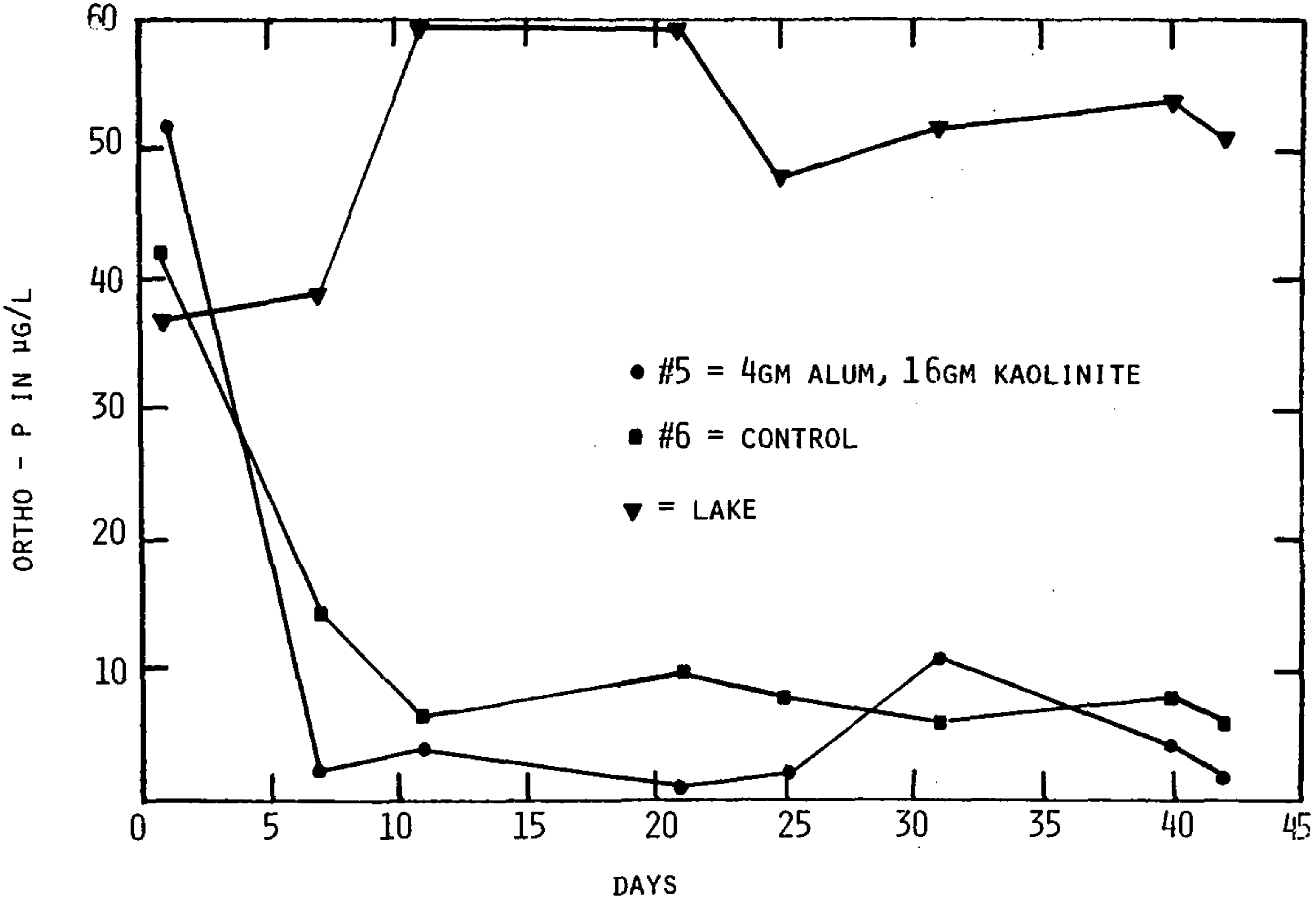

Figure 41. Temporal variation of orthophosphate in suppression tubes (5,6) and in lake water, October 26 to December 13, 1973.

lake water and Tube No. 6, which served as the control. The initial concentrations in the tubes ranged from 42 to 54 µg/l. After treatment as described in Table 3, all of the tubes showed as 80 to 90 percent reduction in orthophosphate concentration. More importantly, the concentrations remained low for the entire test period. However, a 75 percent reduction in orthophosphate was also obtained in Tube No. 6 which was untreated. As will be later discussed, orthophosphate was actually converted to organic phosphate by algal uptake in this tube.

Concentration-time profiles of total phosphate as shown in Figures 42-44 provide a more meaningful interpretation of suppression treatment than corresponding data for orthophosphate. In the untreated Tube No. 6, total phosphate remained high throughout the study period, averaging 63 µg/l. This indicates that an approximate steady-state value of phosphorus was maintained in the untreated reactor. It should also be noted that orthophosphate decreased rapidly in the control tube to a steady-state value of only 8 µg/l. Conversion to organic phosphate by algae is suggested.

The results of suppression tube studies showed a trend of lower total phosphate achieved at equilibrium as chemical dosage was increased. Equilibrium concentration of total phosphate in the overlying water were reduced in Tube No. 1-4 (Figures 42 and 43) 35 to 40 percent. The largest

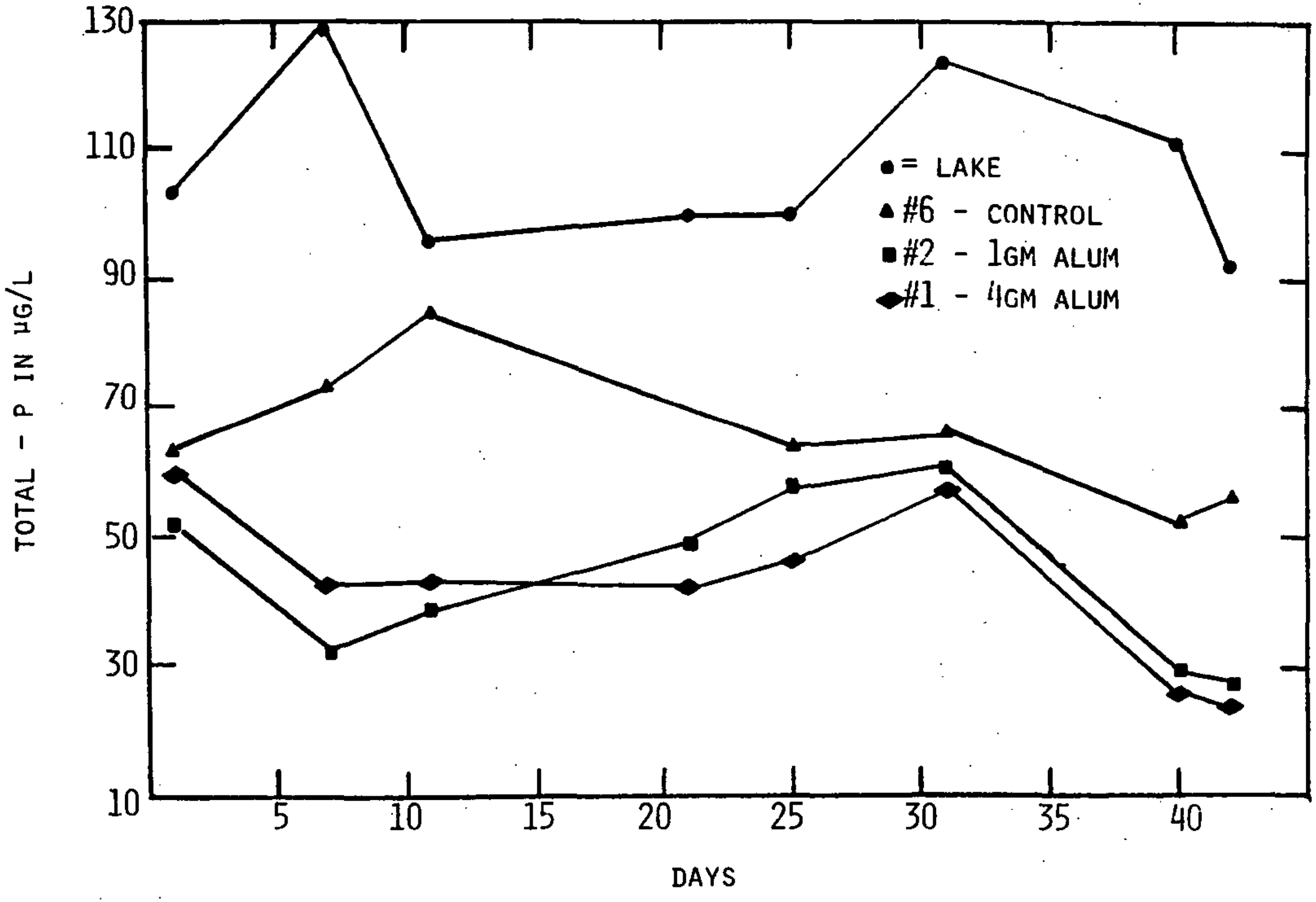

Figure 42. Temporal variation of total phosphate in suppression tubes (1,2,6) and in lake water, October 26 to December 13, 1973.

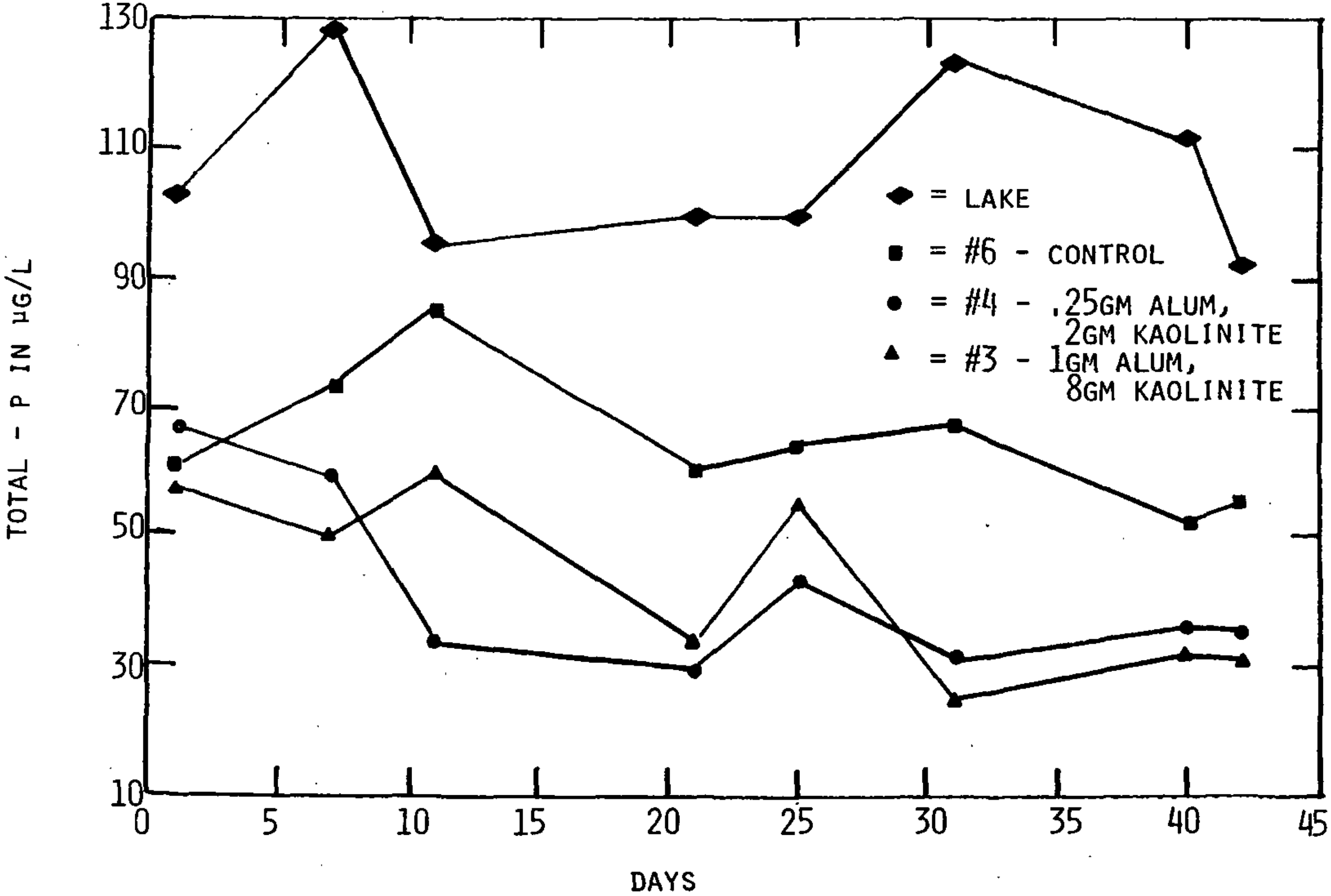

Figure 43. Temporal variation of total phosphate in suppression tubes (3,4,6) and in lake water, October 26 to December 13, 1973.

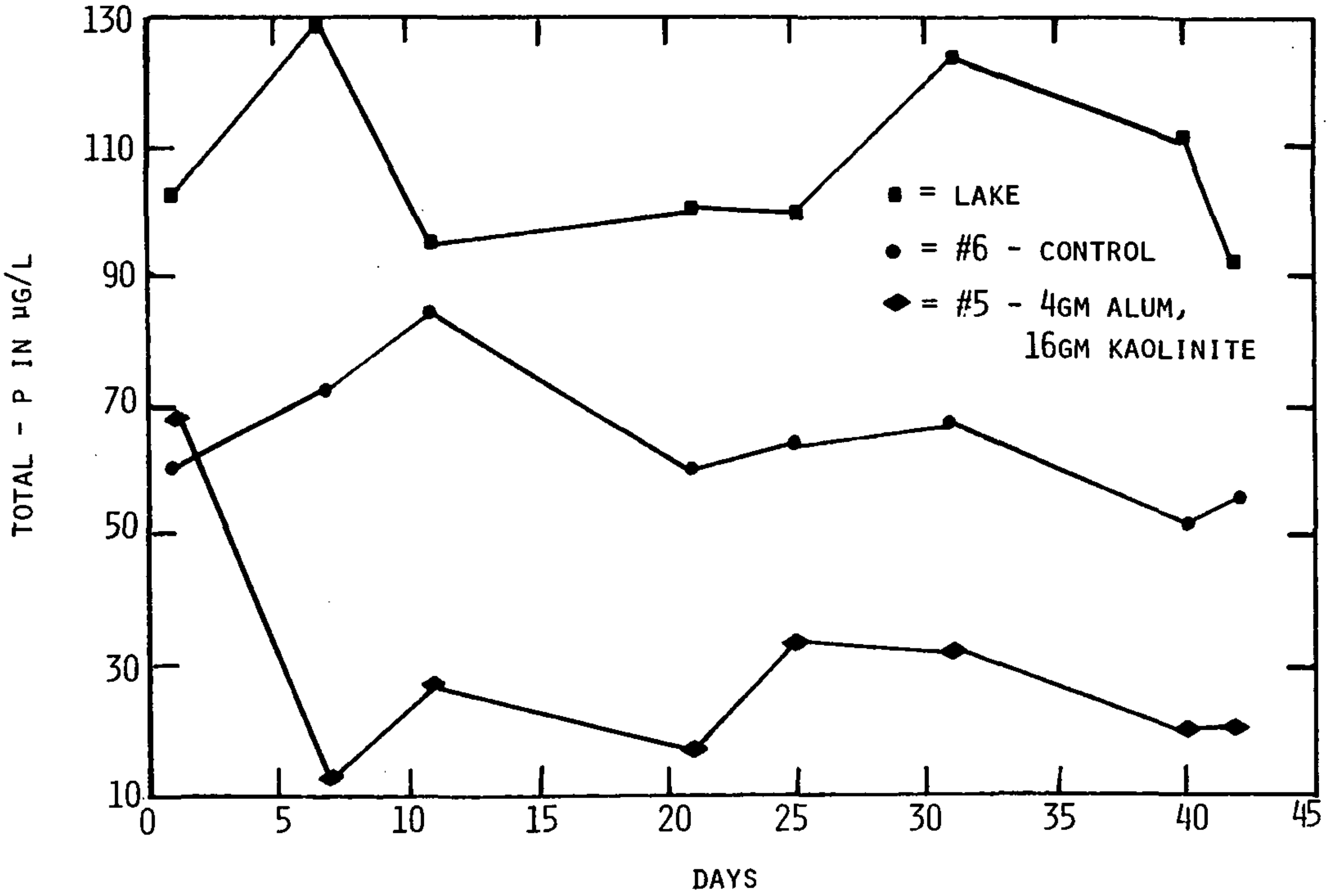

Figure 44. Temporal variation of total phosphate in suppression tubes (5,6) and in lake water, October 26 to December 13, 1973.

dose of kaolinite and alum as applied in Tube No. 5 (Figure 44) produced an average reduction in total phosphate of 61 percent. These reductions are all with respect to results observed in the control tube (Tube No. 6).

Figure 45 shows the changes in iron concentrations in Tubes 1-3 with respect to time. A statistical analysis of the relationship between phosphate and iron in the suppression tubes was attempted. Correlation coefficents for the relationship of iron and phosphate were:

Tube No. 1	$r = .7841$
Tube No. 2	$r = -.0342$
Tube No. 3	$r = .339$
Tube No. 4	$r = .3600$
Tube No. 5	$r = .8484$
Tube No. 6	$r = .1441$

Although phosphate released from the sediment would normally be associated with iron complexes, statistical evidence from this study was insuffcent to prove this relationship. As already mentioned, this could be due to the formation of $Fe(OH)_2$ or FeS within the sediment.

The steady-state concentration of total phosphate in Tube No. 6 compared quite closely to that attained in the large caisson used for determining rate constants during the same time period. This would suggest that the rates of sedimentation and release were similar in both test systems.

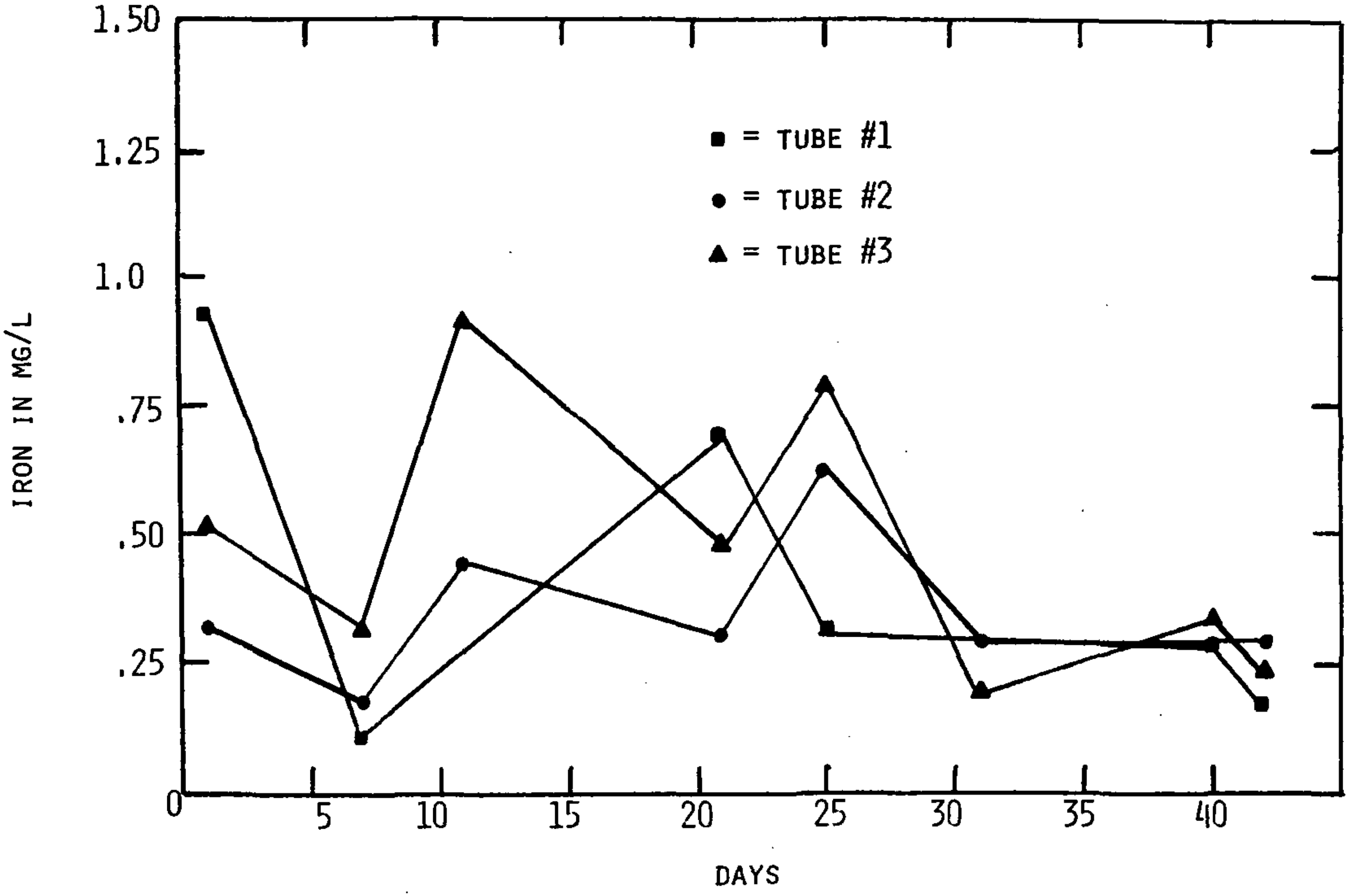

Figure 45. Temporal variation of total iron in suppression tubes (1,2, 3) for October 26 to December 13, 1973.

Determination of Values of Interstitial P for Suppressant Additions

Figure 46 depicts how both a chemically treated and untreated sediment-overlying water system can be visualized for interpretation in the mathematical model. Without suppressants added, the flux from the sediment is K_1 times $(P_i - P_L)$ and sedimentation to the bottom is K_2P_L. Addition of alum and kaolinite decrease the interstitial concentration from P_i to P_i^* and thus, a lower flux, $K_1(P_i^* - P_L)$, occurs. As shown from these studies, the net effect of suppressant addition is to lower phosphate in the overlying water. Thus, the average equilibrium value for a given suppressant dosage can be used to calculate an apparent interstitial concentration, P_i^*. In turn this effective interstitial concentration allows prediction of a lower flux from the sediment in model simulation of a chemically treated lake.

The value of P_i^* required can be obtained by applying the following steady-state model of a batch reactor describing the sediment-overlying water system:

$$P_{L_{eq}} = \frac{\varepsilon \frac{A}{V} K_1 P_i^*}{\varepsilon \frac{A}{V} K_1 + K_2} \qquad (48)$$

The necessary data input to the equation consisted of ε (from Chapter III), K_1 and K_2 (from the third caisson study) and the average equilibrium concentration from suppression studies. Table 4 provides the resulting values of effective

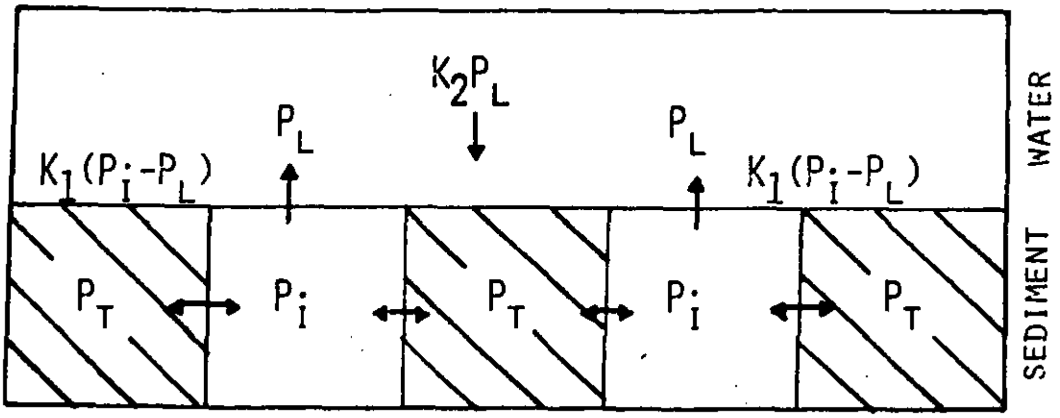

Figure 46. Sediment and water interchange without suppressants.

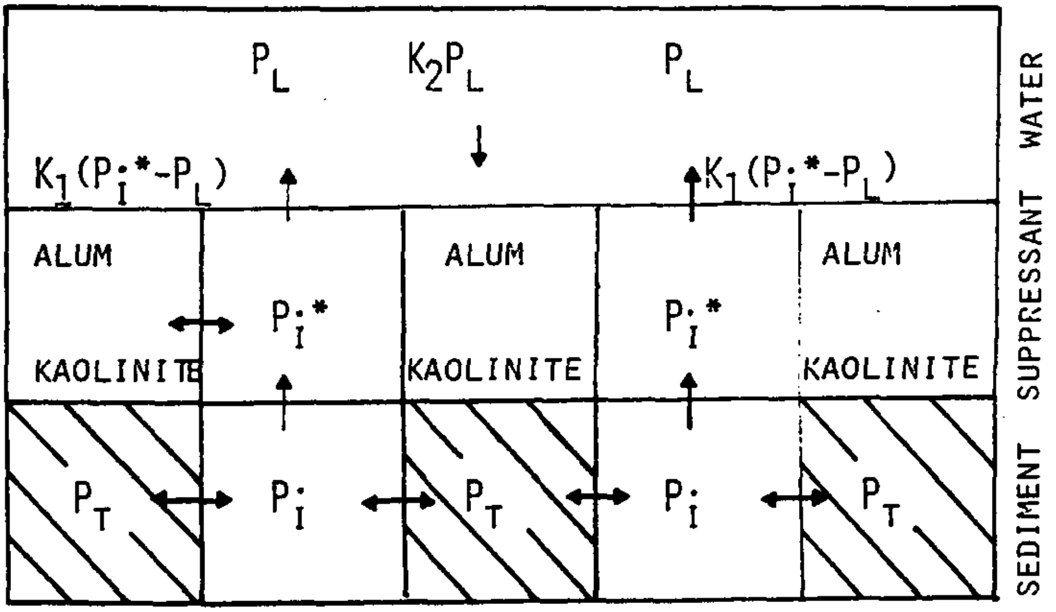

Figure 46. Sediment and water interchange with alum and kaolinite suppressants.

Table 4. Results of Suppression Study

Tube	P_i* µg/l	Dosage in Grams	
		Alum	Kaolinite
1	318	4	0
2	305	1	0
3	298	1	8
4	225	.25	2
5	172	4	16
6	410	0	0

interstitial phosphate concentration with the addition of chemical suppressants. Combined mixtures of alum and kaolinite in a ratio of 1:4 appear to be the best combination in affecting the lowering of phosphate release. This decrease of P_i will be used in the lake predictive model to show the reduction in time needed to attain a lower phosphate concentration in a lake when suppressants are used.

Summary

It should be stressed that the value of K_1 and K_2 were derived from a shallow, highly eutrophic lake and applications of them to stratified lakes or oligotrophic lakes has not been shown. Also, K_1 and K_2 are presumed constant throughout the year and are not adjusted for various temperatures, Eh values of the sediment, or seasons of the year. This is in part due to a lack of sufficient data to make these adjustments. That the constants, K_1 and K_2, remain fairly unchanging is evident from a comparison of results of the July, 1973 run with the December, 1973 run: $K_1 = .087$ m/day versus .091 m/day and $K_2 = .183$/day versus .176/day, respectively. There is only a 4 percent difference between the rate constants obtained at two different temperatures and at two different seasons of the year. This consistency in the values of K_1 and K_2 has made it possible to apply them to the predictive model as constants although future research may determine how each varies with temperature, redox potential, pH, and season of the year.

CHAPTER VI

APPLICATION OF PHOSPHORUS EXCHANGE MODEL

Model Input Data Requirements

Background Development. The ultimate utility of the proposed mathematical model is to predict the approach to a new, steady-state phosphate concentration in a shallow lake after phosphate loading has been reduced or suppressants added. The necessary phosphate release and sedimentation rate constants, K_1 and K_2, for application to Lake Warner have been developed in Chapter V. In addition, the equilibrium relationship between interstitial and sediment phosphate required to account for depletion of this phosphate reservoir over long periods of time was derived within Chapter IV. In this chapter, the appropriate steady and non-steady state models describing phosphate release and sedimentation will be applied to Lake Warner.

To apply these models to Lake Warner, it was first necessary to provide estimates of Q,A,V, and $\overline{T}$. The major function of the model is to then predict P_L as a function of time given an initial set of conditions. The most obvious eutrophication control measure is to reduce the influent phosphate concentration, P_o. However, as discussed in Chapter V, it is also possible to reduce the effective interstitial phosphate concentration, P_i, to P_i^*.

A very important factor for proper utilization of the model is estimating the extent of the phosphate reservoir in the sediment. Thus far, this problem has not been addressed directly. However, the model must account for depletion of the reservoir by decreasing the value of P_i over time.

In this chapter, the necessary data and assumptions will first be discussed before applying the model. The steady state plug flow model will be tested and the steady state completely mixed model will be used to show the interdependence of P_o, P_i, and P_L. Then the non-steady state, completely mixed model will be used to generate a historic profile of phosphate in Lake Warner using field data collected in this research for verification. Finally the non-steady state model will be used to project future phosphate concentrations in Lake Warner as a result of either reducing input phosphate loading or suppressing sediment phosphate by chemical additions. Both the rate of approach and the final position of equilibrium between overlying water and sediment can be predicted by this proposed model.

Phosphate Loading to Lake Warner. The Mill River is the major tributary to Lake Warner and, as such, was assumed to contribute most of the phosphate loading. Although, for simplicity, a constant phosphate loading must be used in the model, in actuality the loading is highly variable throughout the year. The principal factor causing this variability in loading is the bypassing of wastewater from the Amherst Primary Treatment Plant during periods when effluent pump capacity is exceeded and not all of the wastewater can be pumped to the Connecticut River.

Considering first the background phosphate concentration in the Mill River due to natural runoff, samples were collected in June, 1973 during a dry period which would eliminate the influence of wastewater bypassing. Figure 47 shows that total phosphate was about 40 μg/l and orthophosphate was 15-20 μg/l, both reasonable values for a natural stream.

Wastewater bypassing was also observed in early spring of 1973. The rate of bypassing could be roughly estimated as between 0.1 and 1 MGD; wastewater total phosphate varied from 3 to 5.5 mg/l. Dilution of this bypass wastewater in the Mill River produced a total phosphate concentration downstream of between 70 and 200 μg/l. Clearly, this is a significant short-term impact on phosphate loading to Lake Warner when wastewater bypassing occurs. However, it should also be noted that soil erosion and agricultural runoff contribute to increased phosphate loadings in the spring.

To provide an estimate of average phosphate concentrations entering Lake Warner, the contribution of wastewater bypassing was included. Obviously, with only minimal data for flow rates and phosphate concentrations for the river and wastewater, such calculations must be regarded as approximate. Nevertheless, this procedure was justified for the purpose of illustrating applications of the proposed lake

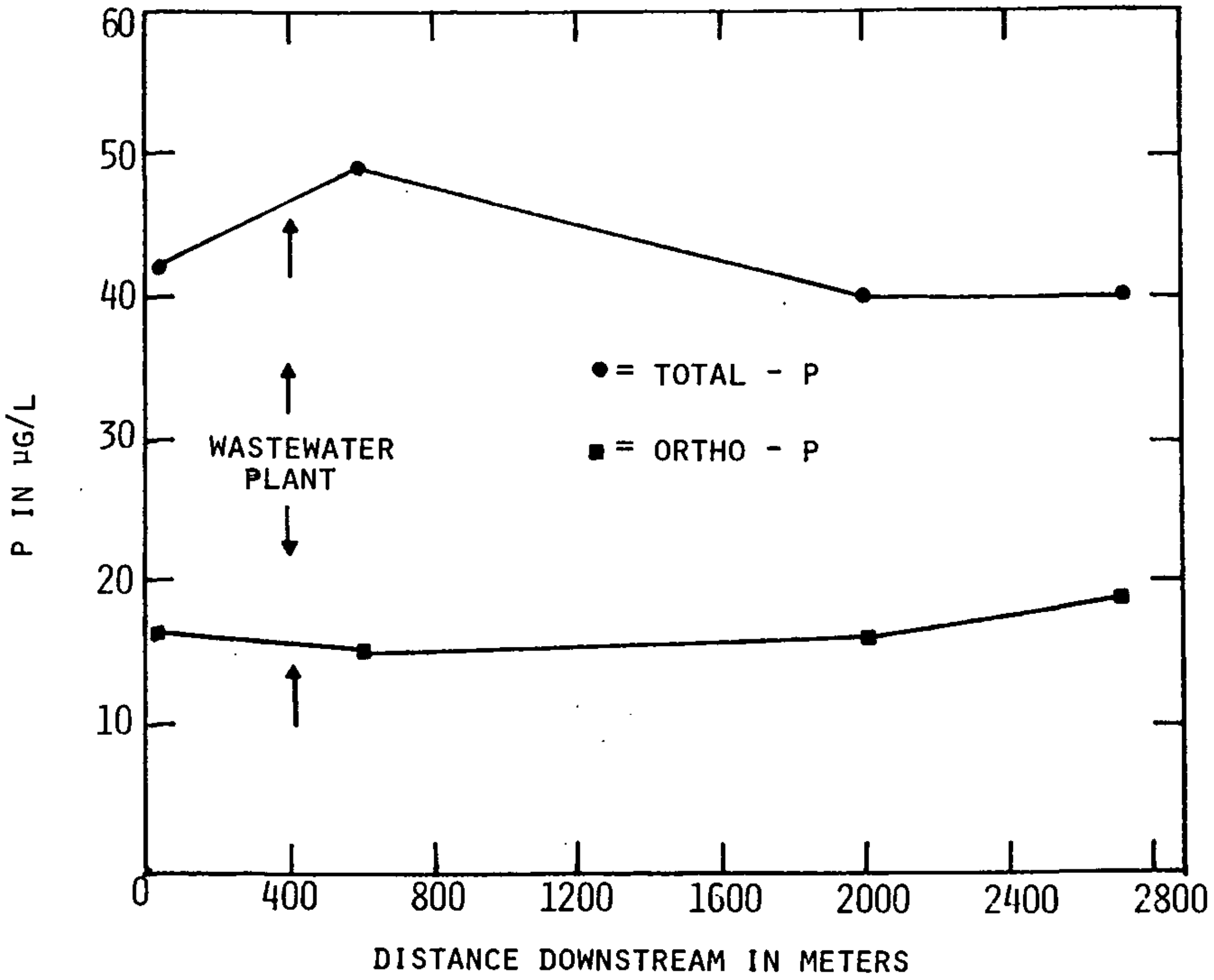

Figure 47. Ortho and total phosphate in Mill River, Arrow indicates location of Amherst Wastewater Treatment Plant, June, 1974.

models. Table 5 provides a summary of the assumptions used to arrive at the annual average concentration of 90 μg/l total phosphate for P_o. This value agrees quite well with data collected in this research and presented in Chapter IV.

Exchange Depth. Table 6 summarizes the depth of sediment assumed by various investigators to represent the zone from which nutrients can be released into the overlying water. This data indicates that long term release from shallow, eutrophic lake sediments will be generated from about 10 cm. The shallow depths indicated in Table 6 were, in general, determined from short term laboratory experiments and were deemed not indicative of long term release. The solid phase concentration of total phosphorus within this zone will be the major control of the interstitial concentration of phosphate in the upper 10 cm of the sediment (Ku, 1975; Fillos, 1975). The exchange depth will be used in the model to provide a limit to the phosphate available in the sediment.

Exchangeable Phosphorus. The amount of solid phase total phosphorus (P_T) that can be exchanged or transferred to the interstitial water is generally believed to be controlled by the Eh, or redox potential, of the sediment environment (Ku, 1975; Li, 1973; Fillow, 1975; Kamp-Nielsen, 1974). Table 7 provides estimates by various investigators of the exchangeable total phosphorus. Much of the data was derived from laboratory studies. The detailed work of Ku

Table 5. Estimate of Phosphate Loading to Lake Warner

Wastewater Characteristics

Average Total Phosphate Concentration = 5 mg/l

Estimated Total Annual Volume of Bypassing (3.3%) = 60 MG

Mill River Characteristics

Average Total Phosphate Concentration = 0.050 mg/l

Total Annual Volume (@ 20 MGD) = 7157 MG*

Annual Average Total Phosphate Entering Lake Warner

$$\text{Total-P } (\mu g/l) = \frac{(60 \text{ MG}) \times (5000\ \mu g/l) + (7157 \text{ MG}) \times (50\ \mu g/l)}{7217 \text{ MG}}$$

$$\text{Total-P} = 90\ \mu g/l = P_o$$

*Estimate of 1 cfs/sq. mile derived by the late Professor George Higgins, Dept. of Civil Eng., Univ. of Mass., Amherst, Mass.

Table 6. Depth into Sediment for Exchange

Depth in centimeters	Reference	
.5	Fillos	(1975)
.5	Mortimer	(1971)
1	Frink	(1967)
1-5	Allen	(1970)
2-5	MacKenthun	(1968)
5-7	Snow	(1973)
5-10	McKee	(1970)
10	Painter	(1968)
10	Kamp-Nielsen	(1974)
10-20	Dobbins	(1970)
15	Forcella	(1970)
20	Bray	(1973)
30	Wentz	(1969)

Table 7. Percentages of Exchangeable Phosphorus Within the Sediment

Amount Exchangeable of Total Phosphorus	Comment	Reference	
17-18 percent	Lake Warner 1.5-2 mgP/gm	Ku	(1975)
12-33 percent	Depending on concentration gradient	Wildung	(1973)
16-24 percent	P desorbed from original amount adsorbed	Lotse	(1973)
22-44 percent	Noncalcareous lakes total-P > 1.5mg/gm	Li	(1973)
up to 50 percent	Lake Mendota	Wentz	(1969)

(1975) and Li (1973) provide the best estimates of exchangeable total phosphorus (25 percent) for noncalcareous, eutrophic lakes such as Lake Warner.

Release Rates. According to Equation 26, the rate-limiting step for phosphate release is transfer across the sediment-water interface. The release coefficient, K_1, relates to the specific properties of the interfacial resistance which determines the transfer rate. For example, resistance to release has already been shown to decrease markedly as the sediment system changes from an oxidized to a reduced state.

Table 8 summarizes the flux or release rates of phosphorus from sediments obtained by various investigators. All data has been converted to express flux in mg/sq m/day. The majority of release rates for reducing eutrophic lake sediments fall between 10-30 mg/sq m/day. Interestingly enough, Fillos (1972, 1973, 1975) also reported release rates for Lake Warner which compare quite closely with the estimate given by using the derived value of K_1 and a concentration gradient across the sediment interface (P_i of 425 μg/l, P_L of 90 μg/l) yielding a release rate of 25.5 mg/sq m/day. It should be noted that in the proposed model, the flux of phosphate from the sediment will depend upon the concentration gradient existing between the interstitial and overlying water. Table 8 is presented here to show that the release rate constant, K_1, and the assumption

Table 8. Release Rates of Phosphorus from Sediments

References		Sediment or Location	Release Rate mg $P/m^2/day$	Comment
Fillos	(1972)	Simulated Sludge	154	anaerobic
Capaccio	(1971)	Muddy River	91	anaerobic
			3	aerobic
Vollenweider	(1968)	Lake Baldeggersee	9-10	anaerobic
Pomeroy	(1965)	Doboy Sound	.03	aerobic marine
Fillos	(1973, 1975)	Muddy River	96	anaerobic (-200mv)
			9.6	aerobic (+200mv)
		Lake Warner	26	anaerobic (-200mv)
			1.2	aerobic (+200mv)
Porcella	(1971)	Shallow eutrophic lakes	50	anaerobic
			5	aerobic
Stumm	(1970b)	Estimates all lakes	.27	-
Krull	(1973)	Lake Sammamish	6	estimate

References	Sediment or Location	Release Rate mg P/m^2/day	Comment
Kamp-Nielsen (1974)	Lake Furensco (eutrophic)	17±5	anaerobic
		2±1.8	aerobic
	Lake Esrom (eutrophic)	12±4	anaerobic
	St. Gribso Lake (oligotrophic)	1.2±.2	anaerobic
		.2±.2	aerobic
Allen (1970)	Lab study on sediment	.7	anaerobic
McKee (1970)	Potting soil	5	aerobic
Welch (1973)	Lake Sammamish	5	estimate
Feng (unpublished)	Pond Sediment	17	3' above sediment
Bray (1973)	Chesapeake Bay	.4	estimate
Snow (this study)	Lake Warner	24-27	*in situ* anaerobic sediment

of a first-order rate of reaction in the model provides as close of an estimate of the flux as obtained by other investigators.

While it is reasonable to assume interstitial phosphate concentration (P_i) remaining constant over the duration of release from the sediment to a fixed volume of overlying water in a batch reactor, P_i will be depleted in a continuous flow reactor under the conditions of continual sediment release. As discussed earlier, P_i is dependent upon exchangeable solid phase phosphorus, P_s. The exchangeable phosphorus is assumed as 25 percent of the total sediment phosphorus, P_T. Determination of total phosphorus in the interstitial water and in the sediment has already yielded an empirical equation which relates P_T to P_s and P_i (Equation 46). Using this empirical equation and the estimated exchangeable phosphorus fraction, P_T and P_i will vary with time as phosphorus is exchanged between sediment and overlying water.

Summary of Data Inputs for Model. Table 9 summarizes the data required to generate model results for application to Lake Warner. For all models, the only two parameters which may change to modify lake phosphate concentration (P_L) are P_o and P_i (or P_i^*). That is, these two parameters directly relate to the two possible mechanisms controlling the concentration of phosphate in the lake; namely, by

Table 9. Summary of Parameters for Use in Phosphate Release Model Applied to Lake Warner

---

K_1 = 0.091 m/day

K_2 = .176/day

P_i = 400 to 450 μg/l Total-P

P_i^* = 175 to 300 μg/l Total-P

P_L = 80 to 90 μg/l Total-P

P_o = 40 μg/l Total-P (Summer)

P_o = 100 μg/l Total-P (During bypassing)

P_T = 1 to 1.6 mgP/gm dry sediment

Q_o = 20 ft^3/sec. (Average)

$\overline{T}$ = 10 days (Average)

ε = .84 (Porosity)

A = 2.572×10^5 m^2 (Area)

V = 4.35×10^5 m^3 (Volume)

Depth of exchange = 10 centimeters

Percentage of P_T exchangeable = 25%

---

altering either the influent loading or the flux of phosphate from the sediment.

Steady State, Plug Flow Model

The parameters shown in Table 9 were applied to the steady state, plug flow model (Equation 43). Comparisons were made between actual and model predicted values of phosphate (P_{L_z}) for various distances (Z) from the inlet using spatial variations of P_{L_z} found in the December 1973 study. However, modeling of this lake as a plug flow reactor proved to be unrealistic as shown from the low correlation coefficent of 0.3 between actual and predicted values of P_L. A better fit of the model to the data (correlation coefficent of 0.9) could be obtained by increasing K_1 from the measured value of 0.091 to 3.1 m/day, increasing K_2 from 0.176 to 3.58/day, and decreasing P_i from 425 to 290 μg/l. The inability of the plug flow model to even approximate the actual lake conditions without tremendous modifications to the measured constants eliminated further studies using this model. The completely mixed reactor model will therefore be used in all subsequent discussion on lake predictive models for phosphate concentrations. Selection of this model is also consistent with findings of the Lake Warner Limnological Survey as summarized at the end of Chapter IV.

Steady-State, Completely Mixed Model

Relationship Between Overlying Water and Interstitial Phosphate. As shown in Chapter III, the steady-state model describing phosphate release and sedimentation in a continuous flow, completely mixed reactor is given by:

$$P_{Leq} = \frac{P_o/\overline{T} + (\varepsilon A/V)\ K_1 P_i}{1/\overline{T} + (\varepsilon A/V)\ K_1 + K_2} \tag{39}$$

For a given input phosphate concentration, P_o, the relationship between the overlying lake phosphate, P_{Leq}, and the interstitial phosphate, P_i, can be obtained by rearranging Equation 39 such that:

$$P_{Leq} = M_1 + N_1\ P_i \tag{49}$$

where:

$$M_1 = \frac{P_o}{1 + (\varepsilon A/V) K_1 \overline{T} + K_2 \overline{T}}$$

$$N_1 = \frac{(\varepsilon A/V) \overline{T} K_1}{1 + (\varepsilon A/V) K_1 \overline{T} + K_2 \overline{T}}$$

Figure 48 shows the predicted relationship between P_{Leq} and P_i based upon the values of M_1 and N_1 calculated from data given in Table 9. For this analysis, the model was applied to Lake Warner with the input phosphate concentration

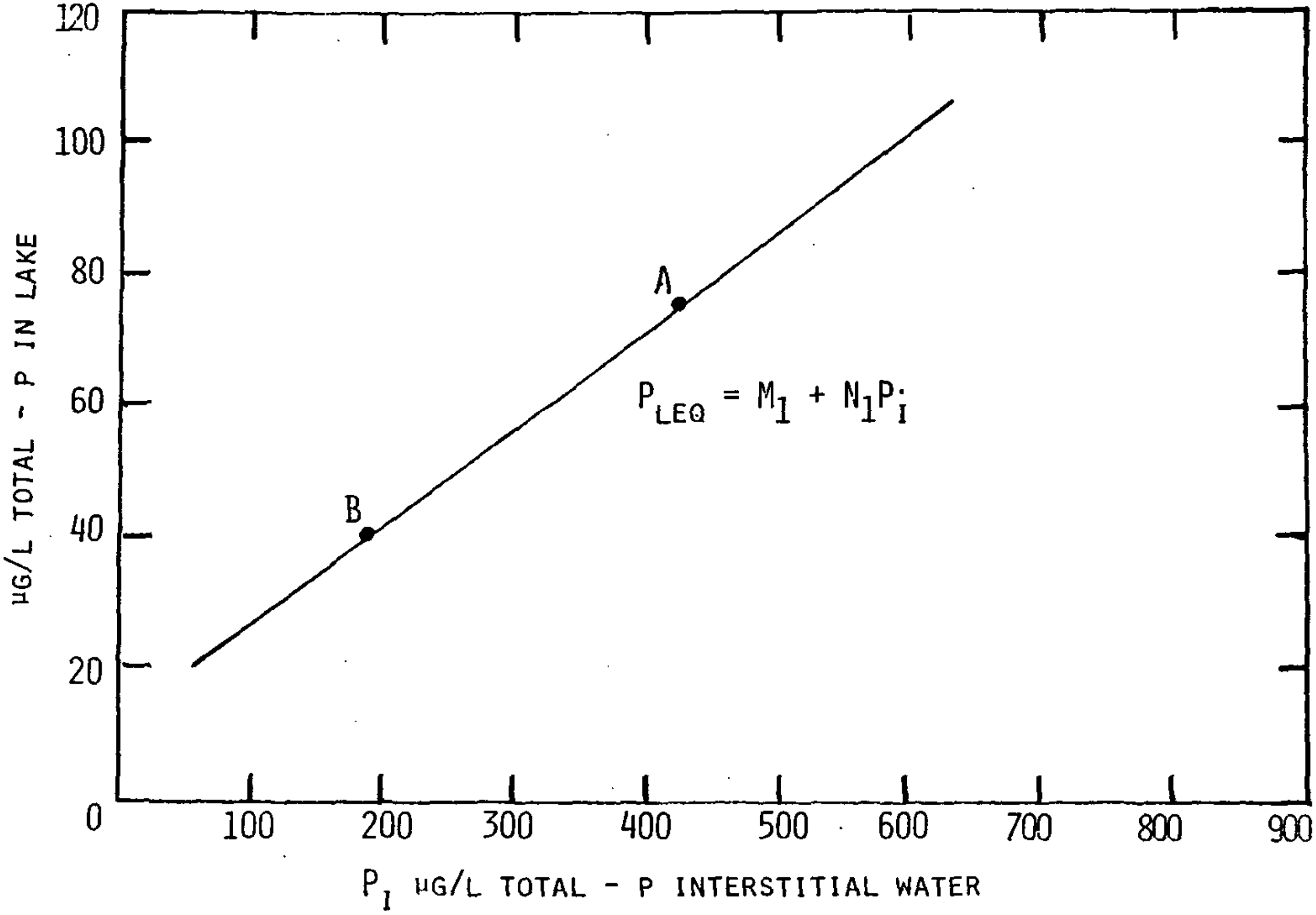

Figure 48. Steady-state simulated data for Lake Warner. $\overline{T}$=10 days, P_o=40 µg/l, A=current conditions, B=ultimate equilibrium.

assumed as 40 μg/l in the absence of wastewater bypassing. Using measurements of lake and interstitial phosphate in Lake Warner during June 1974, there is good agreement with the model (point A). From Figure 48, it is also apparent that lower phosphate in the interstitial water corresponds to lower equilibrium values of lake water phosphate (see also Table 1).

Of particular interest is the ultimate equilibrium. That is, the condition when influent (P_o) and lake phosphate (P_L) concentrations are equal. This condition can be reached by: (1) introducing a steady-state input (P_o) of phosphate equal to 40 μg/l to a "clean" lake whose sediment acts as a sink and adsorbs more phosphate than it releases or (2) reducing the interstitial phosphate (P_i), initially created by high input of phosphate, to lower sediment release. Proceeding from either direction, one intrinsic value of P_i will be reached whereby an equilibrium will be established between sedimentation and release and the influent phosphate (P_o) will equal the lake phosphate (P_L) concentration. This point for Lake Warner is shown in Figure 48 as Point B where P_i is equal to 190 μg/l. In theory, all lakes should attain an ultimate dynamic equilibrium condition. A steady-state model, however, provides no information about the time required to reach this ultimate equilibrium condition.

Sediments as a Phosphate Source or Sink. The steady-state, completely mixed model can also be used to attain a better understanding of the role of sediments in the lake either as a source or sink of phosphate, provided that the existing phosphate concentrations of the input, lakewater, and interstitial volume of the sediment are known. For this purpose, it is convenient to consider the family of linear relationships that are obtained by rearranging Equation 39 such that:

$$P_{Leq} = M_2 + N_2 P_o \qquad (50)$$

where:

$$M_2 = \frac{(\varepsilon A/V)\overline{T}K_1 P_i}{1 + (\varepsilon A/V)K_1\overline{T} + K_2\overline{T}}$$

$$N_2 = \frac{1}{1 + (\varepsilon A/V)K_1\overline{T} + K_2\overline{T}}$$

Here, each of the family of linear steady-state relationships applies to a given interstitial phosphate concentration with varying inputs (P_o). The many possible steady-state conditions for Lake Warner as obtained by applying Equation 50 are graphically depicted in Figure 49. The ultimate equilibrium of input and lake water concentrations is also shown as a line with a 45° slope. Lakes described by phosphate coordinate points below the equilibrium line have sediments which act as phosphate sinks. Lakes whose coordinate points

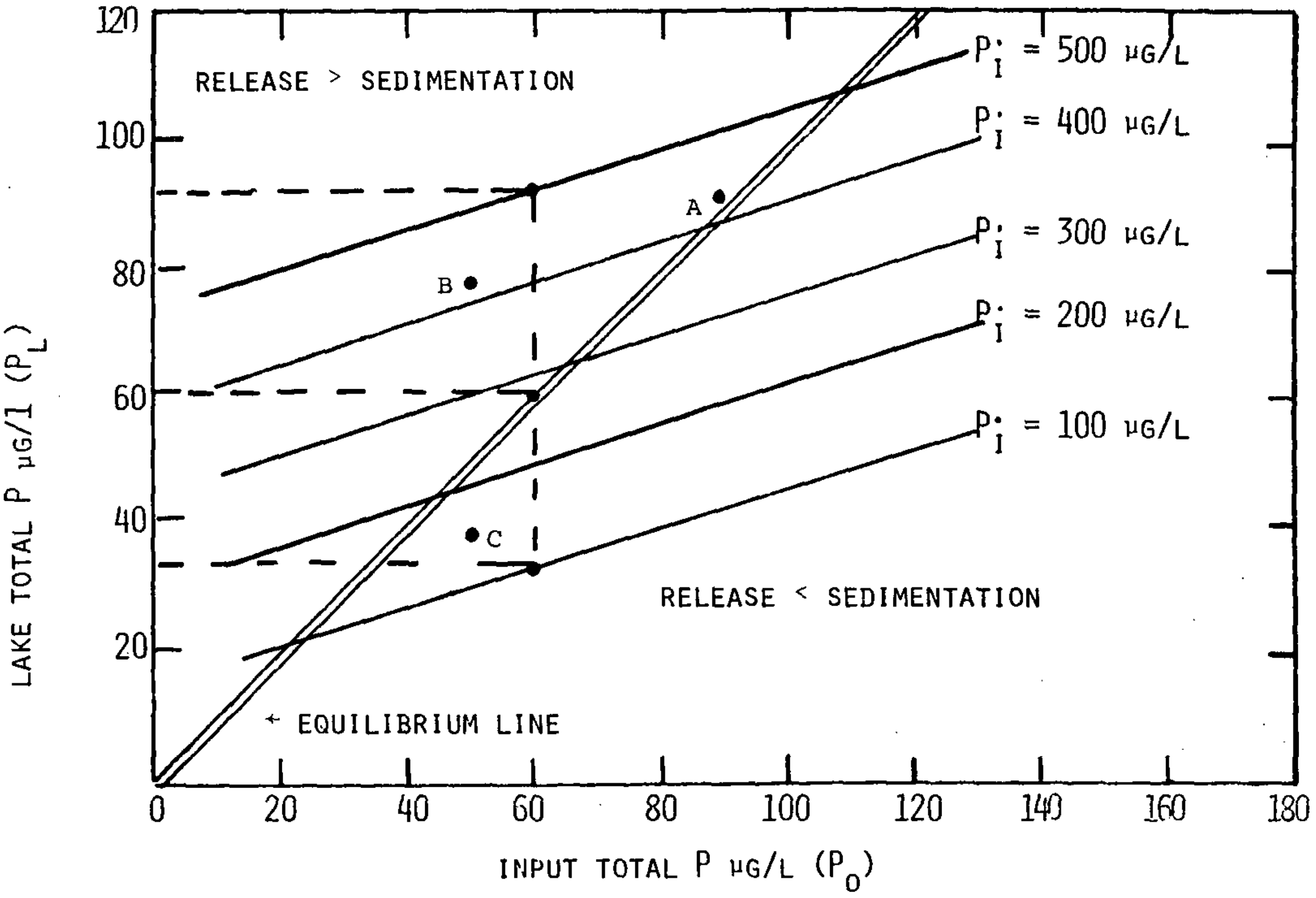

Figure 49. Graphical representation of steady state model using Equation 48 to relate P_L to P_o and P_i for $\bar{T}$=10 days. Points A,B, and C discribed in section titled Application of Steady State Model.

are above the equilibrium line have sediments which release phosphate at a greater rate than sedimentation.

To illustrate the use of Figure 49, if input phosphate (P_o) to Lake Warner was 60 μg/l and measured interstitial phosphate 100 μg/l, then the corresponding pseudo equilibrium value of lake water phosphate (P_{Leq}) would be only 33 μg/l. However, to ultimately equilibrate the system with this phosphate input would require achieving an interstitial phosphate concentration of almost 290 μg/l. Thus, the sediment must act as a sink for phosphate until this condition is reached. As indicated in the literature review, most lakes studied seem to behave as phosphate sinks; that is, the rate of sedimentation is greater than the rate of release. The time required to achieve the equilibrium interstitial phosphate concentration will depend upon the adsorptive equilibrium behavior of the sediment which governs the relationship between solid and interstitial phosphate.

The contrasting example of a sediment acting as a phosphate source can also be clearly shown from Figure 49. In these lakes, excessive phosphate loadings have caused accumulations in the sediment and an increase in interstitial phosphate due to high sedimentation rates. To illustrate, equilibration in Lake Warner such that the interstitial phosphate is 500 μg/l would correspond to a high phosphate input of 109 μg/l and a corresponding value of 109 μg/l in the lake water. If input to the lake were now reduced to

60 μg/l, then the interstitial phosphate concentration would initially remain almost constant and the new pseudo steady-state value of phosphate in the lake water would be 92 μg/l. In this example, the interstitial phosphate must decrease to 290 μg/l to reach dynamic equilibrium with the input phosphate. This would be observed as higher rates of release as compared to sedimentation. Thus, the sediment would act as a source of phosphate rather than a sink until the final equilibrium condition was reached. This example is probably similar to the problems encountered in Lake Sammamish and Shagawa Lake (Chapter II). In both lakes, the influent loadings were reduced but only a slight decrease in the value of P_L was noted. The high pseudo steady-state values were probably maintained by the sediment acting as a source of phosphate.

Application of Steady-State Model. As developed graphically in Figure 49, the steady-state model enables determination of the tendency of the sediments to act as a sink or a source given the present levels of phosphate in the input to the lake, the lake water itself and the interstitial water of the sediment. Moreover, this graphical presentation is useful in analyzing the effect of altering the input loadings. For example, point A in Figure 49 represents the 1974 condition in Lake Warner with bypassing of wastewater from the Amherst Wastewater Treatment Plant contributing significantly to the phosphate loading. By eliminating wastewater bypassing and decreasing the input phosphate loading to 50 μg/l, the initial pseudo steady-state phosphate concentration in the lake would decrease from 90 to only 79 μg/l (Point B). However, to reach the actual steady-state condition of 50 μg/l, interstitial phosphate must decrease from 425 to 232 μg/l. Although impossible to estimate from the steady-state model, the time required to decrease the interstitial phosphate by a factor of almost two would certainly be extensive.

On the other hand, addition of alum and kaolinite to the sediment has been shown in Chapter V to decrease the effective interstitial phosphate (P_i^*) to 150-200 μg/l (Table 4). If, for example, P_i^* were reduced to 150 μg/l, then Point C on Figure 49 would represent the new pseudo steady-state lake condition. This point indicates that the sediment acts more as a sink than as a source, allowing phosphate to increase gradually over time from 38 μg/l to the final steady-state equilibrium value of 50 μg/l (P_L equal to P_o).

The usefulness of the non-steady state model as given by Equation 40 can now be appreciated. This model allows prediction of the time required to move from one position of pseudo steady-state as given in Figure 49 to another position provided that the current values of P_o, P_i and P_L are determined and phosphate control methods, i.e.reduced future loadings (P_o) and/or interstitial phosphate concentrations

(P_i or P_i^*) are known.

Non-Steady State, Completely Mixed Models

Computational Scheme. The non-steady state, completely mixed model can be used to determine transient responses of lake phosphate concentration to a change in either input phosphate (P_o) or interstitial phosphate (P_i or P_i^*). As discussed in Chapter III, an analytic solution to the non-steady state model can be obtained by assuming that interstitial phosphate remains unchanged. Accordingly, Equation 40 was derived as shown again here:

$$P_L = \frac{P_o + (\varepsilon A/V)K_1 P_i \bar{T}}{1 + (\varepsilon A/V)K_1 \bar{T} + K_2 \bar{T}} \left[1 - e^{-\left(\frac{1}{\bar{T}} + [\varepsilon A/V]\ K_1 + K_2\right)t} \right] + P_{L_o} e^{-\left(\frac{1}{\bar{T}} + [\varepsilon A/V]\ K_1 + K_2\right)t} \qquad (40)$$

This model is of only limited value because P_i will decrease with time as phosphate escapes from the sediment.

To account for a decrease in P_i with time, solution of Equation 40 must be considered simultaneously with an equation describing the equilibrium relationship between interstitial and solid phase phosphate. To account for changing sediment phosphate concentration, a phosphate balance on this phase yields:

Rate of Accumulation of P in Exchangeable Phase, P_s within the Sediment	=	Input Rate of P due to Sedimentation	-	Output Rate of P due to Release

That is,

$$V_s \frac{dP_s}{dt} = K_2P_LV_L - \left(\frac{\varepsilon A}{V_L}\right) K_1(P_i-P_L)V_L \qquad (50)$$

Here, the accumulation rate of phosphate in the sediment is dependent upon the rates of sedimentation and release. The sediment volumes, V_s, depends upon the reactive depth, Dr, of the sediment which was approximated as 10 cm. (see Table 6).

To conveniently incorporate the reactive depth into the sediment phosphate balance, V_s may be replaced by:

$$V_s = Dr\ (A) \qquad (51)$$

where A represents the bottom area of the lake, which for all intents, can be assumed equal to the water surface area. Thus, in finite difference form, Equation 50 becomes:

$$P_{s_{t+\Delta t}} = P_{s_t} + \left[\frac{K_2P_LV_L}{DrA} - \frac{\varepsilon}{Dr}K_1(P_i-P_L)\right]\Delta t \qquad (52)$$

Appropriate values of P_i and P_s can be obtained from rearranging the relationship derived in Chapter IV (Equation 46). That is:

$$P_i = \frac{2.19 \times 10^{-3}P_s + 41.87}{\varepsilon} \qquad (53)$$

where:

P_i = concentration of phosphate within the interstitial water of the defined volume

The new value of P_i after a time change Δt can be calculated from:

$$P_{i_{t+\Delta t}} = \frac{2.19\times10^{-3}(P_{s_{t+\Delta t}}) + 41.87}{\varepsilon} \tag{54}$$

Thus, knowing the initial value of P_{s_t} allows projection of the new value of $P_{s_{t+\Delta t}}$. In turn, $P_{s_{t+\Delta t}}$ allows calculation of a new value of P_i from Equation 54. Finally, the new value of P_i is used in the non-steady state model given by Equation 40 to obtain the new value of P_L after time step Δt. The new value of P_L is then used in Equation 52 to calculate a new value of $P_{s_{t+\Delta t}}$. Necessarily,this requires selection of an appropriate time step, Δt, which provides a practical number of iterations realizing that the span of interest may be on the order of years.

For Lake Warner data, an interstitial phosphate concentration of 425 μg/l is in equilibrium with a P_s value of 1.439×10^4 mg P/M^3. Using the finite difference scheme with input phosphate, P_o, set at 90 μg/l shows that for Δt of 10 days, the value of P_s is reduced by only 5 mg P/M^3 and correspondingly, P_i is reduced by only 0.2 μg/l. Lake phosphate concentration (P_L) was reduced from 90.97 μg/l to 90.94 μg/l (only 0.03 μg/l change). Thus, a time increment of 10 days was considered a reasonable estimate of quasisteady state conditions necessary for analytic solution of the model given by Equation 40.

To speed calculation time, the computational scheme was solved by using a digital computer. The program (Appendix E) was initiated with specific values of P_i, P_s, and P_{L_o} prior to changing input phosphate values, P_o. Changes in interstitial concentrations were calculated for each new 10 day period and the corresponding lake concentration was determined. Because most changes in 10 days were shown to be very small, lake and interstitial phosphate concentrations were printed out for 100 day time intervals for the various input conditions tested.

Effect of Input Phosphate on Model Predictions. Figure 50 shows the increase in lake phosphate concentration in the first eight days after the input concentration is increased from 20 to 50 μg/l and from 20 to 100 μg/l. In this model application, lake detention time was assumed to be 10 days, interstitial phosphate (P_i) was 100 μg/l and K_1 and K_2 as 0.091/day and 0.176 m/day, respectively. With an input phosphate of 50 μg/l, the lake concentration (P_L) increased from 20 μg/l to 29.5 μg/l in 8 days. However, the approach to equilibrium slows considerably such that lake phosphate reaches only 31 μg/l after 100 days.

The value of P_i only increased from 100.0 μg/l to 100.3 μg/l during the first 8 days at the higher input phosphate loading. Thus, release rate of phosphate from the

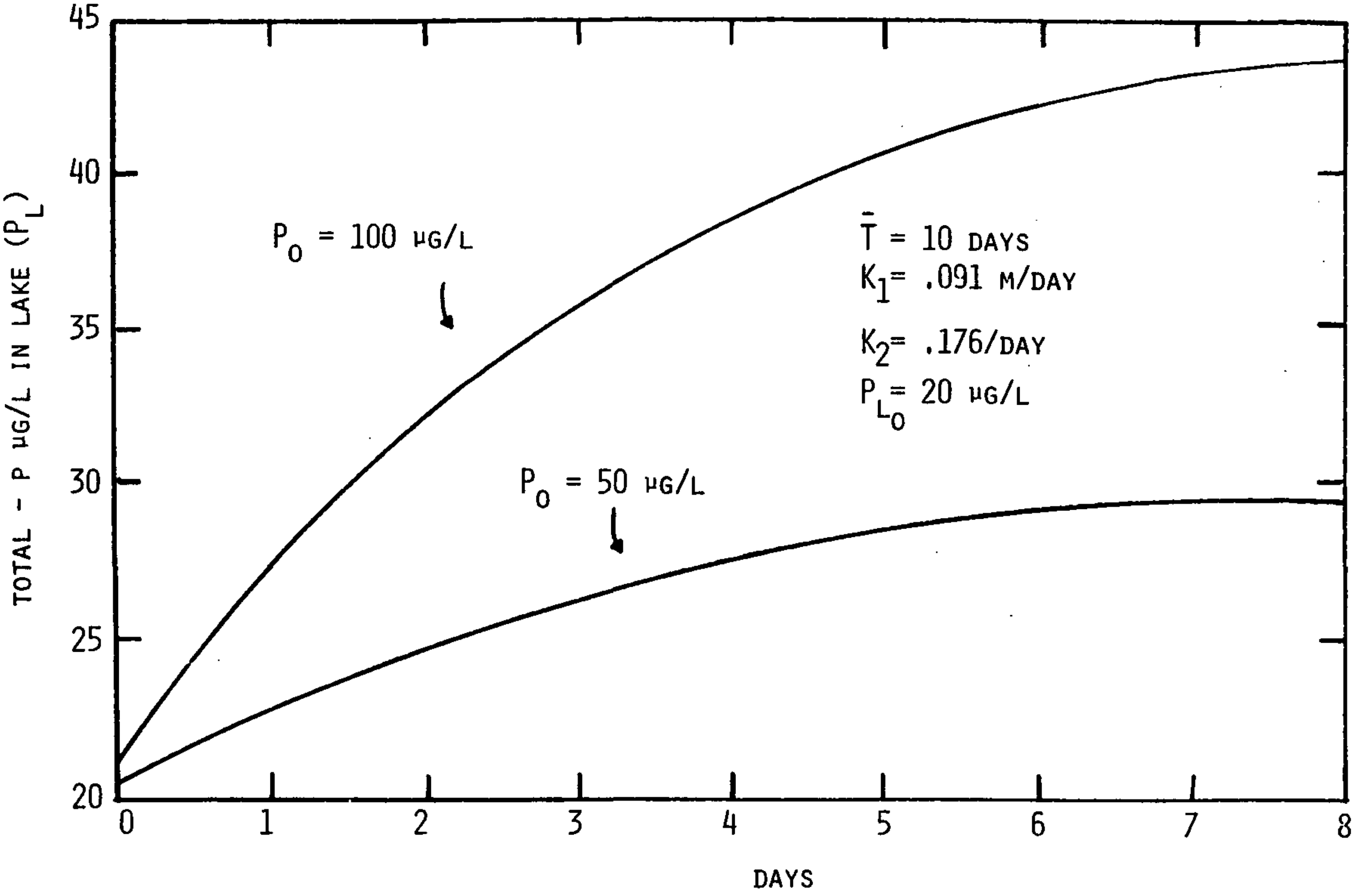

Figure 50. Prediction of P_L as a function of time for step increases in P_o of 50 and 100 μg/l.

sediment actually decreased while the sedimentation rate increased evidenced by the increase in lake phosphate, P_L, during this time.

Figure 50 also indicates that the increase in lake phosphate, P_L, is more rapid for a higher input, P_o, of 100 μg/l with all other conditions being the same. In eight days, the lake concentration, P_L, increased from 20 μg/l to 44 μg/l. As was the case for an input, P_o, of 50 μg/l, the value of P_i only increased from 100.0 μg/l to 100.9 μg/l and again the release rate from the sediment decreased while the sedimentation rate increased.

The rate of change in P_L during the initial period of response to a new P_o is almost entirely controlled by the residence time, $\overline{T}$, in the lake, i.e.the dilution factor. For example, in a larger lake with a $\overline{T}$ of 100 days instead of 10 days, use of this model indicates an increase in phosphate input from 20 μg/l to 100 μg/l would only increase the concentration in the lake from 20 μg/l to 21 μg/l in the first 100 days. This response is in sharp contrast to that given in Figure 50 in which lake phosphate increased from 20 μg/l to 44 μg/l in only eight days with $\overline{T}$ of 10 days. The important point here is that, initially, the dilution effect may be providing a faster response than the interaction of phosphate with the sediment. Thus, the effect of phosphate release from the sediment is a longer term effect which can only be appreciated by calculating P_L on a much greater time scale.

Prediction of Present Phosphate Concentration in Lake Warner. Assuming that input phosphate concentration to Lake Warner has increased at some time in the past due to bypassing of wastewater, it was of interest to predict the present phosphate concentration in the lake and sediment. For purpose of modeling, input phosphate concentration, P_o, was increased from 40 to 90 μg/l to simulate the input of bypassed wastewater. Figure 51 shows that lake phosphate, P_L, finally equilibrates with the input phosphate after about 14 years. Correspondingly, interstitial phosphate, P_i, increased from 185 to 407 μg/l. Using this time-frame of years rather than days, the initial increase in lake phosphate concentration, as shown in Figure 50 can only be indicated by a sharp, almost step, increase followed by a more gradual exponential approach to final equilibrium.

If it is assumed that wastewater bypassing probably started between 1964 and 1967 with the rapid expansion in Amherst, then about 8 to 11 years later, the model predicts a lake phosphate concentration, P_L, of about 85 μg/l and an interstitial phosphate concentration, P_i, of 381 μg/l. These values are actually quite close to those determined in Lake Warner as discussed in Chapter V.

A simple dilution model with no regard to sedimentation and release would yield quite different results. Using Equation 8 (Biffi, 1963) as given below:

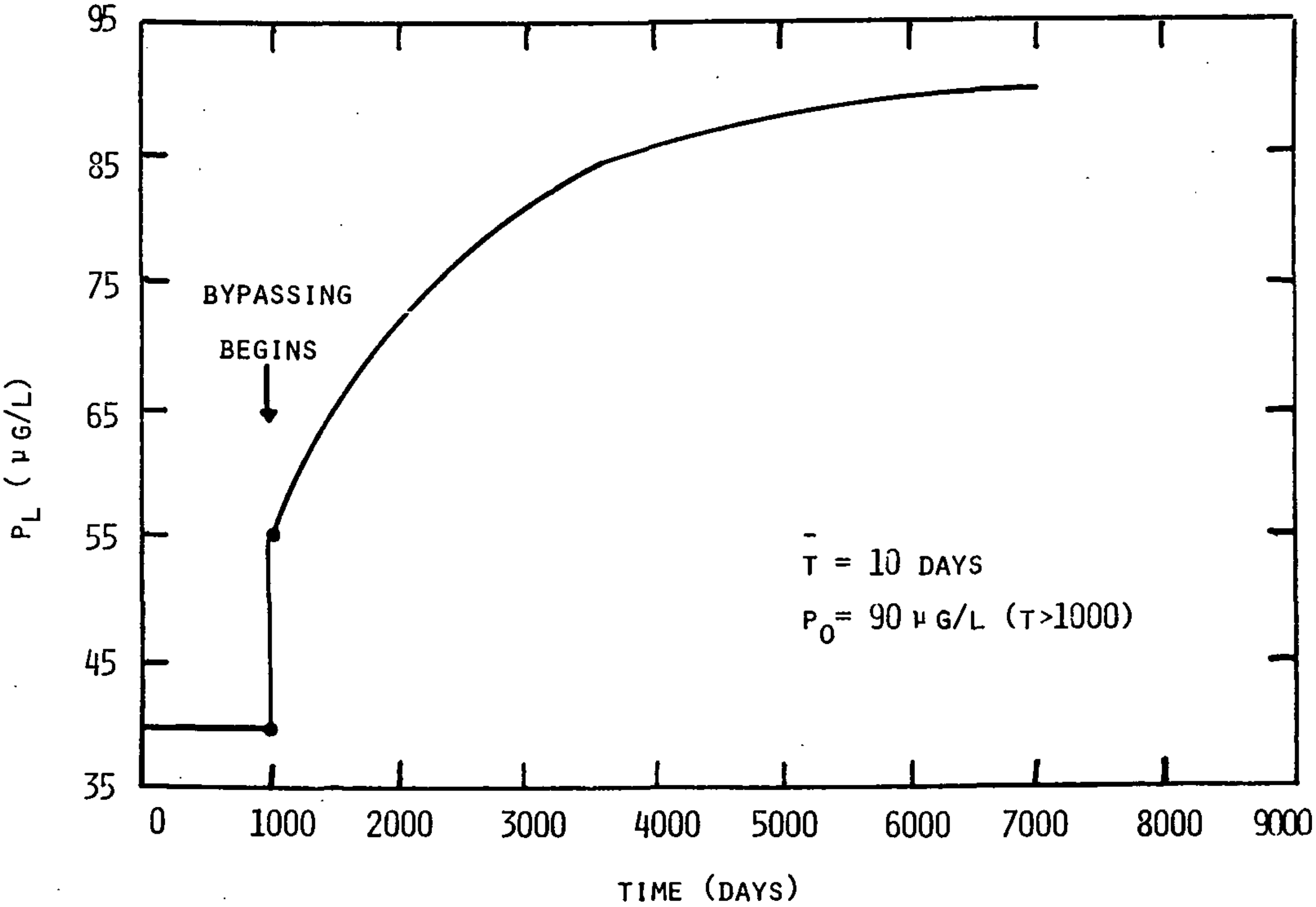

Figure 51. Unsteady state prediction results for historic changes in P_L with wastewater bypassing. At t=0, P_L=40 μg/l, P_i=185 μg/l. At t=5000 days, P_L=88.5 μg/l, P_i=407 μg/l.

$$P_{L_t} = P_o - (P_o - P_{L_o})\, e^{-t/T} \tag{8}$$

indicates that a similar increase in input, P_o, would cause the lake phosphate concentration, P_{L_t}, to increase from 40 μg/l to 88.5 μg/l (i.e.14 years of change in the previous proposed model) in only 35 days. The effect of sedimentation and release with respect to the sediment can obviously be seen; 14 years versus 35 days.

Finally, to determine if the values of K_1 and K_2 derived from the December 1973 caisson study could be used as invariant constants, a comparison was made between the December values (K_1 = 0.091 m/day, K_2 = 0.176/day) and summer values (K_1 = 0.087 m/day, K_2 = 0.183 day) derived in Chapter V. Initial values used were P_o = 50 μg/l, P_i = 100 μg/l, and P_{L_o} = 20 μg/l. After 8.2 years, the predicted values of P_L differed by only 0.8 μg/l (i.e.43.9 μg/l versus 43.1 μg/l). The use of the chosen values of K_1 and K_2 as invariant throughout the year seem reasonably justified since results using summer and early winter derived constants differ by only 1.8 percent.

Prediction of Lake Recovery. Using the non-steady state model (Equation 40) coupled with the finite difference equation for changing P_i and P_s values (Equations 52 and 54), the results of decreasing phosphate loading to the lake can also be predicted. For Lake Warner, the transient responses produced by decreasing input phosphate, P_O, from 90 µg/l to 80, 50, 40, and 20 µg/l are shown in Figure 52. In these predictions, the initial conditions in Lake Warner were assumed to correspond to those in 1974 when bypassing of wastewater produced a lake water phosphate, P_L, of 90 µg/l and interstitial phosphate, P_i, of 425 µg/l.

Obviously, the most rapid decrease in P_L is brought about by the greatest decrease in phosphate loading (20 µg/l). However, even reducing input phosphate to 20 µg/l would not reduce phosphate levels below 30 µg/l for 8 years. Moreover, such a drastic reduction in phosphate loading, P_O, would be impossible without elimination of agricultural and suburban runoff. Thus, this non-steady state model clearly indicates that storage of phosphate in the sediments of shallow lakes can provide a long lasting source which will offset any measure to lower lake phosphate, P_L, by reducing input phosphate, P_O.

From the steady-state model (Figure 49), lake phosphate could be reduced from 90 to 40 µg/l if the interstitial phosphate, P_i, was reduced from 425 to 185 µg/l. However, the non-steady state model has shown that attainment of this desired steady-state condition would require about 14 years due to the influence of the sediment. Obviously, another control strategy besides reducing input phosphate should be examined in order to accelerate lake recovery time.

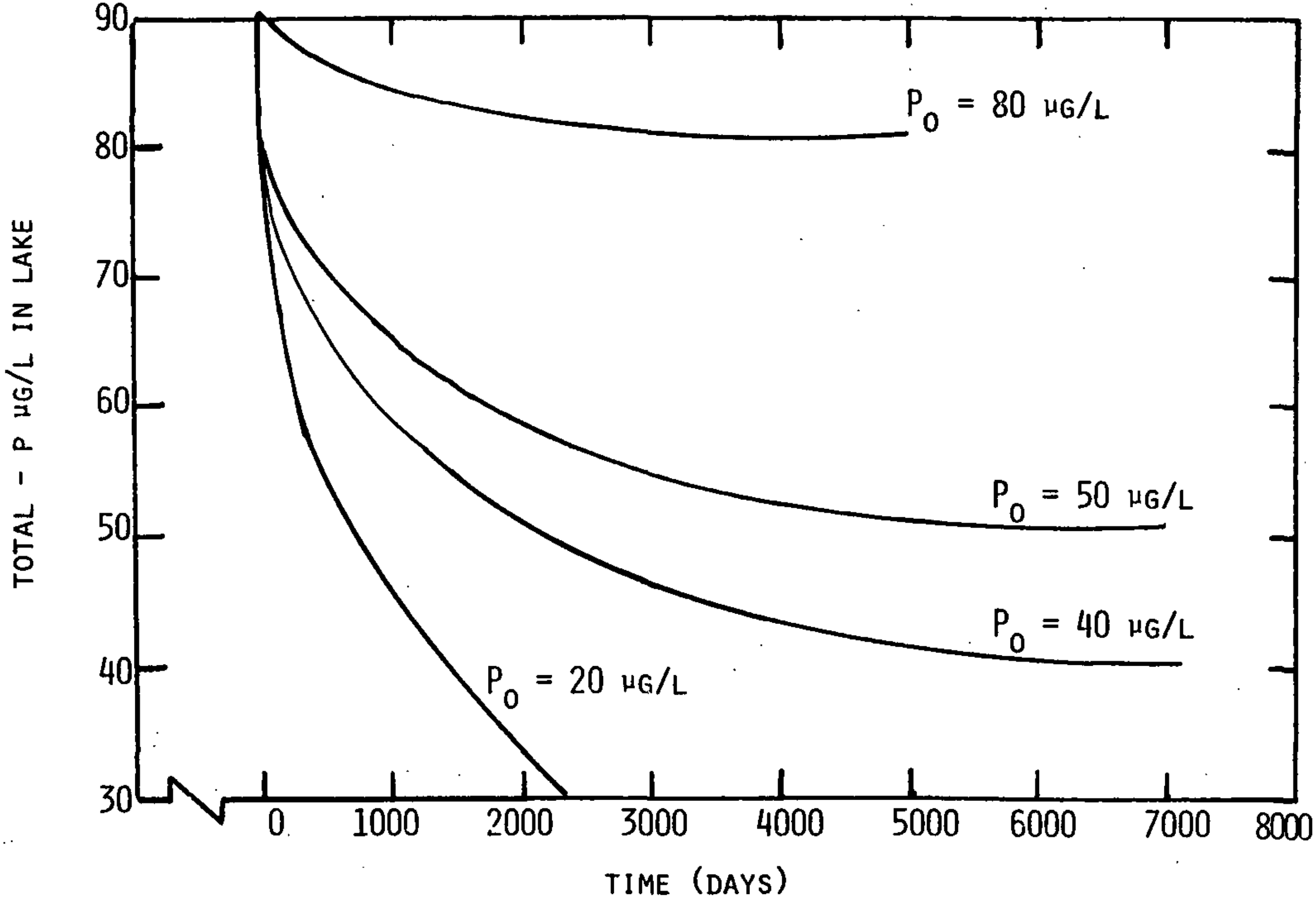

Figure 52. Unsteady state model prediction results for lake recovery. At t=0, P_{L_o}=90 µg/l, P_i=425 µg/l. At t>0, P_o=80,50,40, and 20 µg/l.

Suppression of sediment phosphate by the addition of alum and kaolinite was shown in Chapter V to decrease the effective interstitial phosphate (P_i to P_i^*) thereby retarding the release rate of phosphate. Figure 53 depicts the transient response in P_L for various values of P_i and P_i^*. Without chemical suppression, P_L would decrease to 55 μg/l with P_i initially equal to 425 μg/l in 7.7 years with input phosphate, P_o, being 50 μg/l. If alum and kaolinite were added to decrease P_i from 425 μg/l to 300 μg/l (P_i^*), the same value of P_L (55 μg/l) would be attained in only 3 years. Interestingly enough, using chemical suppressants to lower P_i^* to 200 μg/l or 100 μg/l brings about immediate (about 40 days) reduction in lake phosphate to values less than the final ultimate equilibrium concentration of 50 μg/l. In these instances, input phosphate, P_o, will actually cause an increase in P_L with time since P_L, with t greater than 40 days, is less than 50 μg/l.

According to field study results presented in Chapter V, a dosage of 12 gm of alum and 100 gm of kaolinite per square meter would reduce P_i^* to 200 μg/l in Lake Warner. With an influent of 50 μg/l (without wastewater bypassing), the initial predicted total phosphate in the lake water would decrease from 90 μg/l to 46 μg/l within about 40 days. If 50 percent of the total phosphate is orthophosphate, then the lake could be classified in the mesotrophic range and the control and elimination of the eutrophic state

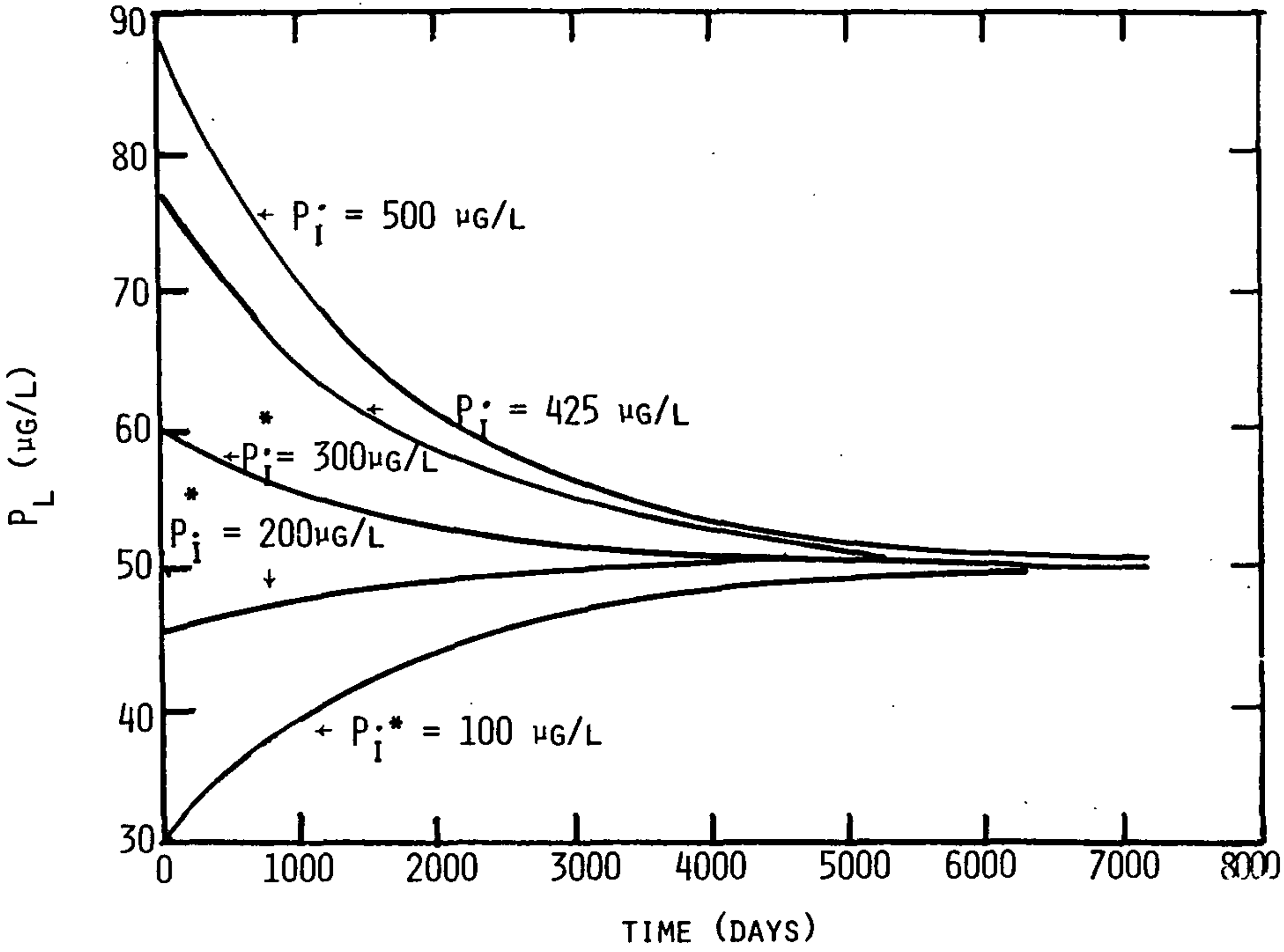

Figure 53. Unsteady state model predictions for Lake Recovery with and without suppressant additions. $\bar{T}$=10 days, P_o=50 μg/l.

would be considered successful.

Summary of Model Predictions Applied to Lake Warner. Predictive model results for Lake Warner are summarized in Figure 54. Here, the arbitrary time zero refers to the start of wastewater bypassing from the Amherst Wastewater Treatment Plant which presumeably increased input total phosphate from 40 to 90 μg/l (see also Table 5 for calculations and assumptions). After about 14 years, the model predicts that lake phosphate concentration, P_L, will reach 89 μg/l and interstitial phosphate, P_i, to reach 407 μg/l. As noted earlier, these model predictions agree with field observations of 1974 and it appears reasonable to assume bypassing of wastewater for at least 10 years prior.

Accounting for discontinuation of the bypass in 1976, input total phosphate, P_o, can be assumed to decrease to 50 μg/l. Without chemical suppression of sediment phosphate, lake phosphate concentration would initially decrease to 77 μg/l and, after about 8 years, approach 54 μg/l. If alum and kaolinite were added to the sediment to decrease interstitial phosphate to a P_i^* level of 200 μg/l, the lake phosphate concentration would be almost immediately decreased to about 45 μg/l. Because of its effectiveness, chemical suppression can actually result in model predictions showing an increase in lake phosphate with time even though input phosphate has been reduced. This situation arises because P_i^* is below the ultimate equilibrium value for that specific

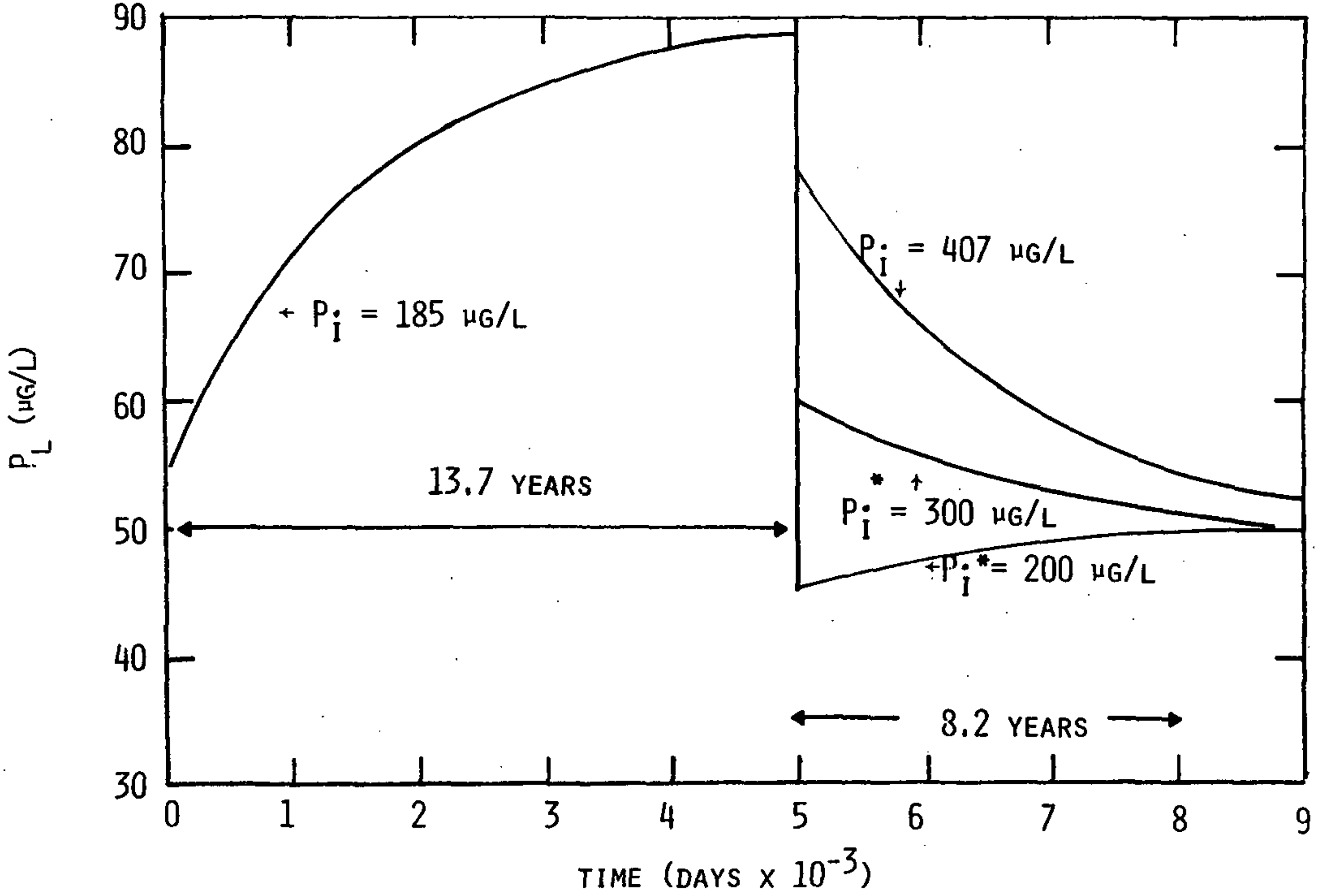

Figure 54. Summary of entire predictive model results for Lake Warner. At t=0, P_i=185 μg/l. At t>0>5000 days, P_o=90 μg/l, final P_i=407 μg/l. At t>5000 days, P_o=50 μg/l.

phosphate input loading (see Figure 49).

Application of Model to Other Lakes. Figure 55 depicts the increase in lake phosphate concentration for a lake having a residence time ($\overline{T}$) of 100 days but subject to the identical exchange processes and loading factor change as Lake Warner with a residence time ($\overline{T}$) of only 10 days (see Figure 54). As should be expected, the greater dilution effect of a larger lake causes a more gradual approach to the new equilibrium concentration. For example, after 11 years, P_L has only increased from 40 to 56 μg/l while this same loading, P_o, increased P_L in Lake Warner from 40 to 87 μg/l during the same time interval.

As shown in Figure 56, addition of suppressants to a hypothetical lake having a residence time ($\overline{T}$) of 100 days and conditions similar to Lake Warner in 1974 would produce a similar initial decrease in P_L. However any subsequent transient response due to K_1 and K_2 is slowed by the greater dilution factor associated with the longer residence time ($\overline{T}$).

Without addition of suppressants to this larger lake, 19 years would be required for P_L to decrease from 90 to 72 μg/l. Addition of suppressants could reduce P_i from 425 μg/l to 200 μg/l (P_i^*) and would almost immediately reduce P_L to about 44 μg/l; moreover, after 19 years, P_L would only have increased to 47 μg/l. This represents an increase of only 3 μg/l over a period of 19 years as the

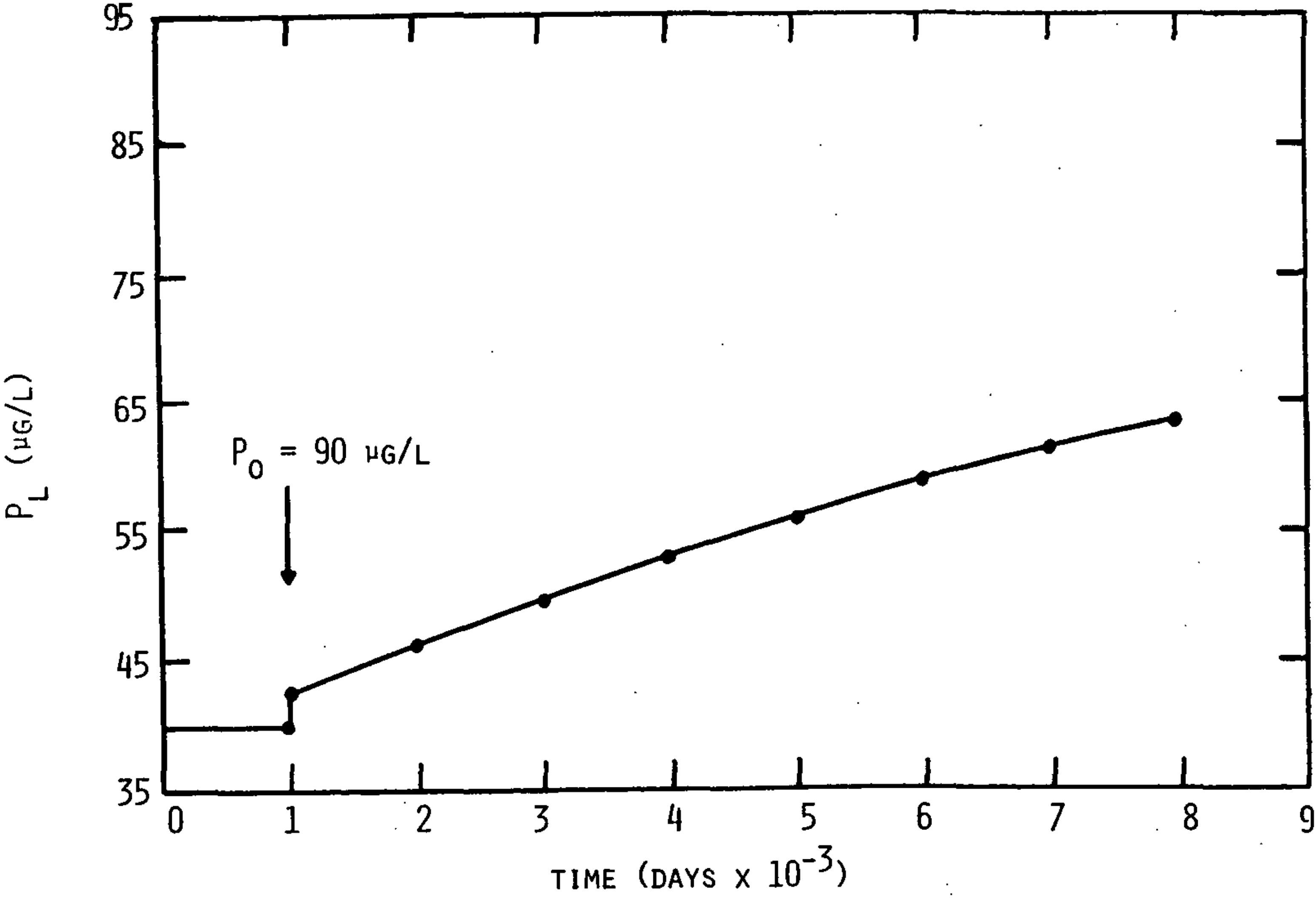

Figure 55. Unsteady state model predictions for larger lake ($\overline{T}$=100days). At 0>t>1000, P_i=185 µg/l, P_o=40 µg/l. At t>1000, P_o µg/l. At t=19 years after change in P_o, P_L=63.5 µg/l, $P_i \cong$ 290 µg/l.

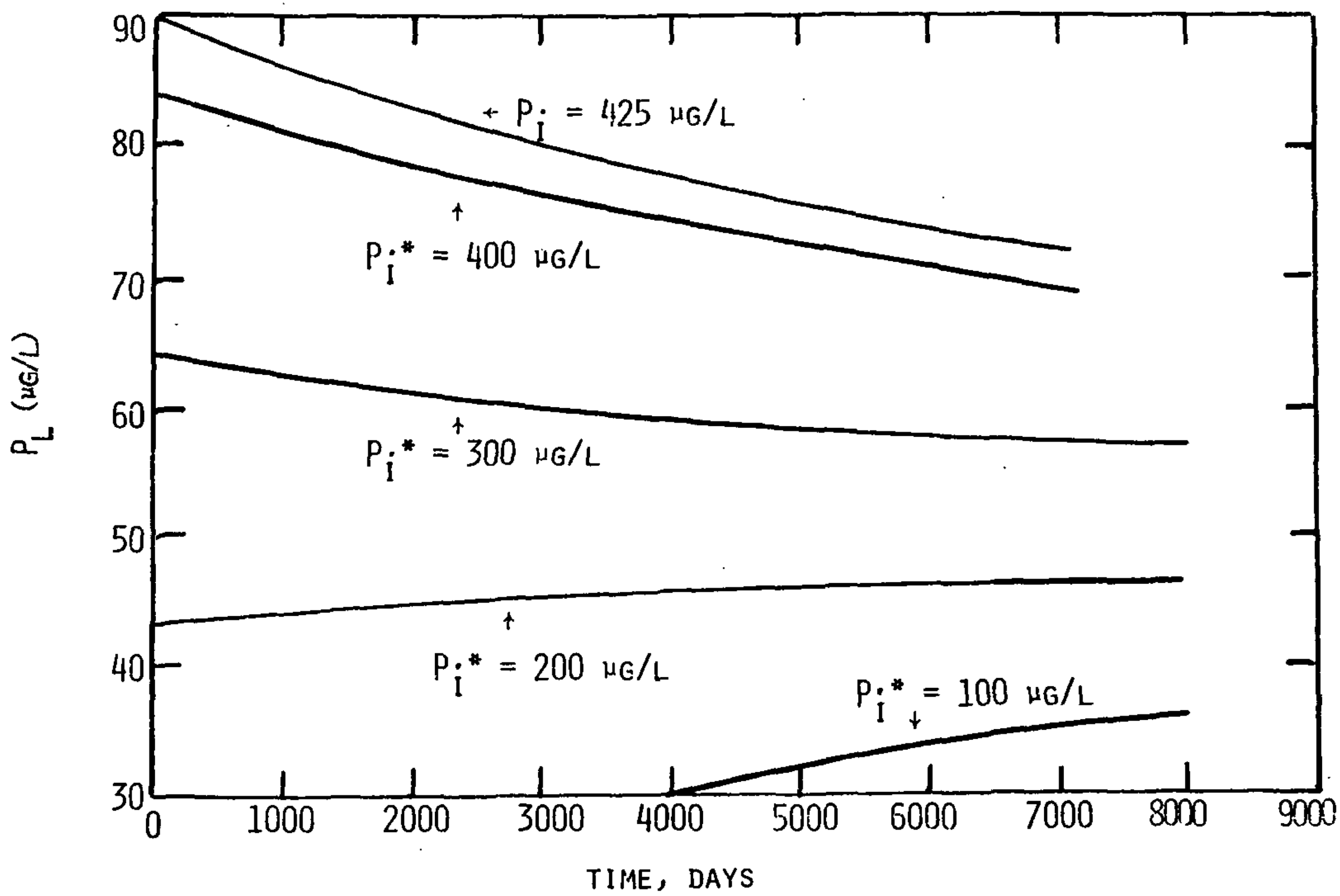

Figure 56. Unsteady state model predictions for larger lake ($\overline{T}$=100 days) for lake recovery with and without suppressant additions. P_i values refer to t=0, P_o=50 µg/l.

lake slowly approaches the ultimate equilibrium where influent phosphate and lake phosphate concentrations become equal.

The use of suppressants can readily be seen to have an immediate effect on transforming an eutrophic lake, as measured by lake water phosphate, to a mesotrophic lake (see Figure 1).

Suppressant addition may be the only economical method to rapidly restore large lakes to meso-oligotrophic conditions and to sustain these conditions for long periods of time even though input phosphate, P_O, may not be drastically reduced.

Summary

In summary, a sediment/water phosphate exchange model has been derived and applied to a shallow eutrophic lake. Using experimentally determined release and sedimentation rate constants and appropriate equilibrium sediment-interstitial phosphate relationships, the model predicts the long term approach to a new steady-state in a lake when phosphate loading, P_O, is increased. The resultant increase in sediment phosphate, P_T, then provides a substantial reservoir, P_S, to be released into the interstitial water, P_i, and subsequently into the lake water, P_L, upon decrease of input phosphate loading.

To illustrate the application of the proposed model, a period of 12 to 14 years is predicted for lake phosphate to be reduced in Lake Warner from 90 μg/l to 50 μg/l given a decrease in phosphate input, P_o, from 90 to 50 μg/l. The model is also useful in determining the effect of alum and kaolinite as suppressants of lake recovery time. Assuming these suppressants decreased interstitial phosphate, P_i^*, to 200 μg/l which would decrease release to the overlying water, an almost immediate decrease (less than 100 days) would occur to lower P_L to less than 50 μg/l. If this model correctly portrays the impact of these two phosphate control strategies, i.e. reducing input phosphate loading (P_o) and lowering interstitial phosphate (P_i^*) by the addition of alum and kaolinite, then both appear necessary to permanently reverse the eutrophic state of lakes similar to Lake Warner. The reversal process for larger eutrophic lakes will take a longer period of time if only input loading, P_o, is reduced and suppressants are not used.

Based on these model results, reducing phosphate input without suppressing or removing phosphate-rich sediments will not result in improvement of lake quality for many years. Generalization of these findings to all shallow eutrophic lakes must be carefully considered. At the least, release and sedimentation rate constants as well as equilibrium relationships between the sediment and interstitial water phosphate must be estimated in each case.

CHAPTER VII

CONCLUSIONS

The eutrophic state of a lake can be controlled by adjusting the concentration of phosphate, especially orthophosphate, in the lake water. In order to alter the trophic state of a lake, the restoration program should include the reduction of influent loading as well as the control of release of phosphate from the sediment. With a decrease in the phosphate concentration in the lake, algal concentrations will be limited. The changes in the chemical, physical, and biological interactions due to this decrease can shift the lake's trophic state from highly eutrophic to mesotrophic and possibly to oligotrophic depending on the amount of loading decrease and the reduction of phosphate release out of the sediment.

In the proposed phosphorus exchange model, both release and sedimentation of phosphate were considered. Release was shown to be proportional to the concentration gradient of total phosphate between lake water and sediment interstitial water. The rate of sedimentation was shown to be first order with respect to total phosphate in the lake water. Field evaluation of the rate constants, K_1 governing release and K_2, governing sedimentation, were obtained from Lake Warner. Additionally, an equilibrium relationship between the interstitial and solid phase sediment phosphorus was obtained.

More specifically, the release of phosphate from the sediment is defined in terms of a rate constant, K_1, reflecting interfacial resistance. This rate constant was found to be 0.091 m/day. In the derived model, the total flux of phosphate from the sediment is dependent on the gradient between total phosphate in the interstitial and lake water. This same constant could be applicable to other small, highly eutrophic lakes with similar biological, chemical, and physical parameters as Lake Warner.

Sedimentation of phosphate from the lake water to the sediment involves the reaction of orthophosphate interacting with various chemical, physical, and biological parameters in the lake water. The entire phenomena of the rate of sedimentation can be closely modeled as a first order rate reaction, K_2P_L, where K_2 is equal to 0.176/day and P_L is the concentration of total phosphate in the lake water.

The amount of exchangeable phosphate which can be released from the solid fraction in the sediment into the interstitial water is a function of the total phosphorus within the solid fraction, as well as the sediment pH, Eh, and temperature. Therefore, each lake will have different amounts of exchangeable phosphate. However, values of 15 to 40 percent of the total sediment phosphorus are common. For Lake Warner, a value of 25 percent yielded reasonable results. Also, it is necessary to determine the depth of influence into the sediment, Dr, from which long term release of phosphate can occur. In this study, 10 cm (0.1m) was selected based on available literature values.

The release of orthophosphate from the sediment can be decreased by the application of suppressants. In this research, alum and kaolinite were tested in-situ in Lake Warner. Both suppressants, adsorb orthophosphate effectively and thereby reduce the interstitial phosphate concentration and the phosphate release rate. A ratio of 1:4 of alum to kaolinite appears to be the best mixture to affect the reduction of interstitial phosphate. The solution of the proposed phosphorus exchange model for the steady-state condition incorporates the effects of release, sedimentation, influent loading, and interstitial phosphate concentration. The results obtained can be used to determine if lake phosphate concentration is currently lower or higher than the equilibrium value predicted on the basis of present input phosphate loading. Also, knowing the present value of interstitial phosphate concentration enables calculation of the final equilibrium value of that parameter upon changing the input phosphate loading. However, this model cannot provide the time required for the lake to reach this new equilibrium condition.

Applications of the non-steady state solution of the proposed phosphate exchange model can be used to determine the transient response of a lake to specific loading changes when coupled with the relationship of interstitial and exchangeable phosphorus retained in the sediment. This model can be used to predict the response of lake phosphate to either increased or decreased phosphate loadings. Further, the interstitial phosphate concentration can be adjusted to account for the effects of the addition of alum and kaolinite on the release of phosphate from the sediment.

The non-steady state model was specifically applied to Lake Warner using the field derived values of K_1 and K_2 which were refined using a gradient search computer program. Both the past and future conditions of Lake Warner were investigated. The model has supported the observation that wastewater bypassing along with a general increase in development in the Mill River drainage basin, has caused total phosphate in the lake water to increase from an estimated 40 μg/l to the present level of 90 μg/l (about 20 μg/l to 45 μg/l orthophosphate) in 10 to 13 years.

Applying this same non-steady state model to predict the impact of discontinuance of bypassing in 1976 shows that the yearly average concentration of total phosphate in the lake would decrease to 54 μg/l in a period of 8.2 years. However, treatment of the lake with approximately 12 gm/m^2 of alum and 100 gm/m^2 of kaolinite, along with the decrease in wastewater bypassing, would reduce total phosphate to about 45 μg/l (about 25 μg/l orthophosphate) within 1-3 months. This prediction rests on the assumption that the suppressant mixture would not be resuspended or washed out due to the velocity of water flowing through the lake or turbulence due to wind action. If, along with the discontinuance of bypassing and suppression treatment, better land use practices were instituted to decrease erosion and the subsequent high phosphate loading due to storm drains, then the influent loading would be low enough to achieve a predicted oligo-mesotrophic level in Lake Warner.

The proposed non-steady state model coupled with the finite difference relationship of interstitial and exchangeable sediment phosphate should be applicable to most small, unstratified lakes using the values of the release (K_1) and sedimentation (K_2) rate constants obtained in this study.

In order to derive a solution using either the plug flow or completely mixed models, these steps are needed:

1) Obtain values for the area (A), volume (V) and average in-flow (Q_o) into the lake;
2) Determine the average yearly loading of total phosphate currently being introduced into the lake to determine the influent concentration (P_o);
3) Determine the present values of lake water concentration (P_{L_o}), interstitial phosphate concentrations (P_i), and total phosphorus (P_T) of the solid fraction according to the procedures described in Chapters IV and V;
4) Assume, unless more extensive research can be pre-

formed, that exchangeable phosphate (P_S) in the solid fraction is 25 percent of P_T, depth of influence (Dr) into the sediment is 10 cm., porosity (ε) is .84, and a similar relationship of P_S and P_i (Equation 46) is applicable;

5) Determine a future value for P_O which can be attained and the appropriate value of interstitial phosphate (current value equal to P_i or suppressed value equal to P_i^*) depending on the option of treatment with alum and kaolinite; and

6) By using the appropriate input data in the computer program presented in Appendix E to apply the non-steady state phosphate exchange model, the transient response of total phosphate in the lake water (P_{L_t}) and the time required to reach an ultimate equilibrium concentration can be predicted. This concentration will have a direct bearing on the future trophic state of the lake.

The ability to predict how much of a reduction of phosphate loading is needed in order to alter the trophic state of a lake will greatly aid engineers and planners in their decision-making processes. The degree of wastewater treatment, land use planning, rezoning, and other political and financial decisions concerning the trophic state of a lake and lake restoration projects can be reasonably arrived at by the application of the proposed methods given in this research.

Literature Cited

1. Allen, J.E., 1970. "Effects of Redox Potential on Equilibrium Distribution of Phosphorus in Mud-Water Systems", M.S. Thesis, Civil Eng. Dept., Univ. of Mass., Amherst, Mass., p. 90.

2. A.S.C.E., 1972. "Fly Ash can be Used Successfully in Reclaiming Dying Lakes", Civil Eng., 3:31.

3. Bailey, G.W., 1968. "Role of Soils and Sediment in Water Pollution Control", Part 1, Report of U.S. Dept. of Interior, Southeast Water Lab.

4. Bartsch, A.F., 1975. "Problems of Lake Quality", Seminar Session No. 2, Water Resources Research Center, Univ. of Mass., Amherst, Mass.

5. Bengtsson, L., and S. Fleischer, 1971. "Sediment Removal Saves Aging Swedish Lakes [Trummen]", Water Poll Control Eng. (G.B.), 109:6:28.

6. Biffi, F., 1963. "Determining the Time Factor as a Characteristic Trait in the Self-Purifying Power of Lage d'Orta in relation to a continual pollution", Atti Internat. Verein. Sci. Lett. Arti, 121:131-136.

7. Bio-Rad Laboratories, 1971. Catalog and Price List W.

8. Bird, B.R., W.E. Stewart, and E.N. Lightfoot, 1960. Transport Phenomena, John Wiley and Sons, N.Y., p. 515.

9. Bostrom, K., 1967. "Some pH-Controlling Redox Reactions in Natural Waters", Equilibrium Concepts in Natural Water Systems, ed. W. Stumm, Am. Chem. Soc., 67:286-311.

10. Bouldin, D.R., 1968. "Models for Describing the Diffusion of Oxygen and other Mobile Constituents Across the Mud-Water Interface", Jour. Ecol. (G.B.), 56:77.

11. Bray, J.T., O.P. Bricker, and B.N. Troup, 1973. "Phosphate in Interstitial Waters of Anoxic Sediments: Oxidization Effects During Sampling Procedure", Science, 180:1362-1364.

12. Brice, R.M., and C.F. Powers, 1969. "The Shagawa Lake, Minnesota, Eutrophication Research Project", in *Proc. Eutrophication - Biostimulation Assessment Workshop*, Ed. Middlebrooks, E.J., Maloney, T.E., Powers, C.F. and Kaack, L.M., Univ. of California, Berkeley, pp. 258-269.

13. Brock, T.D., 1973. "Lower pH limit for the Existence of Blue-Green Algae: Evolutionary and Ecological Implications", *Science*, 179:480-483.

14. Broecker, W.S., 1973. "Environmental Priorities", *Science*, 182:435.

15. Browman, M.G., and R.F. Harris, 1973. "Interaction of Soluble Phosphate with Aluminum Hydroxide in Lakes", Report to Inland Lakes Demonstration Project, Upper Great Lakes Regional Comm., Madison, Wisc.

16. Cahill, T.H., P. Imperato, and F.H. Verhoff, 1974. "Evaluation of Phosphorus Dynamics in a Watershed", Amer. Soc. Civil Eng., *Environ. Eng. Div.*, pp. 439-458.

17. Capaccio, R.S., 1971. "The Rate of Release of Phosphorus from Natural Benthal Deposits", M.S. Thesis, Northeastern Univ., Boston, Mass.

18. Carritt, D.E., and S. Goodgal, 1954. "Sorption Reactions and Some Ecological Implications: *Deep-Sea* and *Oceanog. Abs.*, 1:224-243.

19. Chen, Y.S., J.N. Butler, and W. Stumm, 1973. "Kinetic Study of Phosphate Reaction with Aluminum Oxide and Kaolinite", *Environ. Sci.* and *Technol.*, 7:4:327-332.

20. Crank, J., 1956. *The Mathematics of Diffusion*, Oxford Press, pp. 15.

21. Delfino, J.J., G.C. Berthlenson, and G.F. Lee, 1968 "Distribution of Mn, Fe, P, Mg, K, Na, and Ca in the Surface Sediments of Lake Mendota, Wisc.", *Environ. Sci.* and *Technol.*, 3:1189-1195.

22. Dept. of Natural Resources, 1970. "Cost of Dredging Lakes", Technical Bull. No. 46, Madison, Wisc. pp. 38-47.

23. DiGiano, F.A., 1971. Mathematical Modeling of Nutrient Transport, Pub. #17, Water Resources Research Center, Univ. of Mass., Amherst, Mass., pp. 37.

24. Dillon , P.J., and F.H. Rigler, 1975. "A Simple Method for Predicting the Capacity of a Lake for Development Based on Lake Tropic Status", (in press).

25. Dobbins, D.A., 1970. "Water-Clay Interactions in North Carolina's Pamlico Estuary", Environ. Sci. and Technol., 4:743.

26. Duke, T.W., J.N. Willis, and D.A. Wolfe, 1968. "A Technique for Studying the Exchange of Trace Elements Between Estuarine Sediments and Water", Limnol. and Oceanog., 13:541.

27. Dunst, R.C., et. al., 1974. "Survey of Lake Rehabilitation Techniques and Experiences", Technical Bull. No. 75, Dept. of Natural Resources, Madison, Wisc., pp. 177.

28. Edmondson, W.T., 1970. "Phosphorus, Nitrogen, and Algae in Lake Washington After Diversion of Sewage", Science, 169:690-691.

29. Edzwald, J.K., J.B. Upchurch, and C.R. Omelia, 1974. "Coagulation in Estuaries", Environ. Sci. and Technol., 8:1:58-63.

30. Emery, R.M., C.E. Moon, and E.B. Welch, 1973. "Delayed REcovery of a Mesotrophic Lake After Nutrient Diversion", Jour. Water Poll. Control Fed., 45:5:913-925.

31. EPA, 1971. "Algal Assay Procedure, Bottle Test", U.S. Environ. Protect Agency, National Eutrophication Research Program, Corvallis, Oregon, pp. 51-61.

32. EPA, 1971. "Methods for Chemical Analysis of Water and Wastes", U.S. Environ. Protect. Agency, Water Qualtiy Office, Analytical Quality Control Lab., Cinn., Ohio.

33. Fair, G.M., J.C. Geyer and D.A. Okun, 1968. *Water and Wastewater Engineering*, John Wiley and Sons, N.Y., 2:23.

34. Fanning, K.A., and M.E.Q. Pilson, 1971. "Interstitial Silica and pH in Marine Sediments: Some Effects of Sampling Procedures", *Science*, 173:4003:1228-1231.

35. Feng, T.H., 1967. "Chemical Effects of Bottom Deposits on the Quality of Impounded Waters", Report No. EVE-6-67-6, Civil Eng. Dept., Univ. of Mass., Amherst, Mass.

36. Feng, T.H., 1971. "Control of Benthic Deposits in Lakes", Publ. No. 16, Water Resources Res. Center, Univ. of Mass., Amherst, Mass., pp. 1-16.

37. Feng, T.H., "Sediment-Water Interchange of Plant Nutrients in Lakes", Civil Eng. Dept., Univ. of Mass., Amherst, Mass. (unpublished Manuscript).

38. Fillos, J. and A.H. Molof, 1972. "Effects of Benthal Deposits on Oxygen and Nutrient Economy of Flowing Waters", *Jour. Water Poll. Control Fed.*, 44:644.

39. Fillos, John and W.R. Swanson, 1973. "Effect of Benthal Deposits on the Quality of Natural Waters", Third Annual Environ. Eng. and Sci. Conf., Louisville, Kentucky.

40. Fillos, J. and W.R. Swanson, 1975. "The Release Rate of Nutrients from River and Lake Sediments", *Jour. Water Poll. Control Fed.*, 47:5:1032-1042.

41. Fink, E.A., 1970. "Adsorption of Anionic Detergents by Soils", *Jour. Water Poll. Control Fed.*, 42:2.

42. Fitzgerald, G.P., 1970. "Aerobic Lake Muds for the Removal of Phosphorus from Lake Waters" *Limnol. and Oceanog.*, 15:550-555.

43. Foree, E.G., amd R.L. McCarthy, 1970. "Anaerobic Decomposition of Algae", *Environ. Science and Technol.*, 4:842.

44. Frink, C.R., 1967. "Nutrient Budget: Rational Analysis of Eutrophication in a Connecticut Lake", *Environ. Sci. Technol.*, 1:425-428.

45. Gagnon, J., and L. Geokas, 1972. "Water Quality Survey on the Mill River from North Amherst to Hadley, Massachusetts", Special Project for Course, Dept. of Civil Eng., Univ. of Mass., Amherst, Mass., p. 23.

46. Gahler, A.R., W.D. Sandville, J.A. Searcy, C.F. Powers, and W.E. Miller, "Studies on Lake Restoration by Phosphorus Inactivation", (in preparation), E.P.A. National Eutrophication Program, Corvallis, Oregon.

47. Gahler, A.R., 1969. "Sediment-Water Nutrient Interchange", Proceedings of Eutrophication-Biostimulation Assessment Workshop. Middlebrooks, et. al., ed., Univ. of Calif. Berkeley, Calif.

48. Gaines, J.B., 1973. "Variation of Sludge Porosity with the Concentration of Solids as Affected by Bound Water", M.S. Special Project, Dept. of Civil Eng., Univ. of Mass., Amherst, Mass.

49. Garrels, R., and C. Christ, 1965. *Solutions, Minerals, and Equilibria*, Harper and Row, N.Y., p. 450.

50. Goldman, J.C., D.B. Porcella, E.J. Middlebrooks, and D.F. Toerien, 1971. "The Effect of Carbon and Algal Growth - Its Relationship to *Eutrophication*", Occasional Paper #6, Utah Water Res. Lab., Utah State Univ., Logan, Utah, 55.

51. Greeson, P.E., 1972. "Natural Eutrophication and Improvement of Lake Qualtiy: A Case History, Oneida Lake, N.Y., *Eight Am. Water Res. Conf.*, Ed. Harbaugh, T. and Warner, D., AW.R.A., St. Louis, Mo.

52. Grundy, R.D., 1971. "Strategies for Control of Man-Made Eutrophication", Environ. Sci. and Technol., 5:12:1184-1190.

53. Harriss, R.C., 1967. "Silica and Chloride in Interstitial Waters of River and Lake Sediments", Limnol. and Oceanog. 12:1:8.

54. Harter, R.D., 1968. "Adsorption of Phosphorus by Lake Sediments", Soil Sci. Soc. Amer. Proc., 32:514-518.

55. Hem, J.D., 1968. "Aluminum Species in Water", in, Trace Inorganics in Water, ed. R.A. Baker, Amer. Chem. Soc., 73:98-114.

56. Hemwall, J.B., 1957. "The Role of Soil Clay Minerals in Phosphorus Fixation", Soil Sci., 83:101-108.

57. Herbes, S.E., H.E. Allen, and D.H. Mancy, 1975. "Enzymatic Characterization of Soluble Organic Phosphorus in Lake Water", Science, 187:432-434.

58. Hetling, L.J., 1974. "Observation on the Rate of Phosphorus Input into Lake George and Its Relationship to the Lake's Trophic State", Technical Paper #36, N.Y. Dept. Environ. Cons.

59. Higgins, George, 1973. Personal Communication, Dept. Civil Eng., Univ. of Mass., Amherst, Mass.

60. Horne, A.J., and C.R. Goldman, 1974. "Suppression of Nitrogen Fixation by Blue-Green Algae in a Eutrophic Lake with Trace Additions of Copper", Science, 183:409-411.

61. Hsu, P.H., 1964. "Adsorption of Phosphate by Aluminum and Iron in Soils", Soil Sci. Soc. Amer. Proc., 28:474-478.

62. Hsu, P.H., 1968. "Interaction Between Aluminum and Phosphate in Aqueous Solution", in, Trace Inorganics in Water, ed. R.A. Baker, Amer. Chem. Soc., 73:115-127.

63. Hutchinson, G.E., 1957. A Treatise on Limnology, Geography, Physics, and Chem., John Wiley Pub. Co.

64. Hynes, H.B.N., and B.J. Greib, 1967. "Experiments on Control of Release of Phosphate from Lake Muds", Publ. No. 16, Great Lakes Res. Div., Univ. of Mich., p. 357.

65. Hynes, H.B.N., and B.J. Greib, 1970. "Movement of Phosphate and other Ions from and through Lake Muds", Jour. Fish Res. Bd., Can., 27:653.

66. Jordan, Robert A., and M.E. Bender, 1973. "An In Situ Evaluation of Nutrient Effects in Lakes", E.P.A. - R3-73-018, Office of Res. and Monitoring, Washington, D.C., p. 227.

67. Jubinville, R.A., 1973. "Analysis of Phosphorus Budget of Lake Wyola and Lake Warner, Massachusetts", M.S. Special Project, Dept. of Civil Eng., Univ. of Mass., Amherst, Mass.

68. Kafkafi, V., A.M. Posner, and J.P. Quirk, 1967. "Desorption of Phosphate from Kaolinite", Soil Sci. Soc. Amer. Proc., 31:348-353.

69. Kamp-Nielsen, L., 1974. "Mud-Water Exchange of Phosphate and other Ions in Undisturbed Sediment Cores and Factors Affecting the Exchange Rates", Arch. Hydrobiology, 73:218-237.

70. Kohl, D.M. and G.B. Shearer, Commoner, B., 1971. "Fertilizer Nitrogen: Contribution to Nitrate in Surface Water in a Corn Belt Watershed", Science, 174:4016:1331-1334.

71. Kramer, J.R., 1967. "Equilibrium Models and Composition of the Great Lakes", in, Equilibrium Concepts in Natural Water Systems, ed. W. Stumm, Am. Chem. Soc., 67:243-254.

72. Krull, J., 1973. "Phosphorus Response Model for Lake Sammanish", M.S. Thesis, Civil Eng. Dept., Univ. of Washington.

73. Ku, W.C., and T.H. Feng, 1975. "Equilibrium Adsorption of Inorganic Phosphate by Lake Sediments", Report No. Env. E. 45-75-1, Dept. of Civil Eng., Univ. of Mass., Amherst, Mass.

74. Kuzminski, L.N., and C. Fredette, 1974. "The Effects of Outboard Motor Subsurface Exhausts on the Growth Characteristics of Two Common Freshwater Algal Species". Report No. Env. E. 42-74-5, Dept. Civil Eng., Univ. of Mass., Amherst, Mass.

75. Larsen, D.P., and K.W. Malveg, "Limnology of Shagawa Lake, Minnesota, Prior to Reduction of Phosphorus Loading", U.S.E.P.A., Corvallis, Oregon, (unpublished manuscript).

76. Larsen, D.P., K.W. Malveg, D.W. Schults, and R.M. Brice, "Response of Eutrophic Shagawa Lake, Minnesota, U.S.A., Eutrophication and Lake Restoration Branch, Corvallis, Oregon, (unpublished manuscript).

77. Latterell, J.J., R.F. Holt, and D.R. Timmons, 1971. "Phosphate Availability in Lake Sediments", *Jour. Soil and Water Cons.*, pp. 21-24.

78. Lean, D.R.S., 1973. "Phosphorus Dynamics in Lake Water", *Science*, 179:678-679.

79. Lee, G.F., 1972. "Phosphorus, Water Quality, and Eutrophication of Lake Michigan", Lake Michigan Enforcement Conf., p. 32.

80. Lee, G.F., and A.W. Hoadley, 1967. "Biological Activity in Relation to the Chemical Equilibrium Composition of Natural Waters", in *Equilibrium Concepts in Natural Water Systems*, ed. W. Stumm, Am. Chem. Soc., 67:319-337.

81. Li, W.C., D.E. Armstrong, and R.F. Harris, 1973. "Measurement of Exchangeable Inorganic Phosphate in Lake Sediments", *Environ. Sci.* and *Technol.*, 7:5:454-56.

82. Li, Armstrong, Williams, Harris, Syers, 1972. "Rate and Extent of Inorganic P. Exchange in Lake Sediments", *Soil Sci. Am. Proc.* 36 279, 285 pp. 51-54.

83. Lorenzen, C.J., 1966. "A Method for the Continuous Measurement of *in vivo* Chlorophyll Concentration", *Deep-Sea Res.* and *Oceanog. Abs.* 13:223-227.

84. Lorenzen, M.W., 1973. "Predicting the Effects of Nutrient Diversion on Lake Recovery", in *Modeling the Eutrophic Process*, Proc. of Workshop at Utah State, Ed. Middlebrooks, Falkenborg, and Maloney*, Utah Water Res. Lab., Logan, Utah., N.T.I.S. No. PB227065, pp. 205-210.

85. Lotse, E.G., 1973. "Phosphate Retention by Lake Sediments", Report No. A-016-ME, Univ. of Maine, Land and Water Resources Center, N.T.I.S. No. PB-233-880, p. 36.

86. MacKenthun, K.M., Kevp, L.E., and Stewart, R.K., 1968. "Nutrients and Algae in Lake Sebasticook, Maine", *Jour. Water Poll. Control Fed.*, 40:72.

87. MacPherson, L.B., M.R. Sinclair, and F.R. Hayes, 1958. "Lake Water and Sediment: III, The Effect of pH on the Partitition of Inorganic Phosphate between water and oxidized Mud or its Ash", *Limnol.* and *Oceanog.*, 3:318.

88. Malveg, K.W., D.P. Larsen, D.W. Schults, and H.T. Mercier, "A six-year Water, Phosphorus, and Nitrogen Budget for Shagawa Lake, Minnesota", U.S.E.P.A., Eutrophication and Lake Restoration Branch, Corvallis, Oregon (unpublished manuscript).

89. Malveg, K.W., R.M. Brice, D.W. Schults, and D.P. Larsen, 1973. "The Shagawa Lake Project", Ecological Res. Series, Report No. EPA-R3-73-026, U.S. E.P.A., Corvallis, Oregon.

90. Martin, D.C., and D.A. Bella, 1971. "Effect of Mixing on Oxygen Uptake Rate of Estuarine Bottom Deposits", *Jour. Water Poll. Control Fed.*, 43:1865.

91. McKee, G.D., L.P. Parrish, C.R. Hirth, K.M. MacKenthum, and L.Z. Reup, 1970. "Sediment-Water Nutrient Relationships", Part 1 and 2, *Water and Sewage Works*, 117:203-206:246-249.

92. Minear, R.A., 1972. "Characterization of Naturally Occurring Dissolved Organophosphorus Compounds", *Environ. Sci.* and *Technol.*, 6:5:431-437.

93. Mitchell, D., 1971. "Eutrophication of Lake Water Microcosms: Phosphate vs. Nonphosphate Detergents", *Science*, 174:827-829.

94. Moore, C.A., and M.A. Silver, 1973. "Nutrient Transport by Sediment-Water Interaction", Report No. 65, UILU-WRC-73-0065, Univ. of Illinois, Urbana, Water Resources Center, 4:44.

95. Morgan, J.J., and W. Stumm, 1964. "The Role of Multivalent Metal Oxides in Limnological Transformations, as Exemplified by Iron and Manganese", Second International Conf. on Water Poll. Res., Paper No. 6, Tokyo, Jap.

96. Morris, J.C., and W. Stumm, 1967. "Redox Equilibria and Measurements of Potential in the Aquatic Environment", in, *Equilibrium Concepts in Natural Water Systems*, ed. W. Stumm, Am. Chem. Soc., 67:270-283.

97. Mortimer, C.H., 1971. "Chemical Exchanges Between Sediments and Water in the Great Lakes - Speculations on Probable Regulatory Mechanisms", *Limnol.* and *Oceanog.*, 16:387.

98. Mortimer, C.H., 1941. "The Exchange of Dissolved Substances Between Mud and Water in Lakes", *Jour. Ecol.*, 29:280-329.

99. Mortimer, C.H., 1942. "The Exchange of Dissolved Substances Between Mud and Water in Lakes", *Jour. Ecol.*, 30:147-201.

100. Newfeld, R.D., and G. Thodus, 1969. "Removal of Orthophosphates from Aqueous Solution with Activated Alumina", *Environ. Sci.* and *Technol.*, 3:661-667.

101. Ogunrombi, J.A., and W.E. Dobbins, 1970. "The Effects Benthal Deposits on the Oxygen Resources of Natural Streams", Jour. Water Poll. Control Fed., 142:538.

102. Painter, D.E., 1968. "Where Does the Phosphate Go", Water and Sew. Works, 115:12.

103. Park, P.K., L.I. Gordon, S.W. Hager, and M.C. Cissell, 1969. "Carbon Dioxide Partial Pressure in the Columbia River", Science, 166:3907:867-868.

104. Patrick, W.M., 1964. "Extractable Iron and Phosphorus in a Submerged Soil with Controlled Redox Potentials", Eighth Internat. Cong. of Soil Science, Bucharest, Rumania, 4:605-609.

105. Patrick, W.H., S. Gotch, and B.G. Williams, 1973. "Strengite Dissolution in Flooded Soils and Sediments", Science, 179:4073:564-565.

106. Patrick, W.H., and R.A. Khalid, 1974. "Phosphate Release and Sorption by Soils and Sediments: Effects of Aerobic and Anaerobic Conditions", Science, 186:53-55.

107. Peterson, J.O., J.P. Wall, T.L. Wirth, and A.M. Born, 1972. "Eutrophication Control: Nutrient Inactivation by Chemical Precipitation at Horseshoe Lake, Wisconsin", Bull. No. 62, Dept. of Natural Res. Wisconsin, pp. 20.

108. Piontelli, R., and V. Tonalli, 1964. "The Time of Retention of Lacustrine Waters in Relation to the Phenomena of Enrichment In Introduced Substances with Particular Reference to the Lago Maggiore", Memoirs 1st Italian Indrobiologie, 17:247-266.

109. Pomeroy, L.R., E.E. Smith, and C.M. Grant, 1965. "The Exchange of Phosphate Between Estuarine Water and Sediments", Limnol. and Oceanog., 10:167-172.

110. Ponnamperuma, F.N. "Oxidization - Reduction Reactions", in Soil Chemistry, by C. Chester and J.M. Bremmer, Marcel Dekker, N.Y. (in press).

111. Porcella, D.B., 1970. "Biological Effects on Sediment-Water Nutrient Interchange", Jour. San. Eng. Div., Proc. Amer. Soc. Civil Eng. 96:4:911.

112. Porcella, D.E., K.L. Schmalz, and W.A. Luce, 1971. "Sediment-Water Nutrient Interchange in Eutrophic Lakes", Proc. of Seminar on Eutrophication and Biostimulation, Univ. of Calif., Berkeley, Calif.

113. Sanders, T.G., 1974. "Rational Design Criteria for a River Quality Network", Ph.D. Dissertation, Dept. of Civil Eng., Univ. of Mass., Amherst, Mass., p. 229.

114. Schindler, D.W., 1974. "Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management", Science, 184:897-899.

115. Schindler, D.W., and G.J. Brunskill, 1977. "Atmospheric Carbon Dioxide: Its Role in Maintaining Phytoplankton Standing Crops", Science, 177:1192-1194.

116. Schindler, P., 1967. "Heterogeneous Equilibria Involving Oxides, Hydroxides, Carbonates, and Hydroxide Carbonates", in, Equilibrium Concepts in Natural Water Systems, ed. W. Stumm, Am. Chem. Soc., 67:196-221.

117. Shannon, E.E., and P.L. Brezoniki, 1972. "Relationships Between Lake Trophic State and Nitrogen and Phosphorus Loading Rates", Environ. Sci. and Technol., 6:8:719-725 No. 8, pp. 719-725.

118. Shapiro, J., "Blue-Green Algae: Why They Become Dominant", 1973. Science, 179:4071:382-384.

119. Shapiro, J., et.al., 1971. "Changes in the Chemical Composition of Sediments of L. Washington", Limnol. and Oceanog., 16:437.

120. Shapiro, J., 1967. "Induced Rapid Release and Uptake of Phosphate by Microorganisms", Science, 115:1269-1271.

121. Shih, C.S., and E.F. Gloyna, 1969. "Influence of Sediments on Transport of Solutes", Jour. Hydraul. Div., Proc. Amer. Soc. Civil Eng., 95:4:p:1347.

122. Shukla, Syers, Armstrong, 1972. "Arsenic Interference in Determination of P in Lake Sediment", Jour. of Environ. Quality, 1:292-295.

123. 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., 35:224-249.

124. Sillen, L.G., 1967. "Master Variables with Activity Scales", in Equilibrium Concepts in Natural Water Systems, ed. W. Stumm, Am. Chem. Soc., 67:45-69.

125. Singer, P.C., "Anaerobic Control of Phosphates", 1972. Jour. Water Poll. Control Fed., 44:4:663-669.

126. Skcopintsev, B.A., E.M. Lyubimova, and S.N. Timofeeva, 1964. "Investigations on the Mineralization of the Organic Substances of Dead Plankton Under Anaerobic Conditions", Sb. Vys. Sk. Chem. Technol., Prague, Technol. Vod. (Czech.), 8:209.

127. Snow, P.D. and F.A. DiGiano, 1973. "Relationship Between Trophic State and Chemical Parameters in Sediment-Water Systems of Selected Western Massachusetts Lakes", Report No. EVE 32-73-3, Civil Eng. Dept., Univ. of Mass., Amherst, Mass., p. 91.

128. Sonzogni, W.C., and G. Fred Lee, 1974. "Diversion of Wastewaters from Madison Lakes", Jour. of Env. Eng. Div., Amer. Soc. Civil Eng., 100:153-170.

129. Stein, O.L., "Amherst Sewage Disposal Problem", Botany Dept., Univ. of Mass., Amherst, Mass. (unpublished manuscript).

130. Strickland, J.D.H., 1968. "Continuous Measurement of in vivo Chlorophyll; A Precautionary Note", Deep-Sea, 15:225-227.

131. Stumm, W., and J.J. Morgan, 1970a. Aquatic Chemistry, Wiley Interscience Pub., p. 583.

132. Stumm, W., and J.O. Leckie, 1970b. "Phosphate Exchange with Sediments: Its Rate in the Productivity of Surface Waters", Paper Presented at 5th Inter. Water Poll. Res. Conf., San Francisco, Calif.

133. Stumm, W., 1973. "The Acceleration of the Hydrogeochemical Cycling of Phosphorus", Water Res., 7:1-2:131-144.

134. Sullivan, W.T., 1967. "Chemical Composition of the Mud-Water Interface Zone with the Description on an Interface Sampling Device", Proc. Tenth Great Lakes Res. Conf., p. 390.

135. Sutherland, J.C., J.R. Kramer, J.R.N. Nichols and T. Kurtz, 1966. "Mineral-Water Equilibria, Great Lakes: Silica and Phosphorus", Publication No. 15, Great Lakes Res. Div., Univ. of Michigan, pp. 439-445.

136. Syers, J.K., R.F. Harris, and D.E. Armstrong, 1973. "Phosphate Chemistry in Lake Sediments", Jour. Environ. Quality, 2:1:1-14.

137. Tofflemire, T.J., M. Chen, P.E. Van Alstyne, L.J. Metling, and D.B. Aulenbach, 1973. "Phosphate Removal of Sands and Soils", Technical Paper No. 31, N.Y. Dept. of Environ. Conservation, Albany, N.Y.

138. Upchurch, J.B., J.K. Edzwald, and C.R. O'Melia, 1974. "Phosphates in Sediments of Pamlico Estuary", Environ. Sci. and Technol., 8:1:56-58.

139. Vollenweider, R.A., 1974. "Input-Output Models", Schweiz, Z. Hydrol., (in press)

140. Vollenweider, R.A., 1969. "Possibilities and Limits of Elementary Models Concerning the Budget of Substances in Lakes", Archives of Hydrobiology, 66:1-39.

141. Vollenweider, R.A., 1968. "Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters with Particular Reference to Nitrogen and Phosphorus as a Factor in Eutrophication", Report No. 27, DAS/CIS/68, Organization for Economic Cooperation and Development, Paris, p. 192.

142. Welch, E.B., 1969. "Factors Initiating Phytoplankton Blooms Resulting Effects on Dissolved Oxygen in Duwamish River Estuary, Washington", U.S. Geological Survey, Water Supply Paper, No. 1873-A.

143. Welch, E.B., G. R. Hendrey, and R.K. Stoll, "Nutrient Supply and the Production and Biomass of Algae in Four Washington Lakes", (in press).

144. Welch, E.B., C.A. Rock, and J.D. Krull, 1973. "Long-Term Lake Recovery Related to Available Phosphorus", in Modeling the Eutrophic Process, Proc. of Workshop at Utah State Univ., Sept. 5-7, 1973. Ed Middlebrooks, Falkenborg, and Maloney, Utah Water Res. Lab., College of Eng., Utah State Univ., Logan, Utah, N.T.I.S., No. PB 227065, pp. 5-14.

145. Wentz, D.A., and G.F. Lee, 1969. "Sedimentary Phosphorus in Lake Cores-Analytical Procedure", Environ. Sci. and Technol., 13:750-754.

146. Wentz, D.A., and G.F. Lee, 1969. "Sedimentary Phosphorus in Lake Cores-Observations on Depositional Pattern in Lake Mendota", Environ. Sci. and Technol., 3:754-759.

147. Wildung, R.E., and R.L. Schmidt, 1973. "Phosphorus Release from Lake Sediments", Report EPA-R3-73-024, Office of Res. and Monitoring, U.S. Environ. Protect. Agency, p. 185.

148. Williams, J.D.H., J.K. Syers, D.E. Armstrong and R.F. Harris, 1971c. "Characterization of Inorganic Phosphate in Noncalcareous Lake Sediments", Soil Sci. Soc. Amer. Proc., 35:556-561.

149. Williams, J.D.H., J.K. Syers and R.F. Harris, 1970. "Adsorption and Desorption of Inorganic Phosphorus by Lake Sediments in .1m NaCl Systems", Environ. Sci. and Technol., pp. 517-519.

150. Williams, J.D.H., J.K. Syers, S.S. Shulka, and R.F. Harris, 1971. "Levels of Inorganic and Total Phosphorus in Lake Sediments as Related to other Sediment Parameters", Environ. Sci. and Technol., 5:1113-1120.

151. Wood, E.J.F., 1965. "Marine Microbial Ecology, Reinhold Pub. Corp., N.Y., pp. 114-115.

152. Woodruff, J.R., and E.J. Kamprath, 1965. "Adsorption

Maximum as Measured by the Langmuir Isotherm and its Relationship to Phosphorus Availibility", *Soil Sci. Amer. Proc.*, 29:148-150.

153. Zajicek, O.T., 1970. "Determination of the Feasibility of Removal of Algal Nutrients in Lake Water by Ion Exchange", Pub. No. 12, Water Resources Res. Center, Univ. of Mass., Amherst, Mass., p. 64.

154. __________, 1970. "Costs of Dredging Lakes ", Technical Bull. #46, Dept. Natural Resources, Madison, Wisc., pp. 38-47.

Appendix A

Orthophosphate and Total Phosphate Determination Methods

Isobutanol Extraction Method for Phosphorus Determination

A. Orthophosphate Determination

All glassware are rinsed in 2N sufluric acid, then stored under deionized water. The acid rinse is needed only when the glassware is initially prepared and after every ten or twelve runs

Mixed reagent: 50 ml 5 N sulfuric acid

25 ml Ammonium Molybdate solution (15 gm Ammonium Molybdate in 500 ml dionized water) - store in plastic bottle at 4°C.

10 ml Potassium Antimony Tartrate solution (0.34 gm in 500 ml deionized water).

1.08 gm Ascorbic Acid dissolved in 20 ml deionized water - prepare daily.

Mix the above constituents in the order given to make the mixed reagent. This reagent is to be prepared fresh each time; the unused portion is to be discarded.

<u>Procedure</u>:

1. Transfer 100 ml of each sample to a separatory funnel. Samples A and B are to be deionized water and control stock solution respectively.

2. Add 10 ml of the mixed reagent to each separatory funnel. Shake each funnel vigorously for one minute immediately after the reagent is added.
3. Add 20 ml isobutanol to each separatory funnel and shake the funnel vigorously for one minute immediately after the addition.
4. After all the isobutanol has been added to the funnels and shaking has been effected, shake each funnel once more in turn for one minute.
5. Separate the organic layer (top) from the water layer and discard the water layer. Transfer the organic layer directly to respective calorimeter tubes to which have been added each .8 ml 95 percent ethanol.
6. Swirl tubes to insure mixing of the butanol and ethanol and measure transmittance against the deionized sample at 690 millimicrons. Remember to use the red tube and filter for this measurement. Estimate measurement to 1 percent transmittance.

   (Source: Snow and DiGiano, 1973).

B. Total Phosphorus Determination

1. Add 1 ml of strong-acid solution (310 ml of concentrated H_2SO_4 diluted to 1 liter with distilled water) to a 50 ml sample in a 125 ml Erlenmeyer flask.
2. Add 0.4 gram of ammonium persulfate.
3. Boil gently on a pre-heated hot plate for approxi-

mately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness.

4. Add phenolphathalein and adjust sample to pink with 1N NaOH. Bring back to colorless with one drop of strong acid solution. Cool and dilute the sample to 100 ml. If sample is not clear at this point filter. (Source: EPA, 1971; Ku, 1975)

NOTE: Appendices B through E are not included in this report but can be found in the Ph.D. Dissertation of the same title by Phillip D. Snow, University of Massachusetts/Amherst (July 1976).