A Mathematical Model of Phosphorus in Completely Mixed Lakes with Special Application to Lake Warner, Massachusetts

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Technical Report

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by

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ABSTRACT

The dynamic response of Lake Warner (Hadley, Massachusetts) to pollution abatement was studied by field measurements and mathematical modeling. Stream flow and phosphorus concentration measurements were used to describe phosphorus flow through the lake system. The lake system released phosphorus, presumably from the sediments, during July 1981, but retained phosphorus during the fall of 1981. Seepage through lake sediments was measured using seepage meters and was determined to be insignificant in the water and phosphorus budget of Lake Warner.

Differential equations for the lake water, sediment interstitial water and sediment solid phase phosphorus concentration developed by others in previous studies were solved using a trial function method. Approximate solutions were developed using steady state and pseudo-order assumptions. The analytic solution was programmed on a hand-held calculator. Sensitivity analysis was carried out for model parameters. The analytic expression for the solution to the differential equations describing lake recovery was an important tool for lake planning, management and research purposes.
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$P_s$ Sediment Solid Phase Phosphorus Concentration ($M/L^3$), micrograms per liter

$P_{so}$ Sediment Solid Phase Phosphorus Concentration, Initial Condition ($M/L^3$), micrograms per liter

$P_{so\infty}$ Sediment Solid Phase Phosphorus Concentration, Steady State ($M/L^3$), micrograms per liter

$Q$ Average Annual Flow Rate ($L^3/T$), cubic meters per day

$R_{rel}$ Rate of Release from Lake Bottom ($M/L^3-T$), micrograms per liter per day

$R_{sed}$ Rate of Sedimentation to Lake Bottom ($M/L^3-T$), micrograms per liter per day

$r$ Root of cubic equation ($1/T$), per day

$T$ Hydraulic residence time ($T$), days

$u$ Macro-Seepage Velocity ($L/T$), micrometers per second

$V$ Volume ($L^3$), liters

$V_L$ Lake Water Volume ($L^3$), cubic meters

$V_s$ Volume of Sediment ($L^3$) cubic meters

$X_1, \ldots, X_7$ Lake Model Parameters ($1/T$), per day

$X_8$ Lake Model Parameter ($M/L^3-T$), micrograms per liter per day

$Z$ Lake Mean Depth ($L$), meters

$\varepsilon$ Sediment Porosity

$\lambda, \phi$ and $\gamma$ Lake Model Parameters ($1/T$), per day
CHAPTER I
INTRODUCTION

The eutrophication of many freshwater lakes has been accelerated by cultural activities such as wastewater overflows and nonpoint pollution. Lake restoration, funded under Section 314 of the Federal Water Pollution Control Act Amendments of 1972, includes the diversion of wastewater overflows. After such diversions or other water pollution control measures, lake sediments can act as a nutrient source for biological activity and, therefore, control the rate of recovery of a eutrophic lake.

Lake nutrient budget models can be used by planners and engineers to predict a lake's response to pollution control efforts. When constructing a nutrient budget for a lake one must account for all nutrient sources, such as lake sediments and ground water discharge/recharge, which may effect the recovery of a eutrophic lake.

The recovery of Lake Warner (Massachusetts) was the subject of past studies by Snow and DiGiano (1976) and Bingham and Feng (1980). Wastewater overflows were diverted from Lake Warner in 1975, thus making it a convenient site for testing the lake recovery model developed by Snow and DiGiano (1976). This model predicted that it would take about 14 years for Lake Warner to recover from its eutrophic state. Subsequent field work by Bingham and Feng (1980) showed that Lake Warner had recovered in
just one year. Hence, they modified the Snow and DiGiano model to include a reaction rate ($K_3$) which describes the conversion of sediment solid phase phosphorus to sediment interstitial phosphorus. The value of this reaction rate may control the recovery of a eutrophic lake when sediments contain a significant reservoir of phosphorus.

**Objectives**

The two major goals of this research were to examine the significance of ground water-lake interactions and to seek an analytical solution to the ordinary differential equations describing phosphorus in the lake recovery model. The hypothesis that ground water may act as a transport mechanism for recycling lake sediment nutrients into the lake water was tested by measuring the ground water discharge/recharge through Lake Warner sediments using seepage meters. It was also of interest to ascertain lake sediment phosphorus release through a mass balance on lake water phosphorus.

An analytical solution to the lake recovery model was desired to eliminate the need for a high speed computer used to implement the numerical solutions of past studies. Simplifications of the governing differential equations using approximation techniques were studied in an effort to produce a compact model
for use in lake planning, management and research purposes. A simplified model was deemed acceptable if predictions closely matched the results of the full analytical solution.

Sensitivity analysis was carried out on model parameters to determine the effect variations in the values used have on model predictions. This information can be used to show which parameters must be estimated very accurately and which parameters can be approximated without significantly affecting model predictions.

**Scope**

Many lakes in Massachusetts are similar to Lake Warner in that they are relatively shallow, have short hydraulic residence times and can be treated as being completely mixed for time periods greater than a few hydraulic residence times. Many of these lakes were formed by man diking a stream. This study is concerned with the phosphorus budget in this category of lakes. Lake Warner will be used as an illustrative case study. Quabbin Reservoir illustrates a man-made reservoir whose phosphorus budget is unlikely to be closely described by the methods illustrated in this study.

The role of ground water in affecting the phosphorus budget of a lake has not been clearly illustrated in past studies of Lake Warner. This study reviews literature on observations of
ground water-lake interactions and uses field measurements for assessing the importance of ground water to Lake Warner's water and phosphorus budgets. Field measurements on the Mill River phosphorus loading and on the lake water are used to evaluate the release of phosphorus from Lake Warner sediments. An analytical solution to the Bingham and Feng (1980) mathematical model of the recovery of a eutrophic lake is presented. Equations for the lake water phosphorus, sediment interstitial phosphorus and sediment solid phase phosphorus are presented. These equations provide tools which engineers and scientists can use to determine the values of reaction rates which govern phosphorus cycling in shallow lake systems.

Sensitivity analysis is used to show the effects on model predictions due to marginal variations in input parameters.
CHAPTER II

LITERATURE REVIEW

This section reviews literature on phosphorus chemistry in lake environments. Lake phosphorus budget modeling and mathematical methods for solving the resulting equations are examined. The importance of groundwater seepage in the water and nutrient budgets of lakes is discussed.

Phosphorus Chemistry

Carbon, nitrogen and phosphorus are required by plant life in ratios of approximately 100:15:1, respectively. Phosphorus has no gaseous phase and is relatively scarce, therefore making it a limiting nutrient to plant growth in most natural aquatic ecosystems. Phosphorus in nature generally occurs as phosphate in both dissolved and solid phases. Categories of phosphate can be operationally defined by particle size and acid molybdate reactivity.

Because of complex limnological transformations in lake systems (see Figure 1) dissolved phosphate concentrations are not a good index of the biologically available phosphorus during the growing season. Schindler et al. (1971) claim that the amount of phosphorus supplied rather than the amount in solution at any
Figure 1. Transformations of phosphorus in a hypothetical lake system. This steady state model shows representative phosphorus concentrations for model compartments (μg/l) and numbers on arrows show mass flow rates (μg/l-day) (Stumm and Leckie, 1971).
point in time must be known to predict algal growth. Lee et al. (1978) note that for most water bodies the biologically available phosphorus is between the total phosphorus and soluble orthophosphate loading since some of the particulate phosphorus is solubilized (Stumm and Morgan, 1981).

The concentration of dissolved phosphate in natural waters gives little indication of phosphate availability for biological growth. The residence time of dissolved phosphate in natural waters ranges from 0.0021 to 8.3 days (Stumm and Morgan, 1981). Lean (1973) found that fifty percent of $^{32}$PO$_4$ was taken up by algae in less than two minutes. Schindler et al. (1971) found that dissolved phosphate concentrations were undetectable within an hour after artificially raising the phosphate concentration of a lake to 10 g/l. Dissolved inorganic phosphate concentrations in water fluctuate on a daily cycle (Vollenweider, 1968). Low dissolved phosphate concentrations were found at night and higher phosphate concentrations were found during the day. It was suggested that phosphates were required by phytoplankton for energy conversion at night and that some phosphates were released by growing cells during the day.

Lake bottom phosphorus occurs in the sediment solid phase and in the sediment interstitial water. Phosphate adsorption by lake sediments is governed by sediment composition and by physical and chemical conditions in the sediment such as redox potential, pH and temperature. Under anoxic lake bottom
conditions (which might occur during summer stagnation periods) a
lower redox potential in the sediment might develop causing an
increase in the dissolution of Fe bound phosphorus (Ku et al.,
1978). Also the phosphorus binding capacity of sediments is
greater as pH decreases. Figure 2 shows the effect of pH on Fe
bound phosphate. It is evident that the dissolution of sediment
phosphorus would increase in response to high pH levels which
would occur during summer algal blooms.

Many researchers believe that phosphorus release from lake
bottoms is from sediment interstitial phosphorus (Syers et al.,
1973). Hence the dissolution of sediment solid phase phosphorus
to sediment interstitial phosphorus may govern the release of
phosphorus to the lake water.

Phosphorus released as orthophosphate from lake bottoms
undergoes rapid transformation into other more stable compounds
which are components of total phosphorus. Hence, when measuring
release rates (such as Snow and DiGiano's $K_1$) total phosphorus
is used as a measure of the phosphorus released from lake
bottoms.

Lake Phosphorus Budget Modeling

Lakes which are phosphorus limited exhibit good correlations
between total phosphorus concentration and primary productivity
parameters such as chlorophyll a (Williams et al., 1978; Dillon
and Rigler, 1974; Jones and Bachmann, 1976).
Figure 2. Solubility diagram for iron phosphate (after Stumm and Leckie, 1971).
Phosphate sources to aquatic systems result from natural weathering and dissolution of phosphate minerals, soil erosion, soil fertilization, biological transfer, detergents and domestic and industrial wastewaters (Stumm and Morgan, 1981). Table 1 shows phosphorus export coefficients based on the U.S. Organization for Economic Cooperation and Development (OECD) eutrophication study.

Vollenweider (1968) developed an empirical model which relates total phosphorus loading to a lake's trophic state. When areal phosphorus loading \( L(P) \) was plotted against mean depth \( Z \) on a log-log plot (figure 3), lakes appear to be grouped according to their trophic states. Lines dividing trophic states define critical phosphorus loading boundaries. A line dividing the oligotrophic and eutrophic states has the equation

\[
L_c(P) \text{ (mg/m}^2\text{-yr)} = (25 \text{ to } 50)Z^{0.6}
\]

Dillon (1975) noted that Cameron Lake appeared in the eutrophic zone in this type of plot but did not exhibit the normal characteristics of eutrophy due to a short hydraulic residence time. Vollenweider (1976) refined his criterion axis to include the hydraulic residence time \( T \). The resulting log-log plot (figure 4) of areal phosphorus loading vs \( Z/T \) gives a more widely applicable model of lake trophic status. The line dividing oligotrophic from eutrophic lakes has the equation:
Table 1. Representative watershed total phosphorus export coefficients from the U.S. OECD eutrophication study (after Lee et al., 1978).

<table>
<thead>
<tr>
<th>Land use</th>
<th>Total Phosphorus (g/m²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban</td>
<td>0.1</td>
</tr>
<tr>
<td>Rural/Agriculture</td>
<td>0.05</td>
</tr>
<tr>
<td>Forest</td>
<td>0.01</td>
</tr>
<tr>
<td>Other:</td>
<td></td>
</tr>
<tr>
<td>rainfall</td>
<td>0.02</td>
</tr>
<tr>
<td>dry fallout</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Figure 3. Vollenweider (1968) phosphorus loading -
trophic state criterion axes.

Figure 4. Vollenweider (1976) phosphorus loading -
trophic state criterion axes.
\[ L_c(P) = 100 (Z/T)^{0.5} \]

Vollenweider's phosphorus loading-trophic state criterion axes are useful for establishing maximum allowable phosphorus loadings to lakes. More complex mass balance models of phosphorus dynamics in lake systems are needed to predict the time dependent response of lake phosphorus concentrations to pollution control measures.

Lorenzen (1973) summarizes model derivations which describe the fate of a conservative substance (total phosphorus is the nutrient of concern) in a well mixed lake. Model I (schematically shown in Figure 5) allows for inflow, outflow and sedimentation of phosphorus. Continuous Flow Stirred Tank Reactor (CFSTR) assumptions allow the lake to be treated as completely mixed. Model II (Figure 5) considers the release of phosphorus from the lake bottom. It is assumed that the concentration of phosphorus in the lake bottom does not change over time. Model III (Figure 5) allows for depletion of phosphorus in the lake bottom over time.

Snow and DiGiano (1976) developed a lake nutrient budget model which differs from the Lorenzen Model III in that lake bottom phosphorus release is from the sediment interstitial water. A linear relationship was developed empirically which described the equilibrium concentration of sediment solid phase phosphorus and sediment interstitial phosphorus. This
Figure 5. Schematic representation of mass balance models derived by Lorenzen (1973).
assumption, in effect, allowed an instantaneous conversion rate between sediment solid phase and sediment interstitial phosphorus. The Snow and DiGiano model predicted that it would take Lake Warner about 14 years to recover from its eutrophic state in response to a reduction in phosphorus loading. Bingham and Feng (1980) found through field observations that Lake Warner had recovered from its eutrophic state (or reached equilibrium with the reduced phosphorus loading rate) one year after the diversion of wastewater overflows. Hence, they modified the Snow and DiGiano model to include a rate constant which describes the conversion from sediment solid phase to sediment interstitial phosphorus. There is no experimental evidence for choosing a particular value for this rate constant and it is found by model calibration.

Mathematical Methods

The most complex Lorenzen mass balance model (Model III) consists of two simultaneous ordinary differential equations with constant coefficients. The equations can be solved numerically or by analytical methods (Lorenzen, 1976). The solution of three simultaneous linear first order ordinary differential equations with constant coefficients is required by the modified Snow and DiGiano model and will be considered in the following discussion on mathematical methods. Methods of solving the equations
include the Laplace transform method, the eigenvalue method, the power series method, the trial function method, numerical methods and other methods.

Laplace transform methods are convenient to use for solving the type of equations under consideration here. However, inverse transforms do not always exist (Churchill, 1958) and the solution of more than two simultaneous equations becomes formidable by this method. Similarly, eigenvalue methods (Kaplan, 1957) become complex when the solution of a system of three or more equations is attempted.

Manipulations of the equations can be aided by introducing matrix notation and solving the differential equations by numerical or power series methods (Himmelblau et al., 1968). The power series method (Rinaldi et al., 1979) is useful if the series converges quickly.

The system of equations can be solved by first reducing them to a single equation of a higher order (Elsgolts, 1973). The solution of the higher order differential equation may be easier than the direct solution of the system of differential equations.

Bingham and Feng (1980) solved the lake model equations by numerical integration. The solution was carried out in one day time steps on a high speed computer.

A trial function method (Stockton, personal communication; Kaplan, 1957) is practical for solving a maximum of three
equations. A solution is postulated and unknown constants are found by manipulating algebraic equations. See Appendix B for details of the trial function method.

Order of magnitude analysis can be used to simplify systems of differential equations by focusing attention on the dominant terms and neglecting small terms. The method is most useful when the simplified equations are solvable whereas the original equations are intractable. One of the most widely recognized applications of the method was Prandtl's 1904 development of boundary layer theory to describe fluid motion near a solid surface (Lamb, 1932).

Approximation methods have been extensively applied in the study of chemical reaction kinetics. The pseudo-order approximation method (Freifelder, 1982), combines experimental planning with mathematical simplification to reduce the order of the differential equation describing a reaction. As rates of formation or consumption of reactants are proportional to the product of the concentration of the reactants raised to a power, the chemist is motivated to combine experimental and mathematical wizardry to transform intractable differential equations into those more amenable to solution. The method of pseudo-order approximation accomplishes the reduction of the reaction rate order by treating a reactant which is in large excess as constant.
Another approximation method resembling order of magnitude analysis is used to simplify the mathematical description of certain consecutive chemical reactions. Consecutive chemical reactions occur when the product of one reaction is the reactant in a subsequent reaction. The method referred to as the stationary state approximation (Harris, 1966), is applied when consecutive reactions occur at different rates, sometimes allowing a slowly changing time derivative term, describing the rate of formation or consumption of a chemical species, to be set equal to zero. As a result, an unsteady state equation is approximated by an equilibrium or steady state equation. Appropriately, the quasi-steady state method is known in the Russian literature as "the method of quasistationary concentrations" (Emanuel' and Knorre, 1973).

Ground Water-Lake Interactions

Ground water-lake interactions are poorly understood and are often overlooked in lake water and nutrient budgets (Winter, 1978). Some recent studies have used seepage meters to measure, in situ, the direction and magnitude of seepage flux through lake sediments. The chemical composition of samples taken from seepage meters may be effected by the environment created by these devices.
Karauskas and Anderson (1978) suggest that flow through conditions occur at Nepco Lake (Wisconsin) based on water table contours around the lake. High manganese concentrations down gradient of Nepco Lake were attributed to the dissolution of manganese in the lake sediments. A similar analysis was done by Loeb and Goldman (1979) to estimate the ground water contribution of Ward Valley to Lake Tahoe. Ground water flow during 1975 was found to be 16% of the Ward Creek inflow to Lake Tahoe. Ground water contributions of nitrates and soluble phosphorus were found to be 78% and 90%, respectively, of the Ward Creek loading.

Dilutional pumping was carried out in 1970 to improve the water quality of Snake Lake (Born et al., 1973). With ground water phosphorus concentrations of about 0.050 mg/l it was expected that the lake water phosphorus concentration (0.4 mg/l) would be diluted. Pumping increased ground water velocities from about 3.5 to 28 μm/sec. The initial increases of chloride, nitrogen and phosphorus in the lake water were thought to be caused by flushing from lake sediments due to the high sediment interstitial velocities induced by pumping.

Cartwright et al. (1979) suggest that ground water movement into Lake Michigan explains the distribution of trace elements in bottom sediments. Trace elements decrease in concentration downward from the lake water—sediment interface. Results from piezometer measurements showed that the ground water flux was
from the aquifer into the lake. Hence, the ground water which has twice the mineral content and hardness as the lake water moves through the lake sediments and trace elements are precipitated out near the sediment--lake water interface.

**Seepage Meters**

The direct measurement of aquifer discharge and recharge in lake environments can be made with seepage meters described by Lee (1977) and by Lock and John (1978). Lee (1977) describes a simple device consisting of a 55 gallon drum with one open end and an outlet on the other end for sample collection. Lock and John (1978) describe a seepage meter provided with a container to buffer the sampling vessel from outside water movement. Also, a gas/pressure release valve was mounted on the top of the meter to allow the measurement of gas which may be released from the sediments during the sampling period.

Theoretical models of ground water-lake interactions can be verified using seepage meters. Also chemical analysis of seepage water may provide information on the effect of sediment chemistry on the chemistry of ground water and vice versa.

Patterns of ground water flow through lake sediments were measured using seepage meters (Fellows and Brezonick, 1980; Connor and Belanger, 1981; Lock and John, 1978; Lee et al., 1980;
Brock et al., 1982). Maximum seepage velocities were found to occur near shore and to decrease exponentially with distance from the shore line.

Lee (1976) examined the reliability of seepage meters as ground water collection devices at Lake Sallie (Minnesota). Nutrient concentrations in seepage water became similar to nutrient concentrations in adjacent wells after more than 1,200 liters of water had passed through the seepage meters. Keel (1979) found that ground water nutrient contributions to lakes in the Upper Pelican River Watershed of Minnesota were significant. The average total phosphorus and total nitrogen concentration of seepage water ranged from 1.04-1.63 and 1.59-4.0 mg/l, respectively.

A theoretical model based on ground water contours around Perch Lake (Ontario) was confirmed using seepage meters and a tritium tracer (Frape and Patterson, 1981). The authors suggest that lake water mixing with sediments would be minimal in aquifer discharge areas which generally occur near shore and deeper mixing would be found in deep lake sediments. Accordingly, it was noted that a thick metal zone occurred in deep lake sediments, due to mixing with oxygen rich lake water, while a thin metal enriched zone was found in near shore sediments. Lee et al. (1980) suggest that sediment biology may affect the ground water chemistry as ground water enters a lake and that ground water may flush materials from lake sediments into the lake.
Brock et al. (1982) estimate ground water seepage into Lake Mendota using seepage meters. Because seepage water has a long residence time in the seepage meters, compared with the time it would take for the seepage water to undergo chemical modification, seepage meter samples were not considered reliable for estimating nutrient flux from ground water. Therefore, both dialysis chambers and pipeting were used to gather sediment pore water samples for chemical analysis.

Spatial variability in the chemical composition of sediment pore water was attributed to either differences in groundwater chemistry or the modification of seepage water by lake sediments as the seepage water moved into the lake. The average phosphorus concentration of seepage water was found to be 171.5 \( \mu \text{g/l} \). Seepage meter data show that ground water accounts for one third of the inflowing water to Lake Mendota. Chemical analysis of seepage water shows, however, that seepage represents only 12% of the phosphorus loading to the lake.

Comparisons of seepage water nutrient concentrations with that of wells in the vicinity indicates that seepage water is higher in phosphorus and ammonia than well water. The authors suggest that the phosphorus and ammonia in seepage water was derived from the lake itself and is, therefore, being recycled from the sediments aided by ground water discharge through the lake sediments.
CHAPTER III
FIELD MEASUREMENTS AND DATA COLLECTION

Background

Lake Warner was created in the early 1800's by the construction of a dam on the Mill River (Hadley, Massachusetts). By-passes from the Amherst Wastewater Treatment Plant flowed into the Mill River, approximately 1.5 miles (2.4 (10) \(^3\) m) upstream from Lake Warner, in the late 1960's and early 1970's, causing the lake to experience excessive algal blooms. Wastewater discharges were stopped in November, 1975, with the completion of the new Amherst Wastewater Treatment Plant. Hence, Lake Warner provided a good study area for assessing the effect of reducing nutrient loadings to a eutrophic lake.

The Lake Warner watershed was analyzed by Jubinville (1973). The total area drained by the Mill River was determined to be 32.1 square miles (8313.8 hectares) and the land usage in this watershed is shown in Table 2.

Table 2. Percentage of Land Usage in the Lake Warner Drainage Basin (after Bingham and Feng, 1980)

<table>
<thead>
<tr>
<th>Land Use Type</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agricultural (Dairy Farms)</td>
<td>20%</td>
</tr>
<tr>
<td>Agricultural (Crops)</td>
<td>20%</td>
</tr>
<tr>
<td>Non-Agricultural (Forest)</td>
<td>50%</td>
</tr>
<tr>
<td>Urban</td>
<td>10%</td>
</tr>
</tbody>
</table>
Snow and DiGiano (1976) determined the lake area to be 68 acres (27.5 hectares), the lake volume to be 352 acre-feet (4.35 \(10^5\) m\(^3\)) and the average depth to be 5.15 feet (1.58 m).

Lake Warner sediments were shown to reflect eutrophic lake characteristics (Snow and DiGiano, 1973) based on the high concentration of \(\text{PO}_4^{3-}\) in the sediment which would be available for exchange with the lake water to support algal blooms. Snow and DiGiano (1976) estimated the average porosity of the upper five centimeters of the lake sediment to be 0.84. Also, high sediment solid phase and interstitial phosphorus concentrations were found in Lake Warner sediments. They measured sediment solid phase phosphorus concentrations of 0.9 to 1.6 mgP/g of dry sediment and 320 to 450 \(\mu\)g/1 sediment interstitial total phosphorus concentrations. The lake water total phosphorus concentrations averaged about 90 \(\mu\)g/l in 1973 and 1974. Snow and DiGiano (1976) also found an extreme dissolved oxygen gradient in the lake water during the summer of 1973. Excessive algal blooms (including a blue-green variety) occurred throughout the summers of 1973 and 1974.

Bingham and Feng (1980) found that Lake Warner had recovered from its eutrophic state more quickly than had been predicted by the Snow and DiGiano (1976) lake recovery model. The average total phosphorus concentration of the lake water was found to be 50 \(\mu\)g/l in 1976. Algal blooms were of only very short duration during mid July of 1976. They found that sediment interstitial
total phosphorus concentrations ranged from 150 to 300 \( \mu g/l \) and that the sediment solid phase phosphorus concentration was actually higher than that measured in 1973 by Snow and DiGiano (1976). This was attributed to more consistently oxic lake bottom waters which increased the phosphorus binding capacity of the lake sediments.

Visual observations during the summer of 1981 indicate that Lake Warner has indeed recovered from its former eutrophic state. During the low flow and high temperature period of July algal blooms were of only short duration. Filamentous blue-green species were not excessive but Watermeal \( (Wolffia brasiliensis) \) and Duckweed \( (Lemna minor) \) did cover much of the lake surface during portions of the summer of 1981.

**Materials and Methods**

To follow up the studies by Snow and DiGiano (1976) and Bingham and Feng (1980) the Mill River and Lake Warner were sampled for phosphorus concentration on July 31, 1981 and daily during a period from September 18, 1981 to October 4, 1981. Stream gauging and sampling was carried out on the Mill River (stations shown in figure 6) to estimate the phosphorus budget of Lake Warner and to model the release of phosphorus from the lake bottom. Also, measurements were made on the ground water component of Lake Warner hydrology using seepage meters. Measurements taken during the dry months of July and August are compared to
Symbol

▲ Influent sampling location for mass balance shown in Figure 11.

● Effluent sampling location used in Figure 11.

Sampling locations used in Figures 9 and 10.

Figure 6. Location map and water sampling sites.
measurements taken during October and November of 1981 (see figure 13).

Water samples were analyzed for total and orthophosphate phosphorus using the Heteropoly Blue-Ascorbic acid Spectrophotometric method (Strickland and Parsons, 1972). Samples from Lake Warner were taken at one-third meter below the surface and from one meter above the bottom. Bottom samples were taken with a Kemmerer sampler. Samples were transported to the laboratory in 500 milliliter acid washed bottles. All glassware used in the phosphorus analysis were acid washed.

Water samples were analyzed for both orthophosphate and total phosphorus on the day that they were collected. Samples analyzed for orthophosphate were filtered through 0.45 m filters, using a millipore apparatus, prior to the addition of the composite reagent solution. Total phosphorus samples were autoclaved after the addition of 0.4 ml of 1N H$_2$SO$_4$ and 0.2 grams of potassium persulfate. These samples were allowed to cool to room temperature before pH adjustment and the addition of the composite reagent solution. The absorbance of the prepared samples was measured on a Bausch and Lomb Spectronic 70 spectrophotometer. A ten centimeter cell was used. The calibration curves of total and orthophosphate phosphorus concentration vs. absorbance appear in Appendix A.

Stream gauging was done on the inlet and outlet streams of Lake Warner using the U.S.G.S. mid-section method (Buchanan and Somers, 1969). Stream velocities were measured at 0.6 of the
stream depth with a Gurley pygmy current meter. A stage-discharge curve was developed using stream flow measurements and a staff gauge to measure stream stage. These curves appear in Appendix A. Stream flow on the sampling dates was estimated by measuring the stream stage and finding the flow from the stage-discharge curve.

Seepage through Lake Warner sediments was measured during July, August and November 1981 using seepage meters described by Lee (1977). The basic shell of a seepage meter consists of a 208.2 liter (55 gallon) steel drum cut at 25 centimeters (9.8 in.) from the end (see Fig. 7). The insides of the seepage meters were painted with epoxy resin to prevent corrosion. The seepage meters were installed in the lake bottom by turning them slowly into the lake sediments until approximately ten centimeters of the meter extended above the sediment-lake water interface. Tubes for sample collection were then inserted in the the bung holes which had been cut into the tops of the meter and Ziplock heavy duty freezer bags were attached to them. Five hundred milliliters (0.132 gal.) of distilled water was placed in each bag before it was attached to a seepage meter.

Meters 1 through 5 were installed on the southeast side of Lake Warner and meters 1A through 5A were installed on the opposite side of the lake as can be seen from Figure 8. The meters were placed in the lake sediments 1.5 to 3 meters (five to ten feet) from shore in about 0.6 meters (two feet) of water. Sample bags were changed from a twelve foot aluminum boat.
Figure 7. Section view of seepage meter. a - Ziplock heavy duty freezer bag; b - rubber band; c - 1/4" ID polyethylene tube; d - No. 10 rubber stopper; e - end section of steel drum.
Figure 8. Location map showing seepage meter station and the locations of cross sections.
To estimate seepage rates the net changes in water volume in
the sample bags were measured. Measurements were done by weight
or volumetrically. Thus if, during the sampling period, there
was a net loss of water from the sample bag (each bag was
installed with a content of 500 ml of distilled water) then the
ground water aquifer was being recharged through the lake
sediments. If after the sampling period the sample bag contained
greater than the original 500 ml of water then the ground water
aquifer was discharging to the lake. These measurements
represent a macro-seepage velocity and should not be confused
with average interstitial velocities which can be obtained by
dividing the seepage rate by the porosity of the sediment. The
seepage rates, herein, were estimated by measuring the volume of
seepage water (described above) and the duration of the sampling
period. Given the area of sediment that was enclosed by the
seepage meter the seepage rate can be calculated:

\[ u = \frac{V}{tA} \]  \hspace{1cm} (3.1)

With volume \( V \) in liters and time \( t \) in hours and Area \( A \) of
0.255 m\(^2\) the seepage rate \( u \) in \( \mu \text{m/sec} \) can be expressed as:

\[ u \ (\mu \text{m/sec}) = 1.089 \ (V/t) \] \hspace{1cm} (3.2)
Discussion

Low flow conditions existed throughout the sampling period in this study. Lake water phosphorus concentration data from July 31, 1981 (Fig. 9) shows a typical dry weather phosphorus profile for surface water and bottom water along an east-west transect through Lake Warner. Data from the intensive sampling period of September 18, 1981, to October 4, 1981 are averaged (Fig. 10) and show a phosphorus profile similar to the wet weather data of Bingham and Feng (1980).

Figure 11 shows the Lake Warner phosphorus budget as determined by stream flow measurements and phosphorus analyses. A net export of phosphorus occurred on the July 31, 1981 sampling date and a net retention of phosphorus occurred during the intensive sampling period (September 18, 1981 to October 4, 1981). Lake sediments released phosphorus during periods of high water temperature and low flow conditions while sediment retention of phosphorus occurs at lower water temperatures and reduced biological activity (Bingham and Feng, 1980). Hence, for Lake Warner, sediment release of phosphorus is seasonal and of short duration, thus only temporarily affecting the nutrient balance of the lake.

The hydrogeologic setting of Lake Warner was examined by constructing cross sections through the lake using a Mount Toby U.S.G.S. quadrangle map and a contour map of the bedrock surface (Londquist, 1974). These cross sections of the bedrock and
Figure 9. Lake-water phosphorus concentrations for sampling date 7/31/81.
Figure 10. Average lake water phosphorus concentrations for sampling period 9/18/81-10/4/81.
Figure 11. Mass balance on lake water total phosphorus.
overburden elevations appear in Figure 12 and suggest that ground water may discharge into Lake Warner from the southeast and be recharged on the northeast side of the lake.

Figure 13 shows that ground water enters the lake (hence, positive velocities) at meter locations 1, 2, 3, 5 and 5A, and that lake water flows out of the lake at seepage meter locations 1A, 2A, 3A, 4 and 4A. Hence, a flow through condition exists between cross sections I and III. A flow out of the lake occurs at cross section IV and a flow into the lake occurs at cross section V.

Seepage velocity measurements taken at Lake Warner in November 1981 were generally double those taken during July and August 1981. Reversals in seepage flow that occurred at meter locations 1A, 2A, 3A, 4 and 4A were probably due to ground water mounding caused by the precipitation that occurred in October and November 1981 and the reduction of evapotranspiration by vegetation near the lake.

The importance of ground water to Lake Warner's water budget can be examined by using a seepage rate estimated by field measurements \( u_{\text{max}} \sim 10^{-2} \, \mu \text{m/sec} \) and assuming that this seepage rate occurs throughout the lake bottom (Area\( A = 2.572 \times 10^5 \, \text{m}^2 \)). Then one estimates: Maximum Seepage flow rate \( = A u \sim 222 \, \text{m}^3/\text{day} \)

Average Mill River flow rate \( \sim 48902 \, \text{m}^3/\text{day} \)

Comparing the seepage flow rate (222 m³/day) with the Mill River flow rate (48902 m³/day) makes it clear that seepage flow can be neglected in the water budget of Lake Warner.
Figure 12. Cross sections through Lake Warner showing the bedrock overburden elevations. The locations of cross sections are shown in Figure 8.
Figure 13. Seepage velocities. Negative seepage velocities mean seepage out of the lake. The station locations are shown in Figure 8.
The significance of ground water discharge through lake sediments as a nutrient transport mechanism can be examined by comparing seepage flux with the phosphorus loading from the Mill River. The average flow rate, determined by Snow and DiGiano (1976), \((48902.4 \text{ m}^3/\text{day})\) and the average phosphorus concentration of \(50 \mu g/l\) (as determined by Bingham and Feng, 1980) were used to estimate Mill River phosphorus loading. Average sediment interstitial phosphorus concentrations of \(176 \mu g/l\) as measured by Bingham and Feng (1980) were used. The maximum value for seepage rates, determined in this study to be about \(10^{-2} \text{ mm/sec}\) through Lake Warner sediments were assumed to occur uniformly through the lake bottom. This is also a high estimate as seepage was found to recharge the ground water aquifer over part of the lake bottom during this study. One can then estimate the relative phosphorus loadings from the Mill River and from seepage as:

- **Average Mill River Loading**: \(\sim 2.4(10)^6 \text{ mgP/day}\)
- **Maximum Seepage Loading**: \(\sim 3.9(10)^4 \text{ mgP/day}\)

As can be seen from the above calculation, the maximum expected seepage loading of phosphorus to Lake Warner is very small (\(3.9(10)^4 \text{ mgP/day}\)) compared with the average Mill River phosphorus loading (\(2.4(10)^6 \text{ mgP/day}\)). Hence, phosphorus loading due to ground water discharge to the lake can be neglected in the construction of a phosphorus budget for Lake Warner.
CHAPTER IV
LAKE RECOVERY MODEL

The lake recovery model developed by Snow and DiGiano (1976) consists of three control volumes (on lake water phosphorus, and on lake sediment interstitial and sediment solid phase phosphorus) which are shown in Figure 14. Control volume I shows the mechanisms by which phosphorus is transported through the lake water. Snow and DiGiano (1976) showed that Lake Warner more closely approximated a Continuous Flow Stirred Tank Reactor (CFSTR) than a Plug Flow Reactor. Hence, CFSTR assumptions were used in their lake recovery model. These assumptions are:

i) The lake is completely mixed.

ii) The outflow phosphorus concentration is the lake water phosphorus concentration.

iii) The Mill River flow rate \( Q \) is assumed to be constant on an annual average time scale. The change in lake water storage can therefore be neglected.

iv) The Mill River influent phosphorus concentration \( P_0 \) is constant.

v) The mass transfer rate \( K_1 \) and the reaction rates \( K_2 \) and \( K_3 \) is constant.

Mass balance equations were developed for the control volumes shown in Figure 14 under the assumption that both total phosphorus and water are conservative substances. The following
Figure 14. Control volumes used in the lake phosphorus budget model.
discussion will use the term "phosphorus" as synonymous with total phosphorus which is the conservative substance being modeled in the lake system.

**Release Rate ($K_1$)**

The release of phosphorus from lake bottoms is governed by physical, chemical and biological processes. The rate limiting step for phosphorus release from the sediments could emanate from resistance due to pore diffusion rates through the interstitial water or resistance at the interface of the sediment deposit and the lake water (DiGiano, 1971). Because concentrations of sediment phosphorus in eutrophic lakes is high, it can be assumed that interfacial resistance entirely controls the rate of mass transport. The dominance of the interfacial resistance effect over pore diffusion rates in deeper sediments can be defended by examining the magnitude of the sediment solid phase phosphorus concentration in the upper sediment layers.

The concentration of exchangeable phosphate in Lake Warner sediments is on the order of $10^5 \mu g/l$ (Snow and DiGiano, 1976). With an average lake water depth of about 1.7 meters, 0.1 meters of sediment (0.1 meters is the exchange depth used by Snow and DiGiano, 1976) could replace a lake water phosphorus concentration of 100 $\mu g/l$ about 60 times. Therefore, with an average lake
water residence time of about 10 days the sediments alone contain a phosphorus source capable of keeping the lake water at 100 μg/l for 600 days.

DiGiano (1971) suggests a simple model of interfacial resistance to describe the rate of mass transport in deposit-water systems. In the case of lake bottom phosphorus the release is proportional to the difference in the sediment interstitial phosphorus concentration \(P_i\) and the phosphorus concentration in the overlying water \(P_L\). The release of phosphorus directly from the solid phase to the lake water is negligible because of the small area of sediment solid phase phosphorus in direct contact with the lake water compared with the area in contact with interstitial water. The exchange depth, estimated by Snow and DiGiano (1976) to be 0.1 meters, multiplied by the lake area is the volume of lake bottom allowed to release phosphorus to the lake water. The volume of sediment solid phase phosphorus \(P_s\) is represented by \(V_s\) (rather than \((1 - ε)V_s\)) and the sediment interstitial phosphorus \(P_i\) as \(εV_s\). This is appropriate because \(P_s\) is three orders of magnitude larger than \(P_i\). Snow and DiGiano (1976) carried out an in situ caisson study at Lake Warner to determine the value of the mass transfer coefficient \(K_1\) which has a magnitude of about 0.1 meters/day. Hence, the lake bottom phosphorus release can be described as:

\[
R_{rel} = \frac{εA}{V_s} K_1 (P_i - P_L)
\]

4.1
The removal of phosphorus from the lake water to the sediment can be modeled by assuming a first order reaction rate ($K_2$) which describes all physical, chemical and biological processes in the lake (Snow and DiGiano, 1976). $K_2$ has a magnitude of about 0.1/day. The rate of removal of phosphorus from the lake water (assumed to be proportional to the lake water phosphorus concentration) to the sediment can be described as:

$$R_{sed} = K_2 P_L$$

The modification of the Snow and DiGiano (1976) model by Bingham and Feng (1980) to include the reaction rate $K_3$ required the introduction of a mass balance equation on sediment interstitial phosphorus.

The reaction rate ($K_3$) describes the conversion of sediment solid phase phosphorus ($P_s$) to sediment interstitial phosphorus ($P_i$). It is a composite parameter which describes all physical, chemical and biological processes in the sediment. $K_3$ is assumed to be constant although seasonal fluctuations in $K_3$ values might be expected due to variations in Mill River water quality and flow rate which affects lake water temperature, dissolved oxygen, biological activity and sediment redox potential.
The rate of conversion from sediment solid phase to interstitial phosphorus is assumed to be proportional to the sediment solid phase phosphorus concentration.

\[
\text{Rate of conversion from solid to interstitial phosphorus in sediment} = K^P_{s} \quad 4.3
\]

**Mass Balance Equations**

The basic equation for the conservation of a reactive material is:

\[
\text{Rate of Mass Input} - \text{Rate of Mass Output} + \text{Rates of Reaction} = \text{Rate of Mass Accumulation} \quad 4.4
\]

The terms of the above mass balance equation for the lake water phosphorus control volume (control volume I in Fig. 14) become:

\[
\begin{align*}
\text{Mass Input Rate} & = QP_{o} + \xi AK_{1}(P_{i} - P_{L}) \\ 
\text{Mass Output Rate} & = QP_{L} \\ 
\text{Rate of Reaction} & = V_{L}K_{2}P_{L} \\ 
\text{Rate of Mass Accumulation} & = V_{L} \frac{\Delta P_{i}}{\Delta t}
\end{align*} \quad 4.5, 4.6, 4.7, 4.8
\]

Substituting equations (4.5, 6, 7 and 8) into equation (4.4) and letting the deltas go to zero yields:
The terms for the mass balance equation for the sediment solid phase phosphorus control volume (control volume II in Fig. 14) become:

\[ \frac{dP}{dt} = \frac{V_k P}{L^2} - \frac{V_L P}{L} + \Delta A \frac{K}{I} (P_i - P_L) \] 4.9

Mass input rate = \( V_k P \) 4.10
Mass output rate = \( \frac{V_L P}{L} \) 4.11
Rate of Mass Accumulation = \( \frac{\Delta P}{\Delta t} \) 4.12

Substituting equations (4.10, 11 and 12) into equation (4.4) and letting the deltas go to zero yields:

\[ \frac{dP}{dt} = \frac{V_k P}{L^2} - \frac{V_L P}{L} \] 4.13

The terms for the mass balance equation for the sediment interstitial phosphorus control volume (control volume III in Fig. 14) become:

Mass Input Rate = \( \frac{V_L P}{L} \) 4.14
Mass Output Rate = \( \Delta A \frac{K}{I} (P_i - P_L) \) 4.15
Rate of Mass Accumulation = \( \frac{\Delta P_i}{\Delta t} \) 4.16

Substituting equations (4.14, 15 and 16) into equation (4.4) and letting the deltas go to zero yields:
\[ V_s \frac{dP_i}{dt} = V_s K_i P_s - \varepsilon AK_1 (P_i - P_L) \quad 4.17 \]

Hence, the modified Snow and Digiano (1976) model as presented by Bingham and Feng (1980) is:

**Sediment Solid Phase Phosphorus**

\[ V_s \frac{dP_s}{dt} = -V_s K_s P_s + V_L K_P P_L \quad 4.13 \]

**Sediment Interstitial Phosphorus**

\[ V_s \frac{dP_i}{dt} = V_s K_i P_s - \varepsilon AK_1 (P_i - P_L) \quad 4.17 \]

**Lake Water Phosphorus**

\[ V_L \frac{dP_L}{dt} = Q_P - Q_{P_{L}} + \varepsilon AK_1 (P_i - P_L) - V_L K_P P_L \quad 4.9 \]

The above equations can be rewritten in a form which is more convenient for solution by grouping the coefficients:

**Sediment Solid Phase Phosphorus**

\[ \frac{dP_s}{dt} = X_1 P_s + X_2 P_L \quad 4.18 \]

**Sediment Interstitial Phosphorus**

\[ \frac{dP_i}{dt} = X_3 P_s + X_4 P_i + X_5 P_L \quad 4.19 \]
Lake Water Phosphorus

\[
\frac{dp_L}{dt} = x_6 p_i + x_7 p_L + x_8
\]

4.20

where:

\[
\begin{align*}
    x_1 &= -x_3 \\
    x_2 &= \frac{k_2 v_L}{v_S} \\
    x_3 &= \frac{k_3}{c} \\
    x_4 &= -\frac{ak_1}{v_S} \\
    x_5 &= \frac{ak_1}{v_S} \\
    x_6 &= \frac{c ak_1}{v_L} \\
    x_7 &= -(q + \frac{c ak_1 + k_2 v_L}{v_L})/v_L \\
    x_8 &= \frac{p_o}{v_L}
\end{align*}
\]

This system of ordinary, first order, linear differential equations with constant coefficients (equations 4.18, 19, and 20) can be solved numerically (Bingham and Feng, 1980) or analytically. Analytical methods of solving these equations were explored including the Laplace transform method, the power series method, the trial function method and approximation methods. The Laplace transform method was not chosen because the inverse transform appeared formidable. The power series method was rejected after calculations using a digital computer showed the series did not approach convergence after evaluating one hundred terms.
The trial function method was successful in leading to the solution of equations (4.18, 19 and 20). Application of approximation techniques allowed these equations to be simplified sufficiently so that they could be solved readily. Both the trial function method and the approximation techniques are discussed more fully in the following sections.

**Trial Function Method**

The trial function method (Stockton, personal communication) is useful for solving a small number of simultaneous ordinary first order linear differential equations with constant coefficients. The number of algebraic equations to be manipulated to determine unknown coefficients grows exponentially with the number of simultaneous differential equations to be solved so that three simultaneous differential equations may be a practical upper limit for the method. The lake model requires the simultaneous solution of 12 algebraic equations. The non-homogeneous differential equations in the lake model were converted to homogeneous equations to simplify algebraic manipulations. Details of the trial function method appear in Appendix B. The equations for the lake water ($P_L(t)$), sediment interstitial ($P_i(t)$) and sediment solid phase ($P_s(t)$) phosphorus concentration as determined by the trial function method are:
\[ P_L(t) = P_{L \infty} + (P_{L0} - P_{L \infty}) \left[ \left( \frac{E(BF-CE)}{(E-D)(BF-CE) - (E-F)(BD-AE)} \right) e^{(E-F)/((E-D)(BF-CE) - (E-F)(BD-AE)) t} + \right. \]
\[ \left. \left[ \frac{F(CD-AF)}{(F-E)(CD-AF) - (F-D)(CE-BF)} \right] e^{(F-D)/((F-E)(CD-AF) - (F-D)(CE-BF)) t} + \right. \]
\[ \left. \left[ \frac{D(AE-DB)}{(D-F)(AE-DB) - (D-E)(AF-CD)} \right] e^{(D-E)/((D-F)(AE-DB) - (D-E)(AF-CD)) t} \right] \]

\[ + \left( P_{i0} - P_{i \infty} \right) \left[ \left( \frac{E(F-A)}{(E-D)(AE-DB) - (E-F)(AF-CD)} \right) e^{(E-F)/((E-D)(AE-DB) - (E-F)(AF-CD)) t} + \right. \]
\[ \left. \left[ \frac{F(C-A)}{(F-E)(CD-AF) - (F-D)(CE-BF)} \right] e^{(F-C)/((F-E)(CD-AF) - (F-D)(CE-BF)) t} + \right. \]
\[ \left. \left[ \frac{D(A-E)}{(D-F)(AE-DB) - (D-E)(AF-CD)} \right] e^{(D-A)/((D-F)(AE-DB) - (D-E)(AF-CD)) t} \right] \]

To use equation (4.21) substitute the values for the initial and steady state conditions and make the following substitutions:

\[ A = \left( \frac{(\alpha - X_4)(\alpha - X_7) - X_5 X_6}{X_3 X_6} \right) \quad 4.21.1 \]
\[ B = \left( \frac{(\gamma - X_4)(\gamma - X_7) - X_5 X_6}{X_3 X_6} \right) \quad 4.21.2 \]
\[ C = \left( \frac{(\gamma - X_4)(\gamma - X_7) - X_5 X_6}{X_3 X_6} \right) \quad 4.21.3 \]
\[ D = \left( \frac{X_2 X_3 + X_5 (\alpha - X_4)}{(\alpha - X_4)(\alpha - X_1)} \right) \quad 4.21.4 \]
\[ E = \left( \frac{X_2 X_3 + X_5 (\gamma - X_4)}{(\gamma - X_4)(\gamma - X_1)} \right) \quad 4.21.5 \]
\[ F = \left( \frac{X_2 X_3 + X_5 (\gamma - X_4)}{(\gamma - X_4)(\gamma - X_1)} \right) \quad 4.21.6 \]
\[
P_i(t) = P_i^\infty + \left( P_{i0} - P_i^\infty \right) \left[ \left( \frac{E(BF-CE)}{(E-D)(BF-CE) - (E-F)(BD-AE)} \right) e^{(t)} + \left( \frac{F(CD-AF)/[(F-E)(CD-AF) - (F-D)(CE-BF)]}{e^{(t)}} \right) + \left( \frac{D(AE-DB)/[(D-F)(AE-BD) - (D-E)(AF-CD)]}{e^{(t)}} \right) \right]
\]

- \left( P_{s0} - P_s^\infty \right) \left[ \left( \frac{E(E-F)}{(E-D)(BF-CE) - (E-F)(BD-AE)} \right) e^{(t)} + \left( \frac{F(D-E)/[(F-E)(CD-AF) - (F-D)(CE-BF)]}{e^{(t)}} \right) + \left( \frac{D(A-E)/[(D-F)(AE-BD) - (D-E)(AF-CD)]}{e^{(t)}} \right) \right] 4.22

To use equation (4.22) substitute the values for the initial and steady state conditions and make the following substitutions:

\[
A = \frac{X_2X_5}{(\alpha - X_1)(\alpha - X_7)} 4.22.1
\]

\[
B = \frac{X_2X_5}{(\bar{\theta} - X_1)(\bar{\theta} - X_7)} 4.22.2
\]

\[
C = \frac{X_2X_5}{(\bar{\gamma} - X_1)(\bar{\gamma} - X_7)} 4.22.3
\]

\[
D = \left[ (\alpha - X_1)(\alpha - X_4)(\alpha - X_7) - X_2X_3X_6 \right] / X_5(\alpha - X_1)(\alpha - X_7) 4.22.4
\]

\[
E = \left[ (\bar{\theta} - X_1)(\bar{\theta} - X_4)(\bar{\theta} - X_7) - X_2X_3X_6 \right] / X_5(\bar{\theta} - X_1)(\bar{\theta} - X_7) 4.22.5
\]

\[
F = \left[ (\bar{\gamma} - X_1)(\bar{\gamma} - X_4)(\bar{\gamma} - X_7) - X_2X_3X_6 \right] / X_5(\bar{\gamma} - X_1)(\bar{\gamma} - X_7) 4.22.6
\]
\[ P_s(t) = P_{s\infty} + (P_{s0} - P_{s\infty}) \left[ \frac{E(BF-CE)}{(E-D)(BF-CE) - (E-F)(BD-AE)} e^{\alpha t} + \frac{F(CD-AF)}{(F-E)(CD-AF) - (F-D)(CE-BF)} e^{\beta t} + \frac{D(AE-DB)}{(D-F)(AE-BD) - (D-E)(AF-CD)} e^{\gamma t} \right] \]

\[ + (P_{L0} - P_{L\infty}) \left[ \frac{E(E-F)}{(E-D)(BF-CE) - (E-F)(BD-AE)} e^{\alpha t} + \frac{F(F-D)}{(F-E)(CD-AF) - (F-D)(CE-BF)} e^{\beta t} + \frac{D(D-E)}{(D-F)(AE-BD) - (D-E)(AF-CD)} e^{\gamma t} \right] \]

\[ - (P_{i0} - P_{i\infty}) \left[ \frac{E(E-C)}{(E-D)(BF-CE) - (E-F)(BD-AE)} e^{\alpha t} + \frac{F(C-A)}{(F-E)(CD-AF) - (F-D)(CE-BF)} e^{\beta t} + \frac{D(A-B)}{(D-F)(AE-BD) - (D-E)(AF-CD)} e^{\gamma t} \right] \]

4.23

To use equation (4.23) substitute the values for the initial and steady state conditions and make the following substitutions:

\[
\begin{align*}
A &= (\alpha - x_1) & 4.23.1 \\
B &= (\beta - x_1) & 4.23.2 \\
C &= (\gamma - x_1) & 4.23.3 \\
D &= x_3/[(\alpha - x_4 - x_6x_7)/(\alpha - x_7)] & 4.23.4 \\
E &= x_3/[(\beta - x_4 - x_6x_7)/(\beta - x_7)] & 4.23.5 \\
F &= x_3/[(\gamma - x_4 - x_6x_7)/(\gamma - x_7)] & 4.23.6
\end{align*}
\]
In the above equations $\alpha$, $\beta$, and $\gamma$ are the roots ($r_1$, $r_2$ and $r_3$) of the following equation.

$$r^3 - (X_1 + X_4 + X_7)r^2 + (X_1X_4 + X_1X_7 + X_4X_7 - X_4X_6)r + \frac{X_1X_4X_7 - X_1X_4X_6 - X_2X_3X_6}{X_1X_4} = 0 \quad 4.24$$

and

$$P_{L\infty} = P_0$$
$$P_{i\infty} = P_0 \frac{X_2}{X_5} \gamma + P_0$$
$$P_{s\infty} = -P_0 \frac{X_2}{X_1}$$

These equations appear formidable but can be programmed on a TI-59 programmable calculator. The program coding for the equations (4.21, 22 and 23) appears in Appendix C. It is suggested that terms that contain $\gamma t$ and $\beta t$ in the exponent position be neglected in applications of the equations. $\beta$ and $\gamma$ are very large ($\beta = \frac{10^{-1}}{10}$ and $\gamma = [1]$, respectively) compared to $\alpha$ ($\alpha = [10^{-3}]$). Hence as $t$ grows large ($t \geq 100$ days) terms with large negative rate constants ($\beta$ and $\gamma$) in the exponent go to zero quickly and can be neglected.

**Approximation Techniques**

**Short term predictions.** Over short time steps the value of the interstitial phosphorus concentration can be considered constant (DiGiano and Snow, 1976). The value of $P_i$ in equation
(4.9) is large relative to the other terms (see order of magnitude analysis in Appendix B) and can therefore be considered constant. This is similar to pseudo-order assumptions which allow species in excess in a chemical reaction to be considered constant to simplify the expression for the differential rate equation. In the initial period \( t<3T \) after phosphorus loading is reduced, dilution plays an important role in lake recovery. Hence, holding \( P_i \) constant and integrating equation (4.9) to give equation (4.25) yields a short term model that is most influenced by the dilution process but allows for phosphorus release from the lake bottom.

\[
P_L(t) = -\frac{(x_8 + x_6 p_{io})}{x_7} + \left[\frac{(x_8 + x_6 p_{io})}{x_7} + p_{lo}\right]e^{7t} \quad 4.25
\]

Figure 15 compares predictions of the short term model (equation 4.25) with predictions of the trial function solution (equation 4.21). Figure 16 compares the same equations on an expanded time scale. It is evident that the short term predictions are accurate for only two or three hydraulic residence times (the average annual hydraulic residence time for Lake Warner is 10 days).

After the initial rapid reduction of the lake phosphorus concentration due to dilution, phosphorus release from the lake bottom may control lake recovery.
Figure 15. Comparison of model predictions \( P_i(t) \), Trial Function Solution (eq. 4.21), Approximate Short-Term Curve (eq. 4.25) and Approximate Curve (eq. 4.31).
Figure 16. Expanded time scale. Comparison of model predictions ($P_p(t)$), Trial Function Solution (eq. 4.21) and Approximate Solution (eq. 4.25).
Intermediate term predictions. Figure 17, obtained from equation (4.21), shows that after the initial recovery period the lake water phosphorus concentration reaches a quasi-steady state condition. The rate of recovery of the lake is controlled by phosphorus release from the lake bottom, hence, sediment interstitial and solid phase phosphorus concentrations are allowed to change over long time horizons (several years to a decade). In a similar manner in which intermediate chemical species are considered constant to simplify differential rate equations the rate of change of the lake water phosphorus concentration can be considered zero. An algebraic expression for \( P_L \) can be found by setting the left hand side of equation (4.20) equal to zero and solving for \( P_L \).

\[
P_L = -\frac{X_8}{X_7} - \frac{X_6P_i}{X_7}  \tag{4.26}
\]

Substituting equation (4.26) into equations (4.18) and (4.19) yields:

\[
\frac{dP_s}{dt} = \frac{X_1P_s - X_2X_6/X_7 - X_2X_6P_i/X_7}{X_1} \tag{4.27}
\]

\[
\frac{dP_i}{dt} = \frac{X_3P_s + P_i(X_4 - X_5X_6/X_7) - X_5X_8/X_7}{X_3} \tag{4.28}
\]
Figure 17. Lake water response to reductions of phosphorus loading ($P_o$) from 90 to 70, 50 and 30 ($\mu g/l$).
Equations (4.27) and (4.28) can be solved simultaneously by Laplace transform methods to yield:

\[
P_i(t) = \left[ \left[ \frac{X_3}{r} - P_{io} (G-r) \right] / 2r \right] e^{-t(H-r)}
- \left[ \frac{X_3}{r} - P_i (G+r) \right] / 2r \right] e^{-t(H+r)}
+ \left[ \frac{X_3}{r}X_8/X_7 - X_5X_8/X_7 (G+r) \right] / 2r(H+r) \right] \left[ 1 - e^{-t(H+r)} \right]
- \left[ \frac{X_3}{r}X_8/X_7 - X_5X_8/X_7 (G-r) \right] / 2r(H-r) \right] \left[ 1 - e^{-t(H-r)} \right]
\]

4.29

\[
P_s(t) = \left[ \left[ \frac{X_3}{r} - P_{so} (G+r) \right] - P_{io} \frac{X_3}{r} \right] / 2r \right] e^{-t(H-r)}
- \left[ \left[ \frac{X_3}{r} - P_i (G-r) \right] - P_{io} \frac{X_3}{r} \right] / 2r \right] e^{-t(H+r)}
+ \left[ \frac{X_3}{r}X_8(X_6X_5/X_7) - 1 \right] \frac{X_3}{r} / 2r(H+r)X_7 \right] \left[ 1 - e^{-t(H+r)} \right]
+ \left[ \frac{X_3}{r}X_8(X_6X_5/X_7) - 1 \right] \frac{X_3}{r} / 2r(H-r)X_7 \right] \left[ 1 - e^{-t(H-r)} \right]
\]

4.30

Substituting the equation for \( P_i(t) \) (equation (4.29)) into equation (4.26) yields a time dependent equation for \( P_L \):

\[
P_L(t) = -X_8/X_7 \left[ \left[ \frac{X_3}{r} - P_{io} (G-r) \right] / 2r \right] e^{-t(H-r)}
- \left[ \left[ \frac{X_3}{r} - P_i (G+r) \right] / 2r \right] e^{-t(H+r)}
+ \left[ \frac{X_3}{r}X_8/X_7 - X_5X_8/X_7 (G+r) \right] / 2r(H+r) \right] \left[ 1 - e^{-t(H+r)} \right]
- \left[ \frac{X_3}{r}X_8/X_7 - X_5X_8/X_7 (G-r) \right] / 2r(H-r) \right] \left[ 1 - e^{-t(H-r)} \right]
\]

4.31
where:

\[
G = \frac{(X_5X_6 - X_4X_7 + X_1X_7)}{2X_7}
\]
\[
H = \frac{(X_5X_6 - X_4X_7 - X_1X_7)}{2X_7}
\]
\[
x = \left[\left(\frac{(X_5X_6 - X_4X_7 - X_1X_7)}{X_7}\right)^2 - 4 \left(\frac{X_2X_3X_6X_7}{X_7} - \frac{X_1(X_5X_6 - X_4X_7)}{X_7}\right)\right]^{1/2}
\]

and

\[
X_1 = -K_3
\]
\[
X_2 = K_2V_L/V_s
\]
\[
X_3 = K_3\epsilon
\]
\[
X_4 = -AK_1/V_s
\]
\[
X_5 = AK_1/V_s
\]
\[
X_6 = \epsilon AK_1/V_L
\]
\[
X_7 = -(Q + \epsilon AK_1 + K_2V_L)/V_L
\]
\[
X_8 = P_o/T
\]

Figures 15, 18 and 19 compare the approximate lake model equations with the solutions obtained from the trial function method. The approximate curves compare favorably with the curves produced by the analytical equations obtained from the trial function method.

Program coding for the use of equations (4.29, 30 and 31) on a TI-59 programmable calculator appear in Appendix C.
Figure 18. Comparison of model predictions, Trial Function Solution (eq. 4.22) and Approximate Solution (eq. 4.29).
Figure 19. Comparison of model predictions ($P_s(t)$), Trial Function Solution (eq. 4.23) and Approximate Solution (eq. 4.30).
Sensitivity Analysis

Figures 20 through 24 show sensitivity of the lake model equations (4.21, 22 and 23) to parameters $K_1$, $K_2$, $K_3$, $Q$ and $Dr$. Table 3 shows the initial conditions and parameter values used in the sensitivity analysis. Figure 20 shows that variations of the release rate $K_1$ by two orders of magnitude has little effect on the prediction of lake water phosphorus concentration. An explanation might be that the sediment desorption rate $K_3$ controls the release of phosphorus from the lake bottom to the lake water. Sediment solid phase and interstitial phosphorus concentrations are sensitive to variations as small as 1% in the value of $K_1$.

Figure 21 shows that a 5% variation in the sedimentation rate ($K_2$) affects the lake water phosphorus concentration in the early stages of the lake recovery. The effect of variations of $K_2$ diminishes as the time horizon increases. In contrast, varying $K_2$ affects long term predictions of the sediment solid phase and interstitial phosphorus concentrations.

Figures 22 and 23 show that the sensitivity of the lake water equation to the phosphorus desorption rate ($K_3$) and sediment reactive depth ($Dr$) is comparable to the sensitivity to $K_2$. The value of $K_2$, $K_3$, or $Dr$ used is most important when making predictions of less than five years. The sediment interstitial phosphorus concentration is significantly affected by varying the values of $K_3$ and $Dr$ ($t < 5$ years) but grows sensitive to $K_2$ for
Figure 20. Sensitivity of model to release rate constant $K_1$. 
Figure 21. Sensitivity of model to release rate constant $K_2$. 
Figure 22. Sensitivity of model predictions to sediment phosphorus desorption rate constant $K_3$. 
Figure 23. Sensitivity of model to sediment reactive depth Dr.
Figure 24. Sensitivity of model to flow rate $Q$. 

- $-10\% \ Q = 4.4 \times 10^4 \ m^3/\text{day}$
- $\ Q = 4.9 \times 10^4 \ m^3/\text{day}$
- $+10\% \ Q = 5.3 \times 10^4 \ m^3/\text{day}$
Table 3. Values for initial conditions and model parameters used in sensitivity analysis.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial conditions:</strong></td>
<td></td>
</tr>
<tr>
<td>Lake Water Phosphorus Concentration ( (P_{Lo}) )</td>
<td>90 ( \mu g/l )</td>
</tr>
<tr>
<td>Sediment Interstitial Water Phosphorus Concentration ( (P_{io}) )</td>
<td>440.5 ( \mu g/l )</td>
</tr>
<tr>
<td>Sediment Solid Phase Phosphorus Concentration ( (P_{so}) ) *</td>
<td>2.6769 (mg/g) dry</td>
</tr>
<tr>
<td>Phosphorus Loading ( (t &gt; 0) ) ( (P_{t}) )</td>
<td>50 ( \mu g/l )</td>
</tr>
<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>( K_3 )</td>
<td>( 10^{-3} /day )</td>
</tr>
<tr>
<td>( Dr )</td>
<td>0.1 m</td>
</tr>
<tr>
<td>( Q )</td>
<td>( 4.89(10)^4 ) m(^3)/day</td>
</tr>
<tr>
<td>( V_L )</td>
<td>( 4.35(10)^5 ) m(^3)</td>
</tr>
<tr>
<td>( A )</td>
<td>( 2.572(10)^5 ) m(^2)</td>
</tr>
<tr>
<td>Exchangeable Sediment Solid Phase Phosphorus ( (% \text{ Exch.}) )</td>
<td>25.0%</td>
</tr>
</tbody>
</table>

\*Sediment solid phase phosphorus concentration \( (P_{so}) \) is calculated by:
\[
P_{so} = P_{s} (\text{mg/g})_{\text{dry}} \times 10^6 \times (\% \text{ Exch.})/(\text{sp. Gr.} = 2.5)\]
t > 5 years. Long term predictions of more than 5 years of sediment solid phase phosphorus concentrations are sensitive to the value of $K_2$ and $K_3$ chosen.

Varying the flow rate ($Q$) (Figure 24) in the lake model equations produces small changes in predicted phosphorus concentrations. The sensitivity of the lake water equations to $Q$ is constant over time. The sensitivity of the sediment interstitial and sediment solid phase phosphorus concentration to $Q$ increases slightly over time.

Prediction of the dynamic response of the lake water phosphorus concentration from 90 to 70, 50 and 30 ($\mu g/l$) are shown in Figure 17. Significant reduction in lake water phosphorus concentration occurs within a few hydraulic detention times due to dilution. The rate of reduction in phosphorus concentration is controlled thereafter by sedimentation and internal phosphorus cycling.

It is expected that the sensitivity to input parameters of the equations obtained by approximation techniques, would be very similar to the sensitivity characteristics shown by the equations obtained by the trial function method.
Phosphate, an essential plant nutrient, is often limiting to plant growth in natural aquatic ecosystems. Total phosphorus is the best index of the biologically available phosphorus. Mass balance models on lake water total phosphorus are useful for predicting the dynamic response of lake phosphorus concentration to pollution control measures. Eutrophic lake bottoms often contain a significant reservoir of phosphorus which may be released to the overlying water and delay the recovery of eutrophic lakes.

Investigations of the hydrogeologic setting of a lake can provide good "first cut" information on the importance of ground water-lake interaction. Seepage meters can be used to measure the magnitude, direction and distribution of ground water interaction with lakes. However, these devices are not considered reliable for sampling seepage water for chemical analysis.

Lake Warner received wastewater overflows from the Amherst Wastewater Treatment Plant for about ten years and began to exhibit eutrophic characteristics. Wastewater overflows were stopped in November, 1975, making Lake Warner a good site for testing mathematical models for the recovery of a eutrophic lake.

Field measurements on the lake phosphorus budget indicated sediment phosphorus release during high water temperature and low
flow conditions. A cursory hydrogeologic study of Lake Warner suggested that ground water would discharge into the lake on one side and recharge the ground water aquifer on the other side. Field measurements using seepage meters verified this hypothesis, but showed that ground water was an insignificant component of Lake Warner's water and phosphorus budget and could therefore be neglected in the phosphorus mass balance model. Seepage water samples were not considered representative of sediment pore water chemical composition.

A mass balance on Lake Warner phosphorus indicated that the lake sediments released phosphorus on the July 1981 sampling date and retained phosphorus during September 1981.

The analytical expression for the lake recovery model is a valuable tool for predicting the response of completely mixed lakes, with short water residence times, to changes in phosphorus loading. The implementation of the model for planning, management and research purposes has been facilitated by the development of an analytical expression of the model as opposed to numerical solutions which require the use of high speed computers.

The approximate solutions to the lake model equations are more easily programmed and convenient to use on the TI-59 programmable calculator than are the analytical equations obtained from the trial function method. The short term lake
phosphorus equation (equation (4.25)) is very easy to use and can be programmed on calculators with only limited programming capabilities.

The close agreement between the curves obtained by the two solution methods suggests the use of the approximate equations for "first cut" predictions of lake recovery.

Future research on the behavior of conservative materials in deposit-water systems as well as planning and management activities is facilitated by the convenience of the analytical expression of the lake recovery model. Sensitivity analysis on equation (4.21) shows that the value of parameters $K_2$, $K_3$ and $D_r$ significantly affect model predictions in the early stages of lake recovery. Care should be taken in estimating the value of these parameters for use in the lake model.

It is recommended that researchers seek to refine the values of reaction rates for particular lakes and that field data used in conjunction with sensitivity analysis be carried out for a wide range of lake systems. As a wider range of lake systems are studied, and more data are accumulated on physical, chemical and biological characteristics of lake bottoms, efforts should be made to compile guidelines which can be employed by model users for choosing the values of reaction rates which would apply to lakes under consideration.

Although beyond the scope of this study it is suggested that efforts be made to relax the assumption of a constant conversion rate ($K_3$) between sediment solid phase phosphorus and sediment
interstitial phosphorus. A time-dependent $K_3$ would, however, increase the mathematical complexity of the model. Some of the following suggestions might be considered:

1) Use low values of $K_3$ for the winter season and high values of $K_3$ for the summer season. Calculate new parameters for each season. Determine the values of the seasonal $K_3$ values by field investigations.

2) Concentrate on determining the value of $K_3$ which would accurately depict sediment conditions in the summer. Sediment phosphorus release during the summer supports biological activity and is, therefore, of interest.
REFERENCES


APPENDIX A

1. MILL RIVER STAGE DISCHARGE CURVES
2. ORTHOPHOSPHATE CALIBRATION CURVE
3. TOTAL PHOSPHORUS CALIBRATION CURVE
Figure 25. Stage-discharge curve of the Mill River (low flow) at the inlet of Lake Warner.
Figure 26. Stage-discharge curve of the Mill River (low flow) at the outlet of Lake Warner.
Figure 27. Orthophosphate calibration curve.
Figure 28. Total phosphorus calibration curve.
APPENDIX B

MATHEMATICAL METHODS
Introduction

The modified Snow and DiGiano (1976) lake recovery model consists of a system of linear first order ordinary differential equations with constant coefficients. Methods for solving such a system of differential equations include:

i) The Laplace transform method

ii) The power series method

iii) The eigenvalue method

iv) The trial function method

v) Numerical methods

iv) Other methods

Snow and DiGiano (1976) and Bingham and Feng (1980) used numerical methods to solve the lake recovery model. The analytical expression for the lake recovery model presented here was developed using the trial function method. In the trial function method the number of homogeneous differential equations (n) to be solved simultaneously is related to the number of algebraic equations (N) needed to solve for the unknown coefficients by equation (7.1):

\[ N = n^n + n \]  \hspace{1cm} 7.1

As can be seen from Table 3 the trial function method was a reasonable approach for the solution of the lake recovery model
as there are three differential equations to be solved simultaneously. These simultaneous differential equations are probably the maximum which can be conveniently solved by the trial function method.

Table 4. Number of algebraic equations needed to solve for the coefficients in a system of homogeneous ordinary differential equations.

<table>
<thead>
<tr>
<th>Number of Ordinary Differential Equations</th>
<th>Number of Simultaneous Algebraic Equations to Solve for the Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>N</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>260</td>
</tr>
<tr>
<td>5</td>
<td>3,130</td>
</tr>
<tr>
<td>6</td>
<td>46,662</td>
</tr>
</tbody>
</table>

The form of the trial function to be postulated for the solution of homogeneous and nonhomogeneous linear first order ordinary differential equations with constant coefficients is discussed below.
Homogeneous case. Given a simple ordinary differential equation:

\[ \frac{dX}{dt} = C_1 X \]  

7.2

with initial conditions:

\[ X(0) = X_0 \]  

7.3

a trial function of the form

\[ X(t) = m e^{\alpha t} \]  

7.4

should be postulated. Taking the derivative of equation (7.4) with respect to \( t \) yields:

\[ \frac{dX}{dt} = m e^{\alpha t} \]  

7.5

substituting (7.4) and (7.5) into equation (7.2) yields:

\[ \alpha m e^{\alpha t} = C_1 m e^{\alpha t} \]  

7.6

Hence, the rate coefficient (\( \alpha \)) can be found by solving a linear equation:

\[ \alpha = C_1 \]  

7.7

The initial conditions

\[ X(0) = X_0, \quad t = 0 \]  

7.3
can be applied to equation (7.4) to yield:

\[ X(0) = m \]  

Substituting equation (7.8) into equation (7.3) yields:

\[ m = X_0 \]  

The solution for the homogenous equation (7.2), therefore, is:

\[ X(t) = X_0 e^{C_1 t} \]  

which is the same equation that one would obtain by integration of equation (7.2) and the application of the initial conditions.

Similarly one would postulate trial functions of the form:

\[ X(t) = m_1 e^{\alpha_1 t} + m_2 e^{\alpha_2 t} \]  
\[ Y(t) = n_1 e^{\alpha_1 t} + n_2 e^{\alpha_2 t} \]

to represent a system of homogeneous ordinary differential equations of the form:

\[ \frac{dX}{dt} = C_1 X + C_2 Y \]  
\[ \frac{dY}{dt} = C_3 X + C_4 Y \]

Here, the values of \( \alpha_1 \) and \( \alpha_2 \) would be the roots of a quadratic equation.
Nonhomogeneous case. There are two possible forms of trial function that one could postulate to represent the solution to an ordinary nonhomogeneous differential equation of the form

\[
\frac{dX}{dt} = C_1 X + C_2
\]

with \( X = X_0, \quad t = 0 \)

\[ X = X_\infty, \quad t \to \infty \]

One form of trial function that one might postulate as a solution to equation (7.15) is:

\[
X(t) = m_1 (1 - e^{-\alpha t}) + m_2 e^{\alpha t}
\]

where the first term on the right-hand side of equation (7.18) represents the nonhomogeneous portion of the solution to equation (7.15) and the second term allows for a finite initial condition.

Solving the (n) simultaneous algebraic equations to find the coefficients of the trial function that represent (N) ordinary differential equations can be simplified by converting the nonhomogeneous ordinary differential equations to homogeneous ordinary differential equations. This can be done by setting the left-hand side of the ordinary nonhomogeneous equation equal to zero and solving for the dependent variables. A change of variable is then employed such that the nonhomogeneous ordinary differential equation becomes homogeneous. This is the method employed in the solution to the lake recovery model.
The modified Snow and DiGiano model presented by Bingham and Feng (1980) to which the trial function method is applied is:

- **Sediment Solid Phase Phosphorus**

\[
V_s \frac{dP}{dt} = V_L K_{PL} - V_{s} K_{PS} \tag{4.13}
\]

- **Sediment Interstitial Phosphorus**

\[
\mathcal{E} V_s \frac{dP_i}{dt} = V_s K_{PS} - \mathcal{E} \Lambda K_{1} (P_i - P_L) \tag{4.17}
\]

- **Lake Water Phosphorus**

\[
V_L \frac{dP_L}{dt} = QP_O - QP_L + \mathcal{E} \Lambda K_{1} (P_i - P_L) - V_{L} K_{2} P_L \tag{4.19}
\]

rearranging

\[
\frac{dP}{dt} = X_{1} P_s + X_{2} P_L \tag{4.18}
\]

\[
\frac{dP_i}{dt} = X_{3} P_s + X_{4} P_i + X_{5} P_L \tag{4.19}
\]

\[
\frac{dP_L}{dt} = X_{6} P_i + X_{7} P_L + X_{8} \tag{4.20}
\]
where

\[ x_1 = -K_3 \]
\[ x_2 = K_2 V_L/V_s \]
\[ x_3 = K_3/\varepsilon \]
\[ x_4 = -AK_1/V_s \]
\[ x_5 = AK_1/V_s \]
\[ x_6 = \varepsilon AK_1/V_L \]
\[ x_7 = -(Q + \varepsilon AK_1 + K_2 V_L)/V_L \]
\[ x_8 = P_0 Q/V_L \]

These nonhomogeneous ordinary differential equations were converted to homogeneous equations by employing a change of variables so that the function \( h \) describes the departure from steady state conditions.

Figure 29. The function \( h \) describes the departure from steady state conditions.
\[ h_s(t) = P_s(t) - P_s^\infty \] 7.19
\[ h_i(t) = P_i(t) - P_i^\infty \] 7.20
\[ h_L(t) = P_L(t) - P_L^\infty \] 7.21

Hence, the homogeneous expression for the lake recovery model becomes:

\[ \frac{dh_s}{dt} = X_1 h_s + X_2 h_L \] 7.22
\[ \frac{dh_i}{dt} = X_3 h_s + X_4 h_i + X_5 h_L \] 7.23
\[ \frac{dh_L}{dt} = X_6 h_i + X_7 h_L \] 7.24

The steady state conditions \( P_s^\infty, P_i^\infty \) and \( P_L^\infty \) were found by setting the left hand sides of equations (4.13, 4.17 and 4.9) equal to zero and solving for \( P_s, P_i \) and \( P_L \), respectively.

\[ P_s^\infty = \frac{K_v P_o}{K_3 V_s} \] 7.25
\[ P_i^\infty = \frac{K_v P_o}{\xi K_i A} + P_o \] 7.26
\[ P_L^\infty = P_o \] 7.27

After a change of variable has been employed (equations 7.19, 20 and 21) to convert nonhomogeneous equations to homogeneous equations the trial function must satisfy the initial conditions:

\[ h = h_o, \quad t = 0 \]
Hence, the trial function for the sediment solid phase phosphorus concentration \( h_s(t) \), the sediment interstitial phosphorus concentration \( h_i(t) \) and the lake water phosphorus concentration \( h_L(t) \) can be postulated:

\[
\begin{align*}
  h_s(t) &= S_1 e^{\alpha t} + S_2 e^{\beta t} + S_3 e^{\gamma t} & \text{7.28} \\
  h_i(t) &= I_1 e^{\alpha t} + I_2 e^{\beta t} + I_3 e^{\gamma t} & \text{7.29} \\
  h_L(t) &= L_1 e^{\alpha t} + L_2 e^{\beta t} + L_3 e^{\gamma t} & \text{7.30}
\end{align*}
\]

with initial conditions

\[
\begin{align*}
  h_s(0) &= S_1 + S_2 + S_3 & \text{7.31} \\
  h_i(0) &= I_1 + I_2 + I_3 & \text{7.32} \\
  h_L(0) &= L_1 + L_2 + L_3 & \text{7.33}
\end{align*}
\]

Taking the derivatives of equations (7.28, 29 and 30) yields:

\[
\begin{align*}
  \frac{dh_s}{dt} &= \alpha S_1 e^{\alpha t} + \beta S_2 e^{\beta t} + \gamma S_3 e^{\gamma t} & \text{7.34} \\
  \frac{dh_i}{dt} &= \alpha I_1 e^{\alpha t} + \beta I_2 e^{\beta t} + \gamma I_3 e^{\gamma t} & \text{7.35} \\
  \frac{dh_L}{dt} &= \alpha L_1 e^{\alpha t} + \beta L_2 e^{\beta t} + \gamma L_3 e^{\gamma t} & \text{7.36}
\end{align*}
\]

Applying equations (7.28, 29, 30, 34, 35 and 36) to equations (7.22, 23 and 24) yields:

\[
\begin{align*}
  \alpha S_1 e^{\alpha t} + \beta S_2 e^{\beta t} + \gamma S_3 e^{\gamma t} &= x_1 [S_1 e^{\alpha t} + S_2 e^{\beta t} + S_3 e^{\gamma t}] + x_2 [L_1 e^{\alpha t} + L_2 e^{\beta t} + L_3 e^{\gamma t}] & \text{7.37}
\end{align*}
\]
Equating the coefficients of $e^{at}$, $e^{bt}$ and $e^{ct}$ in equations (7.37, 38 and 39) yields three sets of equations.

\[
\alpha I_1 e^{at} + \varnothing I_2 e^{bt} + \gamma I_3 e^{ct} = X_3 \left[ S_1 e^{at} + S_2 e^{bt} + S_3 e^{ct} \right] + X_4 \left[ L_1 e^{at} + L_2 e^{bt} + L_3 e^{ct} \right] + X_5 \left[ L_1 e^{at} + L_2 e^{bt} + L_3 e^{ct} \right] + X_7 \left[ L_1 e^{at} + L_2 e^{bt} + L_3 e^{ct} \right]
\]

Equating the coefficients of $e^{at}$, $e^{bt}$ and $e^{ct}$ in equations (7.37, 38 and 39) yields three sets of equations.

\[
\alpha S_1 = X_1 S_1 + X_2 L_1 \\
\alpha I_1 = X_3 S_1 + X_4 I_1 + X_5 L_1 \\
\alpha L_1 = X_6 I_1 + X_7 L_1 \\
\varnothing S_2 = X_1 S_2 + X_2 L_2 \\
\varnothing I_2 = X_3 S_2 + X_4 I_2 + X_5 L_2 \\
\varnothing L_2 = X_6 I_2 + X_7 L_2 \\
\gamma S_3 = X_1 S_3 + X_2 L_3 \\
\gamma I_3 = X_3 S_3 + X_4 I_3 + X_5 L_3 \\
\gamma L_3 = X_6 I_3 + X_7 L_3
\]

The above yields 9 equations and 12 unknowns. Three more equations that make the solution possible are the initial conditions:
\[ h_{so} = S_1 + S_2 + S_3 \]  
\[ h_{io} = I_1 + I_2 + I_3 \]  
\[ h_{lo} = L_1 + L_2 + L_3 \]  

Solving for \( \alpha, \beta \) and \( \gamma \). Each set of equations (7.40.1, 2 and 3), (7.41.1, 2 and 3) and (7.42.1, 2 and 3) can be reduced by substitution, to a cubic equation in \( \alpha, \beta \) and \( \gamma \), respectively. As an example, equations (7.40.1, 2 and 3) will be solved to arrive at the cubic equation.

Solving for \( S_1 \) in equation (7.40.1) yields:

\[ S_1 = \frac{X_2 L_1}{(\alpha - X_1)} \]  

Solving for \( I_1 \) equation (7.40.3) yields:

\[ I_1 = \frac{L_1 (\alpha - X_7)}{X_6} \]  

Substituting equations (7.43) and (7.44) into equation (7.40.2) yields a cubic equation in \( \alpha \).

\[ \alpha^3 - (x_1 + x_7 + x_4)\alpha^2 + (x_1 x_7 + x_1 x_4 + x_4 x_7 - x_5 x_6)\alpha \\
+ x_1 x_2 x_5 x_6 - x_1 x_4 x_7 - x_2 x_3 x_6 = 0 \]  

Using a similar procedure on equation sets (7.41.1, 2 and 3) and 7.42.1, 2 and 3) identical equations in \( \beta \) and \( \gamma \) can be found.
Hence values for $\alpha$, $\varphi$ and $\gamma$ to be used in the lake recovery model are determined to be the roots of equation (4.24).

The roots of equation (4.24) are found using a trigonometric formulation described by Tuma (1979). The general form of equation (4.24) can be expressed as:

$$ar^3 + br^2 + cr + d = 0$$  \hspace{1cm} 7.45.1

The roots $r_1$, $r_2$ and $r_3$ of equation 7.45.1 are:

$$r_1 = 2 \sqrt{|P|/3} \cos \varphi/3 - b/3a$$  \hspace{1cm} 7.45.2

$$r_2 = -2 \sqrt{|P|/3} \cos (\varphi + \pi)/3 - b/3a$$  \hspace{1cm} 7.45.3

$$r_3 = -2 \sqrt{|P|/3} \cos (\varphi - \pi)/3 - b/3a$$  \hspace{1cm} 7.45.4

with

$$P = \frac{[3(c/a) - (b/a)^2]/3}{3}$$  \hspace{1cm} 7.45.5

$$\varphi = \cos^{-1} \left[ -\frac{q/2}{\sqrt{|P|^{3/2} 7}} \right]$$  \hspace{1cm} 7.45.6

where

$$q = \left[ 2(b/a)^3 - 9(b/a)(c/a) + 27(d/a) \right]/27$$

Solving for $P_{L}(t)$, $P_{I}(t)$ and $P_{S}(t)$. Finding the solution to equations $P_{L}(t)$, $P_{I}(t)$ and $P_{S}(t)$ requires the evaluation of the constants $L_1$, $L_2$, $L_3$, $I_1$, $I_2$, $I_3$, and $S_1$, $S_2$, $S_3$ in equations (7.30), (7.29) and (7.28), respectively. This was done by applying equations (7.40.1) through (7.42.3) to the equations defining the initial conditions (equations 7.31, 32 and 33). For
example, to find the constants $L_1$, $L_2$ and $L_3$, equations (7.40.1) through (7.42.3) are employed to find expressions for the constants $S_1$, $S_2$, $S_3$, $I_1$, $I_2$ and $I_3$ in terms of the constants $L_1$, $L_2$ and $L_3$. Hence, for the example of the lake water equations, one obtains:

\[
\begin{align*}
  h_{so} &= AL_1 + BL_2 + CL_3 & \text{(7.46.1)} \\
  h_{io} &= DL_1 + EL_2 + FL_3 & \text{(7.46.2)} \\
  h_{lo} &= L_1 + L_2 + L_3 & \text{(7.46.3)}
\end{align*}
\]

where $A$ through $F$ are defined by equations (4.21.1) through (4.21.6), respectively.

To find $P_L(t)$ the algebraic equations (7.46.1), (7.46.2) and (7.46.3) must be solved simultaneously to find $L_1$, $L_2$ and $L_3$. Substituting the expressions for $L_1$, $L_2$ and $L_3$ into equation (7.30) yields equation (4.21). A similar procedure is used to find the solutions for $P_i(t)$ and $P_s(t)$.

**Order of Magnitude Analysis**

A common method for simplifying a differential equation is to examine the order of magnitude of the terms in the equation. The order of magnitude of parameters in the lake model equations are:
\[ P_s = O [10^5 \mu g/l] - \text{sediment solid phase phosphorus} \]

\[ P_i = O [10^3 \mu g/l] - \text{sediment interstitial phosphorus} \]

\[ P_L = O [10^2 \mu g/l] - \text{lake water phosphorus} \]

\[ Dr = O [10^{-1}] \text{m} - \text{sediment reactive depth} \]

\[ Z = O [1] \text{m} - \text{lake mean depth} \]

\[ T = O [10] \text{days} - \text{lake detention time} \]

\[ K_1 = O [10^{-1}] \text{m/day} - \text{sediment release rate} \]

\[ K_2 = O [10^{-1}] \text{m/day} - \text{sedimentation rate} \]

\[ K_3 = O [10^{-3}] \text{m/day} - \text{sediment desorption rate} \]

\[ \varepsilon = O [1] - \text{sediment porosity} \]

Order of magnitude of the terms in equation (4.18).

\[ O [K_3 P_s] = O [10^2] \]

\[ O [Z K_2 P_L / Dr] = O [10^2] \]

Hence:

\[ O [Z K_2 P_L / Dr] = O [K_3 P_s] \]

Order of magnitude of the terms in equation (4.19).

\[ O [K_3 P_s / \varepsilon] = O [10^2] \]

\[ O [K_1 P_i / Dr] = O [10^3] \]

\[ O [K_1 P_L / Dr] = O [10^2] \]

Hence:

\[ K_3 P_s / \varepsilon, K_1 P_L / Dr \ll K_1 P_i / Dr \]
Order of magnitude of terms in equation (4.20).

\[ O \left( \frac{P_L}{T} \right) = O [10] \]
\[ O \left( \mathcal{E} K P_L / Z \right) = O [10^2] \]
\[ O \left( \mathcal{E} K P_L / Z \right) = O [10] \]

Hence:

\[ P_L / T , \mathcal{E} K P_L / Z \ll \mathcal{E} K P_L / Z \]

Order of magnitude analysis indicates that the order of \( P_i \) is greater than the other terms in equation (4.20). This fact allowed the simplification of the lake water equation for intermediate term predictions.
APPENDIX C

CODING FOR LAKE MODEL EQUATIONS

(TEXAS INSTRUMENTS 59 PROGRAMMABLE CALCULATOR)
PARAMETERS

This program calculates the parameters \((X_1, X_2, X_3, X_4, X_5, X_6, X_7, \alpha, q, \gamma)\) and values of \(P_{i0}, P_{so}, P_{i\infty}\) and stores them in data registers 16, 17, 19 and 20, respectively, for use in the lake recovery model equations \(P_L(t), P_i(t)\) and \(P_s(t)\).

USER INSTRUCTIONS

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Enter</th>
<th>Press</th>
<th>Display</th>
</tr>
</thead>
<tbody>
<tr>
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<td>STO21</td>
<td>(K_1)</td>
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<tr>
<td></td>
<td>(K_2)</td>
<td>STO22</td>
<td>(K_2)</td>
</tr>
<tr>
<td></td>
<td>(-K_3)</td>
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<td>(-K_3)</td>
</tr>
<tr>
<td></td>
<td>(e)</td>
<td>STO24</td>
<td>(e)</td>
</tr>
<tr>
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<td>(D_r)</td>
<td>STO25</td>
<td>(D_r)</td>
</tr>
<tr>
<td></td>
<td>(Q)</td>
<td>STO26</td>
<td>(Q)</td>
</tr>
<tr>
<td></td>
<td>(V_L)</td>
<td>STO27</td>
<td>(V_L)</td>
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<td></td>
<td>(A)</td>
<td>STO28</td>
<td>(A)</td>
</tr>
<tr>
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<td>(P_o)</td>
<td>STO29</td>
<td>(P_o)</td>
</tr>
<tr>
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<td>(P_{LO})</td>
<td>STO30</td>
<td>(P_{LO})</td>
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<tr>
<td>2. Run Program</td>
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<td>R/S</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>3. Continue Program</td>
<td>R/S</td>
<td></td>
<td>(\beta)</td>
</tr>
<tr>
<td>4. Continue Program</td>
<td>R/S</td>
<td></td>
<td>(\delta)</td>
</tr>
<tr>
<td>Parameter</td>
<td>DATA REGISTER</td>
<td>Parameter</td>
<td>DATA REGISTER</td>
</tr>
<tr>
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<td>--------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>input:</td>
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<td></td>
</tr>
<tr>
<td>$K_1$ m/day</td>
<td>21</td>
<td>$X_3$ /day</td>
<td>06</td>
</tr>
<tr>
<td>$K_2$ /day</td>
<td>22</td>
<td>$X_4$ /day</td>
<td>07</td>
</tr>
<tr>
<td>$-K_3$ /day</td>
<td>23</td>
<td>$X_5$ /day</td>
<td>08</td>
</tr>
<tr>
<td>$\mathcal{C}$</td>
<td>24</td>
<td>$X_6$ /day</td>
<td>09</td>
</tr>
<tr>
<td>Dr meters</td>
<td>25</td>
<td>$X_7$ /day</td>
<td>10</td>
</tr>
<tr>
<td>$Q$ m$^3$/day</td>
<td>26</td>
<td>$P$</td>
<td>30</td>
</tr>
<tr>
<td>$V_L$ m$^3$</td>
<td>27</td>
<td>$Q$</td>
<td>31</td>
</tr>
<tr>
<td>$A$ m$^2$</td>
<td>28</td>
<td>$\phi$</td>
<td>32</td>
</tr>
<tr>
<td>$P_0$ $\mu$g/l</td>
<td>29, 18</td>
<td>$b$</td>
<td>34</td>
</tr>
<tr>
<td>$P_{lo}$ $\mu$g/l</td>
<td>15</td>
<td>$c$</td>
<td>35</td>
</tr>
<tr>
<td>$t$ days</td>
<td>00</td>
<td>$d$</td>
<td>36</td>
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Calculated by parameter program:

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<td>16</td>
</tr>
<tr>
<td>$P_{so}$ $\mu$g/l</td>
<td>17</td>
</tr>
<tr>
<td>$P_{l\infty}$ $\mu$g/l</td>
<td>18</td>
</tr>
<tr>
<td>$P_{i\infty}$ $\mu$g/l</td>
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</tr>
<tr>
<td>$\alpha$ /day</td>
<td>01</td>
</tr>
<tr>
<td>$\phi$ /day</td>
<td>02</td>
</tr>
<tr>
<td>$\gamma$ /day</td>
<td>03</td>
</tr>
<tr>
<td>$X_1$ /day</td>
<td>04</td>
</tr>
<tr>
<td>$X_2$ /day</td>
<td>05</td>
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</table>
Figure 30. Coding for TI-59 Programmable Calculator, Parameters Program.
Figure 30. (continued)
LAKE WATER PHOSPHORUS CONCENTRATION

The following program calculates the lake water phosphorus concentration ($P_L(t)$) (equation (4.21)) in response to a change in phosphorus inflow concentration ($P_o = P_L^0$, $t < 0$; $P_o = P_L\infty$, $t \geq 0$). The parameters $X_1$, $X_2$, $X_3$, $X_4$, $X_5$, $X_6$, $X_7$, $\alpha$, $\varphi$ and $\gamma$ from the parameters program must be used.

USER INSTRUCTIONS

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<th>Display</th>
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<td>t</td>
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<td>2. Run program</td>
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<td>E</td>
<td>$P_L(t)$</td>
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<tr>
<td>3. Enter time (days)</td>
<td>t</td>
<td>STO00</td>
<td>t</td>
</tr>
<tr>
<td>4. Run program</td>
<td></td>
<td>R/S</td>
<td>$P_L(t)$</td>
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</table>
Figure 31. Coding for TI-59 Programmable Calculator. The lake model equation \( P(t) \) (4.21) solved by the Trial Function Method.
Figure 31. (continued)
Figure 31. (continued)
SEDIMENT INTERSTITIAL PHOSPHORUS CONCENTRATION

The following program calculates the sediment interstitial phosphorus concentration ($P_i(t)$) (equation (4.22)) in response to a change in the phosphorus inflow concentration ($P_o = P_{LO}$, $t < 0$; $P_o = P_{L\infty}$, $t \geq 0$). The parameters $X_1, X_2, X_3, X_4, X_5, X_6, X_7$, $\alpha$, $\phi$ and $\gamma$ from the parameters program must be used.

USER INSTRUCTIONS

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<th>Procedure</th>
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<td>$P_i(t)$</td>
</tr>
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<td>3. Enter time (days)</td>
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<td>t</td>
</tr>
<tr>
<td>4. Run program</td>
<td></td>
<td>R/S</td>
<td>$P_i(t)$</td>
</tr>
</tbody>
</table>
Figure 32. Coding for TI-59 Programmable Calculator. The model equation \( P(t) \) (4.22) solved by the Trial Function Method.
Figure 32. (continued)
Figure 32. (continued)
SEDIMENT SOLID PHASE PHOSPHORUS CONCENTRATION

The following program calculates the sediment solid phase phosphorus concentration \( P_s(t) \) (equation (4.23)) in response to a change in the phosphorus inflow concentration \( P = P_{Lo}, \ t < 0; \ \ P = P_{Lo}, \ t \geq 0 \). The parameters \( X_1, X_2, X_3, X_4, X_5, X_6, X_7, \infty, \ \phi \) and \( \gamma \) from the parameters program must be used.

USER INSTRUCTIONS

<table>
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<tr>
<th>Procedure</th>
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<th>Press</th>
<th>Display</th>
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</thead>
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<td>ST000</td>
<td>( t )</td>
</tr>
<tr>
<td>2. Run program</td>
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<td>( P_s(t) )</td>
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<tr>
<td>3. Enter time (days)</td>
<td>( t )</td>
<td>ST000</td>
<td>( t )</td>
</tr>
<tr>
<td>4. Run program</td>
<td></td>
<td>R/S</td>
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Figure 33. Coding for TI-59 Programmable Calculator, trial model equation $P(t)$ (4.23) solved by Trial Function Method.
Figure 33. (continued)
0.006305994 01
-2596287671 02
-9726868917 03
-0.00175 04
2.976671851 05
0.0020633333 06
-0.91 07
0.91 08
0.0451962483 09
-3211962483 10
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0.0000000000 12
0.0000000000 13
0.0000000000 14
90. 15
450. 16
375000. 17
50. 18
243.3 19
213000. 20
0.001194006 21
-2578787671 22
-9709368917 23
0.0021922903 24
0.002359698 25
0.0245186247 26
0.0000166436 27
-0.001735783 28
0.000154494 29

Figure 33. (continued)
Equations (4.29, 30 and 31) obtained by approximation techniques.
LAKE WATER PHOSPHORUS CONCENTRATION

Approximate Equation

The following program calculates the lake water phosphorus concentration \( P_L(t) \) (equation (4.31)) in response to a change in the phosphorus inflow concentration \( P_o = P_{Lo}, t < 0; P_o = P_{L\infty}, t \geq 0 \).

USER INSTRUCTIONS

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Figure 34. Coding for TI-59 Programmable Calculator, lake model equation $P_L(t)$ solved by Approximation techniques.
Figure 34. (continued)
SEDIMENT INTERSTITIAL PHOSPHORUS CONCENTRATION

Approximate Equation

The following program calculates the sediment interstitial phosphorus concentration \( P_i(t) \) (equation (4.29)) in response to a change in phosphorus inflow concentration \( P_o = P_{Lo}, \ t < 0; \ P_o = P_{L\infty}, \ t \geq 0 \).

USER INSTRUCTIONS

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Figure 35. Coding for TI-59 Programmable Calculator, lake model equation $P_1(t)$ solved by Approximation techniques.
Figure 35. (continued)
**SEDIMENT SOLID PHASE PHOSPHORUS CONCENTRATION**

**Approximate Equation**

This program calculates the sediment solid phase phosphorus concentration \( P_s(t) \) (equation (4.30)) in response to a change in phosphorus inflow concentration \( P_o = P_{lo}, \ t < 0; \ P_o = P_{l\infty}, \ t \geq 0 \).

**USER INSTRUCTIONS**

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3. Run program | E | \( P_i(t) \) |

4. Enter time (days) \( t \) | ST000 | \( t \) |

5. Run program | R/S | \( P_i(t) \) |
Figure 36. Coding for TI-59 Programmable Calculator, lake model equation P(t) solved by Approximation techniques.
Figure 36. (continued)