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
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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
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University of Massachusetts
Amherst, Massachusetts 01002

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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.
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*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).
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\( \bar{T} \) Detention time (T)

\( t \) Time (T)

\( V \) Volume of Lake Water (L³)

\( V_s \) Volume of Sediment (L³)

\( v \) Velocity (L/T)

\( Z \) Lake Depth (L)

\( z \) Distance (L)

\( \varepsilon \) Porosity (dimensionless)

\( \Delta t \) Finite Time Difference (T)

\( \Delta z \) 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 mesotrophic 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 $\text{PO}_4^{3-}$ 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 \( \text{HCO}_3^- \) or \( \text{CO}_2 \), \( \text{NO}_3^- \), and \( \text{PO}_4^{3-} \). 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 \( \text{CO}_2, (\text{H}_2\text{CO}_3) \), or \( \text{HCO}_3^- \) 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) at .2gm/m²/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, \( \text{CO}_2 \) generated from the breakdown or organics in the benthic sediments adds to the atmospheric derived \( \text{CO}_2 \) (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 \( \text{CO}_2(\text{H}_2\text{CO}_3) \) in solution and (2) a gradual rise in water temperature which also decreases the solubility of \( \text{CO}_2 \). 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 \( \text{CO}_2 \) (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 \( \text{CO}_2 \) 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) \( \text{CO}_2 \) influx is still occurring; (2) \( \text{HCO}_3^- \) and \( \text{CO}_3^- \) can be converted to \( \text{CO}_2 \) 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 \( \text{N}_2 \) to nitrate (Shapiro, 1973); and (5) the breakdown of dead algal cells by bacteria liberates \( \text{CO}_2 \) 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, \( \text{NO}_3^- \), 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 \( \text{N}_2 \) gas to nitrates. Horne (1974) has estimated that one-half of yearly nitrogen budget in an eutrophic lake was derived from \( \text{N}_2 \) 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 \( \text{N}_2 \). 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 emanating 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 \( \text{HPO}_4^{2-} \) or \( \text{H}_2\text{PO}_4^{-} \), 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)

\[
\text{106CO}_2 + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 8\text{I}_2\text{O} + 18\text{H}^+ + \text{trace elements} + \text{light}
\]

\[
\begin{align*}
\text{photosynthesis} & \quad \text{respiration} \\
\text{C}_{106}\text{H}_{181}\text{O}_{45}\text{N}_{16}\text{P} + 150\text{ O}_2
\end{align*}
\]

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 \( \text{O}_2 \)) 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 concen-
tration in lake or on phosphorus loading (ie. gm P/m²/yr). This
direct and highly correlated dependence of algal population:
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; Ponnampuruma, 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)

<table>
<thead>
<tr>
<th>Lake</th>
<th>µg/l lake water</th>
<th>µg/l interstitial water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laurel</td>
<td>.1</td>
<td>(4/40)</td>
</tr>
<tr>
<td>Warner</td>
<td>.15</td>
<td>(70/464)</td>
</tr>
<tr>
<td>Wyola</td>
<td>.1</td>
<td>(18/179)</td>
</tr>
<tr>
<td>Mattawa</td>
<td>.11</td>
<td>(7/64)</td>
</tr>
<tr>
<td>Norwich</td>
<td>.08</td>
<td>(13/160)</td>
</tr>
<tr>
<td>Aldrich</td>
<td>.135</td>
<td>(55/410)</td>
</tr>
</tbody>
</table>
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, AlPO₄ and FePO₄, 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, \( \text{Ca}_{10} \left( \text{PO}_4 \right)_6 \left( \text{OH} \right)_2 \), 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 (Ponnampерума, 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:

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

(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$_4 \cdot 2$H$_2$O), 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):

$$
FePO_4 \cdot 2H_2O + 2H^+ + e^- \rightleftharpoons Fe^{+2} + H_2PO_4^- + 2H_2O
$$

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$_4$)$_2 \cdot 8$H$_2$O, 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)$_3$. nH$_2$O 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:

\[
\begin{align*}
\text{Fe (OH)}_3 \cdot n\text{H}_2\text{O}^+\text{PO}_4^{-3} & \rightarrow \text{Fe(OH)}_2\text{PO}_4 \quad (4) \\
\text{Fe (OH)}_n + \text{H}_2\text{PO}_4^{-1} & \rightarrow \text{Fe(H}_2\text{PO}_4)_n(\text{OH})_{3-n} \quad (5) \\
\text{Fe (OH)}_n + \text{PO}_4^{-3} & \rightarrow \text{Fe(OH)}_x(\text{PO}_4)_1-x/3 \quad (6)
\end{align*}
\]

Exchange of OH$^{-1}$ or H$_2$O for PO$_4^{-3}$ in the amorphous hydrated oxides of iron is favored over coprecipitation of FePO$_4$ within the iron gel (Ponnampерума, 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\textsubscript{4}\textsuperscript{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\textsubscript{4} which releases the PO\textsubscript{4}\textsuperscript{3-} (Wood, 1965). Along with this reaction, H\textsubscript{2}S 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).

\[
\text{FePO}_4 + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2\text{PO}_4^{-1}
\]  

(7)

This iron therefore cannot recombine with PO\textsubscript{4}\textsuperscript{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\textsubscript{4}\textsuperscript{3-} from Fe\textsuperscript{3+} - PO\textsubscript{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\textsubscript{4}\textsuperscript{3-} on the ferric iron complexes and release PO\textsubscript{4}\textsuperscript{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 $\text{Fe}^{+2}$), tends to dissolve. At pH5, $\text{FePO}_4$ will be in equilibrium with $0.1 \text{ mg/l of PO}_4^{--3}$, while at pH6, $\text{FePO}_4$ will be in equilibrium with $1 \text{ mg/l of PO}_4^{--3}$ (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 $\text{PO}_4^{--3}$ (Ponnampemuna, in press). Hence, desorption of $\text{PO}_4^{--3}$ from ferric iron hydroxometal complexes increases as pH increases, as Eh decreases, and as temperature increases (Ku, 1975; Morgan, 1974). Adsorption of $\text{PO}_4^{--3}$ by ferric iron will, therefore, usually occur in the winter and spring and cause the $\text{PO}_4^{--3}$ 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 $\text{PO}_4^{--3}$ back into the lake water is most likely to occur when algal blooms are in progress.

**Aluminum System.** Aluminum phosphate, $\text{AlPO}_4$, and its amorphous hydrated complexes act in a way similar to iron in adsorbing and reacting with $\text{PO}_4^{--3}$. Direct formation of $\text{AlPO}_4\cdot2\text{H}_2\text{O}$ (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. $\text{Al}^{+3}$ ions exhibit $\text{OH}^{-1}$ bridging and are coordinated with water molecules to form $\text{Al(}\text{H}_2\text{O})_6^{+3}$ and $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{+4}$. The positive charge attracts $\text{PO}_4^{--3}$ and $\text{PO}_4^{--3}$ is adsorbed to complex (Hem, 1968; Hsu, 1968). The complex later tends to exchange
OH⁻ ions for PO₄⁻³ and form either vascarite, aluminum hydroxide-phosphate, Al(OH)ₓ(PO₄)₁₋ₓ/₃ (Stumm, 1970a), or hydrated amorphous aluminum phosphate (Williams, 1971; Shukla, 1971; Ku, 1975). The latter form exhibits dissolution properties similar to AlPO₄ (Ku, 1975). At pH6, AlPO₄ is in equilibrium with 10 µg/l PO₄⁻³-P, which is 100 times lower than the equilibrium level with respect to FePO₄. The equilibrium concentration of PO₄⁻³ increases with pH but the level of PO₄⁻³ in solution is still much lower: e.g., at pH7, the PO₄⁻³ 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 PO₄⁻³ which could diffuse back into the lake water.

Clay System. Small, colloidal clay minerals, especially kaolinite, have been also found to adsorb PO₄⁻³. Kaolinite, Al₄(Si₄O₁₁)(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 $\text{PO}_4^{-3}$ (Hemwall, 1957; Stumm, 1970a). Also, exchange of $\text{OH}^-$ for $\text{PO}_4^{-3}$ occurs at the edges (Ponnampereuma, in press; Stumm, 1970a). Aluminum hydroxy complexes are also found attached to kaolinite; phosphate will be adsorbed to the surface or exchanged for $\text{H}_2\text{O}$ or $\text{OH}^-$ in the aluminum complex (Lotse, 1973). Adsorption of $\text{PO}_4^{-3}$ 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 $\text{PO}_4^{-3}$ adsorbed was desorbed. This would indicate that $\text{PO}_4^{-3}$ was bound to the clay or had formed an aluminum-phosphate complex (Edzwald, 1974; Stumm, 1970a).

Adsorption to form $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8\cdot\text{PO}_4$ can occur in rivers where fine grained sediments come in contact with $\text{PO}_4^{-3}$. 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 $\text{PO}_4^{-3}$ from the lake water and increasing the $\text{PO}_4^{-3}$
stored in the sediment (Carritt, 1954). Release of some of the \( \text{PO}_4^{3-} \) will occur in the summer when the pH rises and ionic strength in the interstitial water increases. The ability of kaolinite to retain \( \text{PO}_4^{3-} \) 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 hypolimnric 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 re-
move 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 $\text{PO}_4^{-3}$, low in $\text{O}_2$) 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 FeCl₃, 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/m² 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 phosphorus 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 $\text{PO}_4^{3-}$;
2. the adsorption and retention of $\text{PO}_4^{3-}$ onto iron and aluminum amorphous hydroxide complexes;
3. the adsorption of $\text{PO}_4^{3-}$ onto clay minerals; and
4. the uptake of $\text{PO}_4^{3-}$ by algae.

Increases in the $\text{PO}_4^{3-}$ concentration in lakes are governed by:

1. an increase in the influent concentration, and
2. release of interstitial $\text{PO}_4^{3-}$ 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 $\text{PO}_4^{3-}$ 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. Biffl (1963) assumed a constant input of a nutrient with no chemical or physical reactions in a completely mixed system as given by Equation 8:

\[
V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L
\]

or

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

where:

- \(V\) = Volume of lake (L³)
- \(Q_o\) = Flow in and out of lake (L³T⁻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)
\[ P_{L_0} = \text{Initial } PO_4^{-3} - P \text{ concentration in lake at } t = 0 \ (ML^{-3}) \]
\[ t = \text{Time (T)} \]
\[ T = \text{Detention time} = \frac{V}{Q_o} \ (T) \]

Biffi's model is then used to find the half-life or time it would take for a lake to reach \[ P_L = \frac{1}{2} P_{L_0} \]
if \[ P_o = 0 \] at \[ t = 0 \]. Thus:
\[
P_{L_t} = P_{L_0} e^{-t/T} \quad (9)
\]

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:
\[
V \frac{dP_L}{dt} = Q_o P_o - r Q_o P_o - Q_o P_L \quad (10)
\]

At steady state, Equation 10 reduces to:
\[
P_{L} = (1-r) P_o \quad (11)
\]
Where:

\[ r = \text{sedimentation coefficient} \]

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.

\[
P_{Lt} = P_o (1-r) (1-e^{-t/T}) + P_{Lo} e^{-t/T} \quad (12)
\]

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.

\[
V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L - K P_L V \quad (13)
\]

or, at steady state:

\[
P_L = \frac{P_o}{1 + K T} \quad (14)
\]

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:

$$K = \frac{P_O - P_L}{-2 - P_L} \tag{15}$$

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 $P_L$ at $t = 0$ and $P_L$ at $t = t$:

$$P_L = \frac{P_O}{1 + KT} \left[ 1 - e^{-\left(\frac{t}{T}\right) + KT} \right] + P_{LO} e^{-\left[\frac{(t/T) + KT}\right]} \tag{16}$$

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

$$P_L = \frac{QO}{A} \frac{P_O}{KZ + QO} = \frac{N}{KZ + QO} \tag{17}$$

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/m²/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**

<table>
<thead>
<tr>
<th>Trophic State</th>
<th>Chlorophyll $a$ (ug/l)</th>
<th>Total P (ug/l)</th>
<th>Secchi depth - ft.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligotrophic</td>
<td>7</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Mesotrophic</td>
<td>12</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>Eutrophic</td>
<td>3-200</td>
<td>10-150</td>
<td>6</td>
</tr>
</tbody>
</table>

**Shannon's Trophic State Index**

<table>
<thead>
<tr>
<th>Trophic State</th>
<th>Trophic State Index</th>
<th>Loading (gm P/M³/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligotrophic</td>
<td>1 - 2.5</td>
<td>0.02 - 0.06</td>
</tr>
<tr>
<td>Mesotrophic</td>
<td>2.5 - 4</td>
<td>0.06 - 0.10</td>
</tr>
<tr>
<td>Eutrophic</td>
<td>4 - 16</td>
<td>0.09 - 0.28</td>
</tr>
</tbody>
</table>
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.

\[ V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L - K_S A P_L + K_R A P_S \]  
(18)

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

\[ + P_o e^{-(Q_o + K_S A/V)t} \]  
(19)

Where:
\[ K^*_R = \text{release coefficient} \]
\[ K^*_S = \text{sedimentation coefficient} \]
\[ P_S = \text{total phosphorus in sediment} \]

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, $V_S$:

$$V_S \frac{dP_S}{dt} = K^*_S P_L A - K^*_R P_S A$$  \hspace{1cm} (20)

Integrating Equation 20 from $P_S = P_{S_0}$ at $t = 0$ to $P_S = P_S$ at $t = t$ yields:

$$P_{S_t} = \frac{K^*_S P_L}{K^*_R} \left[ 1 - e^{-(K^*_R A/V_S)t} \right] + P_{S_0} e^{-(K^*_R A/V_S)t}$$  \hspace{1cm} (21)

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

$$P_S = \frac{K^*_S P_L}{K^*_R}$$  \hspace{1cm} (22)

or

$$K^*_R P_S = K^*_S P_L$$  \hspace{1cm} (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:

\[ Q_o P_o = Q_o P_L \]  \hspace{1cm} (24)

or

\[ P_o = P_L \] \hspace{1cm} (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, \( K^* A_P S \), 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.

\[ V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L \pm \text{Rates of Reaction} \cdot V \] \hspace{1cm} (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) retention 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 $\text{PO}_4^{3-}$. 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:

\[ N_p = K_1 (P_i - P_L) \]  

(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:

\[ R_r = \frac{\varepsilon A}{V} K_1 (P_i - P_L) \]  

(28)

where:

- \( \varepsilon \) = 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,

$$R_{\text{sed}} = K_2 P_L$$

(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 subse-
quently 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.

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

(30)

or, substituting the appropriate rate terms already derived
yields

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

(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, $P_{L_0}$ at $t = 0$ and reaching a concentration $P_L$ at $t = t$ yields

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

$$+ P_{L_0} e^{-\left(\frac{eA}{V} K_1 + K_2\right) t}$$

(32)

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

$$P_L \text{ (equilibrium)} = \frac{e^A}{V} \frac{K_1}{K_1 + K_2} P_i$$

(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 $t$,

$$\frac{dp_L}{dt} = \frac{eA}{V} K_1 (P_i - P_L)$$

(34)
or

\[ p_{L_t} = p_i - (p_i - p_{L_0}) e^{-\frac{\varepsilon A K_1}{V} t} \tag{35} \]

Knowing the physical constants for the system, namely \( \varepsilon \), \( A \), \( V \) 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:
\[ V \frac{dP_L}{dt} = Q_o P_o - Q_o P_L + \frac{eA}{V} K_1 (P_i - P_L) V - K_2 P_L V \]  

(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

\[ P_i = f (P_S) \]  

(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

\[ V \frac{dP_L}{dt} = 0 \]  

(38)

in Equation 36 yields:
\[ P_L \text{ (equilibrium)} = \frac{P_o + \frac{\varepsilon A}{V} K_1 P_i \bar{T}}{1 + \frac{\varepsilon A}{V} K_1 \bar{T} + K_2 \bar{T}} \quad (39) \]

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 \( (\varepsilon A) \) 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 \( P_L = P_{L_0} \) at \( t = 0 \) (when either \( P_o \) or \( P_i \) is reduced) to \( P_L = P_L \) at \( t = t \) yields:

\[
P_L = \left[ \frac{P_o + \frac{\varepsilon A}{V} K_1 P_i \bar{T}}{1 + \frac{\varepsilon A}{V} K_1 \bar{T} + K_2 \bar{T}} \left[ 1 - e^{-\left(\frac{1}{T} + \frac{\varepsilon A}{V} K_1 + K_2 \right) t} \right] - P_{L_0} e^{\left(\frac{1}{T} + \frac{\varepsilon A}{V} K_1 + K_2 \right) t} \right]
\]

\[ + P_{L_0} e^{\left(\frac{1}{T} + \frac{\varepsilon A}{V} K_1 + K_2 \right) t} \quad (40) \]
The value $P_0$ 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 hydroxo-metal 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

\[
V \frac{\partial p_z}{\partial t} = Q_0 p_z \left|_{Z} - Q_0 p_z \left|_{Z+\Delta Z} + \frac{\varepsilon A}{V} \frac{K_1}{V} (p_i - p_z) A_Z \Delta Z 
\right. \right.
\]

- \( K_2 p_z A_Z \Delta Z \) \hspace{1cm} (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\(^{-3}\))
- \( \Delta Z \) = 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

\[
\frac{d p_z}{d Z} = \frac{1}{v} \left[ \frac{\varepsilon A}{V} \frac{K_1}{V} (p_i - p_z) - K_2 p_z \right] \hspace{1cm} (42)
\]

where:

- \( v \) = Velocity in the Z direction \((Q_0/A_Z)\)

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 \( Z = \bar{Z} \) to yield a steady state expression for the plug flow lake system. Thus,

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

(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 \( (\varepsilon) \) 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,

\[ Q = KBH^{3/2} \]  \quad (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 (\( \varepsilon \)) 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/1 PO₄⁻³-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 H₂SO₄ 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 (HNO₃) 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

Physical Features. 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 x 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 \( (T) \) 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 \( (50 \times 10^6 \text{ l/day}) \) with peak (24 hour average) flow being 50 million gallons per day \( (190 \times 10^6 \text{ l/day}) \). 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 \( (1.25 \text{ cm}) \) 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 \( (5.8 \text{ cm}) \). 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 \( (378 \times 10^6 \text{ l/day}) \) 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.

\[ AVERAGE \, \varepsilon = 0.84 \pm 0.025 \]

\[ AVERAGE \, DENSITY = 1.17 \pm 0.08 \]
due to compaction and realignment of platy clay minerals. The value for porosity ($\epsilon = 0.84$) 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 super-
saturation 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 after-
noon 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 photo-
synthetic 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 x 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 $1 \times 10^9$ 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.
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 75\(\mu g/l\) and near-bottom samples increased from 80\(\mu g/l\) at the inlet to 105\(\mu g/l\) in a short distance and then decreased to about 84\(\mu g/l\).

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 30\(\mu g/l\) at the inlet to 55\(\mu g/l\) in approximately 100 meters. The increase (25\(\mu g/l\)) accounts for almost all of the increase in total phosphate (83 to 106\(\mu g/l\) or 23\(\mu g/l\)) which supports the premise that orthophosphate is the main form of sediment released phosphorus. Higher values of orthophosphate (about 55\(\mu g/l\)) 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 usually 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.

**pH and Redox Potential.** 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):

\[
Eh = 1.23 + \frac{0.59}{4} \log \tilde{P}_{O_2} - 0.059 \text{pH}
\]  

(45)

Numerically, the change in O$_2$ concentration has only a slight effect on the Eh compared to the change in pH.

If the above equation is used to define the Eh in terms of the pH and \(\tilde{P}_{O_2}\) (pH 7.0, \(\tilde{P}_{O_2} .21\)), 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 450 μg/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 $3.78 \times 10^{-4}$ 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 0.15 mg of exchangeable phosphorus ($P_s$) and be associated with $3.78 \times 10^{-4}$ 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 $1.5 \times 10^5$ 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:

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

(46)

This relationship of total sediment phosphorus ($P_T$), exchangeable sediment phosphorus ($P_s = 0.25 P_T$), 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 ($0.25 P_t$) 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 90\mu g/l of total phosphate as P.

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

(4) An increase up to about 100\mu g/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:

$$P_L = \frac{\varepsilon A}{V} K_1 P_i \left[ 1 - e^{-\frac{\varepsilon A}{V} (K_1 + K_2) t} \right] - \frac{\varepsilon A}{V} K_1 P_{L_0} e^{-\frac{\varepsilon A}{V} (K_1 + K_2) t}$$

(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 ($P_1$) 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 lower 1.5 ft. of the caisson. Additional concrete anchors were also installed to prevent cai son from overturning. The final caisson measured 5 x 6 ft and 6" in cross section. Having a height of only 350 pounds, the unit was easily lowered and floated on pontoons to the site during early morning and late afternoon. This insured no 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 $21.7 \times 10^{-14}$ moles/day-cm$^2$. This would increase the caisson concentration by only $6.8 \times 10^{-6}$ 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 $P_{L0}$ 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 caisson. 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 $\text{PO}_4^{3-}$ 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:
SYNTHETIC PO₄ WATER
\( Q = 555 \text{ ML/MIN} \)
\( V = 18 \text{ LITERS} \)
\( \text{TIME} = 20 \text{ MIN/CYCLE} \)
ANION BED = 1 FOOT
APPLICATION RATE = 34.6 ML/MIN/CM²
INITIAL \( P' \) = 52 µG/L
FINAL \( P_T \) = 6 µG/L

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/ft² 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
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<th>Tube Number</th>
<th>Alum Added grams</th>
<th>Kaolinite Added grams</th>
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<td>1</td>
<td>4</td>
<td>0</td>
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<td>2</td>
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anionic exchange sites of aluminum, $\text{Al(OH)}_x \text{(PO}_4\text{)}_{1-x/3}$, and kaolinite, $\text{Si}_2\text{O}_5\text{Al}_2\text{(OH)}_4 \cdot \text{PO}_4$.

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 $\mu$g/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, 1977.
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, orthophosphate 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:

\[
P_L = \frac{eA}{V} \frac{K_1P_i}{K_1+K_2} \left[1-e^{-\left(\frac{eA}{V} K_1 + K_2\right)t}\right] + P_{L0} e^{-\left(\frac{eA}{V} K_1+K_2\right)t}
\]

(32)

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

Thus, from Equation 31:

\[
\frac{dP_L}{dt} = \frac{eA}{V} K_1 (P_i - P_L)V
\]

(47)

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

The additional data required for substitution into Equation 47 is:

\[\epsilon = \text{porosity} = .84\]
\[A = \text{sediment area} = 3.5m^2\]
\[V = \text{tank volume} = 8.155m^3\]
\[P_i = \text{measured interstitial P conc.} = 410 \mu g/l \text{ total P}\]
\[P_L = \text{average tank water P. conc.}(0<t<5 \text{ days}) = 53 \mu g/l. \text{ total P.}\]
Solving for $K_1$ yields 0.078 m/day. The steady-state phosphate concentration, $P_{\text{Leq}}$, attained in the batch reactor was shown by letting $t \to \infty$ in Equation 32 such that,

$$
P_{\text{Leq}} = \frac{\frac{\varepsilon A}{V} K_1 P_i}{\frac{\varepsilon A}{V} K_1 + K_2}
$$

An approximate value of $K_2$ was determined as .15/day by substituting known values of $\varepsilon$, $A$, $V$ and estimates of $P_i$, $K_1$ and $P_{\text{Leq}}$ 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 $P_1$ 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:

\[ K_1 = .091 \text{ m/day} \]
\[ K_2 = .176/\text{day} \]
\[ P_i = 430 \text{ u g/l} \]

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 u g/l) and predicted values (430 u g/l) of \( P_i \) were quite close.

Suppression Study Results

Field Observations. 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.

- $K_1 = 0.091 \text{ M/DAY}$
- $K_2 = 0.176 \text{/DAY}$
- $P_I = 430 \text{ \mu G/L}$
- CORR. COEF. = 0.963

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

- $\bullet$ = LAKE
- $\circ$ = #6 - CONTROL
- $\blacksquare$ = #1 - 4GM ALUM
- $\blacktriangle$ = #2 - 1GM ALUM
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.

- #5 = 4GM ALUM, 16GM KAOLINITE
- #6 = CONTROL
- ▼ = LAKE
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.
A 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 coefficients for the relationship of iron and phosphate were:

- Tube No. 1 \( r = 0.7841 \)
- Tube No. 2 \( r = -0.0342 \)
- Tube No. 3 \( r = 0.339 \)
- Tube No. 4 \( r = 0.3600 \)
- Tube No. 5 \( r = 0.8484 \)
- Tube No. 6 \( r = 0.1441 \)

Although phosphate released from the sediment would normally be associated with iron complexes, statistical evidence from this study was insufficient to prove this relationship. As already mentioned, this could be due to the formation of \( \text{Fe(OH)}_2 \) 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.
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 $K_2 P_L$. 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:

$$P_{Leq}^* = \frac{\epsilon A K_2 P_{i}^*}{\epsilon A V K_1 + K_2}$$

(48)

The necessary data input to the equation consisted of $\epsilon$ (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>
<thead>
<tr>
<th>Tube</th>
<th>$P_i^*$ μg/l</th>
<th>Dosage in Grams</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Alum</td>
<td>Kaolinite</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>318</td>
<td>4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>305</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>298</td>
<td>1</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>225</td>
<td>.25</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>172</td>
<td>4</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>410</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
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: $K_1 = .087 \text{ m/day}$ versus $.091 \text{ m/day}$ and $K_2 = .183/\text{day}$ versus $.176/\text{day}$, 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 $T$. 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, $P_0$. 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 waste-
water can be pumped to the Connecticut River.

Considering first the background phosphate concentration
in the Mill River due to natural runoff, samples were col-
lected 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 concentra-
tions 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 approx-
imate. 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 \mu g/l total phosphate for \( P_0 \). 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

<table>
<thead>
<tr>
<th>Wastewater Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Total Phosphate Concentration = 5 mg/l</td>
<td></td>
</tr>
<tr>
<td>Estimated Total Annual Volume of Bypassing (3.3%) = 60 MG</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mill River Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Total Phosphate Concentration = 0.050 mg/l</td>
<td></td>
</tr>
<tr>
<td>Total Annual Volume (e 20 MGD) = 7157 MG*</td>
<td></td>
</tr>
</tbody>
</table>

Annual Average Total Phosphate Entering Lake Warner

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

\[
\text{Total-P} = 90 \mu g/l = P_0
\]

*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

<table>
<thead>
<tr>
<th>Depth in centimeters</th>
<th>Reference</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>.5</td>
<td>Fillos</td>
<td>1975</td>
</tr>
<tr>
<td>.5</td>
<td>Mortimer</td>
<td>1971</td>
</tr>
<tr>
<td>1</td>
<td>Frink</td>
<td>1967</td>
</tr>
<tr>
<td>1-5</td>
<td>Allen</td>
<td>1970</td>
</tr>
<tr>
<td>2-5</td>
<td>MacKenthun</td>
<td>1968</td>
</tr>
<tr>
<td>5-7</td>
<td>Snow</td>
<td>1973</td>
</tr>
<tr>
<td>5-10</td>
<td>McKee</td>
<td>1970</td>
</tr>
<tr>
<td>10</td>
<td>Painter</td>
<td>1968</td>
</tr>
<tr>
<td>10</td>
<td>Kamp-Nielsen</td>
<td>1974</td>
</tr>
<tr>
<td>10-20</td>
<td>Dobbins</td>
<td>1970</td>
</tr>
<tr>
<td>15</td>
<td>Forcella</td>
<td>1970</td>
</tr>
<tr>
<td>20</td>
<td>Bray</td>
<td>1973</td>
</tr>
<tr>
<td>30</td>
<td>Wentz</td>
<td>1969</td>
</tr>
</tbody>
</table>
Table 7. Percentages of Exchangeable Phosphorus Within the Sediment

<table>
<thead>
<tr>
<th>Amount Exchangeable of Total Phosphorus</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-18 percent</td>
<td>Lake Warner</td>
<td>Ku</td>
</tr>
<tr>
<td></td>
<td>1.5-2 mgP/gm</td>
<td>(1975)</td>
</tr>
<tr>
<td>12-33 percent</td>
<td>Depending on concentration</td>
<td>Wildung</td>
</tr>
<tr>
<td></td>
<td>gradient</td>
<td>(1973)</td>
</tr>
<tr>
<td>16-24 percent</td>
<td>P desorbed from original amount</td>
<td>Lotse</td>
</tr>
<tr>
<td></td>
<td>adsorbed</td>
<td>(1973)</td>
</tr>
<tr>
<td>22-44 percent</td>
<td>Noncalcareous lakes</td>
<td>Li</td>
</tr>
<tr>
<td></td>
<td>total-P &gt; 1.5mg/gm</td>
<td>(1973)</td>
</tr>
<tr>
<td>up to 50 percent</td>
<td>Lake Mendota</td>
<td>Wentz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1969)</td>
</tr>
</tbody>
</table>
(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>
<thead>
<tr>
<th>References</th>
<th>Sediment or Location</th>
<th>Release Rate</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fillos (1972)</td>
<td>Simulated Sludge</td>
<td>154</td>
<td>anaerobic</td>
</tr>
<tr>
<td>Capaccio (1971)</td>
<td>Muddy River</td>
<td>91</td>
<td>anaerobic</td>
</tr>
<tr>
<td>Vollenweider (1968)</td>
<td>Lake Baldeggersee</td>
<td>9-10</td>
<td>anaerobic</td>
</tr>
<tr>
<td>Pomeroy (1965)</td>
<td>Doboy Sound</td>
<td>.03</td>
<td>aerobic, marine</td>
</tr>
<tr>
<td>Fillos (1973, 1975)</td>
<td>Muddy River</td>
<td>96</td>
<td>anaerobic, (-200mv)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.6</td>
<td>aerobic, (+200mv)</td>
</tr>
<tr>
<td></td>
<td>Lake Warner</td>
<td>26</td>
<td>anaerobic, (-200mv)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.2</td>
<td>aerobic, (+200mv)</td>
</tr>
<tr>
<td>Porcella (1971)</td>
<td>Shallow eutrophic lakes</td>
<td>50</td>
<td>anaerobic</td>
</tr>
<tr>
<td>Stumm (1970b)</td>
<td>Estimates all lakes</td>
<td>.27</td>
<td>-</td>
</tr>
<tr>
<td>Krull (1973)</td>
<td>Lake Sammamish</td>
<td>6</td>
<td>estimate</td>
</tr>
<tr>
<td>References</td>
<td>Sediment or Location</td>
<td>P Release Rate</td>
<td>Comment</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------</td>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td>Kamp-Nielsen (1974) Lake Furensco (eutrophic)</td>
<td>17±5</td>
<td>anaerobic</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2±1.8</td>
<td>aerobic</td>
</tr>
<tr>
<td>Lake Esrom (eutrophic)</td>
<td>12±4</td>
<td>anaerobic</td>
<td></td>
</tr>
<tr>
<td>St. Gribso Lake (oligotrophic)</td>
<td>1.2±.2</td>
<td>anaerobic</td>
<td></td>
</tr>
<tr>
<td>Allen (1970) Lab study on sediment</td>
<td>.7</td>
<td>anaerobic</td>
<td></td>
</tr>
<tr>
<td>McKee (1970) Potting soil</td>
<td>5</td>
<td>aerobic</td>
<td></td>
</tr>
<tr>
<td>Welch (1973) Lake Sammamish</td>
<td>5</td>
<td>estimate</td>
<td></td>
</tr>
<tr>
<td>Feng (unpublished) Pond Sediment</td>
<td>17</td>
<td>3' above sediment</td>
<td></td>
</tr>
<tr>
<td>Bray (1973) Chesapeake Bay</td>
<td>.4</td>
<td>estimate</td>
<td></td>
</tr>
<tr>
<td>Snow (this study) Lake Warner</td>
<td>24-27</td>
<td>in situ anaerobic sediment</td>
<td></td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>0.091 m/day</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.176/day</td>
</tr>
<tr>
<td>$P_{i_1}$</td>
<td>400 to 450 µg/l Total-P</td>
</tr>
<tr>
<td>$P_{i_1}^*$</td>
<td>175 to 300 µg/l Total-P</td>
</tr>
<tr>
<td>$P_L$</td>
<td>80 to 90 µg/l Total-P</td>
</tr>
<tr>
<td>$P_O$</td>
<td>40 µg/l Total-P (Summer)</td>
</tr>
<tr>
<td>$P_O'$</td>
<td>100 µg/l Total-P (During bypassing)</td>
</tr>
<tr>
<td>$P_T$</td>
<td>1 to 1.6 mgP/gm dry sediment</td>
</tr>
<tr>
<td>$Q_O$</td>
<td>20 ft³/sec. (Average)</td>
</tr>
<tr>
<td>$\bar{T}$</td>
<td>10 days (Average)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.84 (Porosity)</td>
</tr>
<tr>
<td>$A$</td>
<td>$2.572 \times 10^5$ m² (Area)</td>
</tr>
<tr>
<td>$V$</td>
<td>$4.35 \times 10^5$ m³ (Volume)</td>
</tr>
</tbody>
</table>

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 ($P_{Lz}$) for various distances ($z$) from the inlet using spatial variations of $P_{Lz}$ 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 coefficient of 0.3 between actual and predicted values of $P_L$. A better fit of the model to the data (correlation coefficient 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:

\[
P_{\text{Leq}} = \frac{P_0/T + (\epsilon A/V) K_1 P_i}{1/T + (\epsilon A/V) K_1 + K_2} \quad (39)
\]

For a given input phosphate concentration, \(P_0\), the relationship between the overlying lake phosphate, \(P_{\text{Leq}}\), and the interstitial phosphate, \(P_i\), can be obtained by rearranging Equation 39 such that:

\[
P_{\text{Leq}} = M_1 + N_1 P_i \quad (49)
\]

where:

\[
M_1 = \frac{P_0}{1 + (\epsilon A/V) K_1 T + K_2 T}
\]

\[
N_1 = \frac{(\epsilon A/V) TK_1}{1 + (\epsilon A/V) K_1 T + K_2 T}
\]

Figure 48 shows the predicted relationship between \(P_{\text{Leq}}\) 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. $\bar{T}=10$ days,
$P_o=40$ $\mu g/l$, $A$=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 (P₀) and lake phosphate (Pₗ) concentrations are equal. This condition can be reached by: (1) introducing a steady-state input (P₀) 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 (Pᵢ), initially created by high input of phosphate, to lower sediment release. Proceeding from either direction, one intrinsic value of Pᵢ will be reached whereby an equilibrium will be established between sedimentation and release and the influent phosphate (P₀) will equal the lake phosphate (Pₗ) concentration. This point for Lake Warner is shown in Figure 48 as Point B where Pᵢ 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:

\[ P_{\text{leq}} = M_2 + N_2P_0 \]  

(50)

where:

\[ M_2 = \frac{(\epsilon A/V)\overline{T}K_1P_i}{1 + (\epsilon A/V)K_1\overline{T} + K_2\overline{T}} \]

\[ N_2 = \frac{1}{1 + (\epsilon A/V)K_1\overline{T} + K_2\overline{T}} \]

Here, each of the family of linear steady-state relationships
applies to a given interstitial phosphate concentration with
varying inputs \( P_0 \). The many possible steady-state con-
ditions for Lake Warner as obtained by applying Equation 50
are graphically depicted in Figure 49. The ultimate equil-
ibrium 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
Graphical representation of steady state model using Equation 48 to relate $P_L$ to $P_0$ and $P_i$ for $T=10$ days. Points A, B, and C described 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 ($P_0$) 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_0) 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:

\[
P_L = \frac{P_0 + (\varepsilon A/V)K_1P_iT}{1 + (\varepsilon A/V)K_1 + K_2} \left[ 1 - e^{-\frac{(1 + [\varepsilon A/V] K_1 + K_2)t}{T}} \right] + P_{LO} e^{-\frac{(1 + [\varepsilon A/V] K_1 + K_2)t}{T}}
\]

(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, \( \dot{P}_s \) = Input Rate of P due to Sedimentation - Output Rate of P due to Release within the Sediment

That is,

\[
\frac{dP_s}{dt} = K_2 P_L V_L - \frac{(\varepsilon \alpha)}{V_L} K_1 (P_i - P_L) V_L
\]  

(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, \( D_r \), 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:

\[
V_s = D_r \alpha \]  

(51)

where \( \alpha \) 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:

\[
P_{s_{t+\Delta t}} = P_{s_t} + \left[ \frac{K_2 P_L V_L}{D_r \alpha} - \frac{\varepsilon K_1 (P_i - P_L)}{D_r} \right] \Delta t
\]  

(52)

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

\[
P_i = \frac{2.19 \times 10^{-3} P_s + 41.87}{\varepsilon}
\]  

(53)
where:
\[ P_i = \text{concentration of phosphate within the interstitial water of the defined volume} \]

The new value of \( P_i \) after a time change \( \Delta t \) can be calculated from:

\[
P_i^{t+\Delta t} = \frac{2.19 \times 10^{-3} (P_s^t) + 41.87}{c^{t+\Delta t}}
\]  

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 \( \Delta t \). 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, \( \Delta t \), 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 \( \mu g/l \) is in equilibrium with a \( P_s \) value of \( 1.439 \times 10^4 \) mg P/M\(^3\). Using the finite difference scheme with input phosphate, \( P_o \), set at 90 \( \mu g/l \) shows that for \( \Delta t \) 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 \( \mu g/l \). Lake phosphate concentration (\( P_L \)) was reduced from 90.97 \( \mu g/l \) to 90.94 \( \mu g/l \) (only 0.03 \( \mu g/l \) change). Thus, a time increment of 10 days was considered a reasonable estimate of quasi-
steady 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 $P_L$ prior to changing input phosphate values, $P_0$. 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 $P_0$ of 50 and 100 $\mu$g/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, $P_0$, 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, $P_0$, 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 $P_0$ is almost entirely controlled by the residence time, $\bar{T}$, in the lake, i.e. the dilution factor. For example, in a larger lake with a $\bar{T}$ 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 $\bar{T}$ 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
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 $t=0$, $P_L=40 \mu g/l$, $P_i=185 \mu g/l$. At $t=5000$ days, $P_L=88.5 \mu g/l$, $P_i=407 \mu g/l$. 

$T = 10$ DAYS

$P_0 = 90 \mu g/l \ (T>1000)$
indicates that a similar increase in input, $P_0$, 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 $P_0 = 50$ µg/l, $P_i = 100$ µg/l, and $P_{L_0} = 20$ 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 \( t=0 \), \( P_L=90 \) \( \mu g/1 \), \( P_1=425 \) \( \mu g/1 \). At \( t>0 \), \( P_0=80, 50, 40 \), and \( 20 \) \( \mu g/1 \).
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 $\mu$g/l with $P_i$ initially equal to 425 $\mu$g/l in 7.7 years with input phosphate, $P_o$, being 50 $\mu$g/l. If alum and kaolinite were added to decrease $P_i$ from 425 $\mu$g/l to 300 $\mu$g/l ($P_i^*$), the same value of $P_L$ (55 $\mu$g/l) would be attained in only 3 years. Interestingly enough, using chemical suppressants to lower $P_i^*$ to 200 $\mu$g/l or 100 $\mu$g/l brings about immediate (about 40 days) reduction in lake phosphate to values less than the final ultimate equilibrium concentration of 50 $\mu$g/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 $\mu$g/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 $\mu$g/l in Lake Warner. With an influent of 50 $\mu$g/l (without wastewater bypassing), the initial predicted total phosphate in the lake water would decrease from 90 $\mu$g/l to 46 $\mu$g/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. $T=10$ days, $P_0=50$ 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 presumably 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, \( P_Q \), 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 $t=0$, $P_i=185 \mu g/l$. At $t>0>5000$ days, $P_o=90 \mu g/l$, final $P_i=407 \mu g/l$. At $t>5000$ days, $P_o=50 \mu g/l$. 
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 ($\bar{T}$) of 100 days but subject to the identical exchange processes and loading factor change as Lake Warner with a residence time ($\bar{T}$) 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 $\mu g/l$ while this same loading, $P_0$, increased $P_L$ in Lake Warner from 40 to 87 $\mu g/l$ during the same time interval.

As shown in Figure 56, addition of suppressants to a hypothetical lake having a residence time ($\bar{T}$) 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 ($\bar{T}$).

Without addition of suppressants to this larger lake, 19 years would be required for $P_L$ to decrease from 90 to 72 $\mu g/l$. Addition of suppressants could reduce $P_1$ from 425 $\mu g/l$ to 200 $\mu g/l$ ($P_1^*$) and would almost immediately reduce $P_L$ to about 44 $\mu g/l$; moreover, after 19 years, $P_L$ would only have increased to 47 $\mu g/l$. This represents an increase of only 3 $\mu g/l$ over a period of 19 years as the
Figure 55. Unsteady state model predictions for larger lake ($T=100$ days). At $0 < t < 1000$, $P_o = 185 \mu g/l$, $P_i = 40 \mu g/l$. At $t > 1000$, $P_o \mu g/l$. At $t=19$ years after change in $P_o$, $P_L = 63.5 \mu g/l$, $P_i < 290 \mu g/l$. 

$P_o = 90 \mu g/l$
Figure 56. Unsteady state model predictions for larger lake (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, \( P_0 \), 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, \( P_0 \), 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 perman-
ently 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 equil-
ibrium 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, $D_r$, from which long-term re-
lease 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 ex-
changeable 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/m² of alum and 100 gm/m² 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 ($Q_0$) into the lake;

2) Determine the average yearly loading of total phosphate currently being introduced into the lake to determine the influent concentration ($P_0$);

3) Determine the present values of lake water concentration ($P_{LO}$), 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 ($D_r$) into the sediment is 10 cm., porosity ($\varepsilon$) is .84, and a similar relationship of $P_s$ and $P_i$ (Equation 46) is applicable;

5) Determine a future value for $P_0$ 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 ($P_{LT}$) 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


Appendix A

Orthophosphate and Total Phosphate Determination Methods
Isobutanol Extraction Method for Phosphorus Determination

A. Orthophosphate Determination

All glassware are rinsed in 2N sulfuric 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 deionized 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.

Procedure:

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 \( \text{H}_2\text{SO}_4 \) 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 phenolphthalein 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 1975).