PHOSPHORUS UTILIZATION AND RECYCLE IN WASTE STABILIZATION PONDS

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CRWR 203
EHE 83-01

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March 1983

ACKNOWLEDGEMENTS

Gratitude is extended to Gerard A. Rohlich, Dr. Joseph F. Malina, Jr., Dr. Neal E. Armstrong of Environmental Health Engineering, and Dr. Orville Wyss of Microbiology for their precious comments.

Special thanks to Dr. Jose M. Roesset and Dr. Desmond F. Lawler for their gracious advice on computer simulation and analysis, to Mr. Frank Hulsey for his assistance in the experimental work, and to the staff of Govalle Wastewater Treatment Plant, who provided the wastewater samples.

ABSTRACT

Waste stabilization ponds frequently provide the most economic and effective way for wastewater treatment. The fact that waste stabilization ponds do not require as much operation and maintenance and are generally not as expensive to construct as other conventional wastewater treatment processes makes the pond systems attractive.

An investigation was conducted to verify the phosphorus utilization and recycle in waste stabilization pond systems and to evaluate the role of sediment in the recycle of phosphorus. Two pond systems, I and II, were operated under three different loading conditions during a period of 22 months.

System I consisted of series-connected anaerobic, facultative and maturation (polishing) ponds. System II was similar to System I with the exception that there was no anaerobic pond.

Pond performance was evaluated on the basis of organic removal. Total phosphorus, organic phosphorus, and inorganic phosphorus were measured on a routine basis.

Two mathematical models were developed to evaluate phosphorus uptake and recycle in the waste stabilization pond systems. The model-generated data provided reliable results and proved to be consistent with the observed data. System I consisted of series-connected anaerobic, facultative and maturation (polishing) ponds. System II was similar to System I with the exception that there was no anaerobic pond.

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CONCLUSIONS

Based on the results of this study, the following conclusions can be drawn:

1. Both the total phosphorus model and the organic-inorganic phosphorus model, which are based on first-order kinetic reactions, are suitable predictors for phosphorus behavior such as phosphorus recycle, phosphorus release from the sediment and phosphorus removal efficiency in waste stabilization ponds. The organic-inorganic phosphorus provides information on the phosphorus uptake and phosphorus release associated with the synthesis and decomposition of microorganisms.
2. The uptake of inorganic phosphorus was found to occur mainly in the water column of the facultative waste stabilization pond (FWSP) and the maturation waste stabilization pond (MWSP). Only three percent to ten percent of inorganic phosphorus uptake occurred in the anaerobic waste stabilization pond (AWSP). The high uptake rates for the FWSP and the MWSP were related to the algal population in the FWSP and the MWSP.
3. The release rates of phosphorus were greater for the AWSP (0.20-0.27 cm/d) and the FWSP (0.11-0.15 cm/d) as compared to the MWSP (0.004-0.008 cm/d). The release rates for the AWSP and the FWSP were about 25 to 50 times greater than that found for the MWSP. Therefore, the sediments of the AWSP and the FWSP, in case of phosphorus shortage, may be a phosphorus source. On the other hand, the fact that the sediment in the MWSP retained most of the deposited phosphorus, might aid in maintaining receiving water quality control. The low phosphorus release rate from the pond sediment in the MWSP supported the hypothesis that the aerobic layer of the sediment surface played a major role in the phosphorus release mechanism.
4. The phosphorus recycle in the MWSP was obscured because the deposition and release rates for the MWSP were low. There appeared to be little interchange between the phosphorus in the water column and the sediment of the MWSP. The solid deposition rates for the AWSP and the FWSP were about 20 to 60 times greater than than experienced by the MWSP. The incoming settlable solids deposited in the AWSP and the FWSP were largely decomposed by microorganisms. The dissolved inorganic phosphorus, one of the products of the decomposition processes, was released to the pond water column.

5. A series connected system, including AWSP, FWSP and MWSP, appears to be the most effective treatment system for phosphorus recycling and removal. Phosphorus removal from the liquid substrate mainly occurred in the AWSP and the FWSP while the MWSP, excluding algal uptake, did not contribute significantly to phosphorus removal. In the case of phosphorus deficiency in a liquid substrate, the sediments of the AWSP and the FWSP can supply the necessary phosphorus. In the MWSP, the utilization of phosphorus by algae caused the percentage of organic phosphorus to increase. In addition, the sediment in the MWSP may retain most of the phosphorus and not release it into the overlying water because of the predominantly aerobic environment.
6. In the application of the phosphorus models, the important physical, chemical, and biological constants, as well as other pertinent information, have to be determined carefully in order to arrive at accurate predictions. Based on the sensitivity analyses, coefficients K_1, K_2, K_3, k_1, and k_2 were important parameters for estimating concentrations of both phosphorus in the water column and in the sediment, coefficients k_3, u_1, and u_2 were important parameters for evaluating concentration of the phosphorus in the water column, and coefficients k_4, u_3, and u_4 were significant in determining phosphorus levels in the sediment. A constant k_5 value may be used without appreciably affecting either the phosphorus concentrations in the water column or the sediment.
7. The fourth-order Runge-Kutta numerical technique proved to be useful in developing phosphorus uptake and release models. The equations of the phosphorus models provided stable and convergent solutions.

RECOMMENDATIONS

The following points were extracted from this study for future consideration:

1. In this study, only the experimental data were evaluated. The data from field ponds were insufficient for verifying the phosphorus models. Little literature was available for describing benthic processes contributing to the uptake and release of phosphorus. Neither inorganic and organic phosphorus concentrations nor total phosphorus concentration in the sediment was available for model verification. The organic-inorganic phosphorus model can better express the biochemical processes and provide more detailed information. Therefore, the inorganic phosphorus and organic phosphorus fractions, instead of total phosphorus, should be measured.
2. Since this study was conducted in a constant temperature ($20 \pm 1^{\circ}C$) room, no temperature factor was considered in these models. Though the release rate of phosphorus was reported to be independent from temperature (Brown 1975), the precipitation rate, synthetic coefficients, and decomposition coefficients are all functions of temperature.
3. Waste stabilization ponds generally perform in a plug-flow manner. Even with typical wind and thermal influences, completely mixed conditions can not be attained in waste stabilization ponds. Since stratification may exist in field installations, some modification may be necessary when the laboratory derived models are applied. The phosphorus models may be improved if field data become available.

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CHAPTER I

INTRODUCTION

Waste stabilization ponds have long been used for storing and treating municipal, industrial, and agricultural wastewaters. In the past few decades, design for these ponds have been developed and standardized. As a result, they have been used to facilitate the treatment and the disposal of a wide variety of wastewaters. Since the waste stablilization pond systems may be the simplest and the least energy intensive method for wastewater treatment, they are especially preferred by both the developing countries and those areas in which more costly techniques are prohibitively expensive (EPA 1979; Gloyna, 1971 & 1978). In addition, compared to the high-rate biological systems which achieve similar levels of effluent quality, waste stabilization ponds require negligible energy, and this advantage is an important consideration in these days of high energy costs (Gloyna & Tischler 1981).

The effectiveness of the performance of waste stabilization ponds depends on bacterial decomposition of organic matter. In facultative and aerobic waste stabilization ponds, bacterial decomposition mainly occurs under facultative and aerobic conditions. The algae utilize the bacterial decomposition products, such as carbon dioxide, as the primary carbon source. With the aid of solar energy, the chlorophyll in the algal cell produces oxygen photosynthetically. The excess oxygen can be used by aerobic and facultative bacteria to transform complex waste products into simple by-products. Thus, the algal growth in these waste stabilization ponds is an essential factor for purifying wastewater.

Phosphorus, like nitrogen, is essential for the growth of microorganisms involved in biodegradation processes and photosynthetic oxygen production. Therefore, phosphorus utilization and recycle in waste stabilization ponds is an important design consideration. An understanding of the exchange of phosphorus between pond sediments and the overlying water column is important in establishing optimum pond performance. Phosphorus, in contrast to nitrogen, does not enter the pond system by atmospheric fixation. This feature may simplify the predictive phosphorus transfer model.

Mathematical modeling techniques can provide a systematic basis for evaluating the behavior of complex ecosystems. Such models may aid in evaluating various management options for nutrient additions or control. Total phosphorus and organic-inorganic phosphorus models should help in predicting phosphorus concentrations in pond effluents and in establishing the availability of various phosphorus forms. Such information should be useful in evaluating the extent of phosphorus recycling that occurs in waste stabilization ponds.

1.1 OBJECTIVES

The purpose of this study was to illustrate the utilization and recycle of phosphorus in waste stabilization ponds. Specifically, the objective was to develop predictive models that could be used to evaluate the uptake, release and recycle of phoshorus and to predict the phosphorus concentrations in the effluent of anaerobic, facultative and maturation (polishing) waste stabilization ponds.

1.2 SCOPE

This study was limited to the use of predictive models and laboratory studies in which two ponds systems were used. "System I" utilized three ponds in series while "System II" used two series-connected ponds. Organic loadings for the facultative waste stabilization ponds were based in part on a previously developed equation (Gloyna 1971). Three different phosphorus loadings were applied to these ponds. All studies were conducted at a temperature of $20 \pm 1^{o}C$.

An analytical solution of the total phosphorus model was obtained by Laplace transformation while the Rung-Kutta's fourth-order numerical method was used to solve the organic-inorganic phosphorus model.

The observed data were compared with the computed data and all the parameters and coefficients in the phosphorus models were determined by means of multiple regression.

Specific tasks were limited to:

1. develop mathematical models for evaluating phosphorus recycle in waste stabilization ponds;

2. predict the phosphorus concentration in the effluent based on influent phosphorus concentrations and pond operating conditions;

3. validate biological growth coefficients relating to substrate utilization, microbial decay, and biomass yield;

4. evaluate the role of sediments in phosphorus recycle; and

5. test the phosphorus models in the formulation of designs for waste stabilization pond.

CHAPTER 2

LITERATURE EVALUATION

Relevant literature is evaluated in this chapter, and the topics to be discussed include: waste stabilization ponds, nutrient requirements of algae and bacteria, phosphorus regeneration, phosphorus recycle, and models applicable for predicting the reutilization of phosphorus in waste stabilization ponds.

2.1 WASTE STABILIZATION PONDS

Waste stabilization ponds are designed to treat wastes under conditions which favor natural purification. Such waste stabilization pond systems are generally designed to treat raw, settled, or partially treated municipal and industrial effluents. These ponds may be used to pretreat wastes, to serve as secondary biological treatment units, and to reduce the concentration of disease-causing agents.

Although waste stabilization ponds require relatively large space, lower capital and maintenance costs make them attractive as alternative wastewater treatment systems. In addition, waste stabilization ponds are relatively simple to construct and operate.

2.1.1 POND CLASSIFICATION

Waste stabilization ponds are classified in accordance with the desired biological activity: aerobic, facultative, or anaerobic (Gloyna 1978 & 1981; Stander & Meiring 1965; Metcalf & Eddy Inc. 1972; Arceivala et al. 1970).

Aerobic waste stabilization ponds, primarily mechanically aerated waste stabilization ponds (MAWSP), biologically stabilize dissolved and suspended substances through the use of aerobic microbial populations. The required oxygen is supplied mostly by mechanical devices and oxygen transfer at the pond surface, although there may be some algal contribution to the oxygen supply.

The BOD reduction in aerobic ponds frequently ranges between 50 percent to 95 percent. Although a high percentage of BOD can be removed from influent wastewaters, the suspended solids in the effluent wastewater may be relatively high because of the large concentration of bacteria and algae.

Facultative waste stabilization ponds (FWSP) predominantly utilize facultative organisms although there may be anaerobic bacterial populations present at the bottom of the pond. There are usually three zones in facultative and anaerobic zones. The aerobic zone is the surface layer of the pond. The facultative or intermediate zone constitutes the largest volume. The anaerobic bottom zone accumulates the settleable organic material.

Figures 2-1 and 2-2 show the functions and profile of a facultative waste stabilization pond (FWSP). Most of the waste stabilization ponds used today in the United States, as well as in many other countries, are FWSP (Gloyna 1976).

The suspended solids, in the form of algal cells, generally do not impact the receiving water. Gloyna et al. (1981) concluded that algal cells in the effluent from a properly designed and operated pond system do not adversely impact on the dissolved oxygen resources of the receiving waters. Furthermore, algae usually serve as an important link in the food chain present in the receiving water. Frequently, the algal cells augment rather than damage fisheries. Thus, removing solids from waste stabilization pond system effluents, which is considered a costly and energy-intensive process, is a questionable process as far as protection of all water quality is concerned.

The anaerobic waste stabilization ponds (AWSP) are usually 2 to 5 meters (6 to 15 feet) deep. The biological process is similar to that occurring in anaerobic digestion tanks in which organic acid formation is followed by methane fermentation. Although anaerobic ponds may reach BOD removal efficiencies of 85 percent, 60 to 80 percent is more common because the BOD removal efficiency is highly temperature dependent. A major advantage of the anaerobic treatment process is that large land areas are not required as compared to facultative pond systems. However, the anaerobic ponds may produce objectionable odors, and the effluent may exhibit excessive color, suspended solids, and BOD.

2.1.2 POND LAYOUT

Facultative waste stabilization ponds (FWSP) can be used alone or in combination with anaerobic and maturation (polishing) ponds. Parallel operations may also be used. Figure 2-3 shows a number of typical series-connected waste stabilization pond systems (Gloyna 1978).

2.1.3 FACTORS AFFECTING POND PERFORMANCE

Because the performance of waste stabilization ponds depends on the effective use of different biological processes, many operational, environmental, and construction factors must be considered in their design. These factors are listed below:

1. Operational Factors--(a) quantity of waste to be treated; (b) nature of waste, i.e., BOD, suspended solids, pH, toxic substances, temperature, and BOD reaction rate constant "K"; (c) type of pond required, i.e., aerobic, anaerobic, facultative, or combination; and (d) sludge accumulation possibilities,

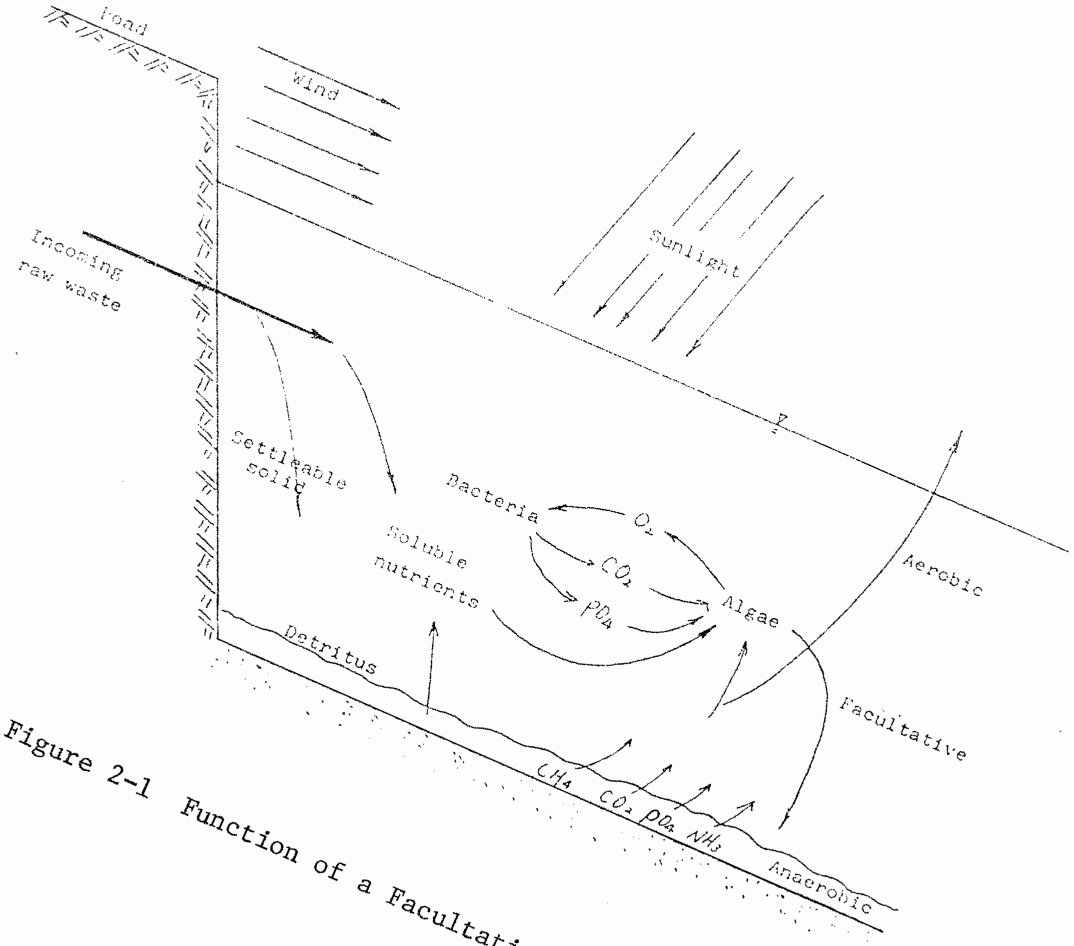


Figure 2-1 Function of a Facultative Waste Stabilization Pond

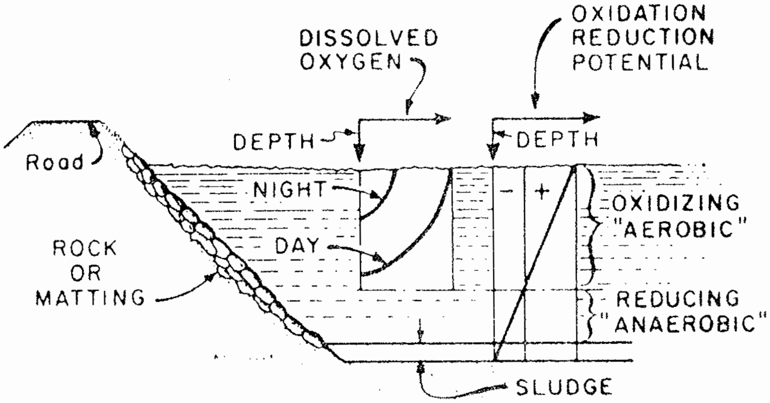
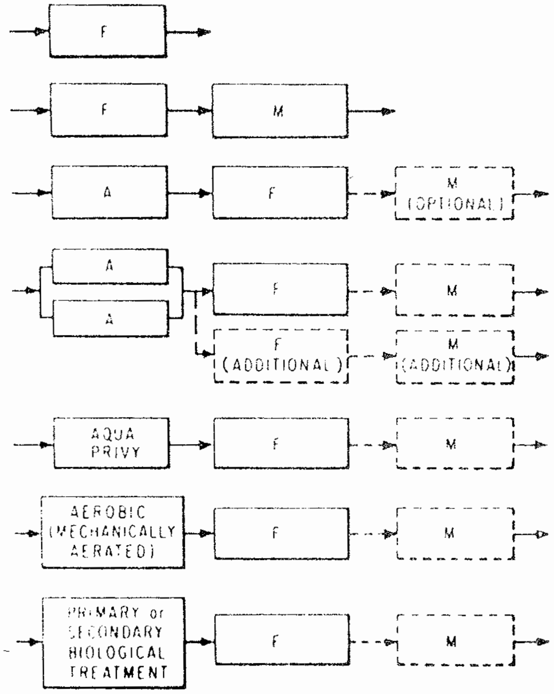


Figure 2-2 A Facultative Waste Stabilization Pond (Gloyna, 1971)



A = Anaerobic Pond.
F = Facultative Pond.
M = Matuation (Polishing) Pond.

Figure 2-3 A Number of Typical Waste Stabilization Pond Systems (Gloyna, 1976)

2. Environmental Factors--(a) water and air temperature, including maximum and minimum temperatures; (b) direction of predominant local winds; (c) light intensity; (d) rainfall; (e) evaporation; (f) topographical features for the selection of the proper site; (g) distance from habitational areas; (h) geological features and soil characteristics; and (i) groundwater level, and

3. Constructional Factors--(a) size, shape, and depth of pond system; (b) embankment requirements; (c) bottom design; and (d) construction consideration such as types of inlets, outlets, and other hydraulic appurtenances.

2.1.4 WASTE STABILIZATION POND DESIGN

A number of studies have been performed on waste stabilization ponds during the past thirty years. However, as shown below, there are limited mathematical models that can be used to either design or predict the performance of waste stabilization ponds.

An empirical equation, which was derived from the experiments using septic tanks in the United States (Weibel et al. 1949) and in Zambia (Vincent et al. 1963), has been suggest for the design of anaerobic ponds. This equation was based on organic loading and detention time. The influent temperature was assumed to be 20°C.

$$L_p = \frac{L_o}{K_n (L_p/L_o)^n \, R + 1} \qquad (2\text{-}1)$$

where

L_o, L_p = influent and effluent BOD respectively, mg/l

R = detention time, days

K_n = BOD removal constant, base e, per day

n = exponent,to be determined by experimentation (for Zambia, $n=4.8$).

For different temperatures, this equation must be changed.

Malina et al. (1976) suggested that anaerobic ponds should be designed on a volumetric loading basis because the anaerobic reactions are affected by detention time and temperature rather than available surface area. The hydraulic detention time in the anaerobic ponds treating municipal wastewaters was suggested to be 2 days during warm weather and 5 days during cool weather because the methane bacteria require relatively long generation times (2 days to 20 days). A pond depth of 6 to 12 feet (2 to 5 meters) should be provided. Enough reserve space should be provided for the accumulated sludge. A volumetric loading from 12 to 25 lbs BOD_5/d/1000 ft^3 (190 to 400 kg BOD_5/d/100 m^3) and/or a surface loading of 400 to 600 lbs BOD_5/ac/d (450 to 700 kg BOD_5/ha/d), and a suspended solid loading of about 100 to 400 lbs/100 ft^3

(1600 to 6400 kg/100 m^3) are also recommended (Gloyna 1971 & 1976; Malina et al. 1976).

The first kinetic model of a facultative waste stabilization pond, which was based on the temperature and rate-dependent theory, was presented by Hermann and Gloyna (1958). Further models were developed by Marais and Shaw (1961), Marais (1966), Huang and Gloyna (1968), and Gloyna and Espino (1969).

Hermann and Gloyna proposed that a first-order reaction took place in a complete mixed pond when the influent BOD was stabilized by facultative organisms. The breakdown, K_T, depends on the temperature as follows:

$$\frac{K_{35}}{K_T} = \theta^{(35 - T)} \tag{2-2}$$

where

T = pond operating temperature, °C

θ = temperature reaction coefficient,

K_{35} = breakdown rate at 35°C.

Marais (1966) analyzed the data obtained by Suwannakarn (1963) from a series of laboratory-scale ponds treating a synthetic, non-settling waste at a number of different temperatures, the values of K_{35} and θ were found to be 1.2 and 1.085 respectively.

The detention time for a fixed percentage of BOD reduction was also temperature dependent. The detention-temperature relationship as originally used by Gloyna (1971) is as follows:

$$\frac{t}{t_o} = \theta^{(T_o - T)} \tag{2-3}$$

where

t = reaction time required at any temperature T, days

t_o = reaction time required at temperature T_o, days

θ = temperature reaction coefficient.

Anaerobic bacteria are not very active below 15°C. The lower temperature retards the activity of many bacteria and algae. The upper temperature limit is imposed by inactivation of many green algal species (Gloyna 1976).

An empirical equation for the design of a facultative waste stabilization pond was established by Gloyna (1971):

$$V = 3.5 \times 10^{-5} Q L_a \theta^{(35 - T)} ff' \tag{2-4}$$

where

V = pond volume, m^3
Q = influent waste flow, l/d
L_a = ultimate influent BOD_u or COD, mg/l
θ = temperature coefficient, 1.085
T = minimum mean monthly temperature of the year, ^{o}C
f = algal inhibition factor:
for domestic wastes, $f = 1$;
for certain industrial pollutants,

$$f = \frac{e^{k}C_o}{K_o t_o + 1},$$

K = chlorophyll inhibition constant for a toxic waste with an observed concentration of C_o,
C_o = observed concentration of a toxic waste,
K_o = observed biodegradation rate constant of the toxic compound,
t_o = reaction time for a rate constant of K and temperature T,
f' = sulfide or other immediate chemical oxygen demand, $f' = 1$ for SO_4^{2-}equivalent ion concentration of less than 500 mg/l.

For conventional units the area of the pond is as follows (Gloyna 1976):

$$A = 2.148 \times 10^{-2} Q L_a \theta^{(35 - T)} f f' \qquad (2\text{-}5)$$

where

A = area of pond for depth of 5 feet (1.5 meter) plus 1 feet (0.3 meter) of sludge storage, acres
Q = waste influent flow, MGD.

The BOD_5 removal efficiency can be expected to be 80 percent to 90 percent as based on unfiltered influent samples and filtered effluent samples. Waste containing significant amounts of sulfates and toxic materials usually require additional detention time and surface area. The recommended minimum depth of a FWSP is one meter. Additional depth to compensate for sludge storage is necessary (Aguirre and Gloyna 1970; Gloyna 1971 & 1976).

Marais and Shaw (1961), in South Africa, observed the maximum BOD load for a FWSP was related to the depth. They introduced the concept of completely mixed waste stabilization ponds, although completely mixed ponds do not exist in natural conditions. Marais and Shaw proposed a kinetic model based on first-order kinetics in completely mixed system with the reaction rate constant independent of temperature:

$$L_p = \frac{L_o}{(K)(R)+1} \qquad (2\text{-}6)$$

where

L_p = influent BOD_5, mg/l
L_o = pond or effluent BOD_5, mg/l
R = detention time, days
K = first order degradation constant, which was found by Marais and Shaw to be about 0.17 days.

This method may be particularly applicable for subtropical areas and domestic wastes containing a high solid-to-water ratio (Gloyna 1976).

Designs of non-mechanically aerated but aerobic ponds are based on the fact that large amounts of algae may be grown (Gloyna 1978). It is important to estimate the density of the algal cells and the oxygen production rate in designing such an aerobic pond. Oswald (1963) formulated the oxygen production rate and the light intensity as shown in Eq. 2-7:

$$O = 0.22\ FI \qquad (2\text{-}7)$$

where

O = oxygen production rate, kg/ha/d
F = light conversion efficiency, which ranges from 0.5 to 0.6 and is a function of light, time, nutrient, and temperature,
I = light intensity, $cal/cm^2/d$.

The algal cell yield has been found to be related to the light conversion efficiency and the solar energy as follows:

$$Y = 0.125\ FI \qquad (2\text{-}8)$$

where

Y = yield of algal cells, kg algae/ha/d.

The ratio between oxygen production and algal cell yield is about 1.6, with the highest BOD removal occurring when the oxygenation factor and the ratio of oxygen produced to oxygen required is at about 1.6.

Since the pathogen control may be one of the important characteristics of waste stabilization ponds, Marais and Shaw (1961) proposed a fecal bacteria relationship:

$$N/No = 1/(KR + 1) \qquad (2\text{-}9)$$

where

N = pond or effluent concentration of fecal bacteria, MPN
No = influent concentration of fecal bacteria, MPN
K = degradation rate constant, per day
R = detention time, days.

The value of K, which was established empirically, was found to be only 0.8 for S. typhi as compared to 2.0 for E. coli (Coetzee and Fourie 1965; Marais 1966). These differences illustrate the fact that it is not appropriate to generalize when extrapolating from indicator organism results to specific disease-causing agents. However, projections made on Eq. 2-9 can provide a useful indication of the degree of general bacterial pollution control that is required (Gloyna 1978).

2.2 ALGAE AND BACTERIA IN FACULTATIVE WASTE STABILIZATION PONDS

Chlamydomonas, Chlorella, Microactinium, Scenedesmus, and Euglena (Allen 1955; Oswald et al. 1957 & 1953; Allen 1955; Gloyna 1971 & 1976; Bold 1978), are generally prominent in facultative waste stabilization ponds. Because of their rapid adaptability to different climatic and environmental conditions, the algal genera mentioned above are found in most of the facultative waste stabilization ponds. Chlorella, Microactinium, and Scenedesmus are non-motile green algae, and Chlamydomonas and Euglena are motile green algae. The former three genera may be unicellular or colonial and are most predominant in aerobic and facultative waste stabilization ponds. The latter two, which have flagella, are able to migrate through the ponds. The other two forms of algae whch are usually found in facultative and aerobic ponds are categorized as blue-green and diatoms.

The blue-green algae are simple forms lacking a defined nucleus. They are frequently termed "nuisance algae" having been associated with odors. Their appearance has been observed to be related to situations of high pH and high temperature. Some common blue-green algae found in facultative waste stabilization ponds are Oscillatoria, Anabaena, and Anacystis. The diatoms have a characteristic silicon dioxide structural framework. The most common diatoms found on ponds are Navicula and Nitzachia.

A simplified expression describing photosynthetic oxygen production is:

$$6CO_2 + 2H_2O \xrightarrow{\text{light}} C_6H_2O_6 + 6O_2 .$$

Algal cell composition is known to vary widely depending on genera, nutrient availability, and other environmental factors. The following are several equations, along with their sources which indicate possible stoichiometry for the major components of cells.

$$106CO_2 + 90H_2O + 16NO_3^- + PO_4^{3-} \longrightarrow C_{106}H_{108}O_{45}N_{16}P + 154.5O_2$$

(Gloyna 1971)

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \longrightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

(Rochow et al. 1974)

$$7.62CO_2 + NH_4^+ + 2.53H_2O \longrightarrow C_{7.62}H_{8.08}O_{2.53}N + 7.62O_2 + H^+$$

(Oswald et al. 1953)

$$5.7CO_2 + NH_3 + 12.5H_2O \longrightarrow C_{5.7}H_{9.8}O_{2.3}N + 6.25O_2 + 9.1H_2O$$

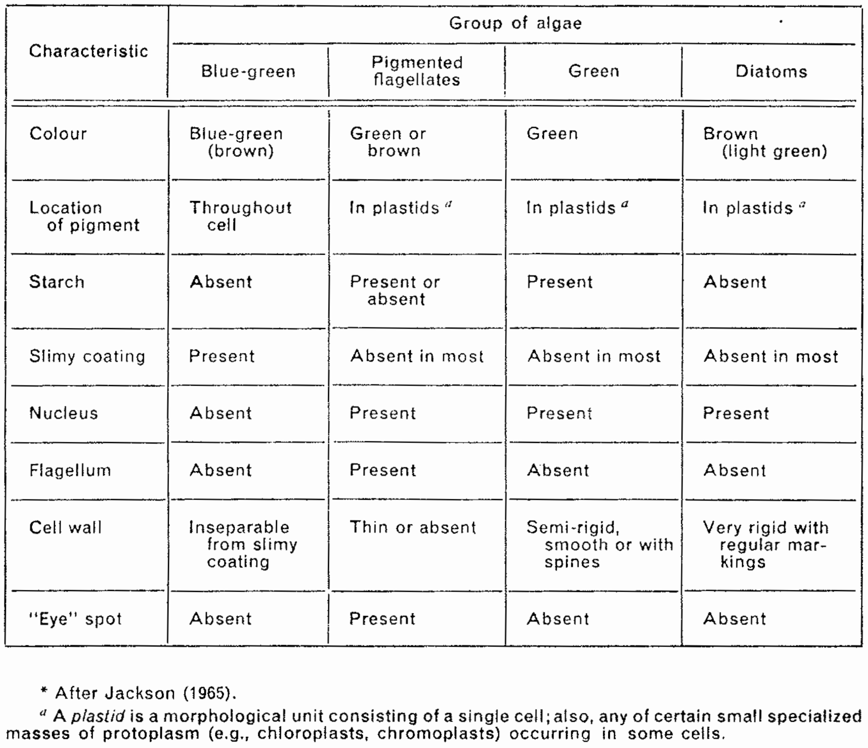
(Fogg 1953)

Table 2-1 describes four algal genera which are important in facultative waste stabilization ponds. Decomposition of the organic matter in wastewaters may progress rapidly and require a considerable amount of oxygen (Gloyna 1971 & 1978; Arceivala 1979; Oswald 1953; Allen 1955; Bold 1978; Oswald & Gotass 1969; Hermann & Gloyna 1958). Bacteria convert complex dissolved organic compounds to simple substances such as carbon dioxide and water. When this conversion takes place, oxygen is consumed rapidly; and bacteria slow down their growth rate. When light and temperature are satisfactory, photosynthetic oxygen is produced by algae. Algae fix available carbon (mostly carbon dioxide) which is mainly produced by bacteria. Figure 2-4 describes the algal-bacterial commensalism carbon cycle (Hermann & Gloyna 1958).

The most important factors which affect algal growth within facultative waste stabilization ponds are (a) light intensity; (b) temperature; (c) detention time; (d) sewage strength; (e) pH; (f) mixing and stratification. However, Stahl and May (1967) and Patil (1972) pointed out that algae production in facultative waste stabilization ponds is commonly limited by light and temperature, and Massy et al. (1971) and Foree et al. (1973) found that the availability of nutrients may be a limiting factor for algal growth.

The major elements required by algae for cell development are carbon, hydrogen, nitrogen, and phosphorus (Massey & Robinson 1971). Due to bacterial respiration,

Table 2-1 Comparison of Four Major Groups of Algae* (Gloyna, 1971)



Characteristic	Group of algae			
	Blue-green	Pigmented flagellates	Green	Diatoms
Colour	Blue-green (brown)	Green or brown	Green	Brown (light green)
Location of pigment	Throughout cell	In plastids [a]	In plastids [a]	In plastids [a]
Starch	Absent	Present or absent	Present	Absent
Slimy coating	Present	Absent in most	Absent in most	Absent in most
Nucleus	Absent	Present	Present	Present
Flagellum	Absent	Present	Absent	Absent
Cell wall	Inseparable from slimy coating	Thin or absent	Semi-rigid, smooth or with spines	Very rigid with regular markings
"Eye" spot	Absent	Present	Absent	Absent

* After Jackson (1965).

[a] A *plastid* is a morphological unit consisting of a single cell; also, any of certain small specialized masses of protoplasm (e.g., chloroplasts, chromoplasts) occurring in some cells.

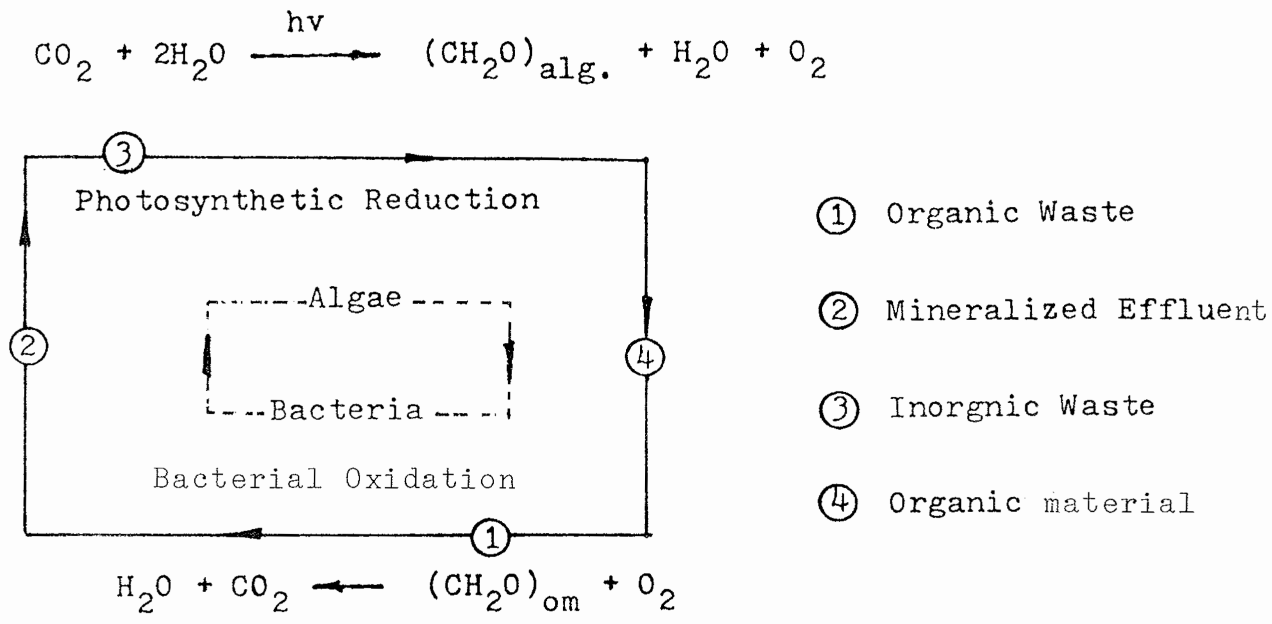


Figure 2-4 Simplified Diagram of Algae-Bacteria Commensalism Based on the Carbon Cycle (Gloyna, 1971)

carbon dioxide is unlikely to be a limiting algal growth factor. Nitrogen and phosphorus are not deficient in domestic wastewater, but some industrial wastes may not contain sufficient quantities of either.

Some trace elements are needed for algal growth. Excessive amounts of some trace elements may cause algal blooms of excessive growth of nuisance species (Gloyna 1971; Arceivala et al. 1970; Massey & Robinson 1971). Some organic nitrogen combinations and polyphosphate forms are not appropriate nutrients for some algal genera unless they are first assimilated by bacterial populations (Gloyna 1976).

2.3 CHEMICAL CHARACTERISTICS OF PHOSPHORUS

Phosphorus forms only about 0.1% of the rocks that make up the bulk of the earth's crust, and thus geochemically this element may be classified as a trace element. Although phosphorus may occur in both the trivalent negative and the quinquevalent positive state, in the lithosphere it occurs almost entirely as the quinquevalent positive ion, which is a part of the orthophosphate ion PO_4^{3-} (McKelvey 1974). Phosphorus in most soils, added in the form of fertilizers, tends to be fixed rather quickly into a relatively stable apatite-form in lime rich soils or an iron or aluminum phosphate in less calcareous ones (Hutchinson 1952). Thus, the availability of phosphorus in soil can be increased by acidifying or by adding phosphate in relatively soluble form, but either effect is likely to be temporary.

Phosphorus is found in wastewater in three principal forms: orthophosphate ion, polyphosphates (condensed phosphates), and organic phosphorus compounds (EPA 1976). There are a number of forms of orthophosphate (PO_4^{3-}) in equilibrium, with the predominant forms changing as the pH changes. The predominant dissolved orthophosphate species over the pH range of 5 to 9 are $H_2PO_4^-$ and HPO_4^{2-} (Stumm and Morgan 1970).

Polyphosphates can be looked upon as polymers of phosphoric acid from which water has been removed. Man-made condensed inorganic phosphates, produced by dehydration and condensation of orthophosphates, are substantial components of synthetic detergents (pyrophosphate and tripolyphospate builder compounds). Polyphosphate and metaphosphate (e.g., so-called "hexametaphosphate") are used in water conditioning operations for scale prevention and corrosion control.

Hydrolysis of polyphosphates is thermodynamically favorable and yields orthophosphate as the eventual product. However, the reaction rates can be slow. Van Wazer (1958) and Clesceri and Lee (1965) found that physical-chemical and biochemical factors such as temperature, pH, and enzymatic activity might influence the rate of hydrolytic breakdown of the condensed phosphate. The presence of bacteria, algae, and enzymes causes a significant increase in the rate of condensed phosphate degradation. While half-lives of pyrophosphate or tripolyphosphate in distilled water are in the order of 4000 to 5000 days, the hydrolysis rates in natural lake and river waters are 100 to 1000 times faster.

Organic phosphorus compounds in wastewaters are the products of biological growth. Rigler (1974) studied the soluble or colloidal organic phosphorus fraction of waters from nine lakes and concluded that the fraction of the total phosphorus that can be described accurately as soluble organic phosphorus is unknown because the optional procedures used to separate soluble and insoluble phosphorus forms vary and provide inconsistent results. Many river samples show significant concentrations of organic phosphorus in both dissolved and suspended forms. While the chemistry of organic phosphorus is complicated, the decomposition of organic phosphorus leads to orthophosphate as complete hydrolysis occurs.

In raw sewage there are substantial amounts of all three principal phosphorus forms. During biological treatment, organic phosphorus is decomposed and converted to orthophosphorus. On the other hand, inorganic phosphorus is utilized in forming biological floc. Polyphosphorus is for the most part converted to orthophosphorus. The result is that in a well treated secondary effluent, a large fraction of the phosphorus is present as orthophosphate (EPA 1976).

The following equations have been suggested for the hydrolysis of some of the condensed phosphates in water (Davis 1966).

Glassy phosphates:

$$(NaPO_3)_n + H_2O \longrightarrow (NaPO_3)_3 + NaH_2PO_4 + (NaPO_3)_{n-4}$$

Trimetaphosphates:

$$(NaPO_3)_3 + H_2O \longrightarrow Na_3H_2P_3O_{10}$$

$$Na_3H_2P_3O_{10} + 2H_2O \longrightarrow 3NaH_2PO_4\text{, or}$$

$$Na_3H_2P_3O_{10} + H_2O \longrightarrow Na_2H_2P_2O_7 + NaH_2PO_4$$

Tripolyphosphates:

$$Na_5P_3O_{10} + H_2O \longrightarrow Na_3HP_2O_7 + Na_2HPO_4$$

Pyrophosphates:

$$Na_2H_2P_2O_7 + H_2O \longrightarrow 2NaH_2PO_4$$

$$Na_3HP_2O_7 + H_2O \longrightarrow NaH_2PO_4 + Na_2HPO_4$$

$$Na_4P_2O_7 + H_2O \longrightarrow 2Na_2HPO_4$$

In the above equations, only the pyrophosphates hydrolyze entirely to orthophophates in one step while the others form polyphosphate intermediates in addition to orthophosphates.

The rate of hydrolysis of the condensed phosphates in waste stabilization ponds is not only affected by biological systems but by physicochemical factors as well. Increases in temperature invariably increase hydroloysis rates. The presence of calcium ions or excess sodium ions usually tends to increase the rate. Occasionally, magnesium ions tend to reduce it. Polyvalent metals generally increase hydrolysis. The longer the chain length, the greater the stability. In addition, clay or other suspended matter increases the rate. Other conditions being equal, the longer the retention time, the greater the amount of reduction to orthoforms (Van Wazer 1958; Clesceri & Lee 1965).

The concentration of phosphorus in natural waters is usually low, ranging from about 1-20 µg of phosphorus per liter. However, domestic sewage is relatively rich in phosphorus compounds. Prior to the development of synthetic detergents, the content of inorganic phosphorus usually ranged from 2 to 3 mg/l and organic forms varied from 0.5 to 1.0 mg/l (Sawyer 1967). Most heavy-duty synthetic detergents contain from 12 to 13 percent phosphorus. The use of these materials as substitutes for soap can greatly increase the phosphorus content of domestic sewage. It has been estimated that domestic sewage probably contains from two to three times as much inorganic phosphorus at the present time as it did before synthetic detergents became widely used. The average total phosphorus concentration in domestic raw wastewater is found to be about 10 mg/l expressed as elemental phosphorus (De Ranzo 1978).

The quantity of phosphorus from industrial sources may be quite variable. For example, wastewater from pulp and paper mills may be phosphorus deficient while that from potato processing plants may contain a high concentration of phosphorus (Mackenthum 1968). Besides potato processing wastes, fertilizer manufacturing wastes (Memerow 1963), animal feedlot wastes (RASWP 1970), certain metal finishing wastes (Anderson 1968), flour processing wastes (Dickerson 1969), dairy wastes (McKee 1957; Lawton 1959), commercial laundry wastes (Flynn 1963), and slaughterhouse wastes (Wymore 1968) have high phosphorus content.

Phosphorus can be found in a variety of forms in water. A list of the more important ones is given in Table 2-2.

All the polyphosphates (molecularly dehydrated phosphates) gradually hydrolyze in aqueous solutions and revert to the ortho-form which they were derived. The rate of reversion is a function of temperature and increases rapidly as the temperature approaches the boiling point. The rate of this reversion is increased by low pH, and it

Table 2-2 Phosphorus Compounds Commonly Encountered in Sanitary Engineering Practice (Sawyer & McCarty, 1978)

NAME	FORMULA
Orthophosphates:	
Trisodium phosphate	Na_3PO_4
Disodium phosphate	Na_2HPO_4
Monosodium phosphate	NaH_2PO_4
Diammonium phosphate	$(NH_4)_2HPO_4$
Polyphosphates:	
Sodium hexametaphosphate	$Na_3(PO_3)_6$
Sodium tripolyphosphate	$Na_5P_3O_{10}$
Tetrasodium pyrophosphate	$Na_4P_2O_7$

is influenced by bacterial enzymes. The rate of reversion is very slow in distilled water but is rapid in wastewaters (Sawyers & McCarty 1978).

2.4 PHOSPHORUS UTILIZATION BY ALGAE AND BACTERIA

Phosphorus plays a very important role in the growth of algae and bacteria. The concept of recycling phosphate bond energy has been proposed by Gest and Kamen (Moore 1969) as early as 1948. They thought that the energy cycle was based on the mechanism where carbon dioxide was reduced by chemosynthesis and photosynthesis. When light energy is sufficient, adenosine diphosphate (ADP) reacts with inorganic phosphate, absorbing energy and forming adenosine triphosphate (ATP).

$$P_i + ADP \xrightarrow{\text{light}} ATP$$

As ATP, energy becomes available to the organism in the form of energy rich bonds. These bonds can yield the required energy when needed for various cellular activities such as locomotion, chemoluminescence, protoplasm syntheses, cell division, respiration, adjustment of osmotic pressure, etc. The total process is called the phosphorylation mechanism (Griffith et al. 1973).

2.4.1 NUTRIENT RELATIONSHIPS

It is known that algae require relatively large amounts of carbon, phosphorus, nitrogen, and small amounts of manganese, iron, chloride, vanadium, potassium, zinc, calcium, boron, molybdenum, cobalt, copper, silicon, sodium, vitamins, and "organic growth factors" (Gloyna 1971; Arceivala 1970; Bold 1978; Hutchinson 1967). Hutchinson (1967) also found that silicon, nitrogen, and phosphorus are most likely to be depleted by algae growth in the fresh water.

Ketchum (1965) concluded four nutrient relationships exist for algae.

1. "The absolute requirement for a nutrient is based upon the postulate that the algae cannot grow, reproduce, or photosynthesize if the nutrient is lacking from the environment, and that no other nutrient can be substituted for it.

2. The normal requirement is the quantity of each nutrient contained in cells produced during active growth of a population while no nutrient is limiting.

3. The minimum requirement is the quantity of a nutrient in the cells when the nutrient is limiting the growth of the population, all other nutrients being present in excess.

4. The optimum concentration or range of concentration will permit the maximum rate of growth, reproduction, or photosynthesis of an algal population."

The "absolute requirement" means the nutrient must be present before the algae can grow. The "optimum requirement" refers to the concentration of a nutrient in the media surrounding the algal cell; and the "normal requirement" refers to the concentration of nutrient in the cellular material.

2.4.2 OPTIMUM PHOSPHORUS LEVELS

The optimum requirement for algal growth differs considerably from species to species even if no other external factor is limiting. The optimum phosphate concentrations for the growth of diatoms and green algae under defined laboratory conditions were studied by Chu (1943). And Chu found that the concentrations below 50 μg/l of phosphorus were limiting, concentrations of about 20 μ g/l were inhibitory, and 100 to 2,000 μ g/l were optimum. Forsberg (1964; 1965 a,b) later found that best growth of Chara occurred at levels below 20μ g/l of phosphorus. Blum (1966) observed saturation of phosphorus uptake by Euglena at 3.1 mg/l of P. However, Batterton and Van Baalen (1968) found limiting growth of blue-green algae at a level below 3.7 mg/l of P.

2.4.3 PHOSPHORUS CONTENT IN ALGAL CELLS

Depending on the phosphorus content of the environment, the phosphorus level in the algal cells may fluctuate widely. Mackereth (1953) noted in his experiments that Asterionella formosa could even accumlate and store phosphorus at as low as 1 μ g/l of phosphorus to provide optimum growth. Borchardt and Azad (1968) also concluded that the normal required concentration for phosphorus in the algal cell is approximately 1% by weight. If an excessive quantity of the element is available, however, the quantity of phosphorus in the algal cell may increase to a level of 5% of the ash-free dry weight.

Redfield et al. (1963) explained these different situations: "As the algae continue to grow, they utilize more of the available phosphorus until the external supply is exhausted. As the algae begin to rely on the cellular phosphorus, the concentration of the limiting nutrient in the cell decreases. The algal growth rate drops until there is a cessation of growth. Cessation of growth rate occurs when the concentration of phosphorus within the algal cell equals or is less than the minimum requirement which appears to be approximately 0.1%."

Phosphorus levels in the algal cells are reported to be 6×10^{-8} to 4×10^{-6} μ g P/cell for Asterionella formosa (Lund 1950); 1×10^{-7} to 1.5×10^{6} μ g P/cell for Chlorella (al Kholy 1956); and 9.2×10^{-7} to 8.7×10^{-6} μ g of P/cell for Scenedesmus (Franzen 1932). Redfield (1963) also found that a cellular phosphorus content of approximately 0.4 to 0.5% will support logarithmic growth of algae.

2.4.4 PHOSPHORUS UPTAKE BY ALGAE AND BACTERIA

Phosphorus uptake rate can be affected markedly by some physical and chemical parameters such as light, pH, temperature, concentration gradient, source of available phosphorus, ion effects, and other factors (Fogg 1973; Shapiro 1968).

Light and/or dark phosphorus uptake has been found to exist in some kinds of algae. Light stimulation of absorption of ^{32}P labelled phosphate has been reported by Talpassayi (1962) for the blue-green algae Anabaena cylindrica. Several reports of assimilation of phosphate in the dark have been made in the green alga Ankistrodesmus brainii (Simonis and Urback 1963), Chlorella (Kanai et al. 1963), Abactstus budykabs (Batterton and Van Baalen 1968), and some other algae (Stewart and Alexander 1971). Harris and Riley (1970) and Fitzgerald (1970) found a dark uptake of phosphate may replenish the phosphorus to the phytoplankton which becomes phosphorus deficient during the day.

Ion effect and pH can also affect the uptake of orthophosphate. Ullrich (1973) found that the uptake rate of ^{32}P labelled phosphate is strongly dependent upon the pH of the culture medium by Ankistrodesmus brainii. Ullrich-Eberius (1973) observed the same result in that maximal uptake rates of phosphate occurred between pH 5.5 and 6.5. Ullrich-Eberius also found that sodium ions could enhance phosphate uptake by Ankistrodesmus brainii (Ullrich-Eberius 1973; Belsky et al. 1970; Ullrich-Eberius and Simonis 1970). Also, they reported that 0.002M sodium chloride could increse phosphate uptake, whereas uptake was constant over a long period of time in the presence of 0.002M potassium ions (potassium chloride). Other ion effects have also been reported in the literature. Polyphosphate formation in Saccharomyces mellis is almost completely inhibited by 0.5M KCl (Weimberg 1970). Baker's yeast, on the other hand, seems to have a specific requirement for potassium ions in the process of phosphate uptake (Schmidt et al. 1946). In fact, 0.01M potassium ions appears to enhance the assimilation of orthophosphate.

Phosphate uptake rate can also be affected by such physical parameters as stream current, concentration of other nutrients, and the aquatic environment itself. Schumacher and Whitfor (1965) found that in a variety of algae, stream currents as low as 1 to 4 cubic meters per second increase the rate of phosphate uptake. Kuenzler and Ketchum (1963) showed that Phaiodactylum tricornutum was able to take up phosphorus from solutions containing less than 11 μg phosphate, and they suggested that concentration levels of phosphate as low as 11 μg do not depress growth rate.

2.5 PHOSPHORUS REGENERATION

The release of phosphorus from algal cells to solution during decomposition leads to more algal growth and the synthesis of new cells. In order to understand this phenomenon, both the quantity of phosphorus which the algal material regenerates and the rate of regeneration must be known.

2.5.1 PHOSPHORUS REGENERATION BY ALGAE AND BACTERIA

Goldeberg (1951) used radioactive phosphate as a tracer to follow the quantity of phosphate in diatoms. Cooper (1935), Grill and Richards (1964) also grew algae in the laboratory and then placed them in the dark to monitor the phosphorus regeneration.

One of the most significant results of these studies on phosphorus regeneration is that a significant fraction of the particulate phosphorus is not regenerated. Cooper, Goldeberg, Grill and Richards reported that there was about 33% of the initial particulate phosphorus remaining after decomposition. Although some investigators have briefly speculated about the reason for the phosphorus remaining, no complete explanation has been provided.

2.5.2 RATE OF PHOSPHORUS REGENERATION BY ALGAE AND BACTERIA

Very little information is available regarding the rate of phosphorus regeneration by algae. Based on the available data, Jewell (1968) used a first order decay rate coefficient to observe the regeneration rate in a range from 0.038 to 0.17 day^{-1}.

Grill and Richards (1964) developed an empirical model with their laboratory phosphorus regeneration experiment which was carried out by diatoms in sea water. The governing differential equations for this model were:

$$dP_I/dt = -K_1P_I \qquad (2\text{-}11)$$

$$dP_B/dt = K_1P_I - (K_1 + K_3)P_B \qquad (2\text{-}12)$$

$$d(P_i + P_r)/dt = (K_2 + K_3)P \qquad (2\text{-}13)$$

where P_I was the available phosphorus in the diatom tissue. P_I decayed at a first order, K_1. Bacterial respiration and the decay of dead bacterial cells gave rise to the inorganic phosphate fraction, P_i, and the refractory organic substances, P_r, which were synthesized during bacterial metabolism and assumed to be the remains of dead bacterial cells. The sum $(K_2 + K_3)$ described the rate of the loss of phosphorus from the bacterial fraction.

Through trial and error, Grill and Richards were able to determine the rate coefficients and to show that the first order kinetics would fit the observed data. Since no basic explanation of the regeneration mechanism was given, this approach defining nutrient regeneration is of little use in other situations. However, the most important contribution of this research is its indication that phosphorus regeneration through bacteria and algae may be described by first order kinetics.

2.6 PHOSPHORUS RECYCLE IN WASTE STABILIZATION PONDS

Waste stabilization ponds generally move water through the system in a plug-flow manner. However, as a result of wind action and series-connected cells, some ponds approach the performance of completely mixed systems. A general mass balance for either a biotic or abiotic substance can be written as follows for a completely mixed reactor:

(inflow) - (outflow) + (reactions) = (accumulation)

Influent and effluent consist of soluble chemical oxygen demand (COD), dissolved oxygen (DO), bacterial mass (X_a), algal mass (X_b), inorganic carbon (C), organic nitrogen (N_o), ammonia (NH_3), nitrate (NO_3^-), alkalinity (ALK), and organic as well as inorganic nitrogen and carbon dioxide into the liquid layer as nutrients for biomass growth.

2.6.1 PHOSPHORUS MASS BALANCE IN WASTE STABILIZATION PONDS

Phosphorus generally occurs in wastewaters as orthophosphates, polyphosphates, and organic phosphorus. For simulation purposes, Di Toro (1975) divided phosphorus into organic and inorganic phosphorus. Souces or organic phosphorus are wastewater inflow and products of algal and bacterial respiration, while sinks are outflow and the decomposition of organic phosphorus into inorganic phosphorus. Based on the assumption of first order reactions with temperature-dependent rate coefficients (Thomann et al. 1971), the mass balance equation was formed as:

$$V \sum_{j=1}^{n} (r_c)_j + Q_i C_i = Q_o C + V\frac{dC}{dt} \tag{2-14}$$

where

r_c = volumetric reaction rate of substance, mg/l/day
C_i = influent concentration of substance, mg/l
C = effluent concentration of substance, mg/l
V(dC/dt) = volumetric rate of change of substance in the reactor, mg/day, and
n = number of reactions that involve the substance.

Fritz et al. (1979) assumed that the influent and effluent flow rates of a waste stabiliation pond were the same. Also, they used a constant pond volume. On this basis they derived Eq. 2-15.

$$\frac{dP_o}{dt} = \frac{P_{oi}}{\theta} - \frac{P_o}{\theta} + r_{1op} + r_{2op} \tag{2-15}$$

where

P_o = organic phosphorus concentration, mg/l,
P_{oi} = influent organic phosphorus concentration, mg/l
r_{1op} = volumetric reaction rate for organic phosphorus production from bacterial and algal decay, mg/l/d
r_{2op} = volumetric reaction rate for inorganic phosphorus transfer, mg/l/d, and
= hydraulic detention time, days.

similarly, the inorganic phosphorus balance was shown to be:

$$\frac{dP_i}{dt} = \frac{P_{ii}}{\theta} - \frac{P_i}{\theta} + r_{1ip} + r_{2ip} + r_{3ip} \qquad (2\text{-}16)$$

where

P_i = inorganic phosphorus concentration, mg/l
P_{ii} = influent inorganic phosphorus concentration, mg/l
r_{1ip} = volumetric reaction rate for assimilation of inorganic phosphorus by biomass for cell synthesis, mg/l/d
r_{2ip} = volumetric reaction rate for organic to inorganic phosphorus transfer, mg/l/d.
r_{3ip} = volumetric reaction rate for inorganic phosphorus production from benthic regeneration mg/l/d_o.

The volumetric reaction rates used by Fritz et al. (1979) are listed in Table 2.3, where k is the substrate utilization kinetic coefficient. The coefficient for organic to inorganic phosphorus transfer, u_p, day^{-1}, was used by Di Toro et al. (1975) as u_p = 0.02T, where T was temperature (°C).

2.6.2 PHOSPHORUS EXCHANGE BETWEEN AQUEOUS PHASE AND SEDIMENTS

Sometimes, waste stabilization pond systems appear to resemble other reservoirs and lakes; for example, sediments act as sources of phosphorus in natural lakes. During the summer time, if stratification has occurred, the phosphorus is liberated into the epilimnion from decaying vegetation of the sediments and littoral region. At the same time, existing vegetation takes up some of this phosphorus. Sedimentation of phytoplankton and other phosphorus-containing microbe and fecal pellets from non-protist groups into the hypolimnion constantly occurs. Phosphorus compounds get into the hypolimnion when sedimentation occurs.

According to Hayes and Phillips (1958), the dynamic interaction between water

Table 2-3 Volumetric Reaction Rate

Reaction	Volumetric Reaction Rate
Organic Phosphorus	
Bacterial and Algal Decay	$r_{1op}=0.009k_aX_a+0.024k_bX_b$
Organic P Inorganic P	$r_{2op}=-u_pP_o$
Inorganic Phosphorus	
Algal and Bacterial Growth	$r_{1ip}=0.009(r_{xa1}+k_aX_a)-0.024(-Yr_s)$
Inorganic P Organic P	$r_{2ip}=-r_{2op}$
Benthic Regeneration	$r_{3ip}=R_p/D$

r_{xa1}=Algal Growth
r_s =Degradable COD Utilization
R_p =Regenerated Phosphorus from the Benthos, mg/cm²/d.

and sediment may be represented as

$$\underset{\text{(a small fraction)}}{\text{P in aqueous phase}} \rightleftharpoons \underset{\text{(a large fraction)}}{\text{P in solid phase}}$$

There is general agreement that chemical interactions of phosphate with Fe (III), Al (clay), and Ca^{2+} are relevant, although the nature of the phosphorus reaction dynamics is still not fully understood.

In waste stabilization ponds, losses of phosphorus appear to be largely from effluent discharge, percolation, and precipitation and not so great due to aquatic insect emergence (Vellentyne 1952). Since algal activity in waste stabilization ponds is more than likely continuous, CO_3^{2-} and HCO_3^- are utilized by algae. Thus, the hydroxyl ion concentration increases and the pH rises. The interaction of calcium, magnesium, and iron with orthophosphate occurs at higher pH values. Thus, it is reasonable to assume that a considerable quantity of calcium-, magnesium-, and ferric-phosphate precipitates. Resuspension of these forms could be accomplished by a decrease in the pH in the detritus region or the depletion of phosphate content in the surface water. The latter does not occur if the waste is domestic sewage which usually has a relatively high phosphorus concentration.

2.6.3 PHOSPHORUS RECYCLE

The investigation of Nesbitt (1974) indicated that phosphorus might occur in the form of organic phosphorus, or as complex inorganic phosphates, or as soluble inorganic orthophosphate (PO_4^{3-}) (the final breakdown product in the phosphorus cycle, and the form in which phosphorus is most readily available for biological utilization). Though Redfield et al. (1963) thought the minimum requirement of phosphorus for algal growth was about 0.1% and Helmers (1952) found that the minimum ratio of BOD_5 and P was 100:1, actually phosphorus could be less. Nesbitt (1974) explained that the situation was due to the recycle of the phosphorus from the anerobic digestion process which occurred at the bottom of the waste stabilization ponds.

The recycle of phosphorus within the epilimnion is as shown in Fig. 2-5. The rapid uptake of PO_4-P by plankton appears to be more general. Approximately the same amount of phosphorus taken by plankton is regenerated by direct release and through grazing with subsequent release by zooplankton. Most of the phosphorus excreted by zooplankton is utlimately regenerated as PO_4-P although part of the phosphorus may be excreted as organic phosphorus compounds. Phytoplankton (greater than 30 um) are pictured as comprising a large phosphorus compartment through which phosphorus is largely regenerated by decomposition.

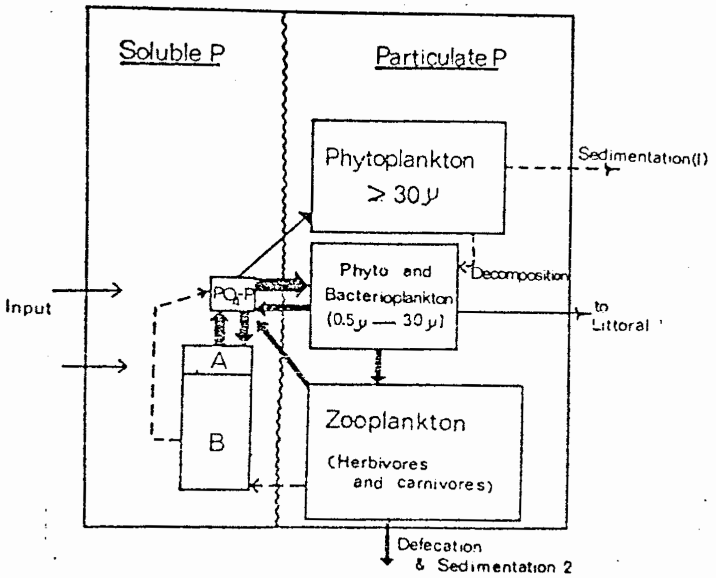


Figure 2-5 Diagrammatic representation of the phosphorus cycle in the epilimnion of eutrophic lakes. The thickness of arrows in Fig. 2-5 is intended to give an impression of the importance of various fluxes. Dashed arrows indicate fluxes of doubtful importance. Soluble P other than PO_4-P is subdivided to indicate that A, the part shown to be exchanging with PO_4-P, is only a small fraction of the total, and is probably different from the material released by zooplankton (B) (Rigler, 1974).

Several different approaches have been taken in the study of phosphorus in aquatic systems. For example, Vollenweider (1969) developed phosphorus budgets that would predict phosphorus concentration from simple parameters such as input and output rates, flushing time, and lake morphometry, while ignoring all biological and temporal complexities. However, detailed studies of phosphorus cycling in the microorganism must also be pursued for better operation design.

CHAPTER 3

PHOSPHORUS MODELS FOR WASTE STABILIZATION PONDS

Mathematical models have been widely used for evaluating the behavior of complex ecosystems. Modeling techniques can provide a systematic basis for research and the comparison of management options.

Models were used in this study to examine the physical, chemical, and biological reactions in waste stabilization ponds. Models can also help to realize the effects of hydrodynamics on phosphorus regeneration from sediments as well as the effect of the phosphorus regeneration on the operation of waste stabilization ponds. It is also expected that models may be used to predict phosphorus uptake, release, and recycle in pond operations.

3.1 THE MECHANISMS OF PHOSPHORUS TRANSFORMATION IN WASTE STABILIZATION PONDS

The mechanisms which are thought to dominate the phosphorus transformations are decomposition and synthesis, while the mechanisms which influence phosphorus changes of location are deposition, release, influent phosphorus loading, and wash-out.

In general, biological processes such as uptake of phosphorus by the algae and the release of phosphorus from the dead plankton, detritus, and sediments dominate the phosphorus recycling. The interrelationships between organic-inorganic phosphorus are also important considerations, and the role of these compounds is mainly governed by biological reactions. The kinetic equations describing the organic and inorganic phosphorus interrelationships are considered in the phosphorus models as a net conversion from organic forms to inorganic forms or vice versa. Similar linear approaches have also been used by Stumm and Leckie (1971), Imboden (1974), and Lung (1975):

$$U_{or} = u_{or} \times C_{or} \times V \tag{3-1}$$

$$U_{io} = u_{io} \times C_{io} \times V \tag{3-2}$$

where

U_{or} = net conversion rate of organic phosphorus, mg/day

U_{io} = net conversion rate of inorganic phosphorus, mg/day

u_{or}, u_{io} = first order kinetic coefficients for phosphorus conversion, per day

V = pond volume, liter
C_{or} = organic phosphorus concentration in the pond, mg/l
C_{io} = inorganic phosphorus concentration in the pond, mg/l.

Deposition of the dead algae and organic material results in a net loss of phosphorus for the supernatant of the pond but a gain of phosphorus for the sediments. This transfer of nutrient from the pond water to the sediment is relatively significant because the algal productivity in a non-anaerobic pond system and the organic loading in an anaerobic pond are both very high. Both the high algal productivity and the high organic loading will result in a considerable amount of phosphorus settling down to the bottom of the pond. The adsorption of phosphorus from the overlying water on the sediment was not considered in the phosphorus models because the adsorption was found by Stumm and Leckie (1971) to be small compared with settling losses. The adsorption phenomenon was also described by Williams and Mayer (1972) and Lung (1975). Lung reported that the phosphorus adsorbed by the sediment was only one-fiftieth to one-tenth of the phosphorus precipitated to the sediment.

The mathematical formulations of the net deposition are:

$$D_{or} = k_{or} \times C_{or} \times A \tag{3-3}$$

$$D_{io} = k_{io} \times C_{io} \times A \tag{3-4}$$

where

D_{or} = deposition rate of organic phosphorus, mg/day
D_{io} = settling rate of inorganic phosphorus, mg/day
k_{or} = deposition velocity of organic phosphorus, cm/day
k_{io} = deposition velocity of inorganic phosphorus, cm/day
A = the water-sediment interface area, m^2.

A first order coefficient was considered for the release of phosphorus from the sediments. The phosphorus release process from the sediment was considered to occur in two steps for organic phosphorus. Organic phosphorus was initially decomposed by microorganisms, resulting in a particulate or dissolved inorganic phosphorus. The first step depended on the biochemical activities as mentioned above. During the second step, the dissolved inorganic phosphorus was transferred to the liquid phase by molecular diffusion and convection. The rate of phosphorus release was assumed to be controlled by the first order coefficient and the difference of the phosphorus concentration in the sediment and in the overlying water. Phosphorus release can be shown by Eq. 3-5.

$$R = k \times C_s \times A \tag{3-5}$$

where

R = net releasing rate of phosphorus from the sediments, mg/day
k = specific rate of phosphorus release from the sediments, cm/day
C_s = phosphorus concentration in the sediments, mg/l

The phosphorus loading, Eq. 3-6, of the waste stabilization pond can be determined by the phosphorus concentration in the waste and the flow rate.

$$L = Q \times C_{in} \tag{3-6}$$

where

L = phosphorus loading, mg/day
Q = flow rate, l/day
C_{in} = phosphorus concentration in the influents, mg/l.

In a completely mixed system, the effluent phosphorus concentration is equal to the phosphorus concentration in the ponds. The phosphorus washed out of the system is:

$$W = Q \times C \tag{3-7}$$

where

W = phosphorus washed out rate, mg/day
C = phosphorus concentration in the ponds which is equal to the phosphorus concentration in the effluents, mg/l.

3.2 MASS BALANCE, TOTAL PHOSPHORUS

The model for total phosphorus as shown in Figure 3-1 is based on mass balance equations for a completely mixed pond system considering input, output, precipitation to sediments, and release from sediments. This model assumes that some of the phosphorus input to the sediments is not available for release. Algal growth and algal cell sedimentation, accompanied by decay and subsequent release of phosphorus from the sediments, are assumed to be first order reactions (Lorenzen et al. 1974; Lung 1976).

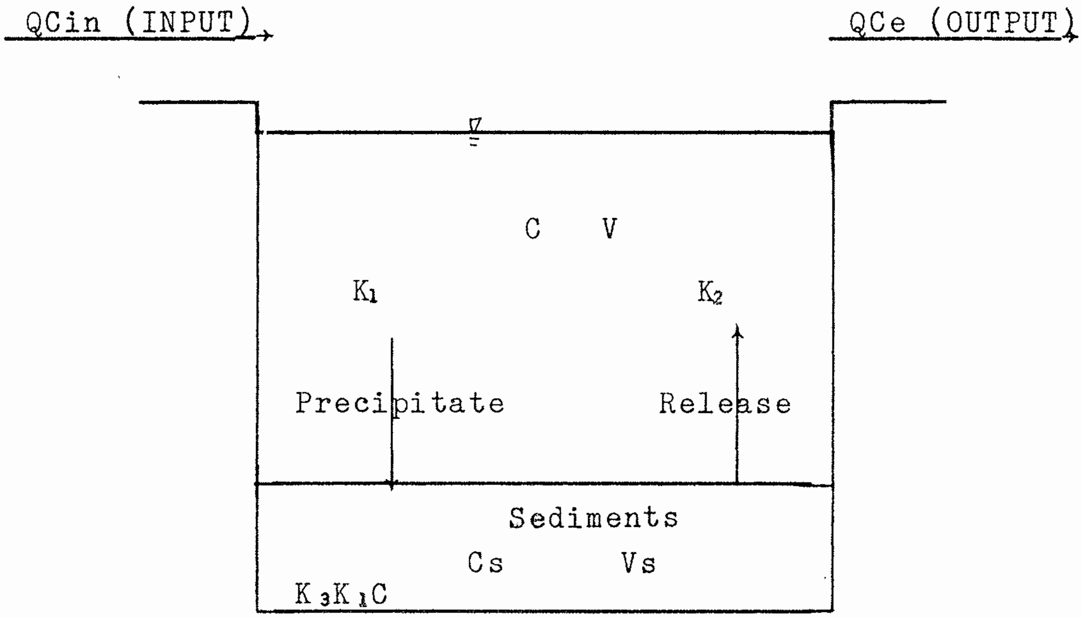


Figure 3-1 Total Phosphorus Mass Balance

The mass balance equation describing the total phosphorus in both the sediment and the overlying water systems can be represented by:

P. content = Input -Output + Release from Sediments - Removal by sedimentation.

That is:

$$V(dC/dt) = QC_{in} - QC + K_2A(C_s-C) - K_1AC \qquad (3\text{-}8)$$

$$V_s(dC_s/dt) = K_1AC - K_2A(C_s - C) - K_1K_3AC \qquad (3\text{-}9)$$

where

C = phosphorus concentration in water column, which is equal to the effluent phosphorus concentration in a completely mixed sytem, mg/l

C_s = phosphorus concentration in the sediments, mg/l

C_{in} = influent phosphorus concentration, mg/l

V = pond volume, l

Q = flow rate, l/day

A = pond surface area that equals sediment area, cm^2

V_s = sediments volume, l

K_1 = specific rate of phosphorus transfer to the sediments, cm/l

K_2 = specific rate of phosphorus release from the sediments, cm/l

K_3 = fraction of total phosphorus input to sediments that is unavailable for the exchange process, percentage.

The analytical solution, solved by integration of the differential equations, will be discussed in Section 3.4.

3.3 MASS BALANCE, INORGANIC AND ORGANIC PHOSPHORUS

Based on mass balance equations for a completely mixed sytem, the concentration of organic phosphorus and inorganic phosphorus in the supernatant and sediments of waste stabilization ponds can be derived as follows:

$$V(\frac{dC_1}{dt}) = QC_{1i} - QC_1 - k_1AC_1 + k_2A(C_3 - C_1) + u_1VC_1 - u_2VC_2 \qquad (3\text{-}10)$$

$$V(\frac{dC_2}{dt}) = QC_{2i} - QC_2 - k_3AC_2 - u_1AC_1 + u_2AC_2 \qquad (3\text{-}11)$$

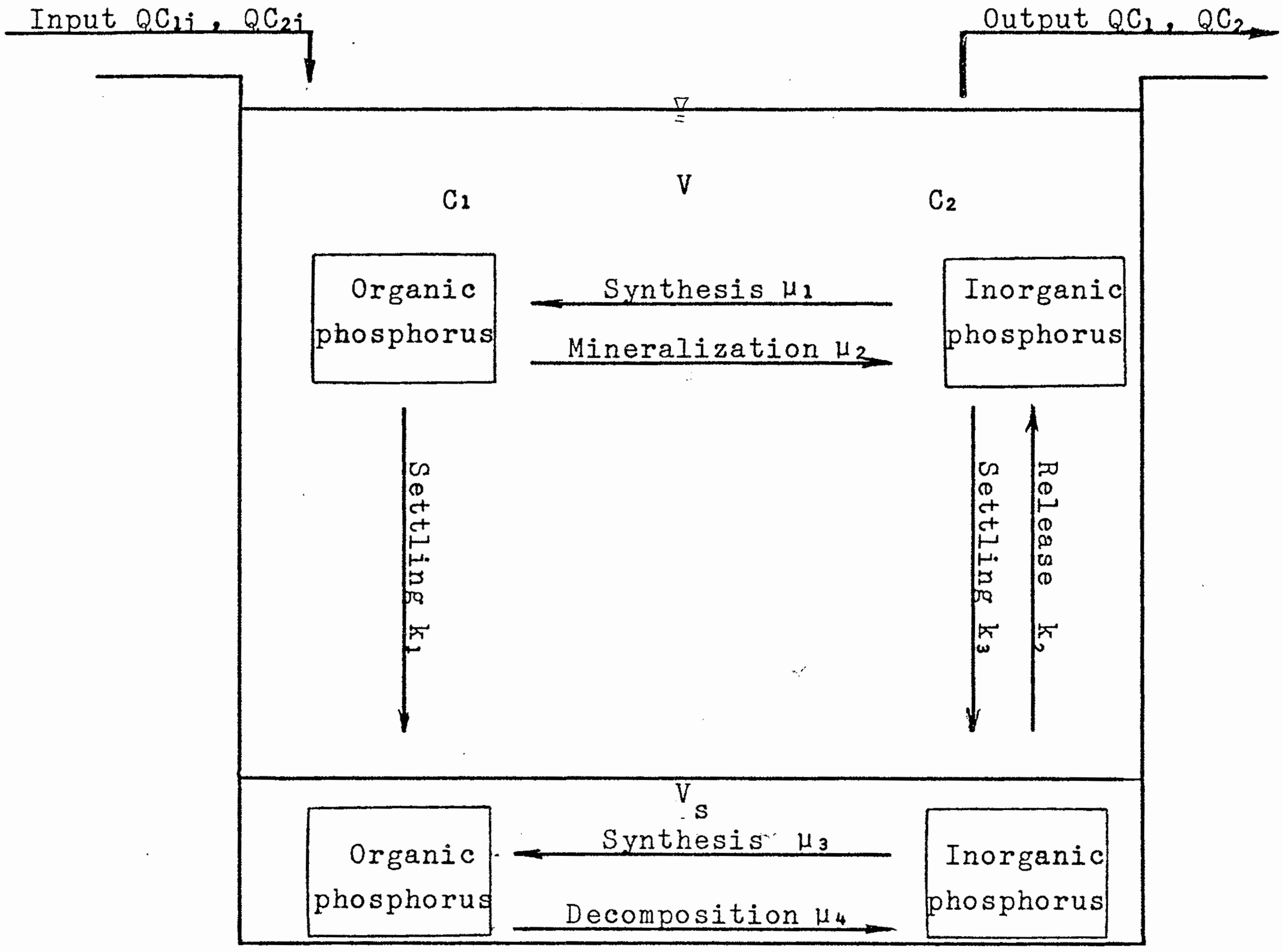


Figure 3-2 Organic and Inorganic Phosphorus Mass Balance

$$V_s(\frac{dC_3}{dt}) = k_1AC_1 - k_2A(C_3 - C_1) - k_1k_4AC_1 - u_3V_sC_3 + u_4V_sC_4 \tag{3-12}$$

$$V_s(\frac{dC_4}{dt}) = k_3AC_2 - k_3k_5AC_2 + u_3V_sC_3 - u_4V_sC_4 \tag{3-13}$$

where

C_1 = inorganic phosphorus concentration in the supernatant, mg/l
C_2 = organic phosphorus concentration in the supernatant, mg/l
C_3 = inorganic phosphorus concentration in sediments, mg/l
C_4 = organic phosphorus concentration in sediments, mg/l
C_{1i} = inflow inorganic phosphorus concentration, mg/l
C_2i = inflow organic phosphorus concentration, mg/l
Q = flow rate, l/day
V = pond volume, l
A = pond surface area, cm^2
V_s = sediments volume, l
k_1 = specific rate of inorganic phosphorus transfer to the sediments, cm/day
k_2 = specific rate of inorganic phosphorus release from the sediments, cm/day
k_3 = specific rate of organic phosphorus transfer to the sediments, cm/day
k_4 = fraction of inorganic phosphorus input to sediments that is unavailable for the exchange process, percentage
k_5 = fraction of organic phosphorus input to sediments that is unavailable for the exchange process, percentage
u_1 = first order kinetic coefficient for decomposition in the supernatant, day^{-1}
u_2 = first order kinetic coefficient for synthesis in the supernatant, day^{-1}
u_3 = first order kinetic coefficient for synthesis in the sediments, day^{-1}
u_4 = first order kinetic coefficient for decomposition in the sediments, day^{-1}.

The equations describing the organic phosphorus and inorganic phosphorus concentrations are based on the following hypotheses:

1. The dissolved inorganic phosphorus is the only one released from the sediments. The particulate phosphorus released from sediments as a result of gaseous release and biological activities will immediately redeposit and remain in the sediments.
2. The dissolved phosphorus adsorbed by the sediments is small compared with deposition losses (Stumm and Leckie 1971) and is not considered in this model.

3.4 INTEGRATION OF EQUATIONS IN PHOSPHORUS MODELS

The total phosphorus model as described in Eqs. 3-8 and 3-9 consists of linear ordinary differential equations with initial values. Thus, these equations may be solved by Laplace transformation. By means of Laplace transformation, the problem of solving a differential equation is simplified and is also reduced to an algebraic problem. The other advantage is that it takes care of initial conditions without the necessity of first determining the general solution and then obtaining from it a particular solution (Kreyszig 1967). The Laplace transformation involves three steps: (a) transform the given differential equation into an algebraic equation (subsidiary equation), (b) solve the subsidiary equations with purely algebraic manipulations, (c) transform the solution of the subsidiary equation by means of inverse transformation, so that it becomes the required solution of the original differential equation.

By Laplace transformation, Eqs. 3-8 and 3-9 can be integrated as follows:

$$V(dC/dt) = QC_{in} - QC + K_2A(C_s - C) - K_1AC \tag{3-8}$$

$$V_s(dC_s/dt) = K_1AC - K_2A(C_s - C) - K_1K_3AC \tag{3-9}$$

By rewriting Eqs. 3-8 and 3-9:

$$dC/dt = E + FC + GC_s \tag{3-14}$$

$$dC_s/dt = HC + IC_s \tag{3-15}$$

Take Laplace transformation of the above equations:

$$zC(z) - C_o = (E/z) + FC(z) + GC_s(z) \tag{3-16}$$

$$zC_s(z) - C_{so} = HC(z) + IC_s(z) \tag{3-17}$$

Rearrange Eqs. 3-16 and 3-17:

$$C(z)\,(z - F) - GC_s(z) = (E/z) + C_o \tag{3-18}$$

$$HC(z) + C_s(z)\,(I-z) = -C_{so} \tag{3-19}$$

Solve C(z) and $C_s(z)$ from Eqs. 3-18 and 3-19, and define:

$$m + n = -(F + I)$$

$$mn = (FI - GH)$$

then

$$C(z) = \frac{-EI}{z(z+m)(z+n)} + \frac{E-IC_o+GC_{so}}{(z+m)(z+n)} + \frac{zC_o}{(z+m)(z+n)} \tag{3-20}$$

$$C_s(z) = \frac{-EI}{z(z+m)(z+n)} + \frac{E+GC_{so}-IC_o}{(z+m)(z+n)} + \frac{zC_o}{(z+m)(z+n)} \tag{3-21}$$

By taking inverse Laplace transformation, the analytical solution of the phosphorus concentration in the water and in the sediments can be described by Eqs. 3-22 and 3-23 (Abramowitz 1972):

$$\begin{aligned} C = {} & \left(\frac{m+I}{m-n}e^{-mt} - \frac{n+I}{m-n}e^{-nt}\right)C_o - \left(\frac{G}{m-n}e^{-mt} - \frac{G}{m-n}e^{-nt}\right)C_{so} \\ & + \frac{EI}{mn}\left(\frac{m+I}{m-n}e^{-mt} + \frac{n+I}{n-m}e^{-nt} - 1\right) \\ & + E\left(\frac{e^{-mt}-e^{-nt}}{m-n}\right) \end{aligned} \tag{3-22}$$

$$\begin{aligned} Cs = {} & -\left(\frac{H}{m-n}e^{-mt} - \frac{H}{m-n}e^{-nt}\right)C_o + \left(\frac{m+n}{m-n}e^{-mt} - \frac{n+F}{m-n}e^{-nt}\right)C_{so} \\ & - \frac{EH}{mn}\left(\frac{m}{m-n}e^{-mt} - \frac{n}{m-n}e^{-nt} - 1\right) \end{aligned} \tag{3-23}$$

where

C_o, C_{so} = total phosphorus concentration in the water and in the sediment

at beginning, mg/l
E = QC_{in}/V, mg P/d
F = $(-Q - K_1A)V$, day^{-1}
G = $(K_2A)/V$, day^{-1}
H = $(K_1A + K_2A - K_1K_3A)/V_s$, day^{-1}
I = $(-K_2A)/V_s$, day^{-1}
$m+n$ = $-(F + I)$, day^{-1}
mn = $(FI - GH)$, day^{-1}.

If both the influent phosphorus loading and the detention time are constant, equilibrium or steady-state concentration will be reached. Values for steady-state phosphorus concentrations in the water, C, and in the sediments, C_s, can be determined by setting $(dC/dt) = (dC_s/dt) = 0$ or setting time equal to infinity. If t = infinity, Eqs. 3-22 and 3-23 become:

$$\underline{C} = \frac{-EI}{FI-GH} = \frac{C_{in}}{1 + \frac{K_1K_3A}{Q}} \tag{3-24}$$

$$\underline{C}_s = \frac{EH}{FI-GH} = \frac{(K_1+K_2-K_1K_3)}{K_2\,(1+\frac{K_1K_3A}{Q})}\,C_{in} \tag{3-25}$$

The same result can be obtained by setting $dC/dt = 0$ and $dC_s/dt = 0$.

From Eqs. 3-24 and 3-25, it is possible to evaluate K_1, K_2, and K_3 if a value for one coefficient is available. At steady-state conditions, the ratio of the phosphorus concentration in the water to the sediment is given by:

$$\frac{\underline{C}}{\underline{C}_s} = \frac{K_2}{K_1+K_2-K_1K_3} \tag{3-26}$$

Eq. 3-26 shows that the ratio of the phosphorus concentration in the water to that in the sediments is independent of the organic loading, detention time, pond volume, and area. The ratio of $\underline{C}/\underline{C}_s$ is only a function of K_1, K_2, and K_3. Also, the steady-state phosphorus concentration in the water, which is described by Eq. 3-24, is independent of the specific release rate from the sediments, K_2. The Runge-Kutta fourth-order numerical method (Gerald 1977) is used to solve the differential equations in the organic-inorganic phosphorus model simultaneously. The fourth-order Runge-Kutta method, which was derived by the German mathematicians Runge and Kutta, is widely used in computer solutions to solve differential equations because of its simplicity in programming, its low truncation error, and its fast convergence. Also, it requires only the initial condition for computation.

The solution represented by the Runge-Kutta fourth-order method, when the time step equals t+1, can be written as:

$$Y_{i+1} = Y_i + (1/6)(w_1 + 2w_2 + 2w_3 + w_4) \tag{3-27}$$

where

w_1 = $Dtf(X_i, Y_i)$,
w_2 = $Dtf(X_i+0.5Dt, Y_i+0.5w_1)$,
w_3 = $Dtf(X_i+0.5Dt, Y_i+0.5w_2)$,
w_4 = $Dtf(X_i+Dt, Y_i+w_3)$, and
Dt = time step interval.

The error associated with the fourth-order Runge-Kutta is $O(Dt)^5$. Because there is no direct method for computing the truncation error, the step size (Dt) is usually halved until the computed result is constant or is within the desired degrees of accuracy. However, as the step size is reduced, accumulation of round-off errors decreases accuracy. There is no simple procedure for determining the optimal time step increment that will yield both accuracy and will minimize round-off errors. A four-hour time step was found by Fritz et al. (1978) to be the appropriate interval yielding consistent results and Ferrara et al. (1978) found that when time step equals to 0.1 day it will lead to satisfactory results.

CHAPTER 4

EXPERIMENTAL PROCEDURES

Two pond systems were utilized for the experimental studies. System I consisted of a series-connected anaerobic waste stabilization pond (AWSP), a facultative waste stabilization pond (FWSP) and a maturation waste stabilization pond (MSWP). System II utilized a FWSP followed by a MWSP.

Test procedures included analyses of pH, chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), total Kjeldahl nitrogen (TKN), orthophosphorus (ortho-P), organic phosphorus, inorganic phosphorus, dissolved phosphorus, particulate phosphorus and total phosphorus.

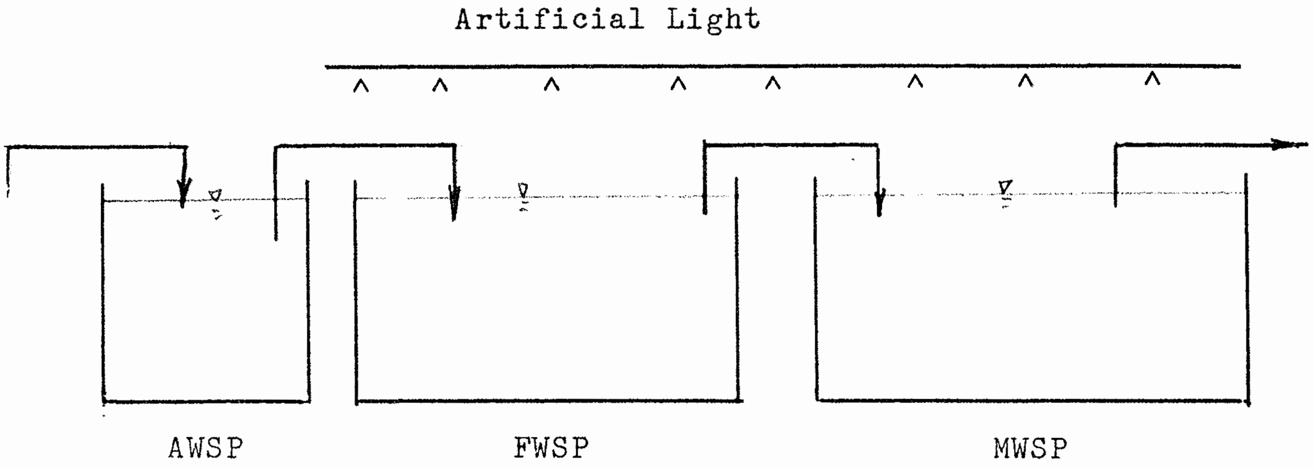
4.1 LABORATORY EQUIPMENT

A 15-liter cylinder, wrapped with aluminum foil, was used as the AWSP in System I. Two 48-liter rectangular aquaria with about 1600 square centimeters of surface area and 60 cm of depth were used as the FWSP's in both Systems I and II. Two 45-liter rectangular aquaria with 1800 square centimeters of surface served as the MWSP in both Systems I and II. The arrangements of these pond systems are shown in Figure 4-1.

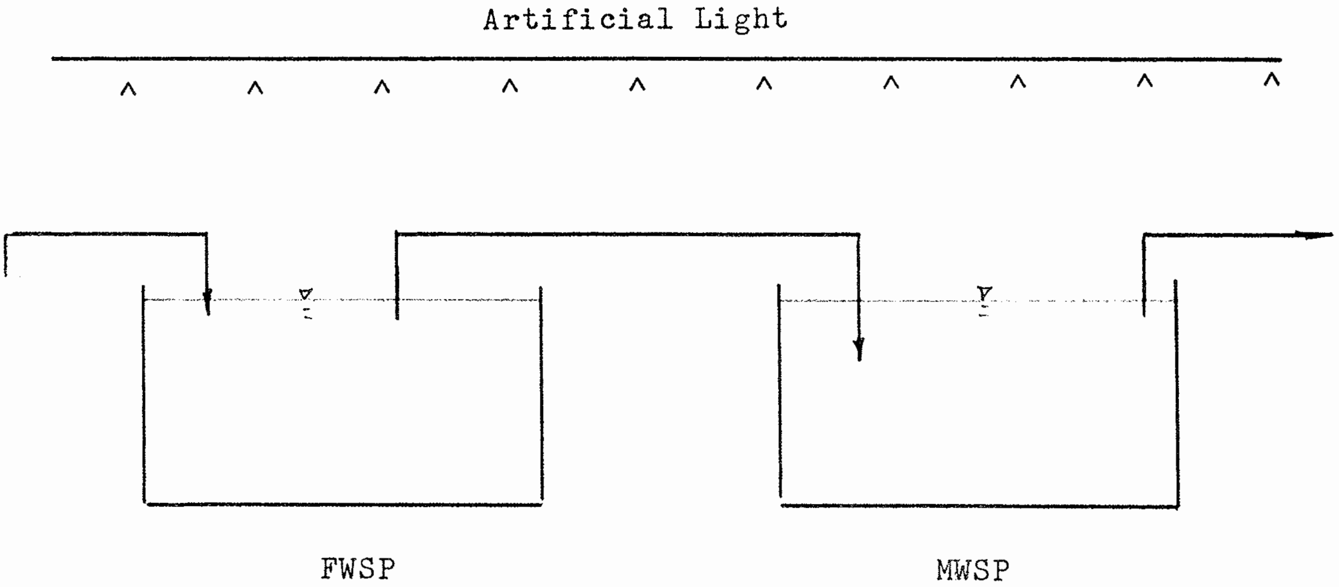
Artificial illumination, which included incandescent and fluorescent lights, was installed about one foot (30 cm) above the surfaces of the FWSP and the MWSP. The lights (which were automatically controlled for 14 hours "on" and 10 hours "off") provided approximately 700 foot-candles at the surfaces of these ponds. Air jets were used to simulate wind action and provide some surface mixing motion. Evaporative losses were made up by adding distilled water daily. All the units in both Systems I and II were maintained at $20 \pm 1^{\circ}C$.

4.2 OPERATING CONDITIONS

Organic loadings were based on facultative pond conditions (Eq. 2-5). The COD loadings and the carbon to phosphorus relationships for both Systems I and II were established for three experimental periods. According to Eqs. 3-22 and 3-23, a steady state condition was obtained in 20 to 120 days for phosphorus in water column and 60 to 200 days for phosphorus in sediment. Therefore, each experimental period was operated for approximately 200 days. The loading conditions were listed as follows:



System I



System II

Figure 4-1 Experimental Waste Stabilization Pond Systems

1. 200% of design loading with C:P = 85:1, (the first period)
2. 100% of design loading with C:P = 85.1, (the second period) and
3. 100% of design loading with C:P = 250:1, (the third period).

Wastewater from the Govalle Wastewater Treatment Plant at Austin was used as influent substrate. Glucose and potassium phosphate was used to adjust the C and P ratio as needed.

At the beginning of the experiment, digested sludge was introduced into the AWSP. Sodium bicarbonate ($NaHCO_3$) was added to keep the pH at near 7 and to promote alkaline fermentation.

Algal water and sediments from facultative waste stabilization ponds of Williamson Creek Wastewater Treatment Plant at Austin, Texas, were used for initiation of the FWSP and the MWSP.

In the first period, 3 liters of influent with 3400 mg COD/l and 40 mg P/l were used for the AWSP of System I and obtained a 3250 kg COD/ha/day surface loading; 3 liters of influent with 1360 mg COD/l and 16 mg P/l were used for the FWSP of System II and obtained a 260 kg COD/ha/day surface loading. In the second period, 1.5 liters of the same wastewater were provided for both systems, which gave 1620 kg COD/ha/day and 130 kg COD/ha/day of organic loading to Systems I and II, respectively. The organic loading of the final period was kept at the same as that of the second period; however, the phosphorus concentration was diluted to only one-third of that of the second period. The operational data are listed in Table 4-1. The ponds were kept at the same water level by adding distilled water to make up those losses due to evaporation.

4.3 SAMPLING PROCEDURES

Water column samples were collected with a volumetric pipet, and the sediment samples were removed by inserting a glass tube into a least three different bottom locations. Initially, the sampling was conducted every other day. After a month, it was apparent that sampling on a four-day schedule was sufficient. Sampling times were scheduled at the same time of the day. The analyses were conducted within an hour after the sampling.

4.4 ANALYTICAL PROCEDURES

Routine measurements were limited to total phosphorus, organic phosphorus, inorganic phosphorus, dissolved phosphorus, particulate phosphorus, COD, TSS, VSS, and pH. Total phosphorus was determined by measuring the orthophosphorus concen-

Table 4-1 Operation Data of Experiment

Pond System			Physical Parameters					Concentration		Loading	
No.	Name	Period	Area (cm)	Vol. (l)	Depth (cm)	DT* (day)	Flow (l/d)	COD (mg/l)	P (mg/l)	COD (kg/ha/d)	P (kg/ha/d)
I	AWSP	1	314	14	45	4.7	3	3400	40	3250	38
		2				9.3	1.5	3400	14	1620	19
		3				9.3	1.5	3400	14	1620	6.7
	FWSP	1	1600	48	30	16	3	1360	32	260	5.9
		2				32	1.5	1360	26	130	1.3
		3				32	1.5	1360	9.4	130	0.9
	MWSP	1	1800	45	25	15	3	290	23	48	3.8
		2				30	1.5	290	18	24	1.5
		3				30	1.5	290	7.5	24	0.6
II	FWSP	1	1600	48	30	16	3	1360	16	260	3.0
		2				32	1.5	1360	16	130	1.5
		3				32	1.5	1360	5.0	130	0.5
	MWSP	1	1800	45	25	15	3	290	12	48	2.0
		2				30	1.5	290	9.0	24	0.8
		3				30	1.5	290	3.3	24	0.3

*DT.=Hydraulic detention time.

tration in the sample in an autoclave for 30 minutes at 120°C (15-20 psi) after the persulfate digestion. Total hydrolyzable phosphorus was measured by colorimetric analysis following the sulfuric acid hydrolysis. Total organic phosphorus was calculated as the difference between the total phosphorus and the hydrolyzable phosphorus which includes orthophosphorus. A Klett Summerson Photoelectric Colorimeter Model 900-3 and wavelength of 880 nm was used for the colorimetric measurement. The phosphorus calibration curve as shown in Figure 4-2, was obtained with high correlation coefficient (0.9992). Prior to each test, a new calibration curve was developed. All phosphorus forms were reported as P mg/l. Other analytical procedures, such as TKN and microscopic algae identification were done on a periodic basis. All sampling and analytical procedures were carried out according to Standard Methods for the Examination of Water and Wastewaters, 14th Edition.

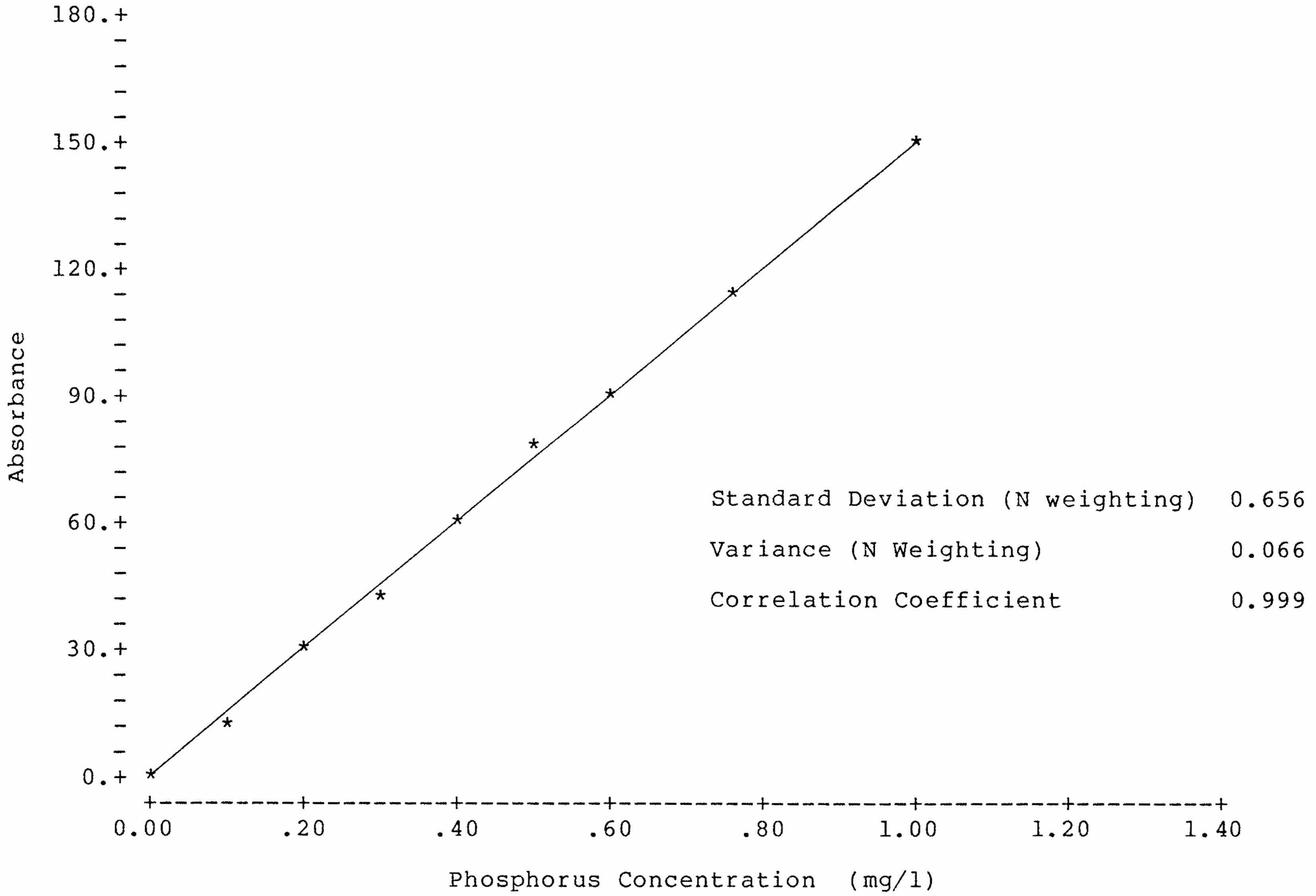


Figure 4-2 Phosphorus Calibration Curve

CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION

The results obtained from the experimental model ponds are presented in this chapter. The phosphorus models were developed to couple the physical, chemical, and biological reactions. Considerable data were required to do statistical analyses for evaluating the parameters in phosphorus models.

The model pond systems were operated for 22 months with three different phosphorus loadings. The data were collected from June 15, 1980 through January 31, 1982. Biochemical coefficients and parameters were evaluated by use of multiple regression analyses. The observed data were compared with computed (expected) data derived using a fourth-order Runge-Kutta numerical technique.

5.1 PARAMETERS AND COEFFICIENTS IN WASTE STABILIZATION PONDS

In order to insure model credibility for predictive purpose, it is necessary to carefully evaluate the parameters in the phosphorus models. In this study two steps were used to estimate the parameters. The first step was to do multiple regression analyses. The second step was to determine the parameters applicable to steady state conditions, Eqs. 3-24 and 3-25, (Chapter Three). The calculated parameters were then compared with the parameters reported in the existing literature.

Minitab, an easy-to-use, flexible, and powerful statistical computing system, as written by Dr. Ryan et al., was used to perform the multiple regression analyses and to calculate coefficients providing the best curve fit. Minitab can also establish the best fit that passes through the point of origin. Besides the coefficient of determination (R-square), Minitab also can be used to calculate F-value and T-ratios. The R-square relationship is defined by Eq. 5-1.

$$\text{R-square} = 100 \times (\text{ssr}/\text{sst}) \qquad (5\text{-}1)$$

where

ssr = sum of square due to regression
sst = total sum of square

R-square is a measure of how well the regression equation fits the observed data, and it also indicates the correlation between the observed data and the predicted values.

The parameters and coefficients obtained from the literature are listed in Table 5-1.

Table 5-1 Values of Biochemical Constants for Waste Stabilization Ponds

	Characteristics	Values	Sources
Y	yield coefficient	0.5 mg/mg	Metcalf & Eddy 1972
K_{20}	max substrate util. rate	5.0 day^{-1}	"
K_s	substr. half sat. const.	50.0 mg/l	"
K_{b20}	bacteria decay coeff.	0.07 day^{-1}	"
K_{bp}	P-bact. half sat. const.	0.01 mg/l	Fritz 1979
S_b	bact. settle. rate	4.5 cm/d	Canale 1976
S_a	algal settle rate	4.5 cm/d	"
M_a	algal growth coeff.	2.0 day^{-1}	"
K_{ap}	p-algal half sat. const.	0.02 mg/l	"
K_a	algal resp. coeff.	0.08 day^{-1}	Ditora 1970
p	$P_o - P_i$ rate coeff.	0.4 day^{-1}	"
K_3	unavailable release portion	60% 20%	Canale 1976 Mckinney 1974, 1976 Goodman et al. 1974 Barsom 1973

5.2 TOTAL PHOSPHORUS MODEL

The laboratory data were first applied to the total phosphorus model.

In each test, the water-sediment interface was considered to be constant. Although the water-sediment interface may have moved upward because of the deposition of particulate matter, compaction occurred as the sedimentation accumulated. With the combination of sediment accumulation and compaction, and the removal of sediment of 5 to 30 ml every two to four days, the interfaces were assumed to be at the same level during each period. Table 5-2 shows that the depths of the pond sediments are almost at the same levels, therefore the assumption of a constant level of water-sediment during each period of experimental test would be reasonable. Williams and Mayer (1972) pointed out that the release rate of dissolved phosphorus from the deeper sediment is much lower than the release rate at the top. A depth of 10 cm for pond sediment evaluation was suggested by Canale (1975) and Ferrara (1980). As shown in Eqs. 3-24 and 3-25, the sediment volumes do not affect the phosphorus concentration in the sediment or the phosphorus concentration in the supernatant. The physical characteristics of the systems are summarized in Table 5-3.

In order to eliminate the possible influence of experimental errors, a best-fit curve was plotted using multiple regression methodology. The resulting parameters and coefficients are listed in Table 5-4. The observed data and the computed data are plotted in Figures 5-2 through 5-31.

The deposition rate (K_1) of the AWSP was much greater than those observed for other ponds. The deposition rate is less in the FWSP and becomes insignificant for the MWSP. The differences of deposition rate in every pond may be accounted for by the differences of particulate matter. In the AWSP, most of the particulate matter is sludge, while in the FWSP and the MWSP algal cells constitute the major fraction of the particulate matter. Anacystis, Chlorella, and Oscillatoria were found in the FWSP while Euglena and Oscillatoria found in the MWSP. Anacystis and Oscillatoria are blue-green algae, are simple forms lacking a true nucleus in the cells, and are classified as procaryotes. Anacystis and Oscillatoria are usually found widely distributed in aerobic and facultative waste stabilization ponds, and these forms are frequently termed "nuisance algae," being associated with odors. Chlorella, which belongs to the family Chlorellaceae, is a unicellular non-motile algae. The spherical, subspherical or ellipsoidal cells are bound by a true cellulosic wall. Chlorella grows very fast under a variety of conditions and its photosynthetic pigments and reserve products are similar to those of higher plants (Kumar 1971). Euglena, which belongs to the family Euglenophyta, is widely distributed in fresh water, polluted water, and mud

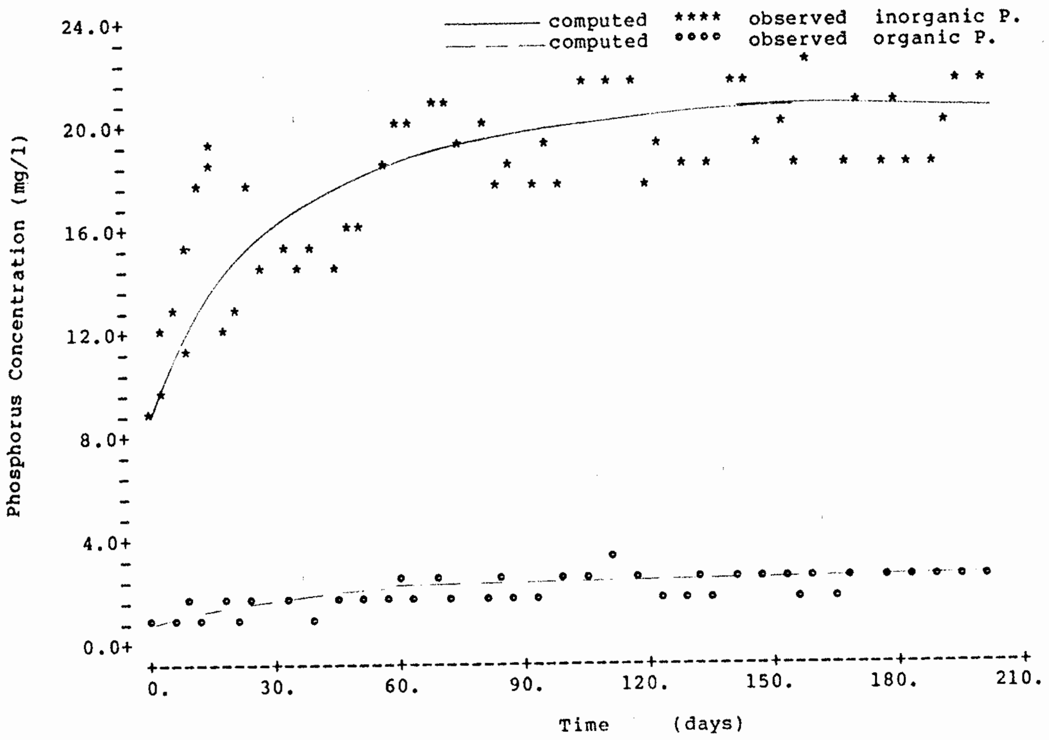


Figure 5-37 Phosphorus in MWSP Supernatant of System I (First Period)

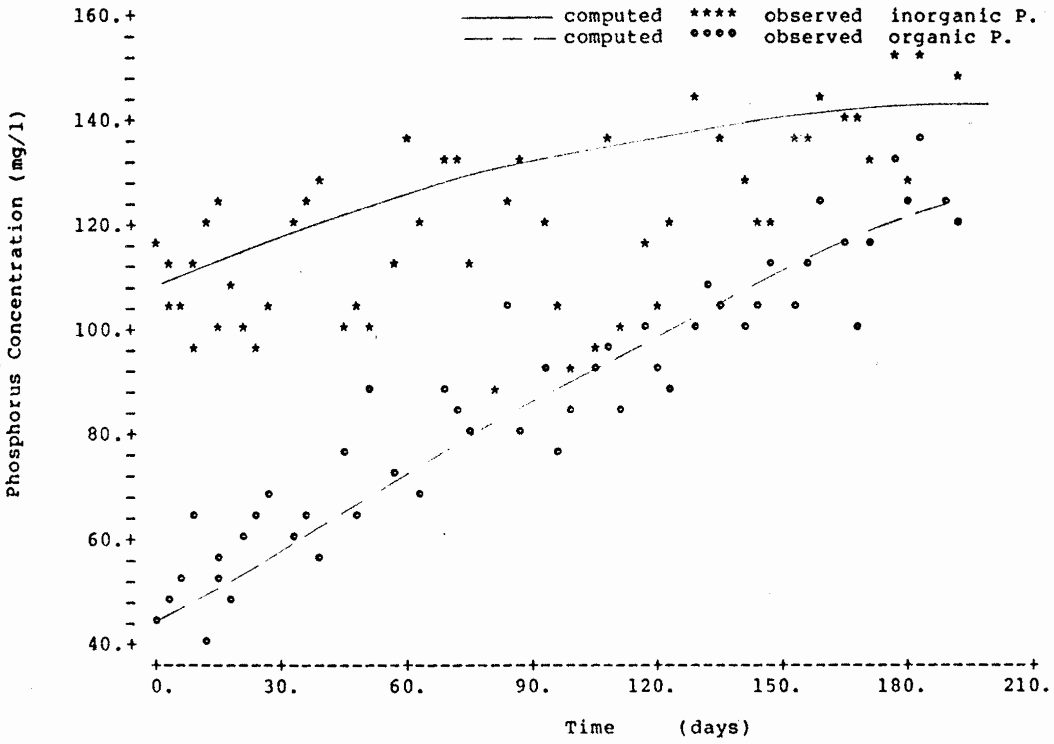


Figure 5-38 Phosphorus in MWSP Sediment of System I (First Period)

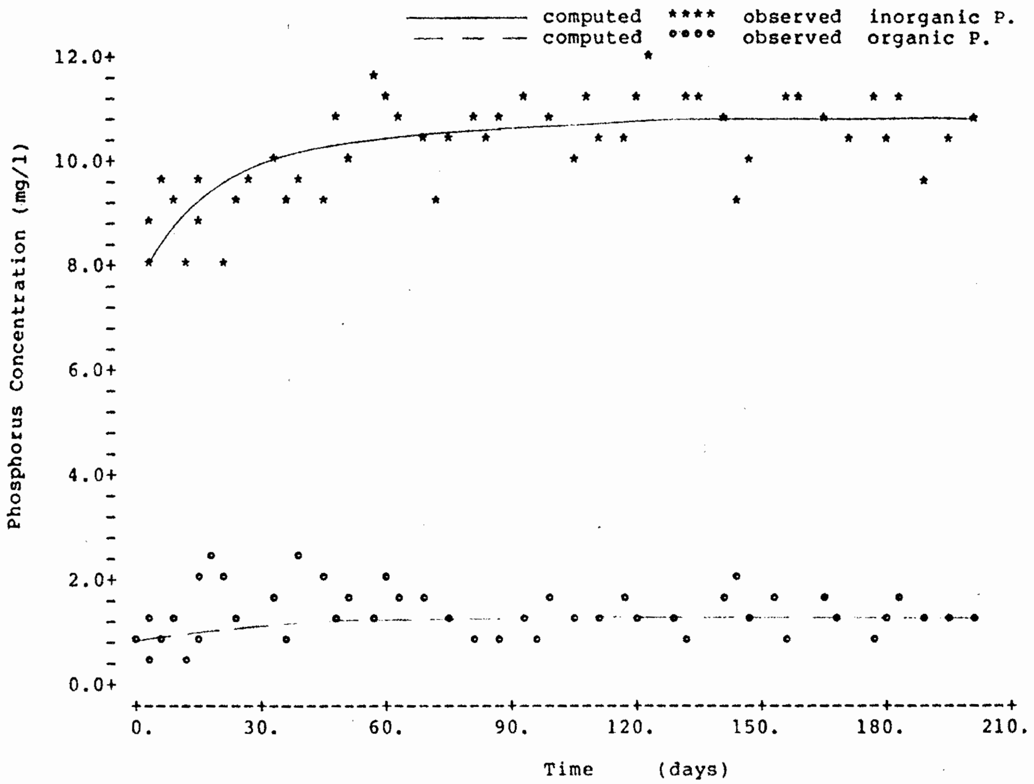


Figure 5-39 Phosphorus in FWSP Supernatant of System II (First Period)

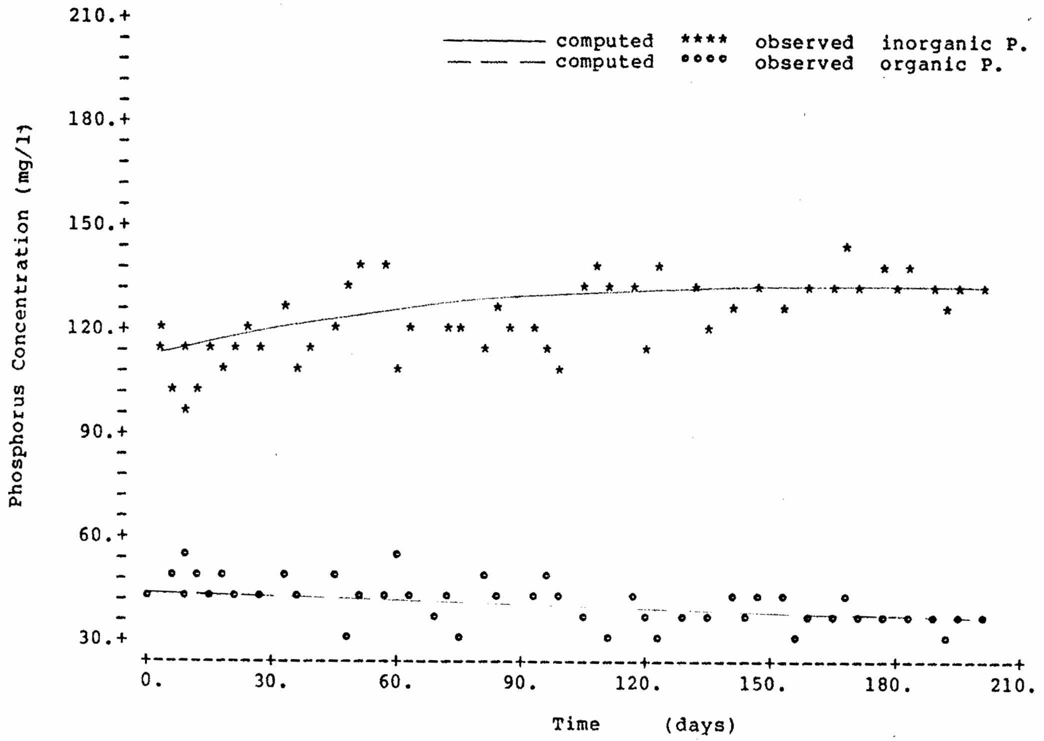


Figure 5-40 Phosphorus in FWSP Sediment of System II (First Period)

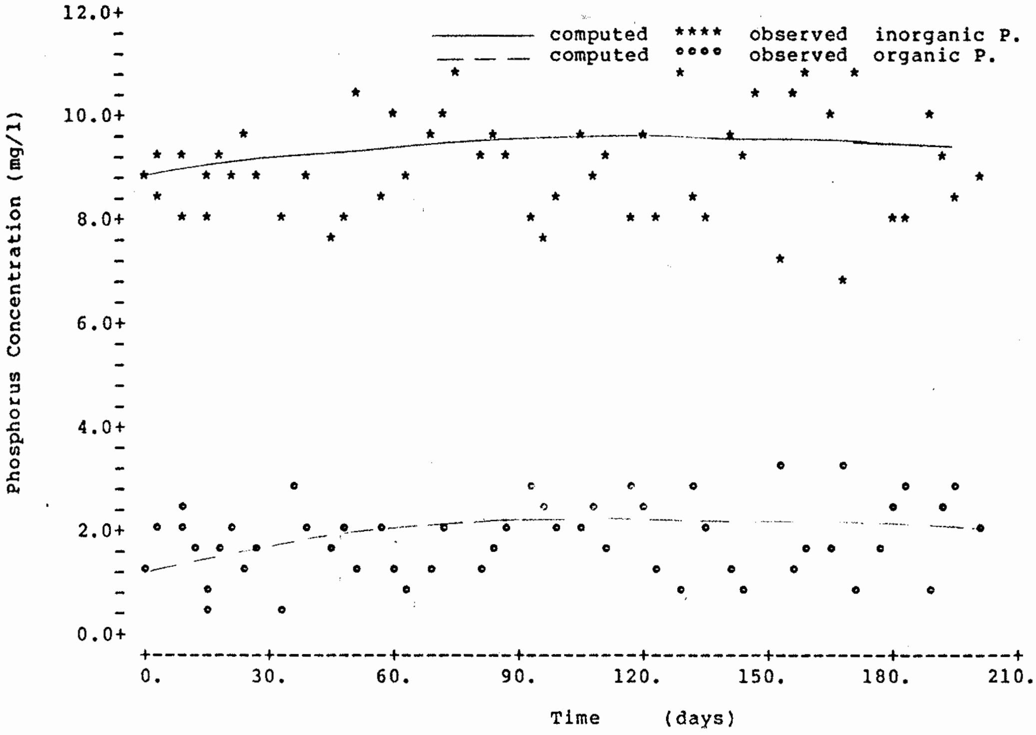


Figure 5-41 Phosphorus in MWSP Supernatant of System II (First Period)

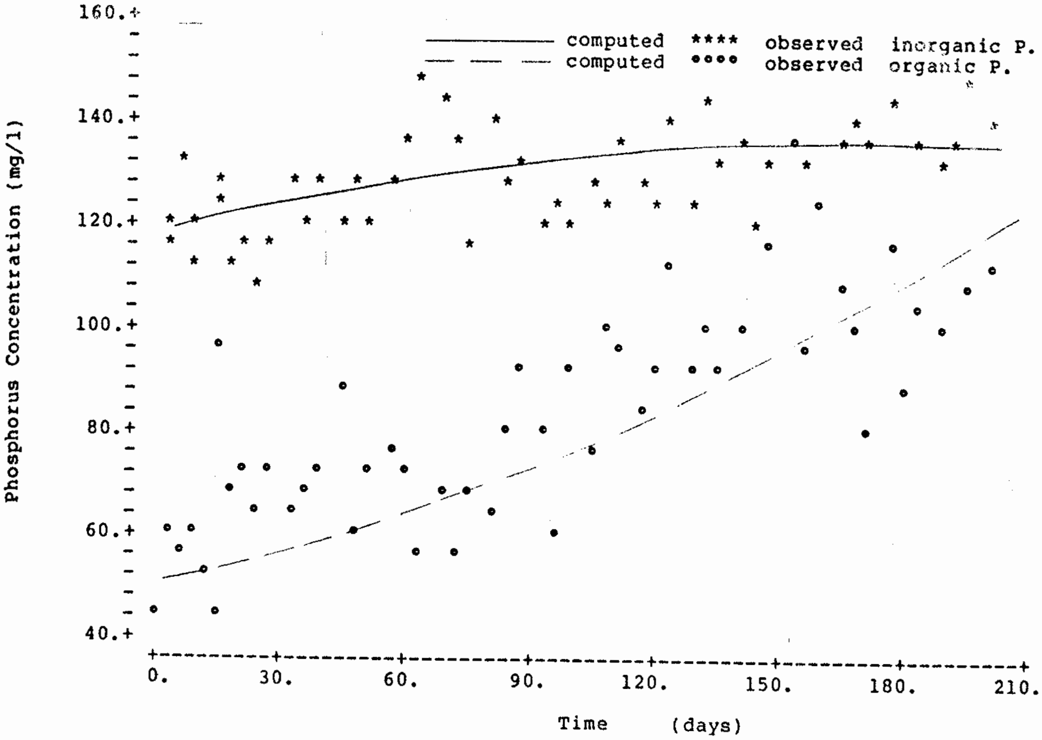


Figure 5-42 Phosphorus in MWSP Sediment of System II (First Period)

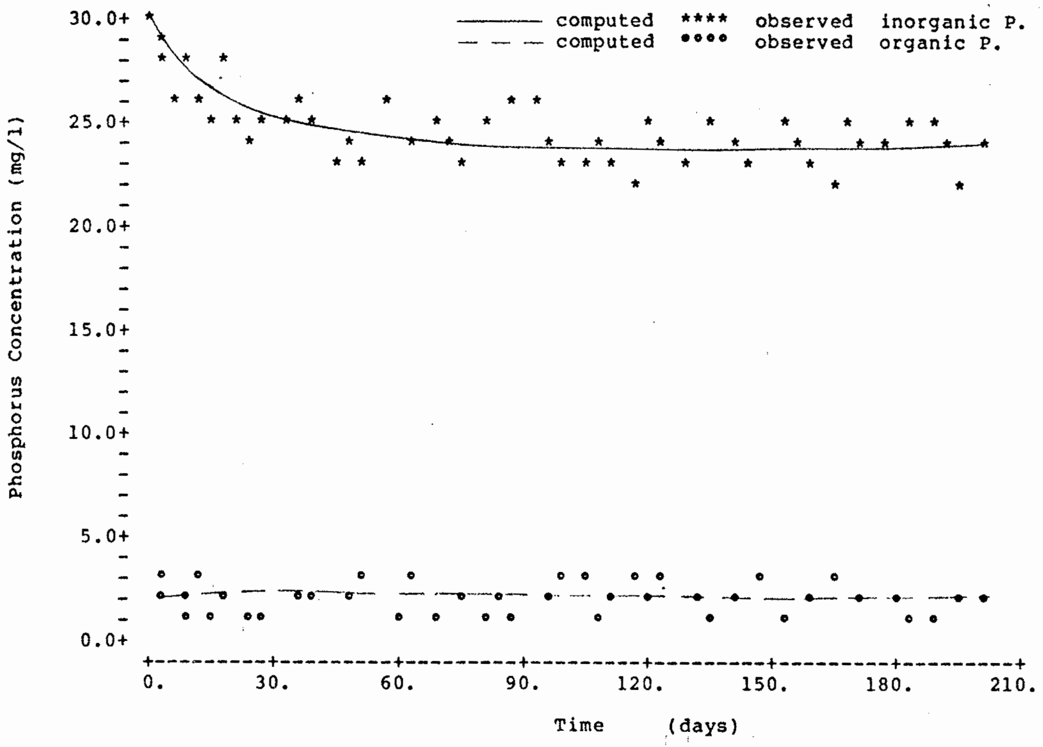


Figure 5-43 Phosphorus in AWSP Supernatant of System I (Second Period)

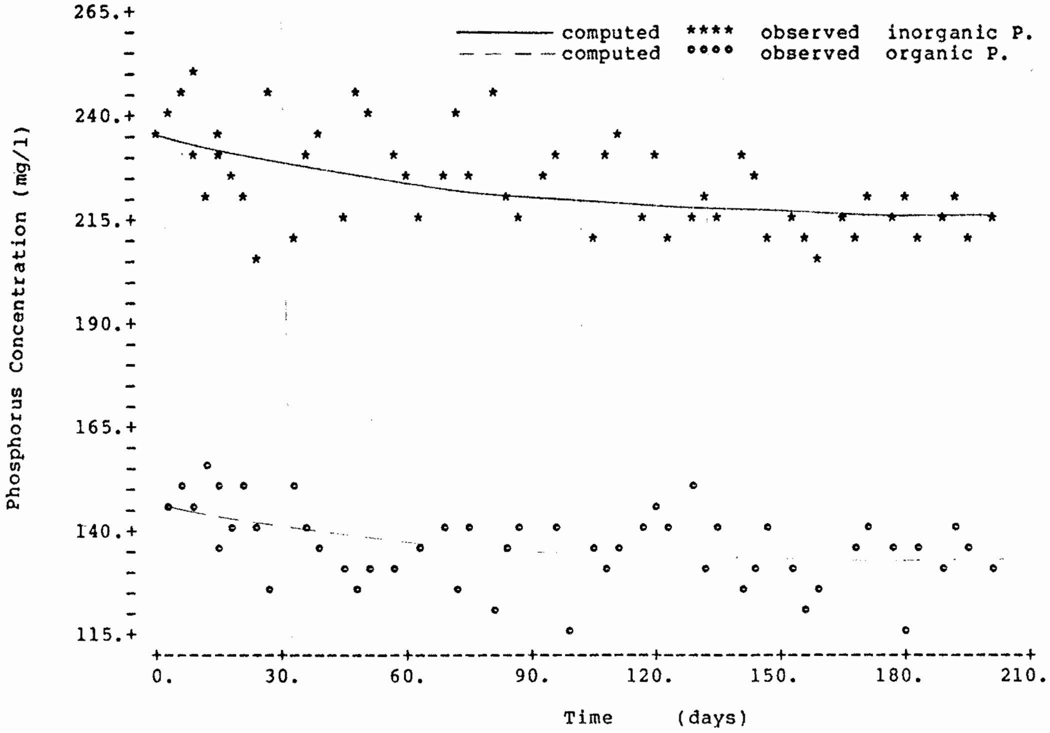


Figure 5-44 Phosphorus in AWSP Sediment of System I (Second Period)

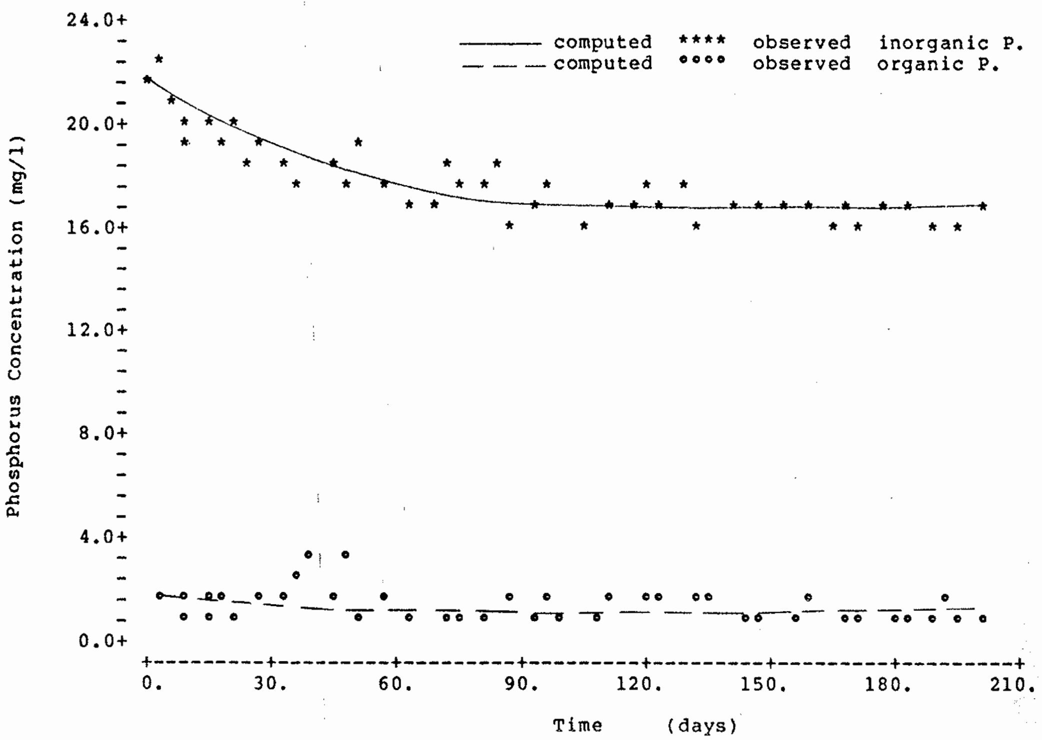


Figure 5-45 Phosphorus in FWSP Supernatant of System I (Second Period)

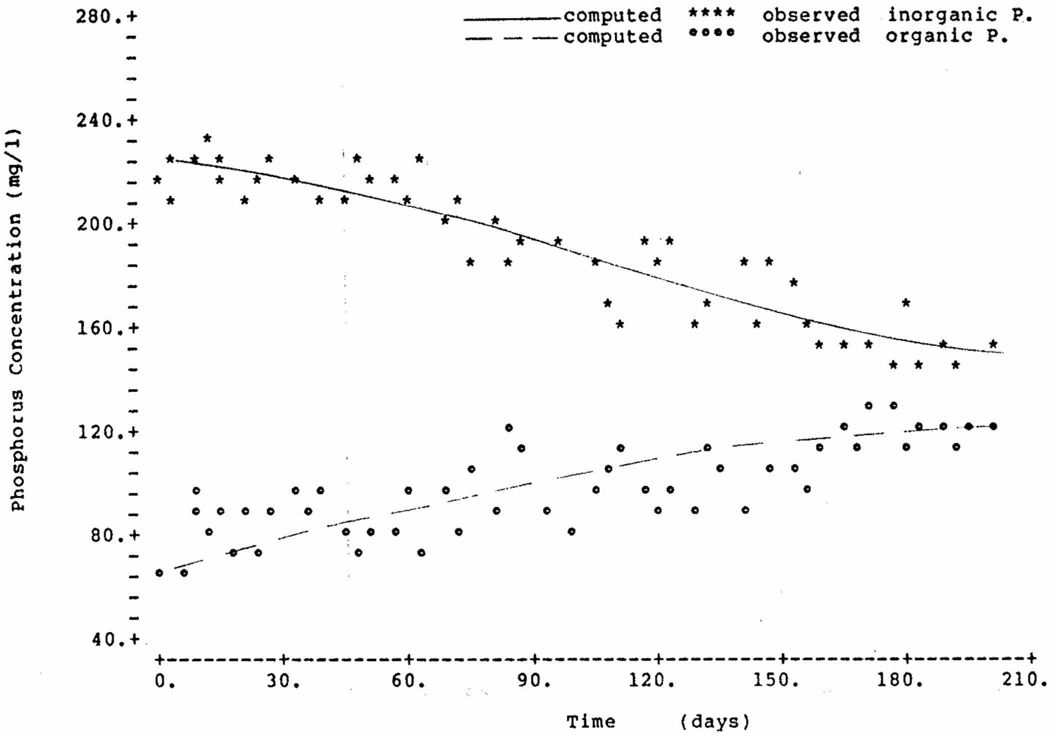


Figure 5-46 Phosphorus in FWSP Sediment of System I (Second Period)

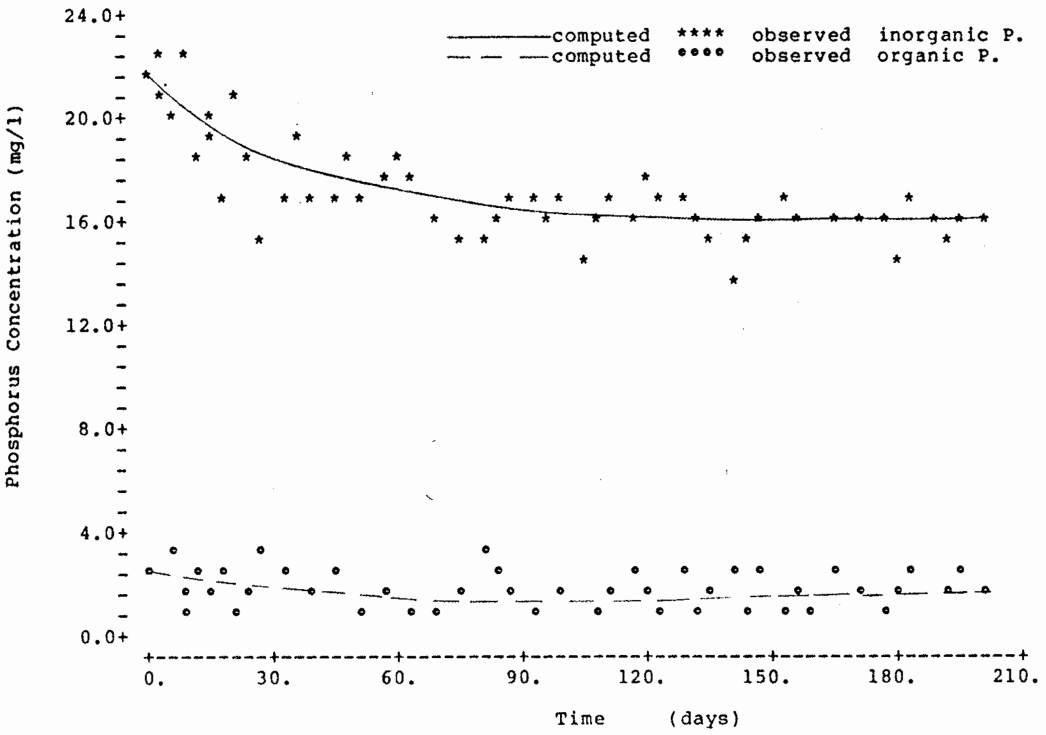


Figure 5-47 Phosphorus in MWSP Supernatant of System I (Second Period)

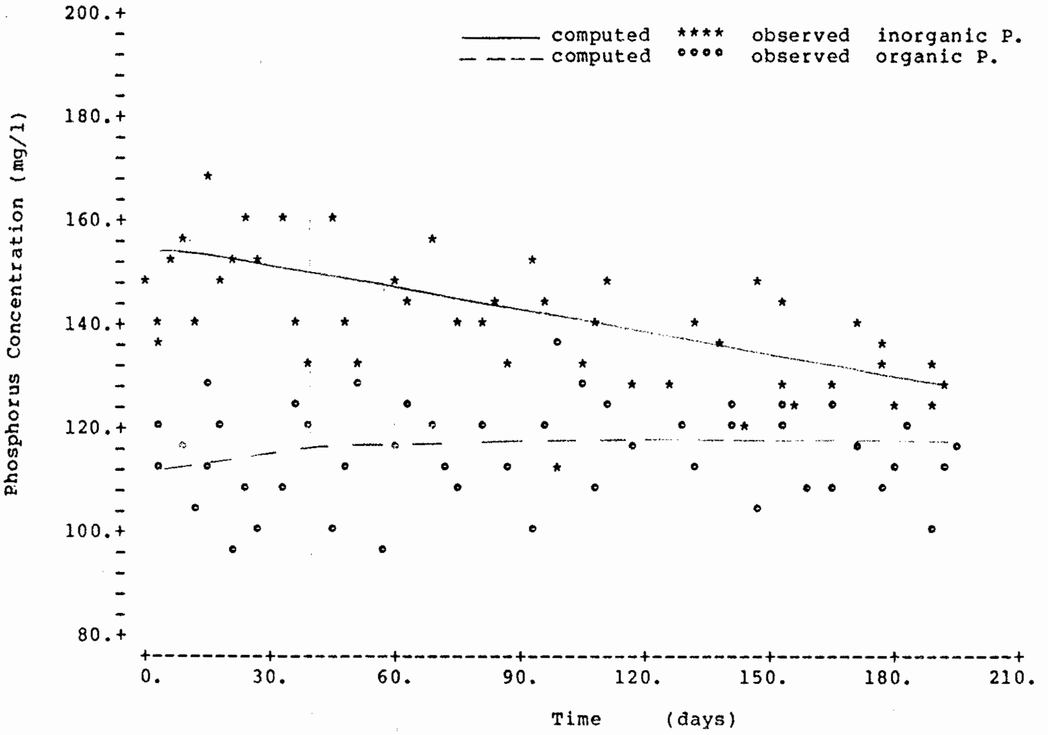


Figure 5-48 Phosphorus in MWSP Sediment of System I (Second Period)

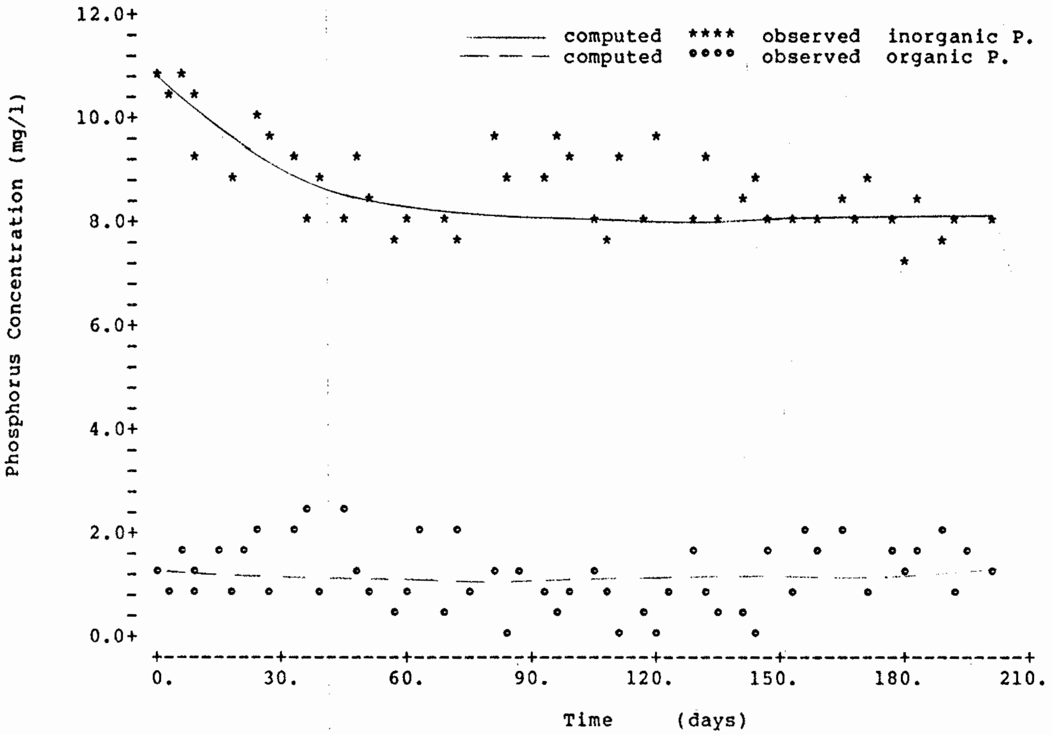


Figure 5-49 Phosphorus in FWSP Supernatant of System II (Second Period)

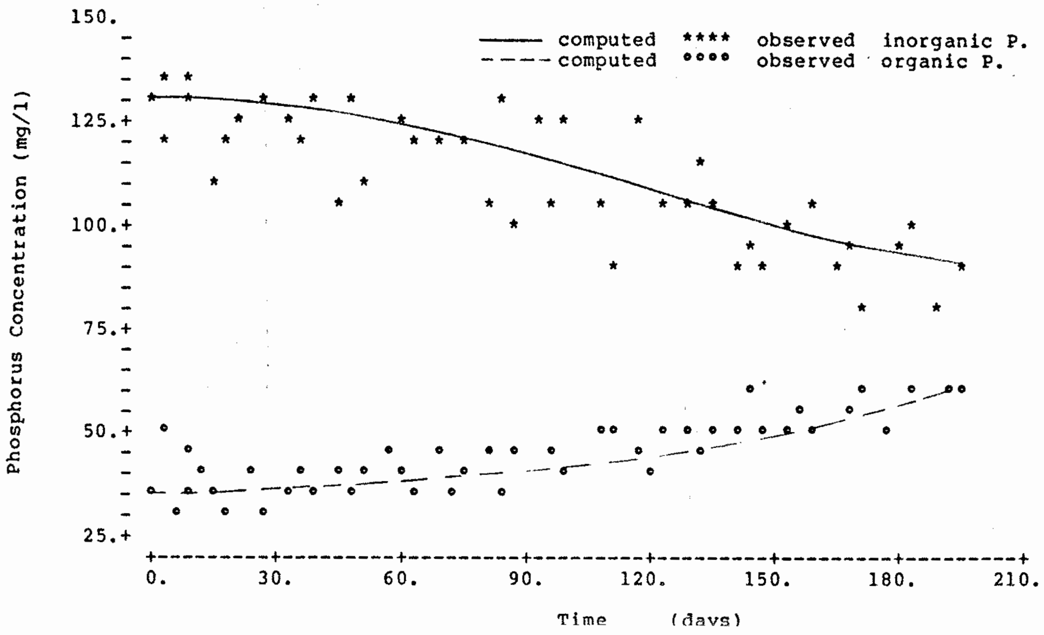


Figure 5-50 Phosphorus in FWSP Sediment of System II (Second Period)

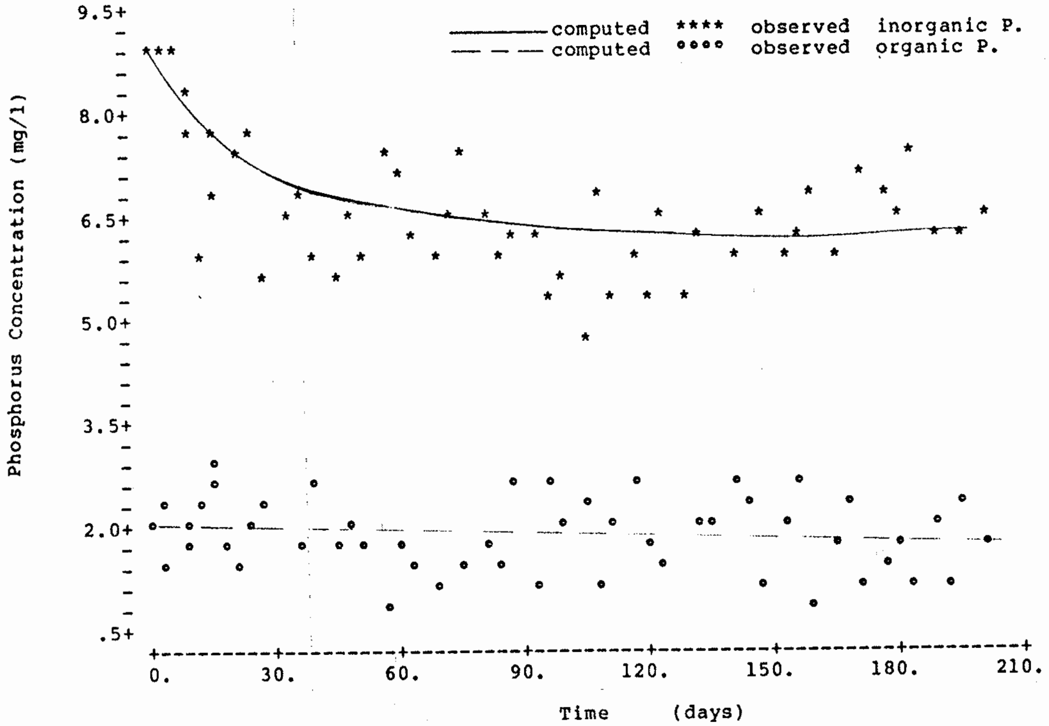


Figure 5-51 Phosphorus in MWSP Supernatant of System II (Second Period)

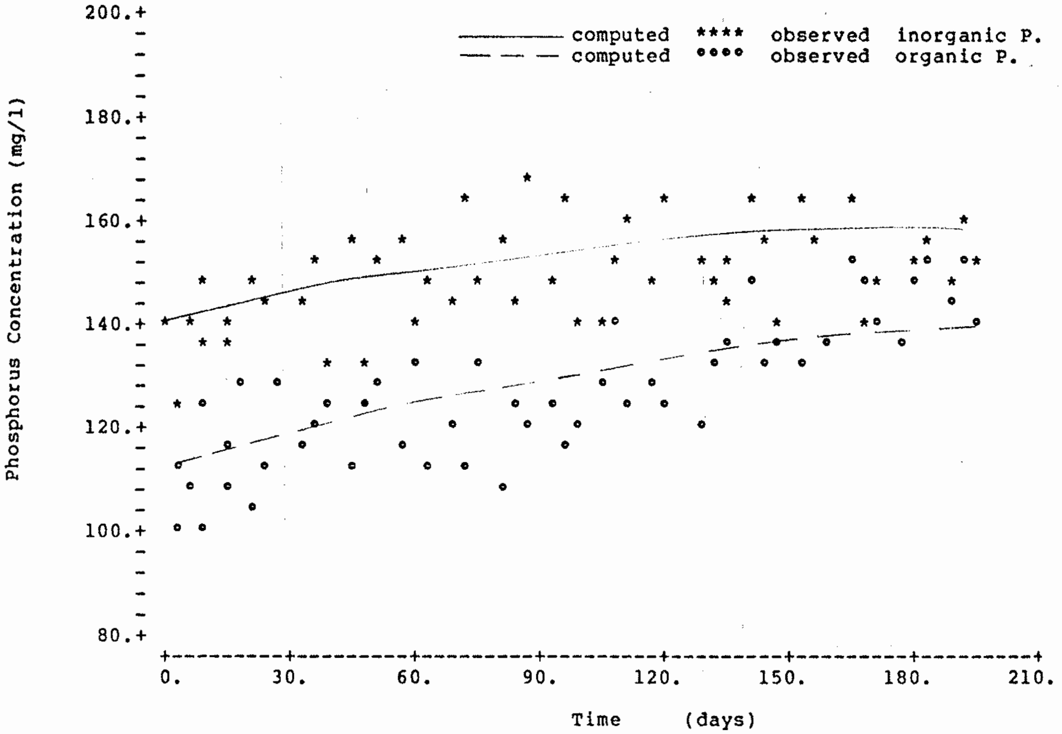


Figure 5-52 Phosphorus in MWSP Sediment of System II (Second Period)

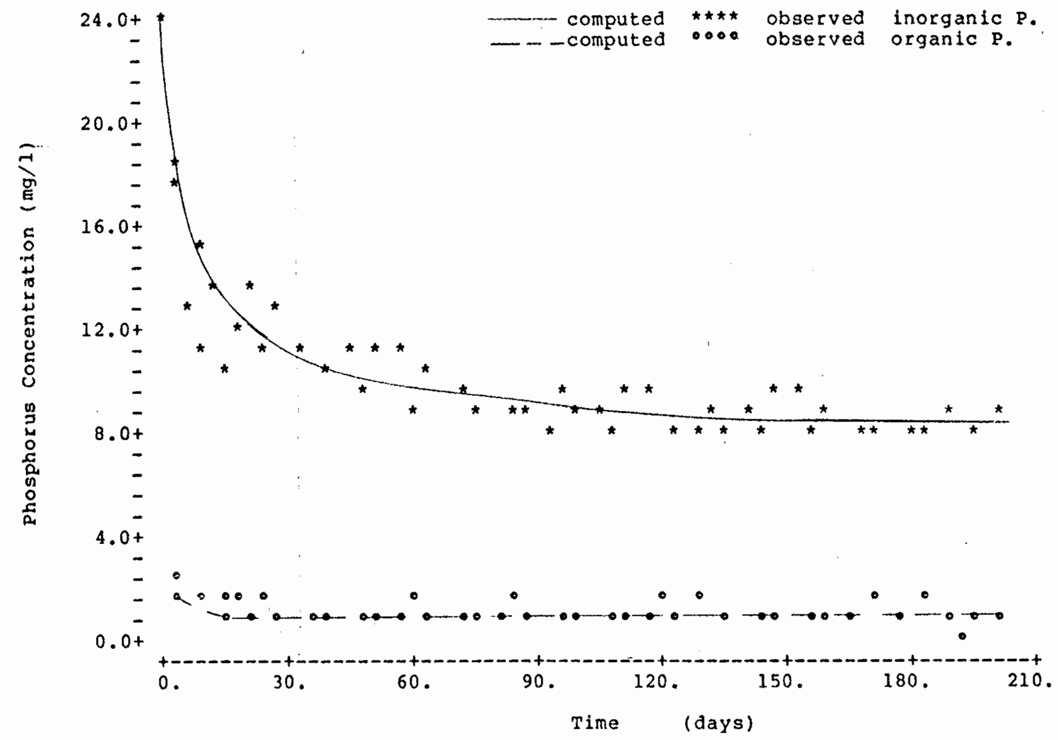


Figure 5-53 Phosphorus in AWSP Supernatant of System I (Third Period)

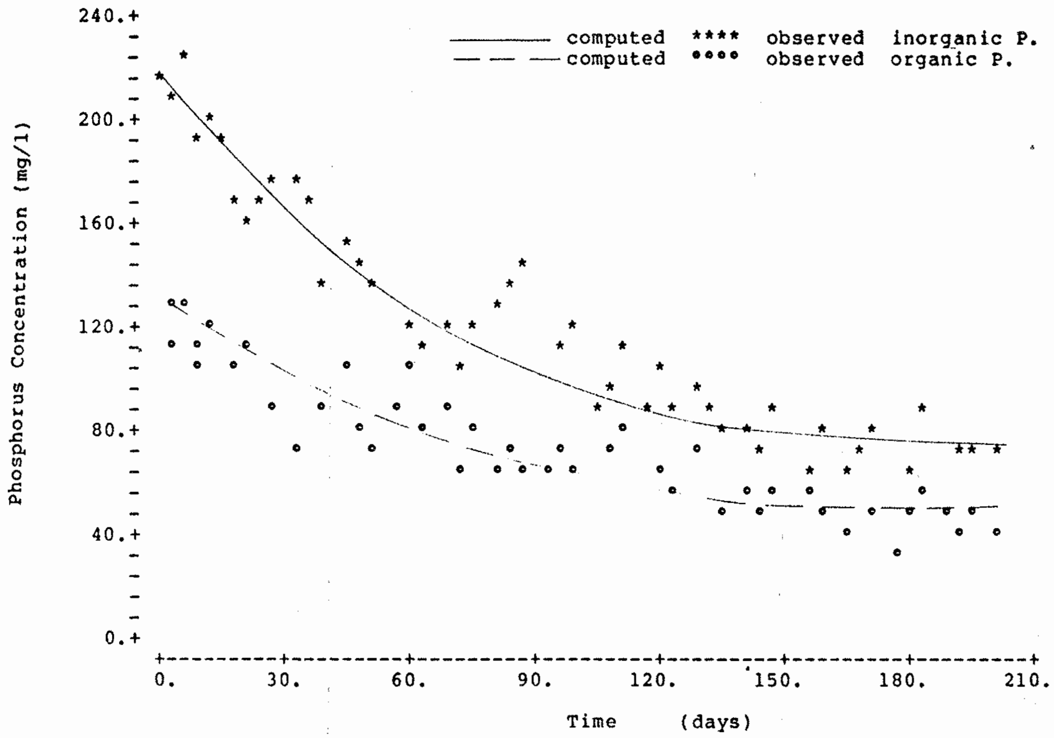


Figure 5-54 Phosphorus in AWSP Sediment of System I (Third Period)

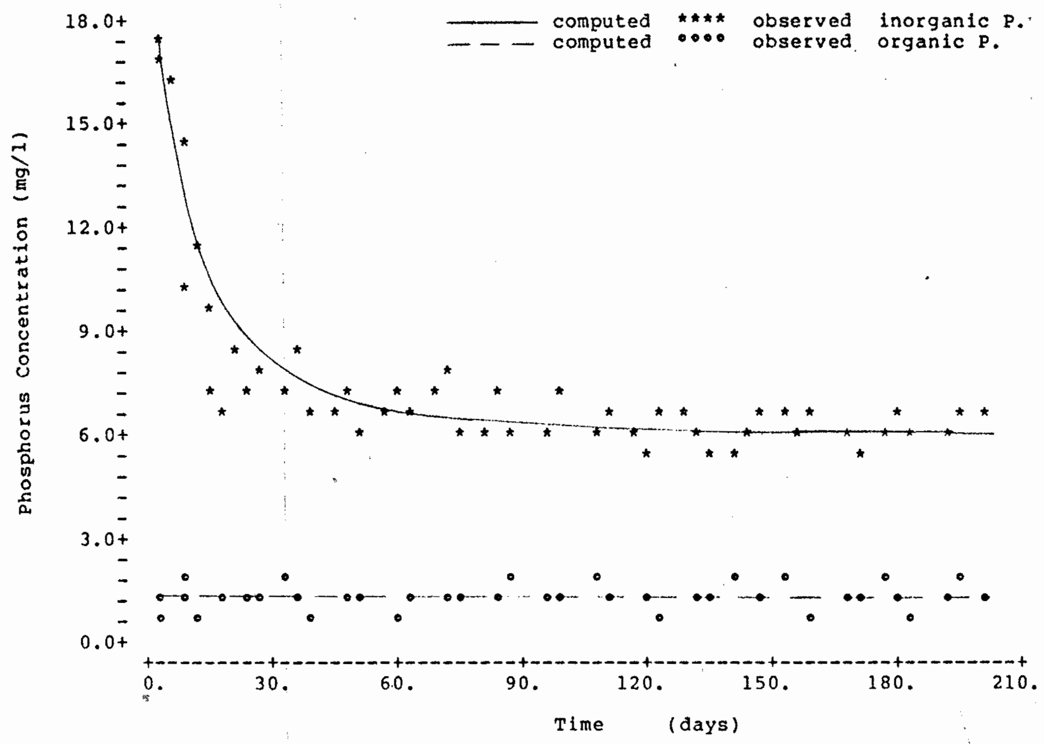


Figure 5-55 Phosphorus in FWSP Supernatant of System I (Third Period)

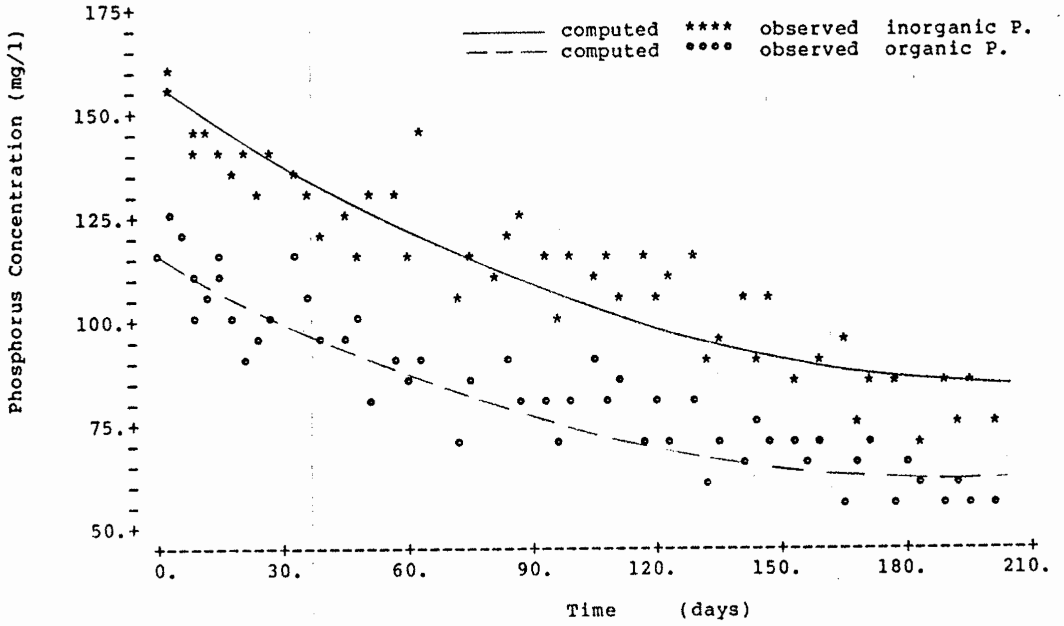


Figure 5-56 Phosphorus in FWSP Sediment of System I (Third Period)

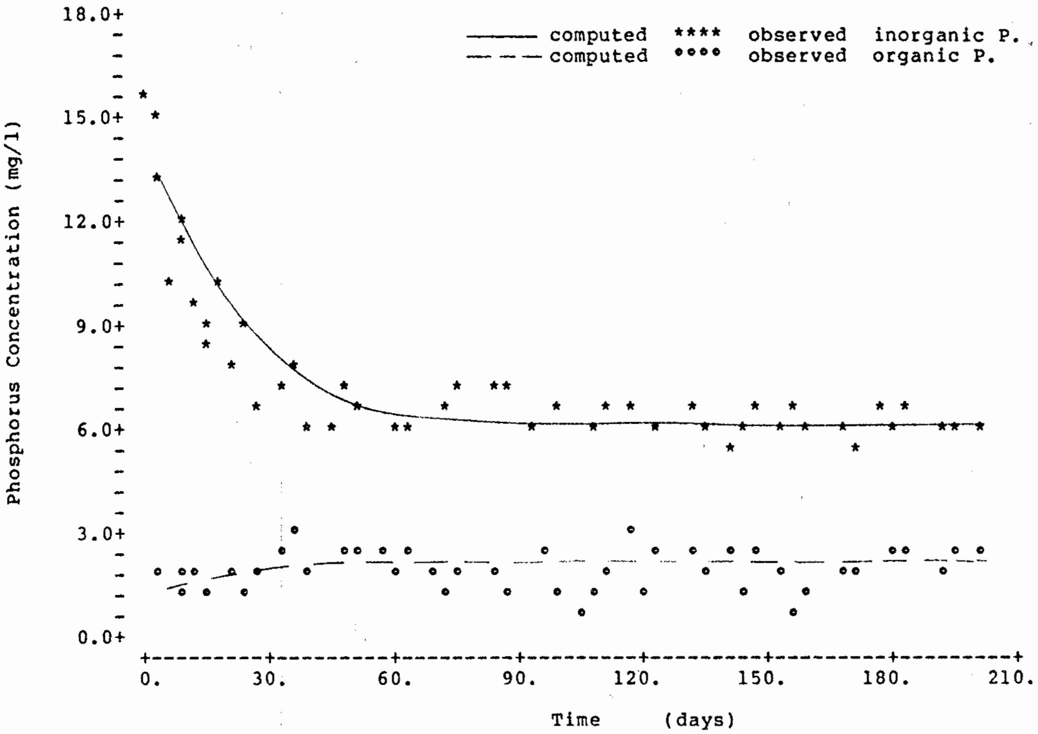


Figure 5-57 Phosphorus in MWSP Supernatant of System I (Third Period)

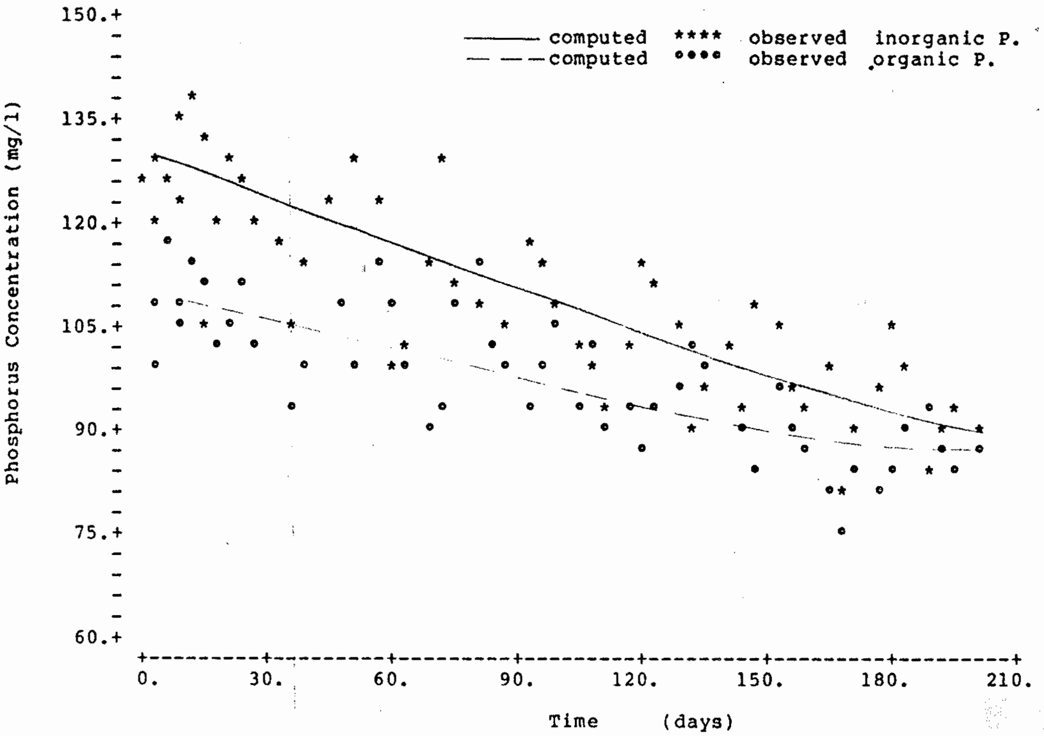


Figure 5-58 Phosphorus in MWSP Sediment of System I (Third Period)

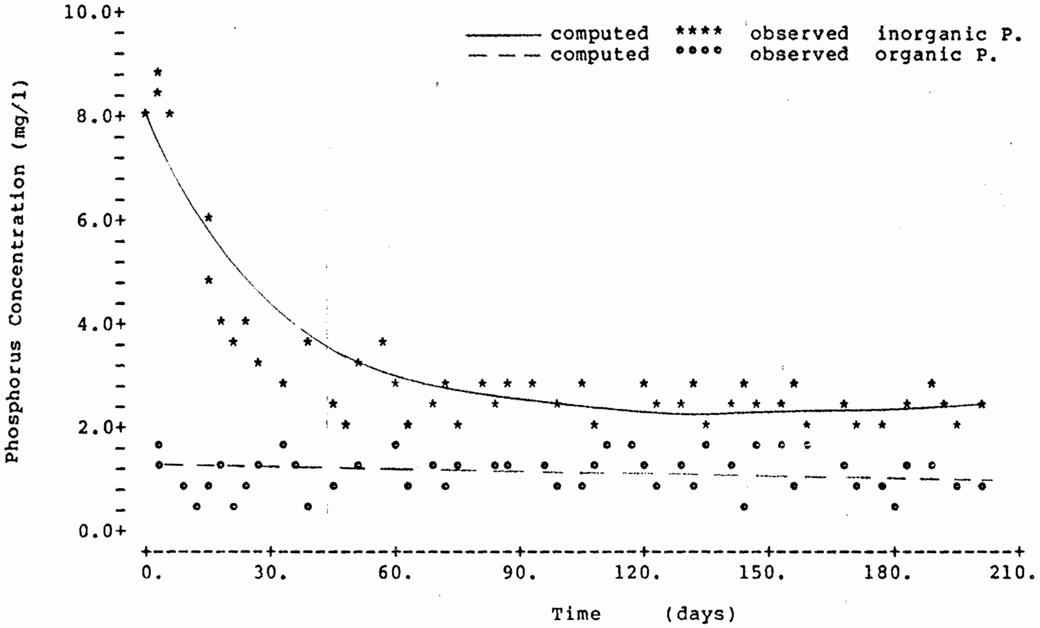


Figure 5-59 Phosphorus in FWSP Supernatant of System II (Third Period)

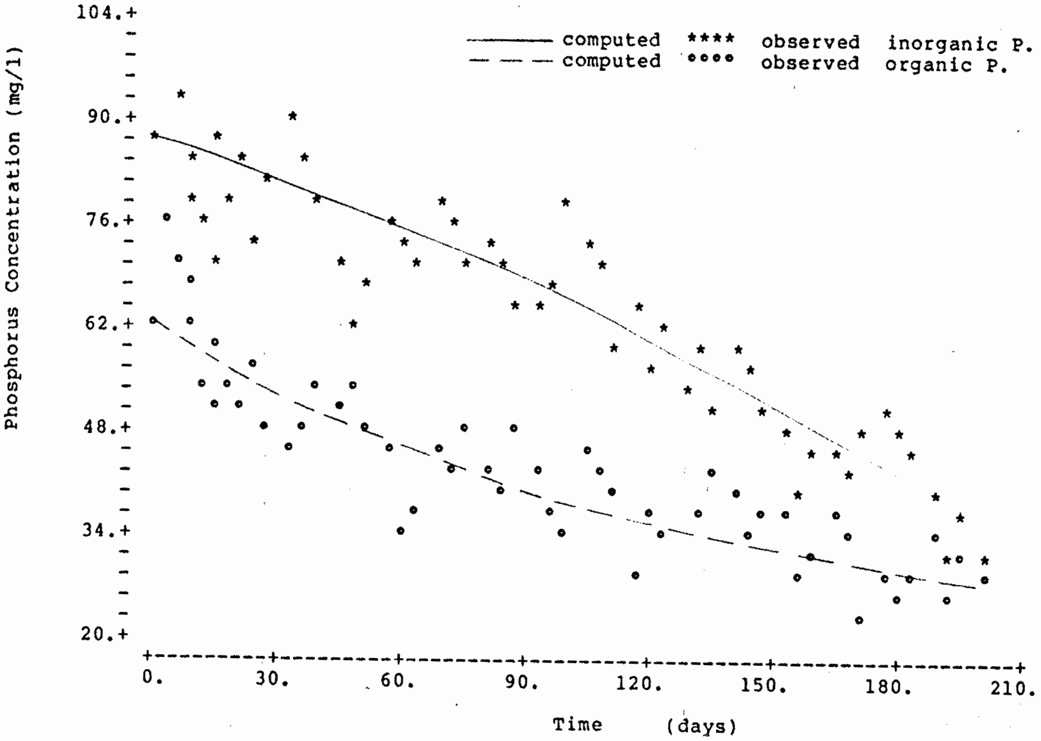


Figure 5-60 Phosphorus in FWSP Sediment of System II (Third Period)

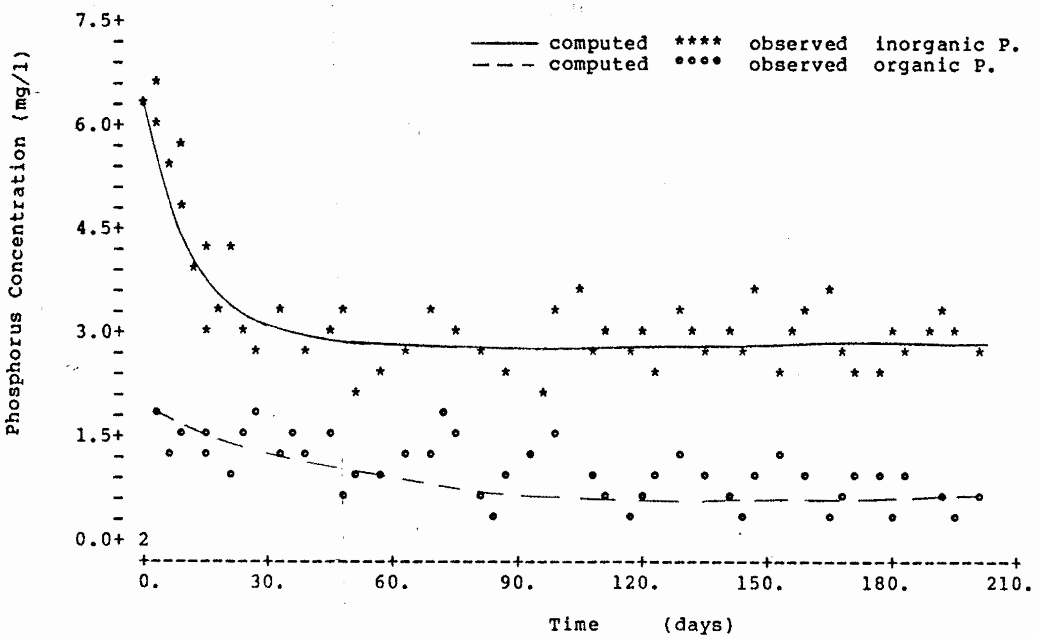


Figure 5-61 Phosphorus in MWSP Supernatant of System II (Third Period)

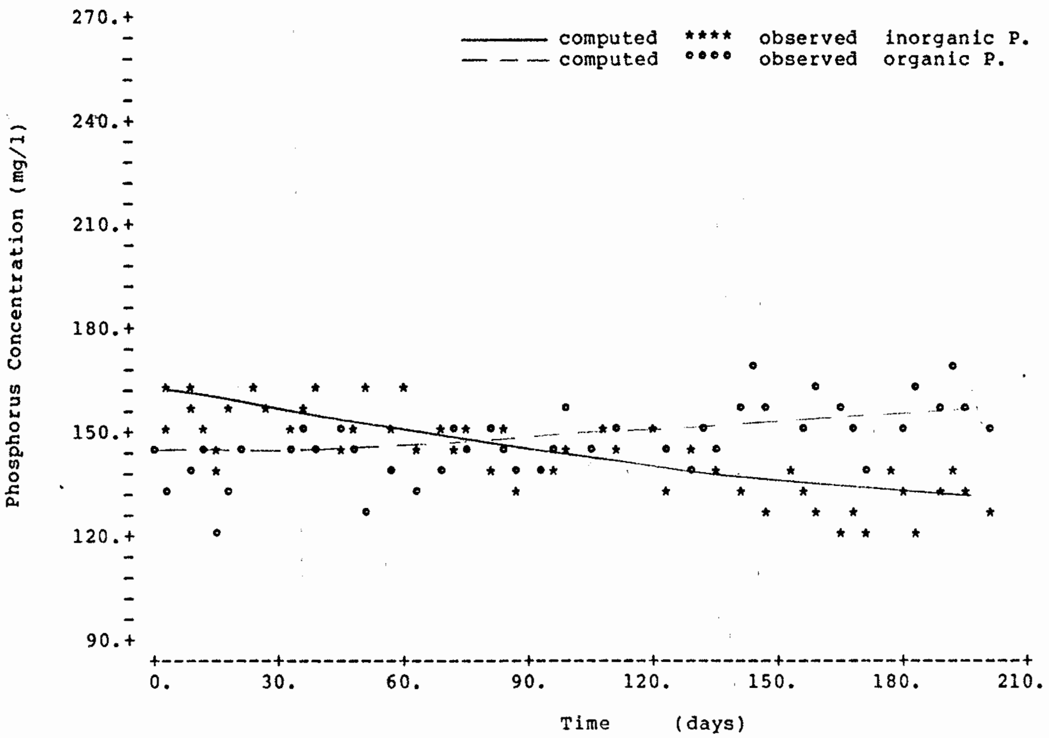


Figure 5-62 Phosphorus in MWSP Sediment of System II (Third Period)

are shown in Figures 5-33 through 5-62. The parameters and coefficients of the organic-inorganic phosphorus model are listed in Table 5-9.

The deposition rate of inorganic phosphorus (k_1) for System I was 5.3 to 5.7 cm/day for the AWSP, 2.5 to 2.6 cm/day for the FWSP, and 0.11 to 0.21 cm/day for the MWSP. Similarly, k_1 for System II was 2.5 to 3.0 cm/day in the FWSP and 0.31 to 0.33 cm/day for the MWSP. The deposition rate of organic phosphorus (k_3) for the same operations for the MWSP was 0.10 to 0.13 cm/day for System I and 0.20 to 0.23 cm/day for System II. The value of k_3 was greater for the AWSP (2.8 to 3.3 cm/day) and for the FWSP (2.0 to 2.4 cm/day for System I and 2.2 to 2.8 cm/day for System II). The value of k_3 fr the AWSP was similar to that found for the FWSP, but the value of k_3 dropped dramatically for the MWSP. The different characteristics of the particulate matter in the ponds could account for the differences of the deposition rates between the FWSP and the MWSP. The release rate of inorganic phosphorus (k_2) was 0.40 to 0.46 cm/day in the AWSP, 0.23 to 0.27 cm/day for the FWSP, 0.11 to 0.33 cm/day for the MWSP (System I), and 0.20 to 0.25 cm/day for the FWSP, 0.001 to 0.022 cm/day for the MWSP (System II). The results also revealed that the AWSP and the FWSP exhibited greater phosphorus release rates as compared to the MWSP.

Phosphorus associated with the sediment may exist in the form of calcium phosphate, aluminum-iron phosphate, organic phosphate or orthophosphate. Phosphate release resulting from biological reactions may occur through dephosphorylation by the phosphatase enzymes. In the degradation of organic matter, organic and inorganic acids are formed. These acids may dissolve inorganic phosphate compounds. Organic acids may also act as chelating and complexing agents for calcium, iron, manganese, and aluminum. Such reactions result in additional solubilization of phosphorus (Bailey 1968). The mineralized phosphorus may be released to the overlying water or be retained by the sediment. Though the exact retention mechanism of phosphorus by the sediment is not known, the aerobic layer of sediment may play a major role. When such an aerobic layer exists, many of the nutrients including phosphorus are retained by the sediment.

The unavailable release portions of inorganic and organic phosphorus (k_4, k_5) for the AWSP of System I and the FWSP in both Systems I and II exhibited almost the same values as those developed for the total phosphorus model. Because of the absence of an AWSP in System II, there was more incoming settlable inorganic matter which settled to pond sediment in the MWSP. The value of k_4 for the MWSP of System I was greater than that of System II.

Table 5-9 Parameters and Coefficients of the Inorganic-Organic Phosphorus Model

Pond System			Parameters					Coefficients			
No	Name	Period	k_1 (cm/d)	k_2 (cm/d)	k_3 (cm/d)	k_4 (%)	k_5 (%)	u_1 d^{-1}	u_2 d^{-1}	u_3 d^{-1}	u_4 d^{-1}
I	AWSP	1	5.7	0.46	3.2	45	48	0.0010	0.0030	0.0021	0.0075
		2	5.7	0.40	3.3	47	45	0.0011	0.0024	0.0020	0.0079
		3	5.3	0.45	2.8	49	42	0.0010	0.0028	0.0017	0.0088
	FWSP	1	2.6	0.25	2.2	29	22	0.0011	0.039	0.0024	0.0092
		2	2.5	0.23	2.0	22	23	0.0008	0.030	0.0035	0.0080
		3	2.6	0.27	2.4	25	24	0.0013	0.049	0.0026	0.010
	MWSP	1	0.21	0.033	0.13	16	25	0.0014	0.057	0.0020	0.0085
		2	0.14	0.011	0.10	17	25	0.0020	0.038	0.0029	0.013
		3	0.11	0.012	0.10	14	24	0.0018	0.042	0.0024	0.019
II	FWSP	1	3.0	0.23	2.8	21	21	0.0010	0.022	0.0017	0.010
		2	2.5	0.20	2.2	29	25	0.0008	0.029	0.0025	0.0072
		3	2.7	0.25	2.2	28	20	0.0010	0.027	0.0020	0.0099
	MWSP	1	0.31	0.022	0.23	25	18	0.0012	0.042	0.0014	0.0075
		2	0.30	0.010	0.22	29	19	0.0019	0.063	0.0019	0.017
		3	0.33	0.009	0.20	29	20	0.0015	0.045	0.0020	0.014

The biological coefficients obtained from the organic-inorganic phosphorus model provided more detailed information. In general, the coefficients developed based on the data derived from the MWSP and the FWSP were greater than those coefficients describing the performance of the AWSP. This phenomenon was found to be consistent with the pH variation in Table 5-5. The photosynthetic activities are related to the diurnal pH variation. As carbon dioxide was consumed, there was a decrease in hydrogen ion concentration and hence an increase in the pH. King et al. (1976) also reported the pH variation in the FWSP and in the MWSP.

The uptake of inorganic phosphorus was found to occur mainly in the supernatant of the MWSP and the FWSP, while the mineralization of organic phosphorus occurred mainly in the anaerobic sediment. Small mineralization rates of organic phosphorus (u_1 = 0.0008 to 0.0020 day^{-1}) were found in both Systems I and II. The uptake rate of inorganic phosphorus (u_2) was found to be between 0.022 to 0.063 day^{-1} in the supernatant for the FWSP and the MWSP, which was about 10 to 30 times greater than that u_2 found in the AWSP. In the AWSP sediment, the mineralization rate of organic phosphorus (u_4) was 0.0075 to 0.0088 day^{-1}, which was higher than the uptake rate of inorganic phosphorus (u_3 = 0.0017 to 0.0021 day^{-1}).

The uptake rate of inorganic phosphorus in the sediment (u_3) of the FWSP and the MWSP in both Systems I and II was 0.0014 to 0.0035 day^{-1} and the mineralization rate of organic phosphorus in the sediment (u_4) was 0.0072 to 0.019 day^{-1}. These data were similar to those found for the sediment of the AWSP (u_3 = 0.0020 day^{-1} and u_4 = 0.0080 day^{-1}). Therefore, the biological reactions in the sediment of both Systems I and II may have occurred mainly under anaerobic conditions.

The volatile suspended solid (VSS) concentration was higher in System II than that found for System I during the third period (Table 5-10); however, the organic phosphorus concentration was lower under the same situation. Kuhl (1974) reported that the phosphorus levels within algal cells might fluctuate widely depending on the phosphorus concentration in the substrate. Mackereth (1953) reported that the phosphorus concentration levels in algal cells (Asterionella formosa) could be as low as 6 x 10^{-8} ug P/cell or as high as 4 x 10^{-6} ug P/cell.

Since the organic-inorganic phosphorus model assumes that all inorganic phosphorus is available for algal and bacterial utilization, differences between the data and the model are to be expected. The percentages of orthophosphorus in inorganic phosphorus are listed in Tables 5-11 and 5-12. The fractions of orthophosphorus in the supernatant were found to be 88 to 97 percent for the AWSP, 88 to 100 percent for the FWSP, 88 to 100 percent for the MWSP (System I), and 90 to 100 percent for the FWSP

Table 5-10 Average SS and VSS Concentrations in Waste Stabilization Ponds for Each Period

Pond System		Characteristics					
No	Name	VSS (mg/l)			SS (mg/l)		
		Period 1	period 2	period 3	period 1	period 2	period 3
I	Influent	204	204	87	238	238	100
	AWSP	64	42	32	81	51	40
	FWSP	148	102	107	181	120	128
	MWSP	110	80	84	132	96	120
II	Influent	102	102	64	120	120	75
	FWSP	182	121	128	220	150	153
	MWSP	120	99	89	148	120	108

Table 5-11 Percentage of Orthophosphorus in Pond Supernatant

Pond System		Characteristics		
No.	Name	Orth-P (mg/l)	Inorg-P (mg/l)	Percentage (%)
I	AWSP	23.2	24.0	97
		24.1	25.3	95
		24.8	28.2	88
		10.0	10.7	93
		8.7	9.6	91
	FWSP	16.0	16.0	100
		16.7	16.7	100
		12.5	14.2	88
		7.4	8.2	90
		5.9	6.3	94
	MWSP	14.1	15.4	92
		15.8	15.8	100
		12.6	13.1	96
		8.4	9.3	91
		5.3	6.1	88
II	FWSP	6.6	7.4	90
		7.8	8.0	97
		9.6	10.1	95
		4.8	4.8	100
		2.7	2.9	94
	MWSP	5.9	6.1	96
		5.3	6.4	83
		6.1	7.2	84
		3.3	3.8	87
		2.5	2.8	89

Table 5-12 Percentage of Orthophosphorus in Pond Sediment

Pond System		Characteristics		
No.	Name	Orth-P (mg/l)	Inorg-P (mg/l)	Percentage (%)
I	AWSP	139	227	61
		147	214	69
		102	154	66
		64	93	65
		45	74	61
	FWSP	133	174	76
		91	154	59
		85	167	51
		56	87	65
		54	73	74
	MWSP	124	142	87
		73	125	59
		82	117	70
		59	87	67
		70	93	75
II	FWSP	69	134	51
		58	88	66
		67	117	57
		36	62	57
		21	31	66
	MWSP	102	142	72
		89	152	59
		75	114	66
		81	126	64
		76	128	59

and 83 to 96 percent for the MWSP (System II). The fractions of orthophosphorus were less in the sediment as compared to the supernatant. These fractions were found to be 61 to 69 percent for the AWSP, 51 to 76 percent for the FWSP, 59 to 87 percent for the MWSP (System I), and 51 to 66 percent for the FWSP and 59 to 72 percent for the MWSP (System II). More than 80 percent of the inorganic phosphorus in the supernatant was orthophosphorus. This form of phosphorus is a ready-to-use nutrient for algae and bacteria. Therefore, it would be reasonable for this model to consider all of the inorganic phosphorus to be available for algal and bacterial utilization. The utilization of inorganic phosphorus by algae and bacteria varies from species to species. However, the growth of many algal species can proceed when orthophosphate is substituted by other sources of phosphorus. Chlorella can utilize inorganic polyphosphates (up to chain length of 55 phosphate units) at the same rate as potassium phosphate (Galloway and Krauss 1963). Stewart (1974) observed that blue-green algae could utilize phosphorus present in phosphorus-based detergents. On the other hand, Overbeck (1961) showed that Scenedesmus quadricanda was unable to use pyrophosphate or some of the organic phosphorus compounds as a phospate source.

5.4 SENSITIVITY ANALYSES

Sensitivity analyses were performed to observe the variations in the values of input variables on the concentrations of total phosphorus, inorganic phosphorus, and organic phosphorus in the supernatant and in the sediment. The variables examined were K_1, K_2, K_3, k_1, k_2, k_3, k_4, k_5, u_1, u_2, u_3 and u_4 (Chapter Three). The effect of the inflow phosphorus concentration was also evaluated. The results of sensitivity analyses for both phosphorus models, total phosphorus model, and organic-inorganic phosphorus model were plotted in Figures 5-63 through 5-92.

The operating data from the FWSP was used for sensitivity analyses. The inflow rate (Q) and inflow phosphorus concentration (C_i), set at 1.5 l/day and 24 mg/l, resulted in a phosphorus loading of 1.2 kg P/ha/day. The hydraulic detention time was 32 days in the 48-liter rectangular aquarium where the volumes of supernatant and sediment, respectively, were set at 45:1 and 5:1.

Figures 5-63 and 5-64 illustrate the changes in total phosphorus concentrations in the supernatant (C) and in the sediment (C_s) as a function of the change of the deposition rate of total phosphorus (K_1). The relationship between C and C_s and the release rate (K_2) as well as the unavailable release portion of total phosphorus (K_3) are shown in Figures 5-65 through 5-68. As shown in Figures 5-63 and 5-67, it is apparent that the choice of values of K_1 and K_3 for C is very important. A 100 percent

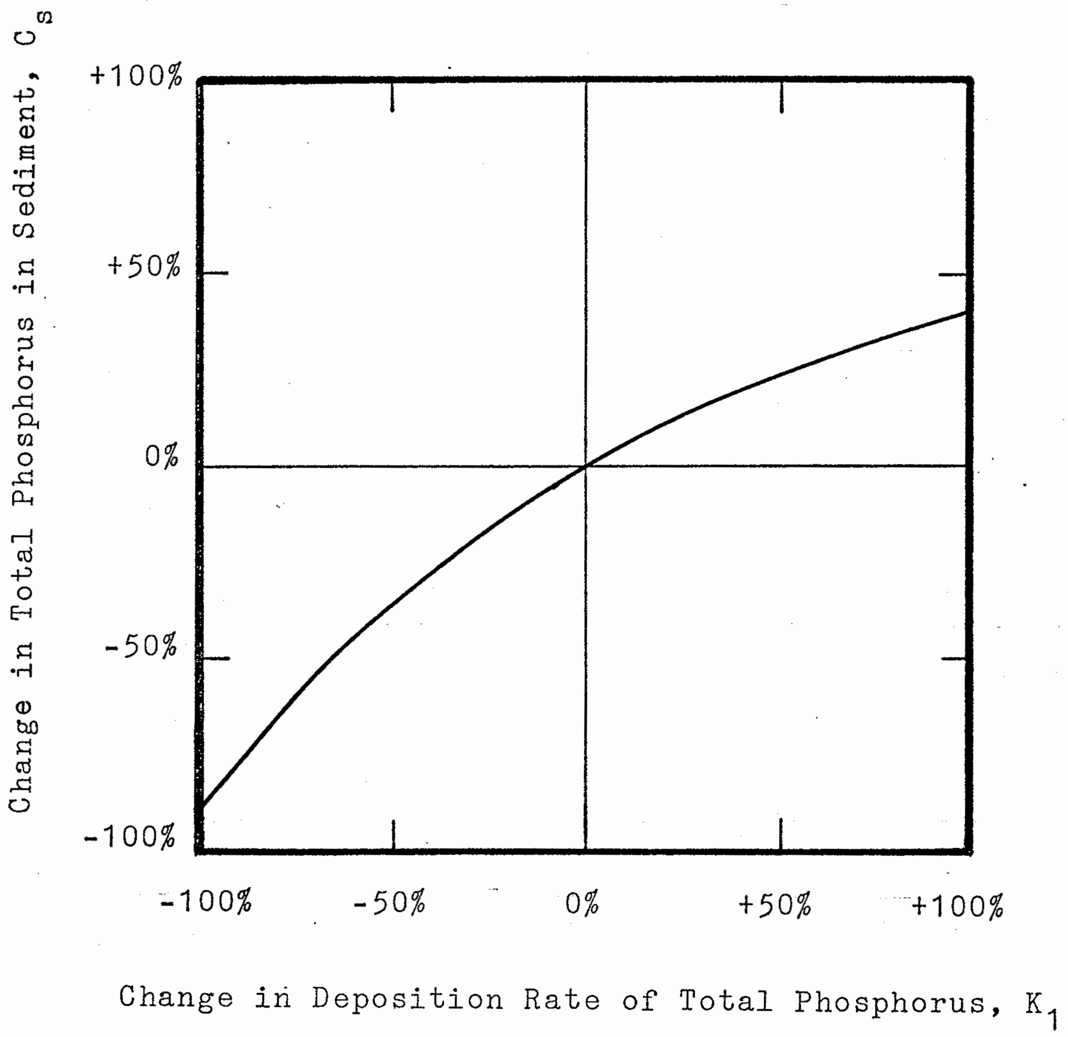


Figure 5-63 Sensitivity Analysis of C to K_1

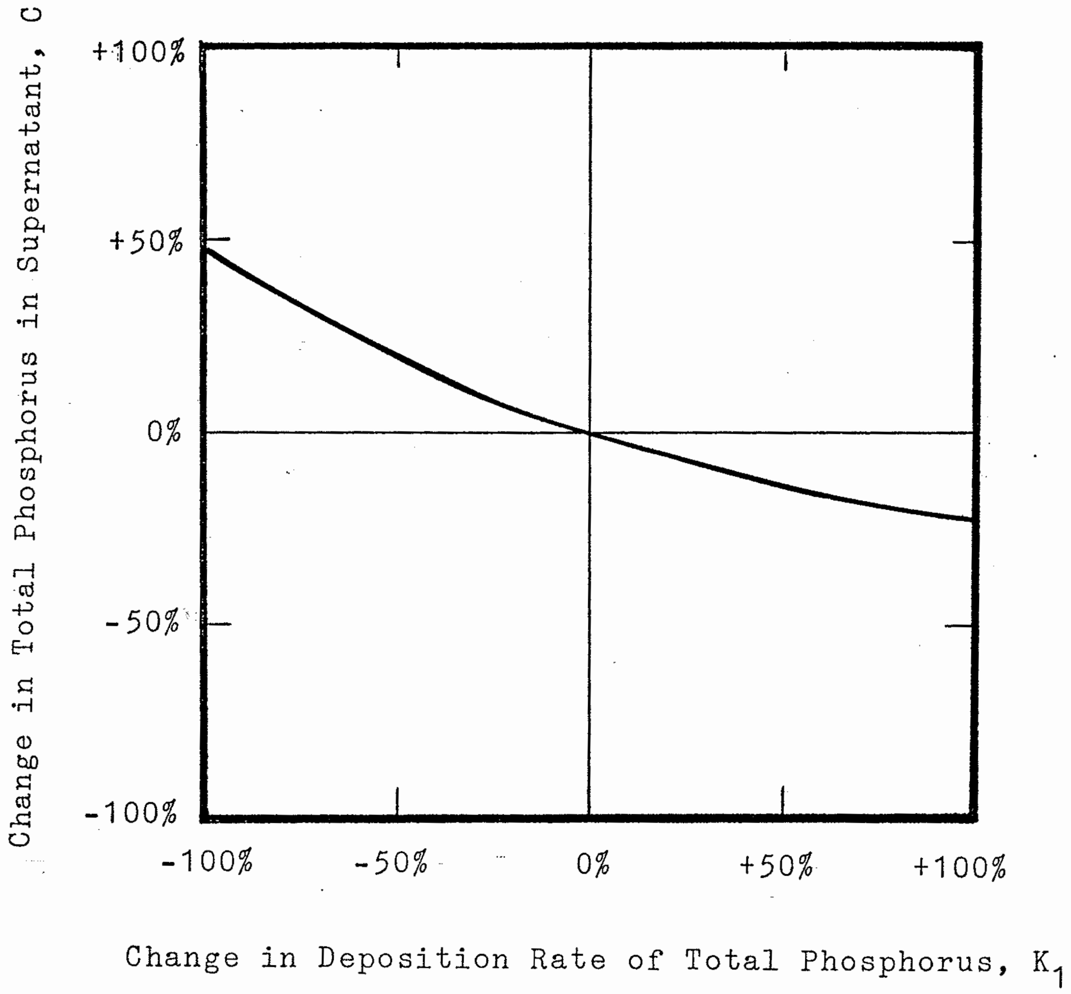


Figure 5-64 Sensitivity Analysis to C_s to K_1

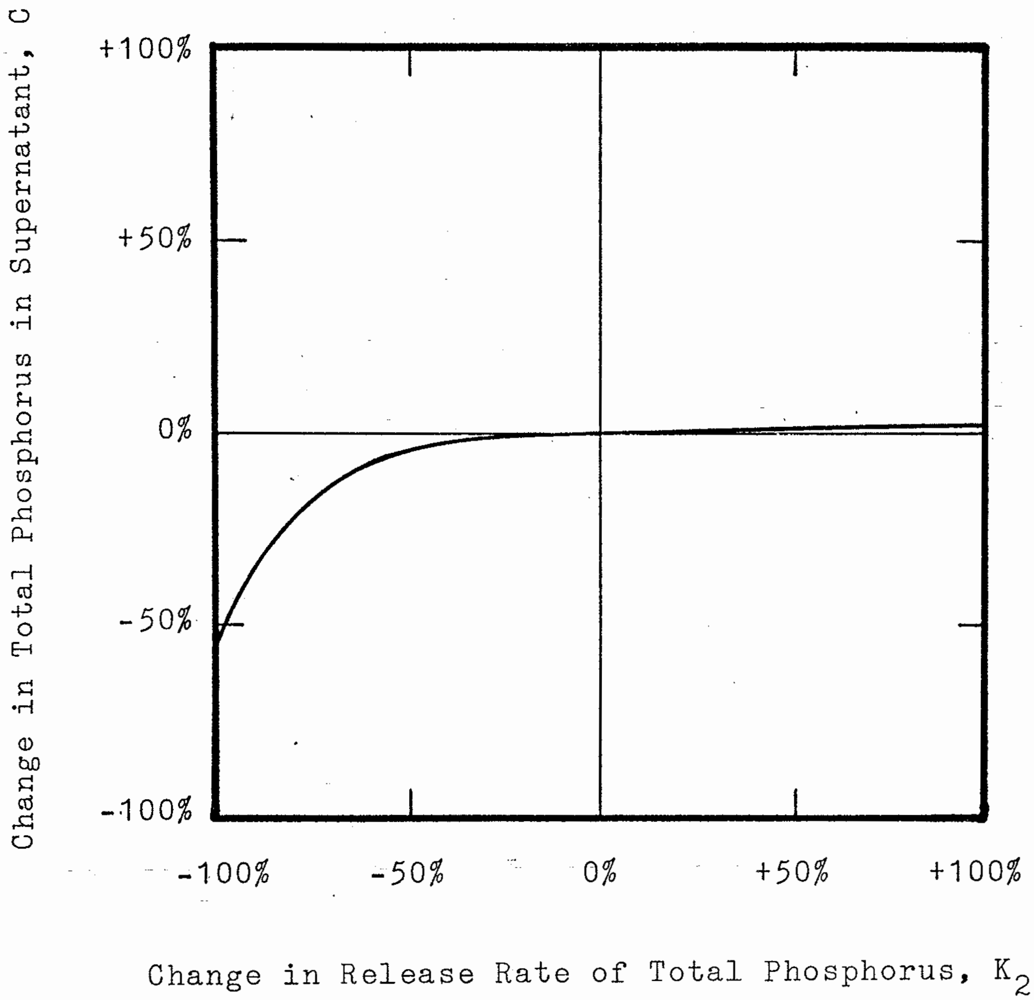


Figure 5-65 Sensitivity Analysis of C to K_2

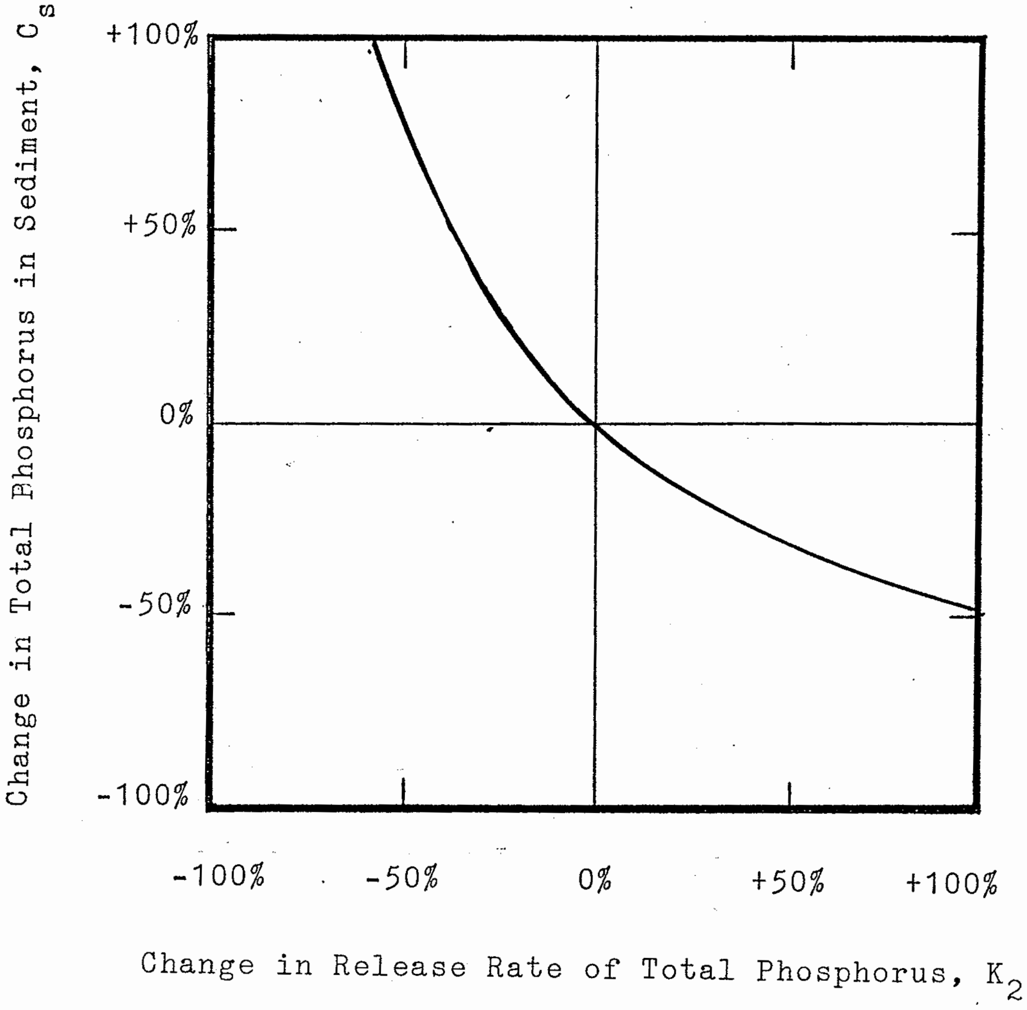


Figure 5-66 Sensitivity Analysis of C_s to K_2

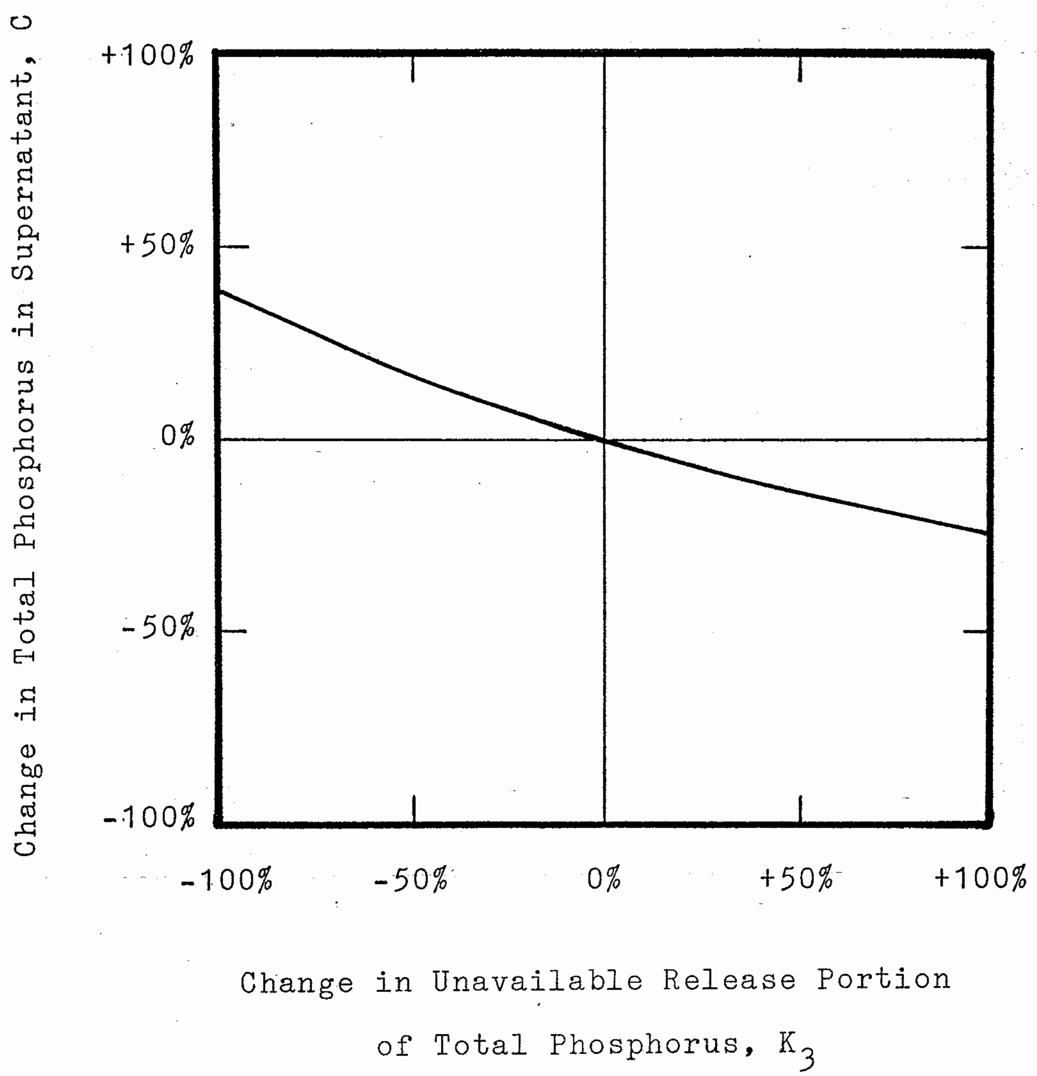


Figure 5-67 Sensitivity Analysis of C to K_3

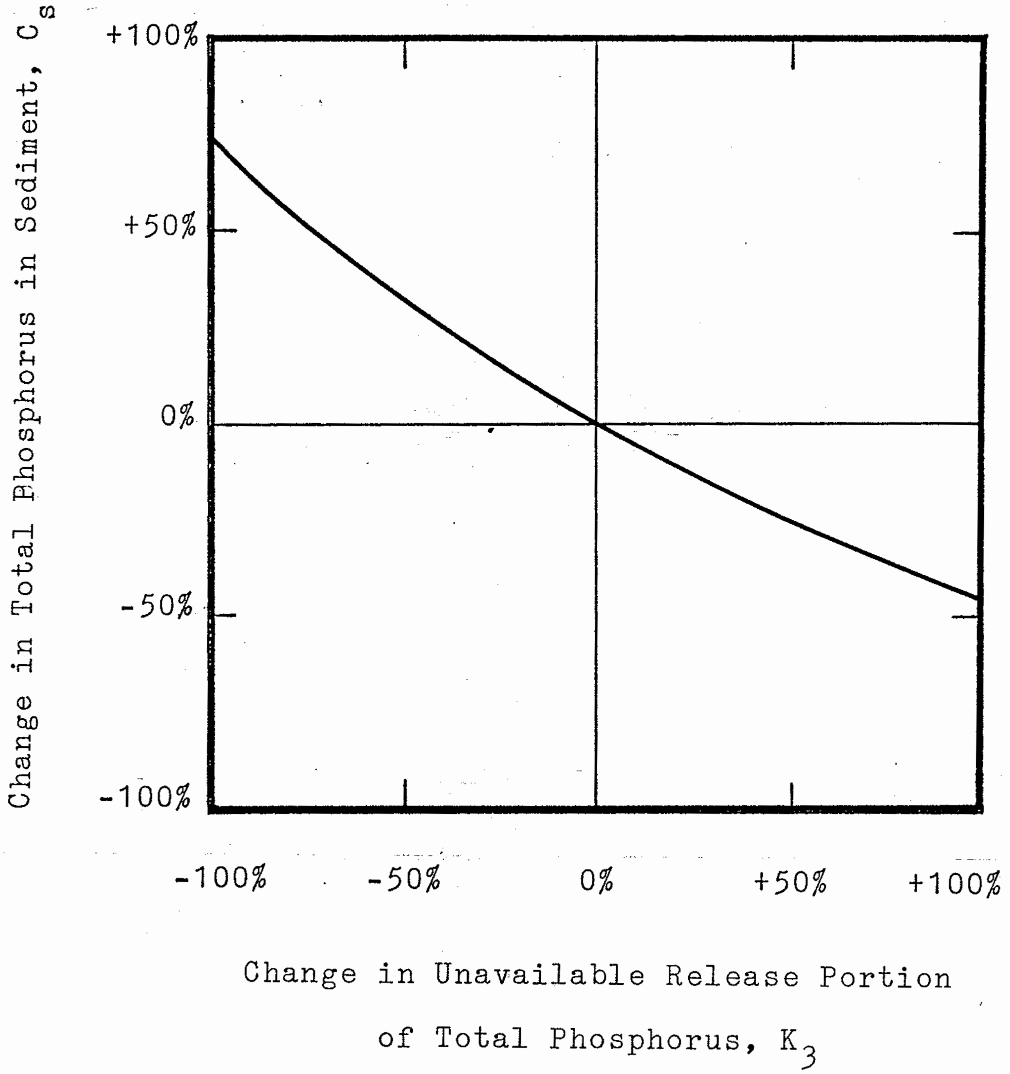


Figure 5-68 Sensitivity Analysis of C_s to K_3

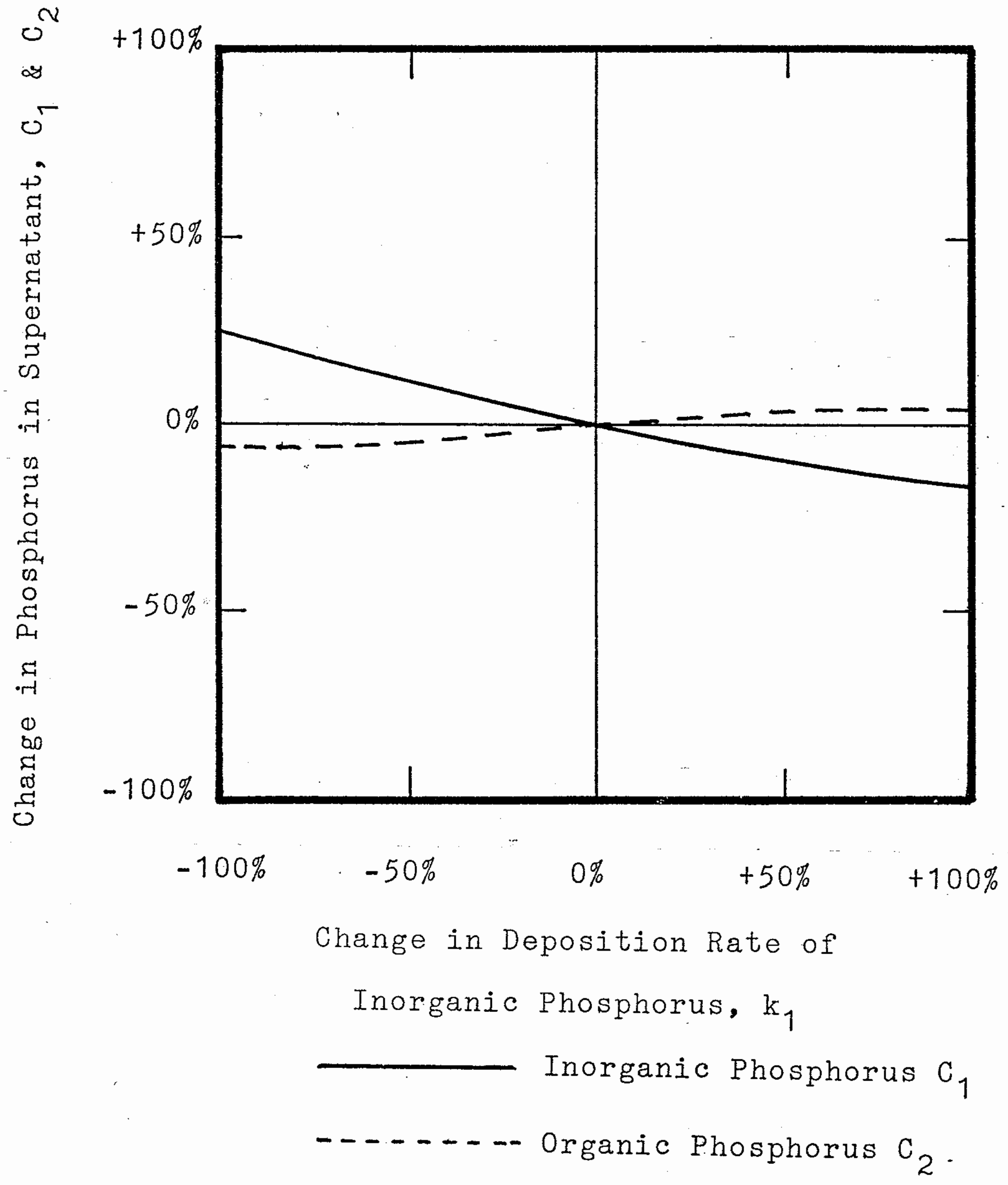


Figure 5-69 Sensitivity Analyses of C_1 & C_2 to k_1

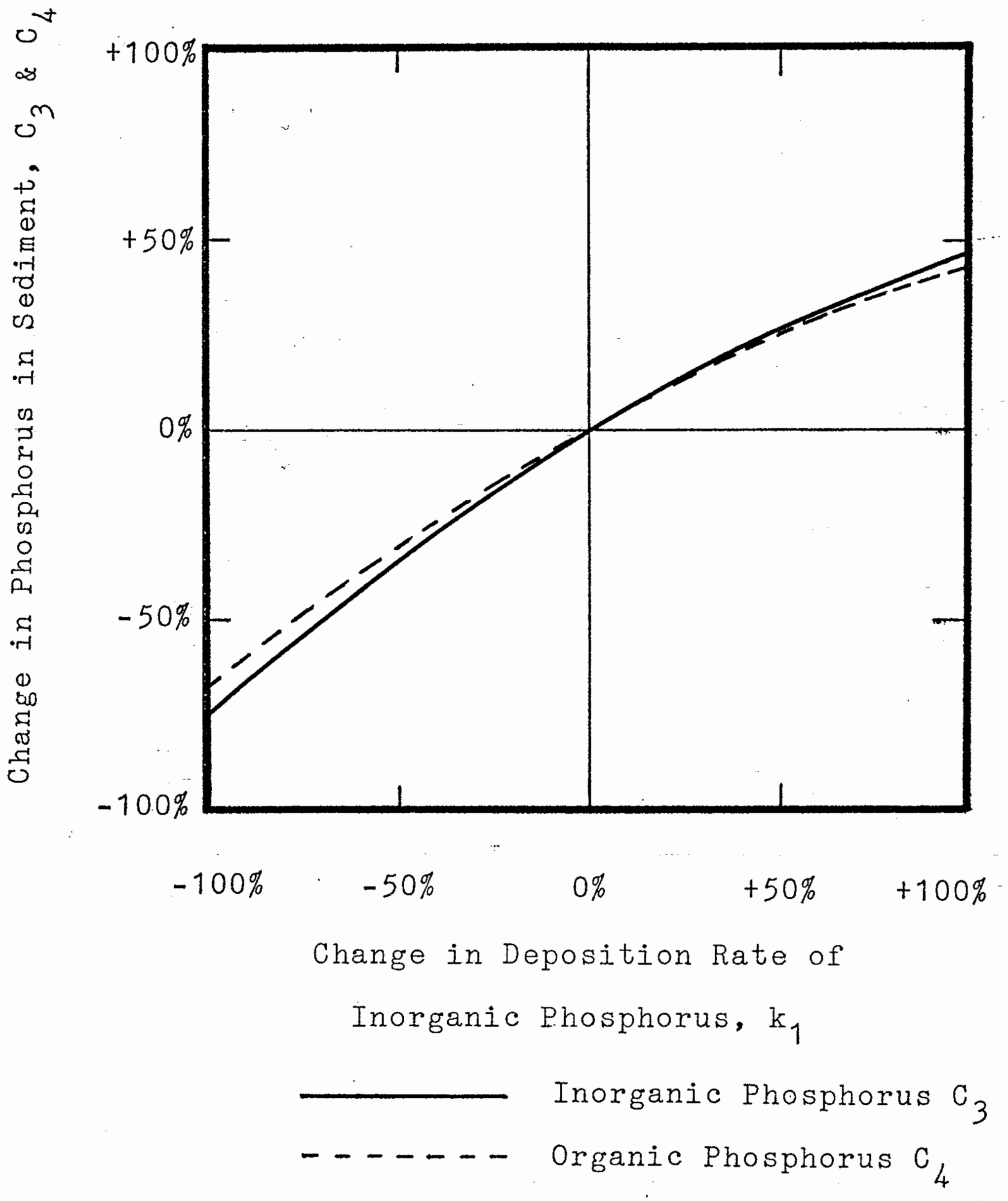


Figure 5-70 Sensitivity Analyses of C_3 & C_4 to k_1

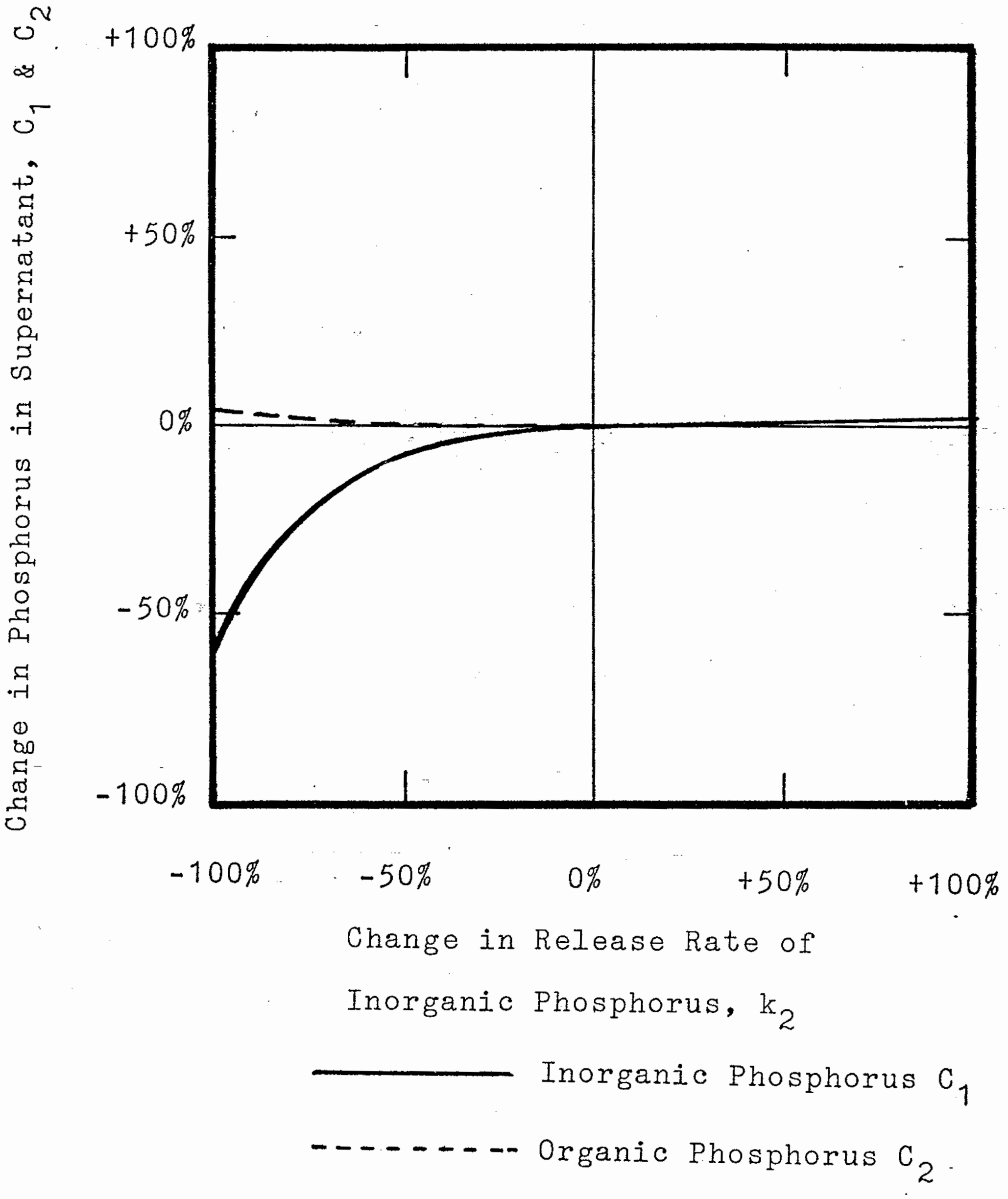


Figure 5-71 Sensitivity Analyses of C_1 & C_2 to k_2

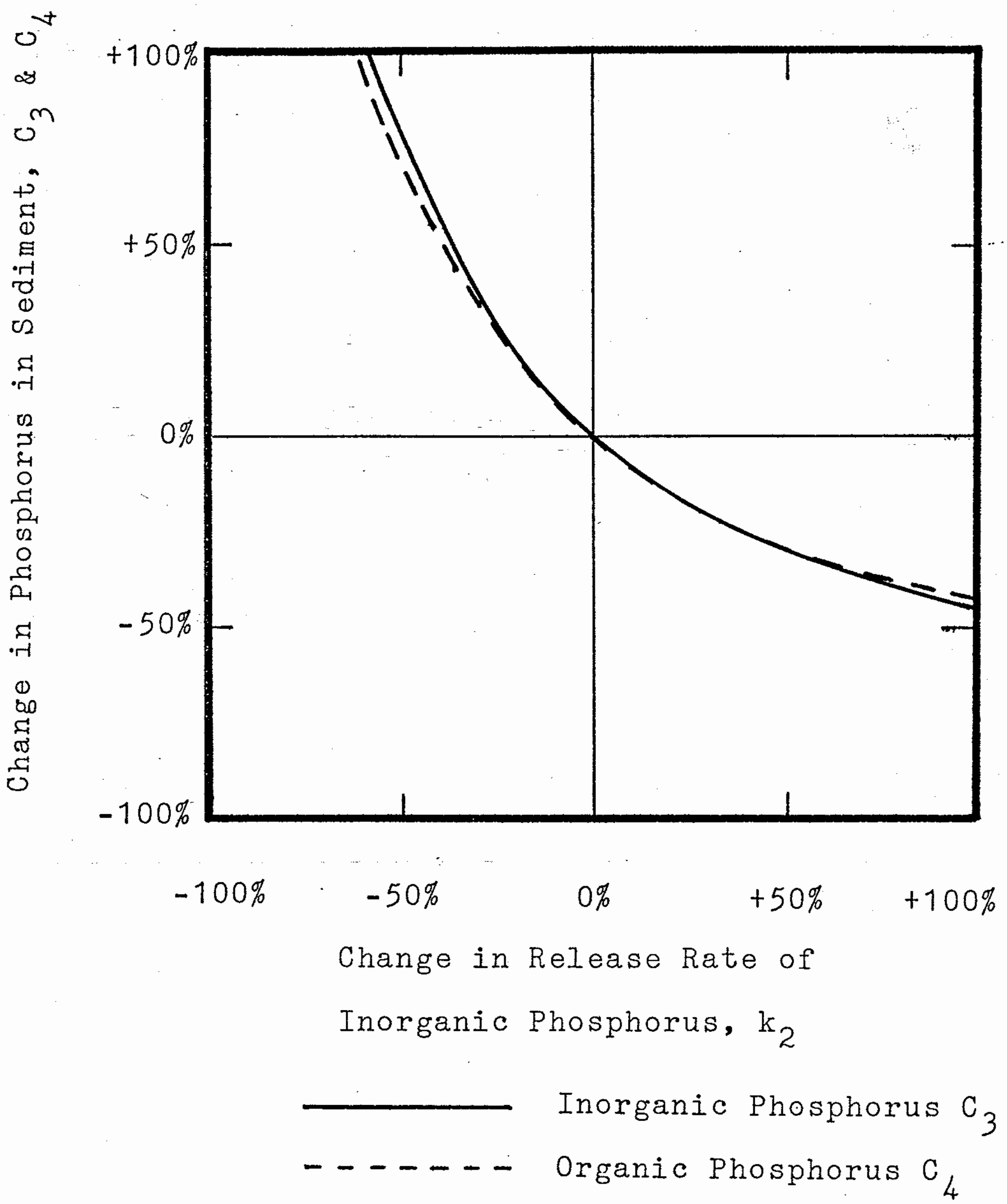


Figure 5-72 Sensitivity Analyses of C_3 & C_4 to k_2

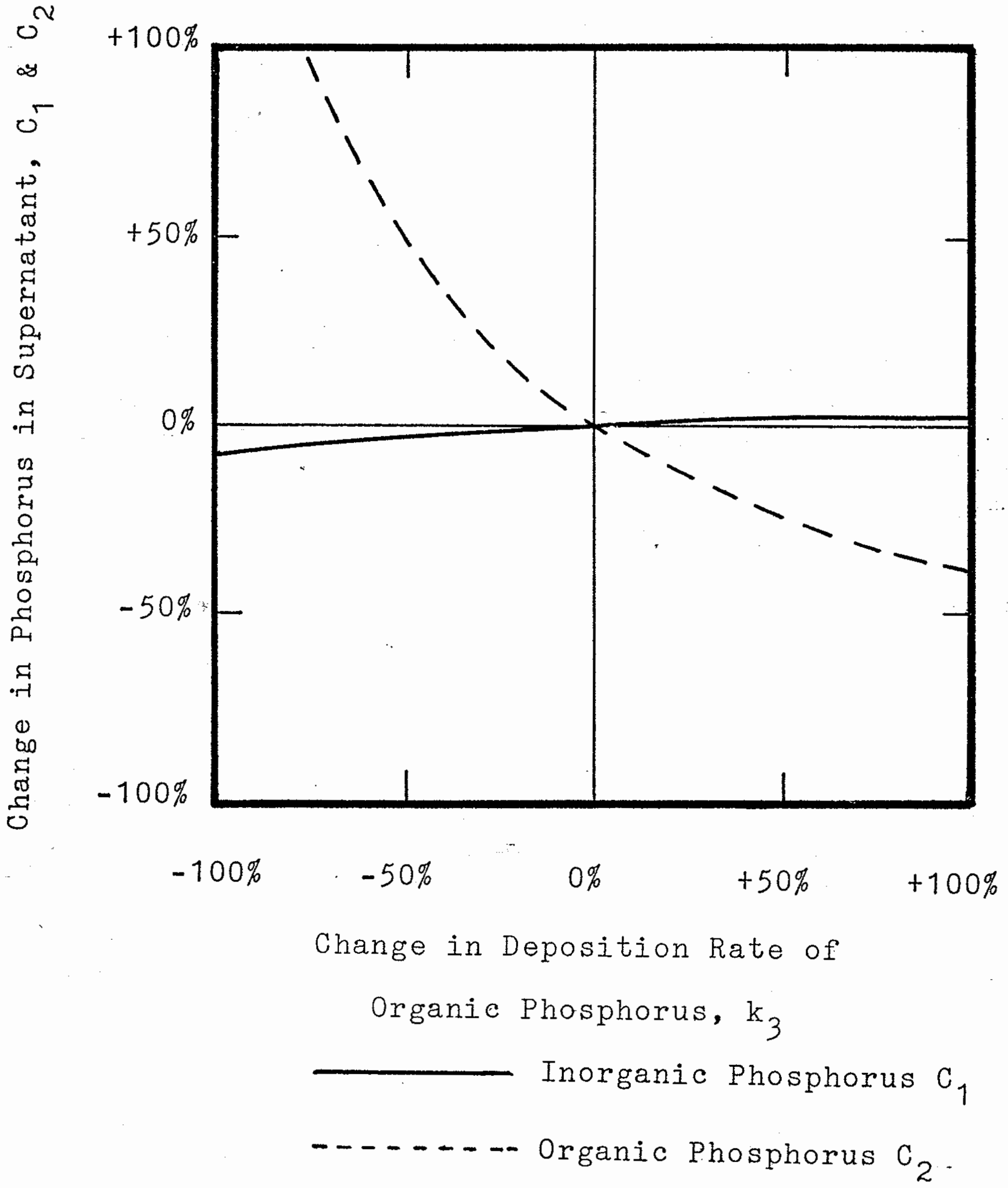


Figure 5-73 Sensitivity Analyses of C_1 & C_2 to k_3

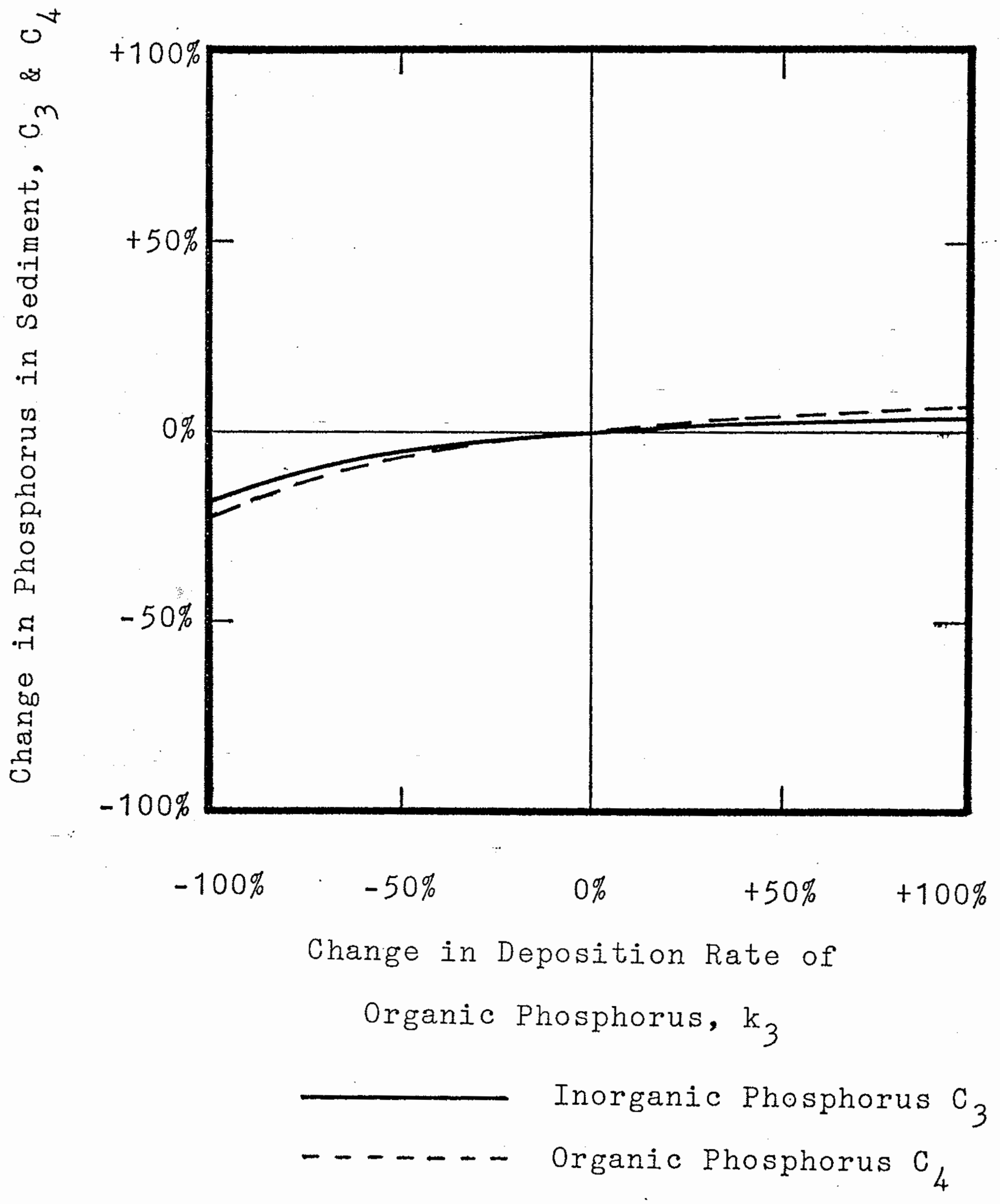


Figure 5-74 Sensitivity Analyses of C_3 & C_4 to k_3

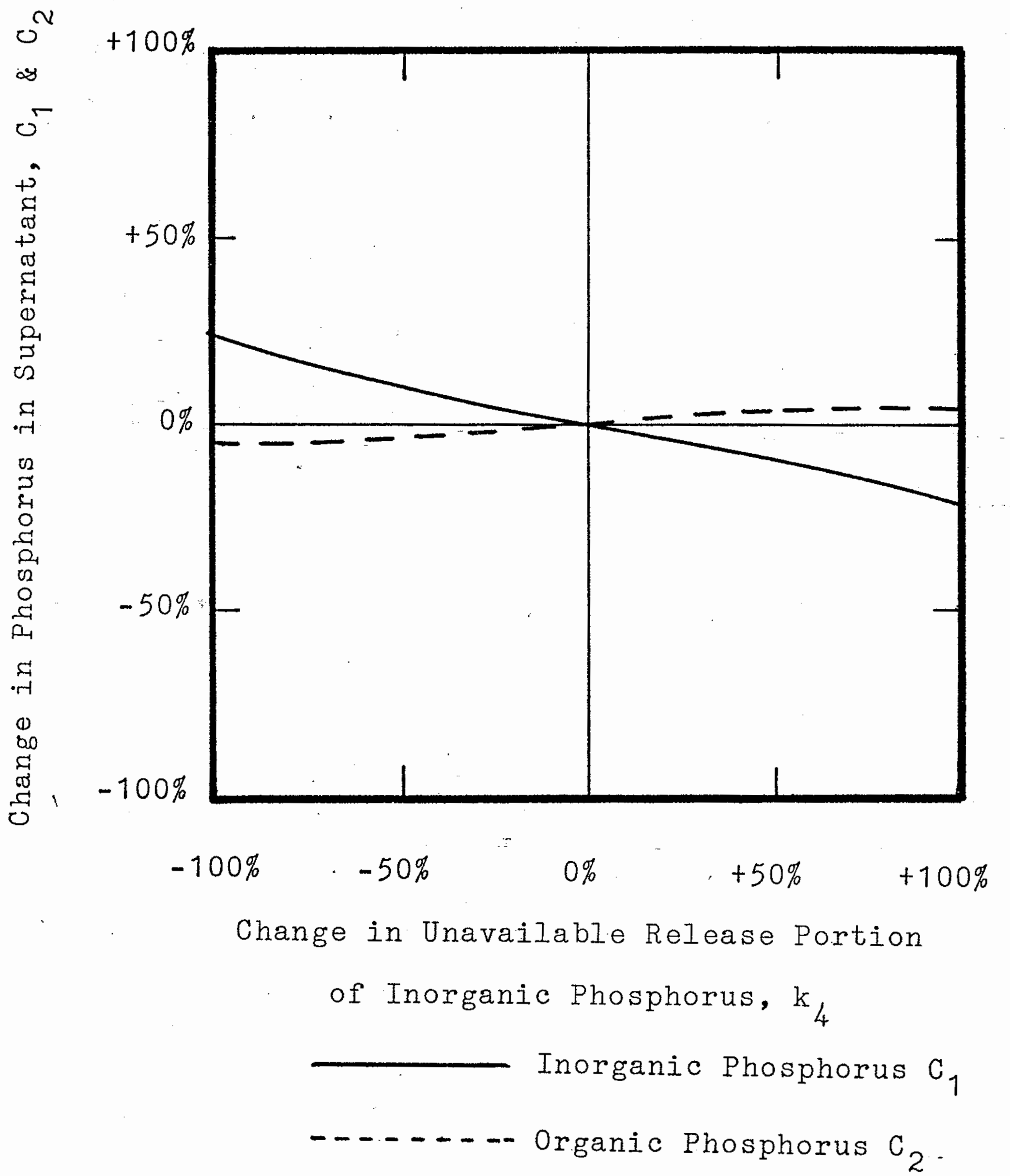


Figure 5-75 Sensitivity Analyses of C_1 & C_2 to k_4

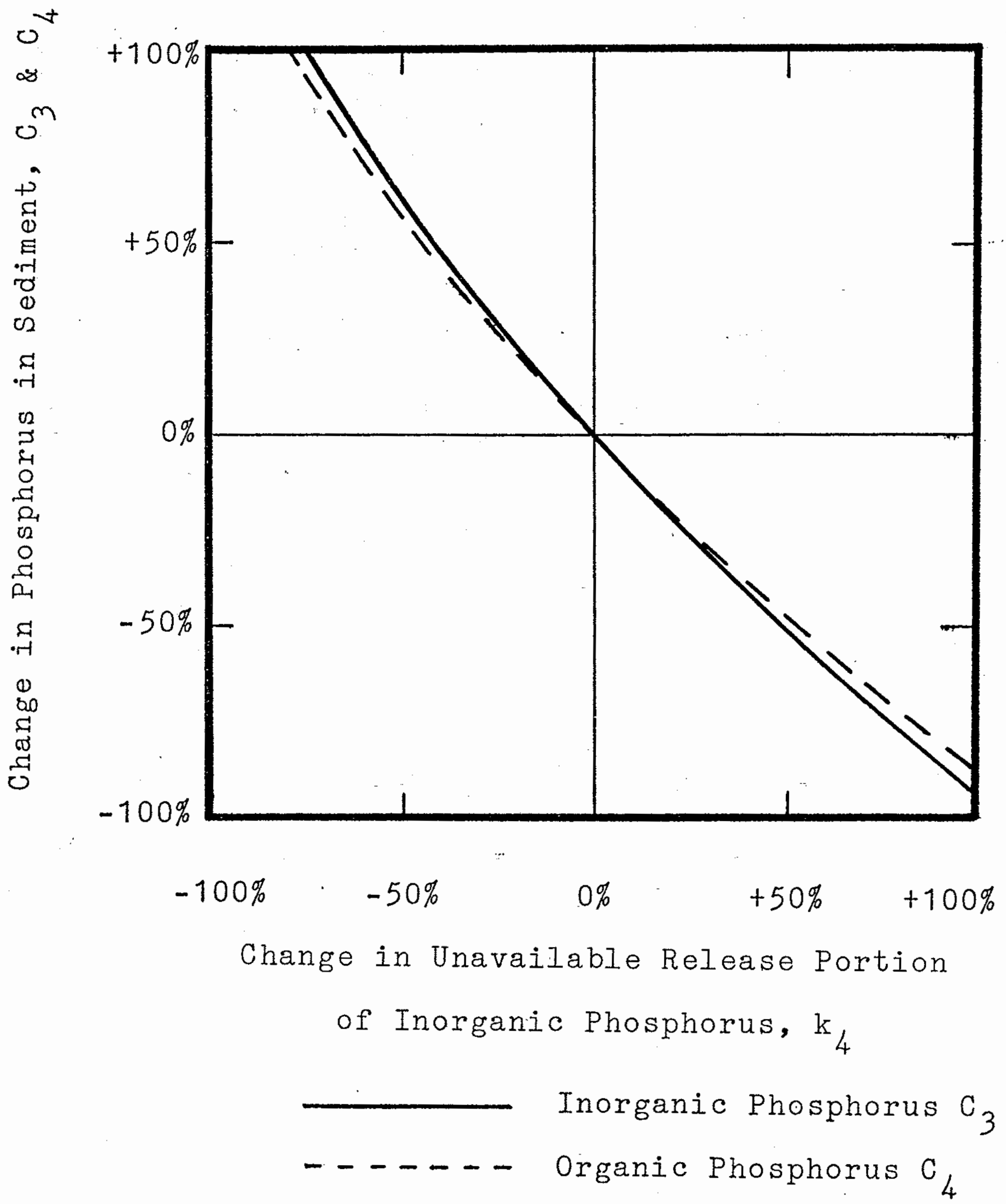


Figure 5-76 Sensitivity Analyses of C_3 & C_4 to k_4

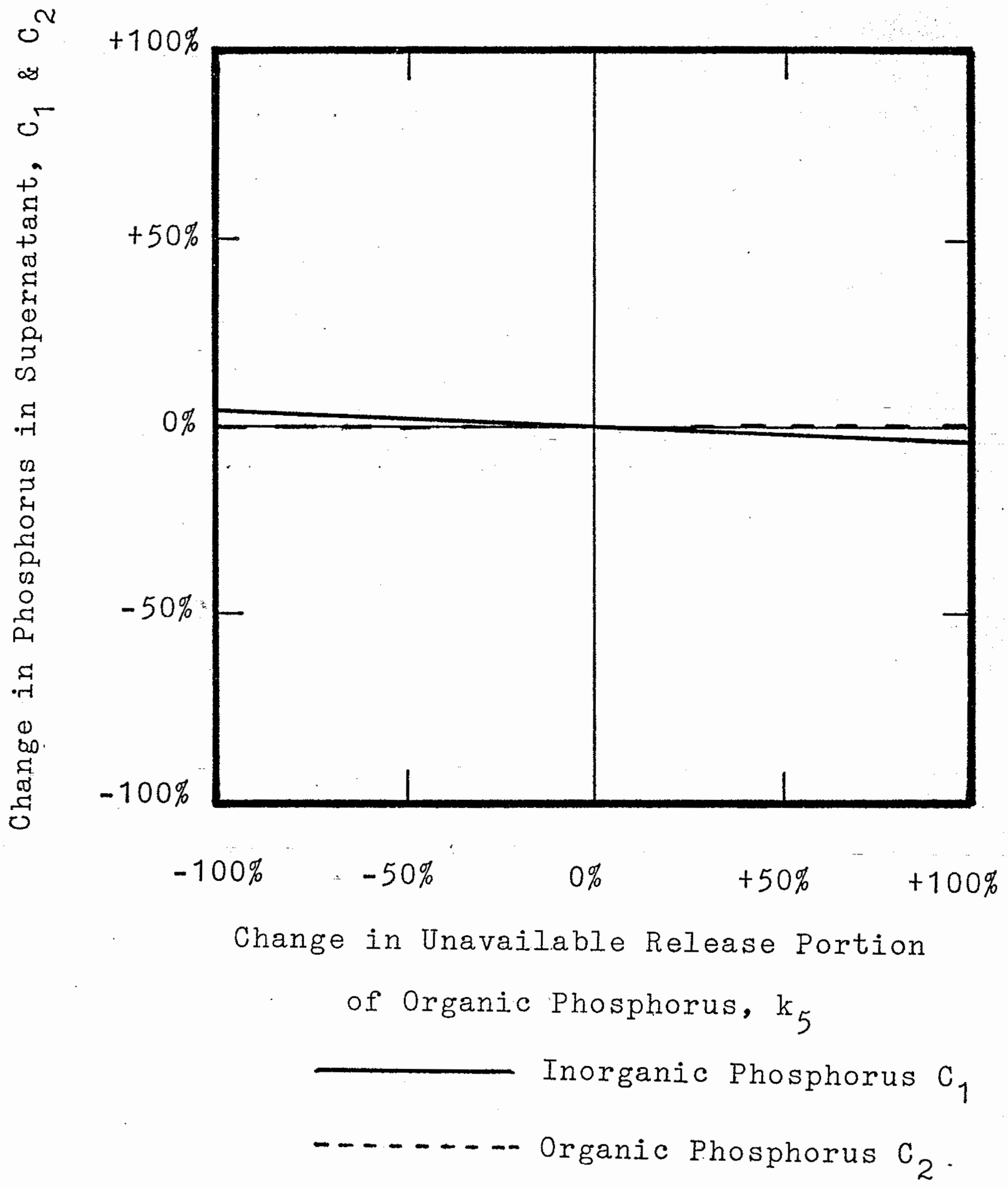


Figure 5-77 Sensitivity Analyses of C_1 & C_2 to k_5

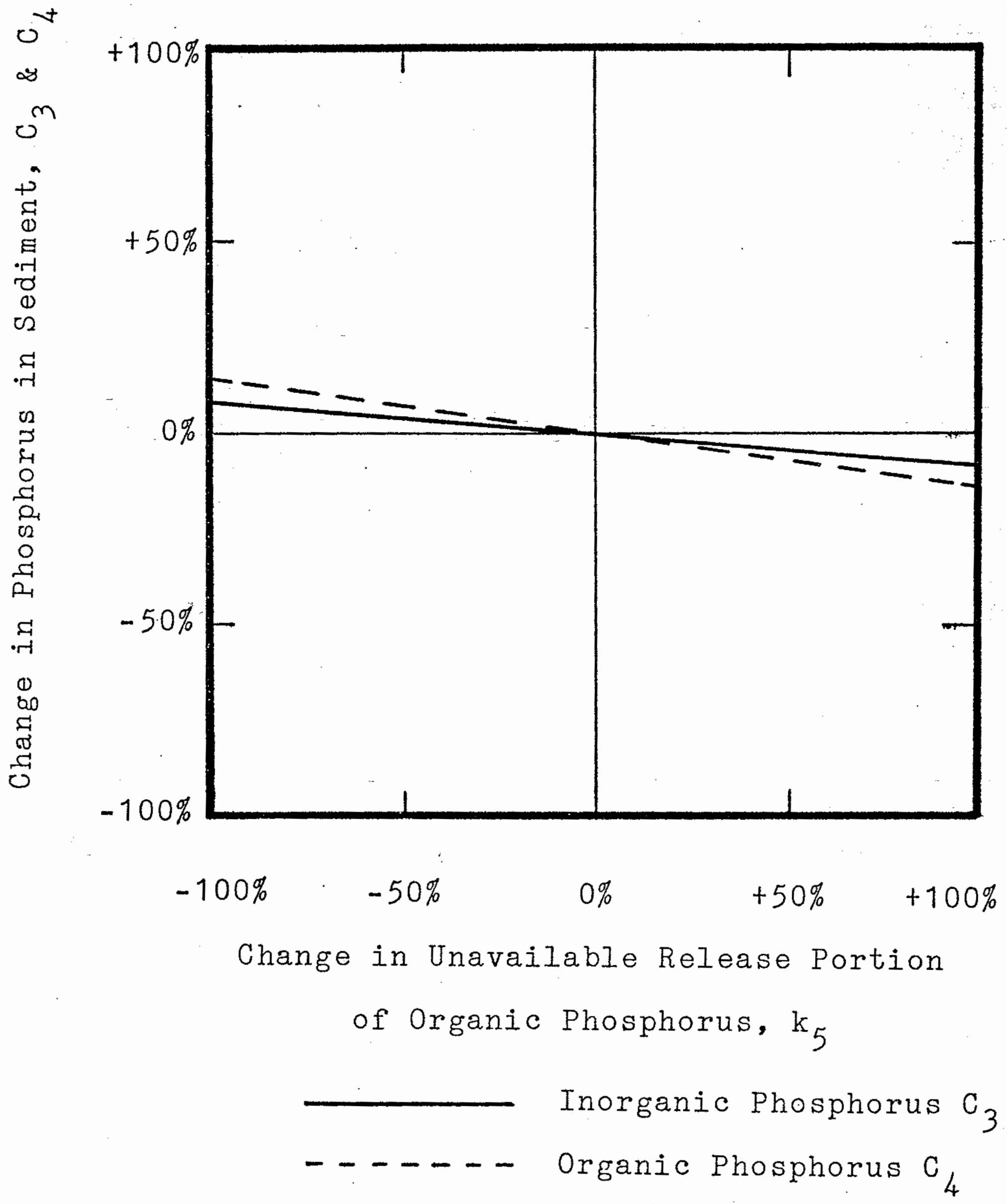


Figure 5-78 Sensitivity Analyses of C_3 & C_4 to k_5

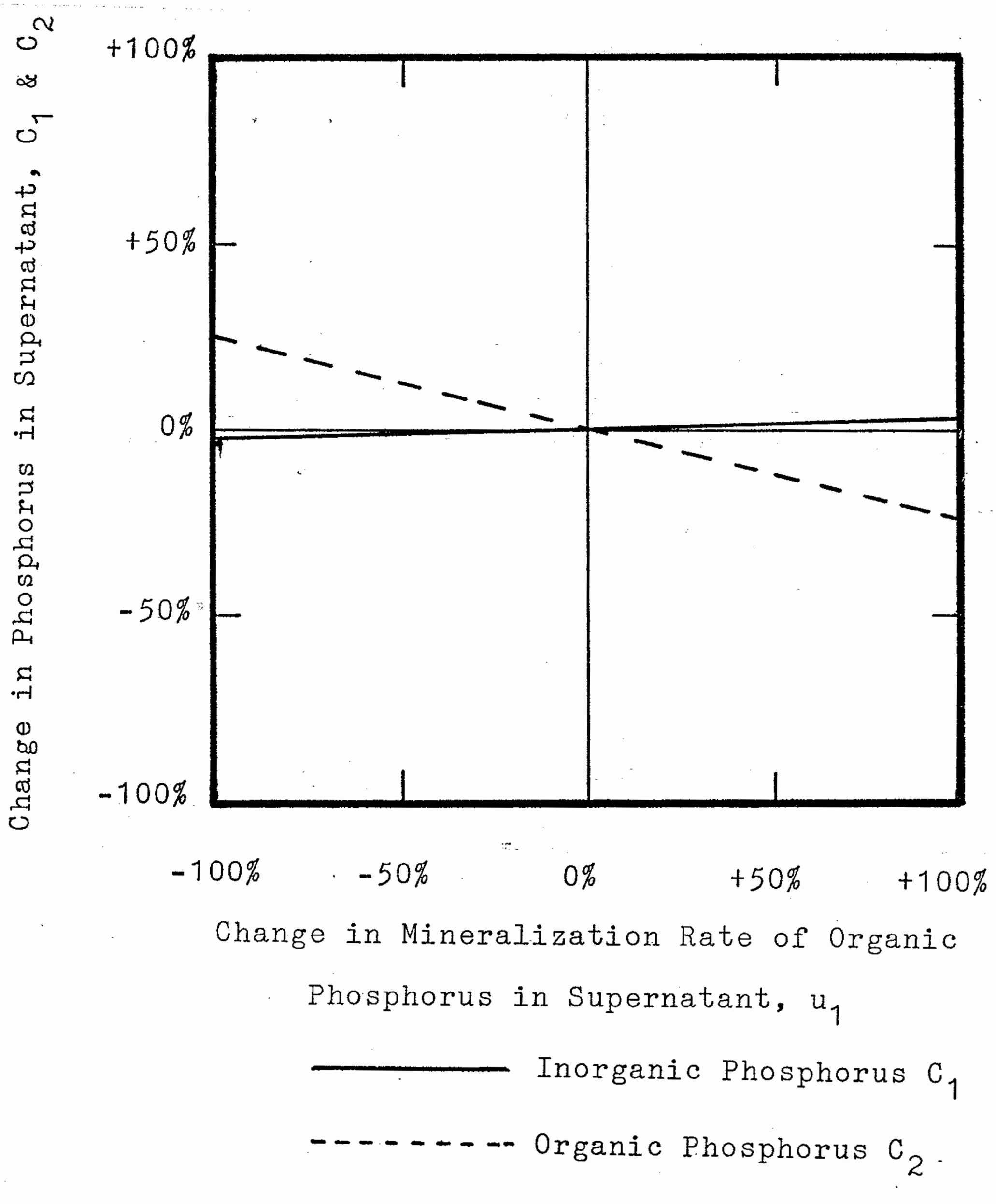


Figure 5-79 Sensitivity Analyses of C_1 & C_2 to u_1

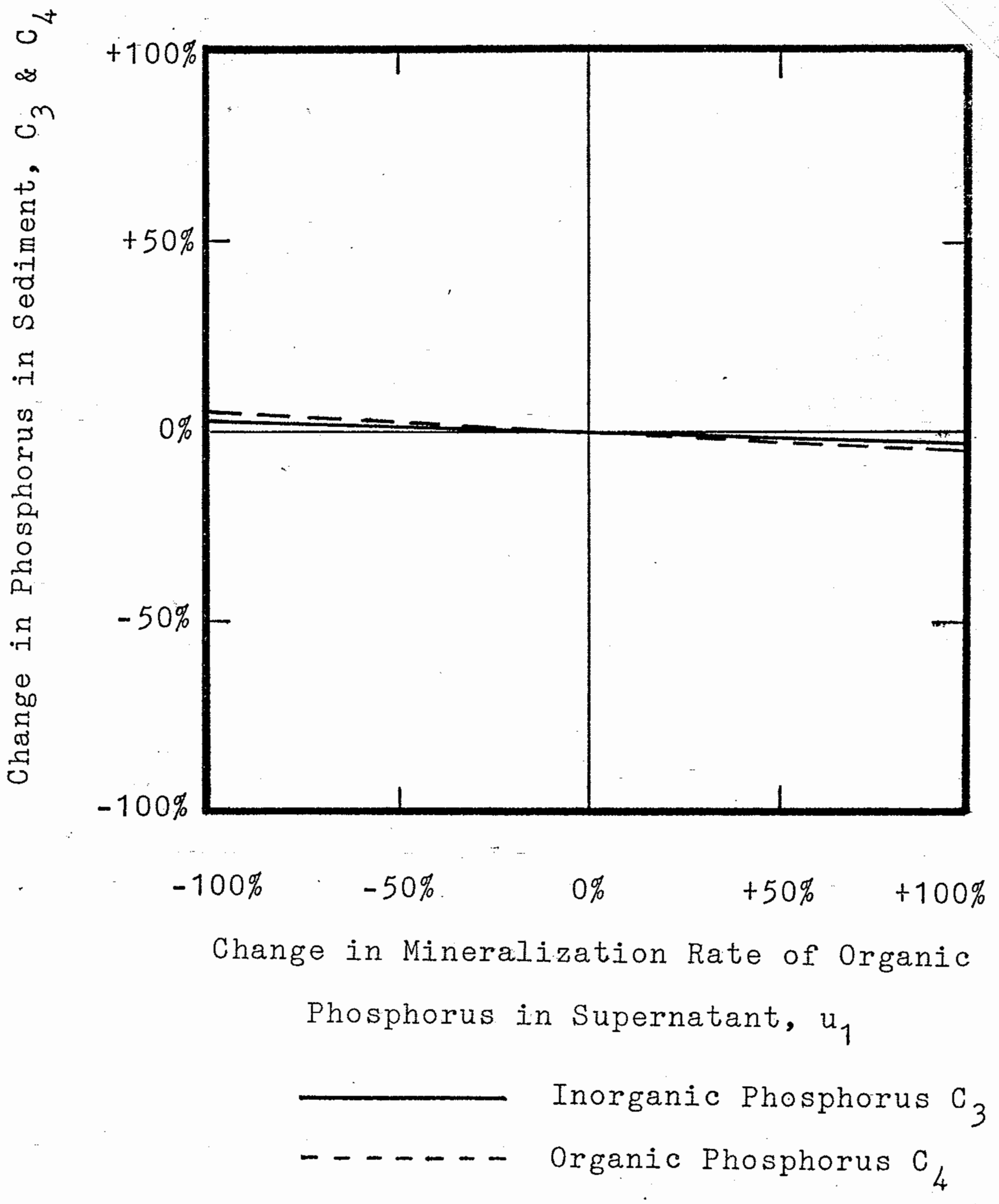


Figure 5-80 Sensitivity Analyses of C_3 & C_4 to u_1

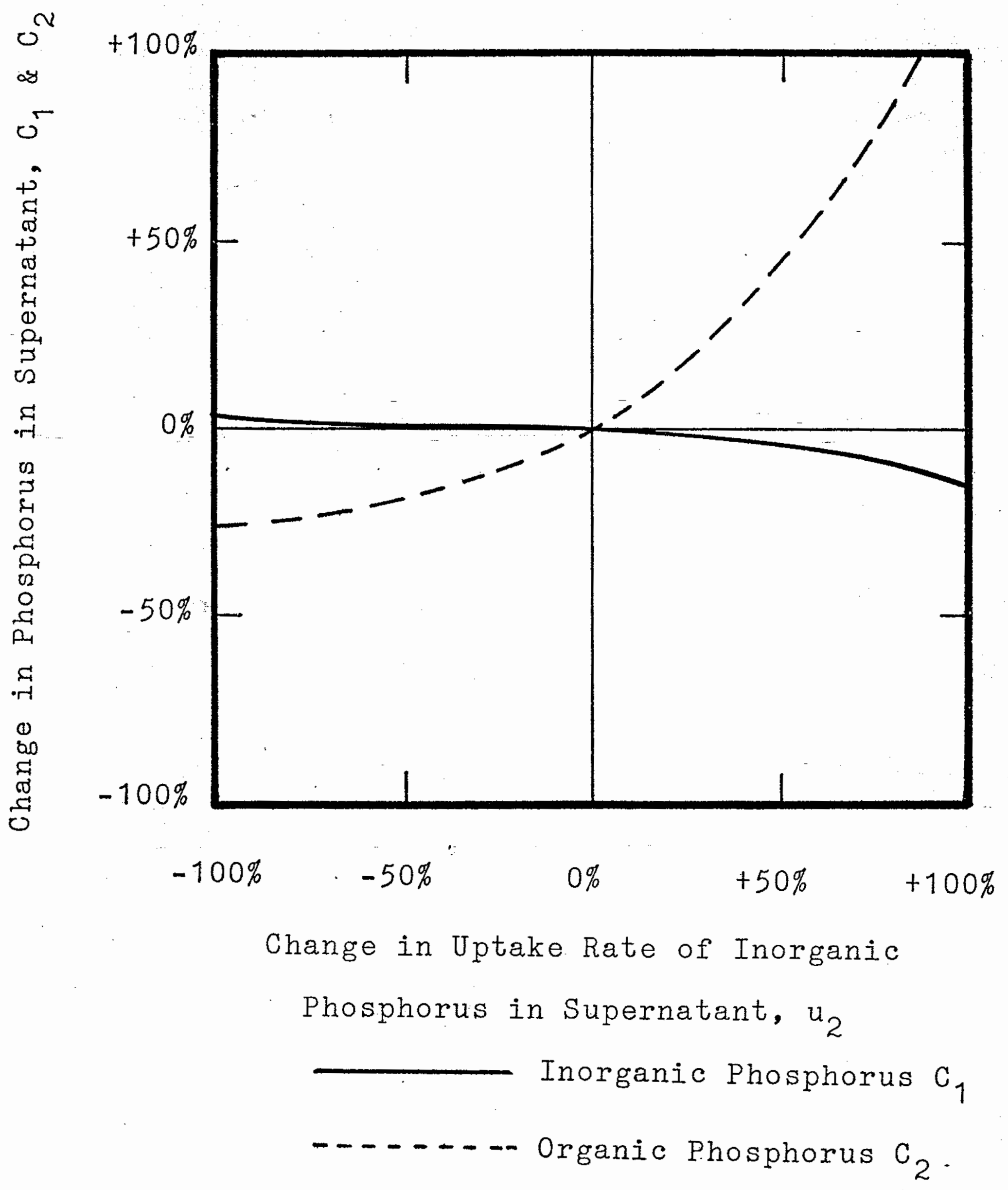


Figure 5-81 Sensitivity Analyses of C_1 & C_2 to u_2

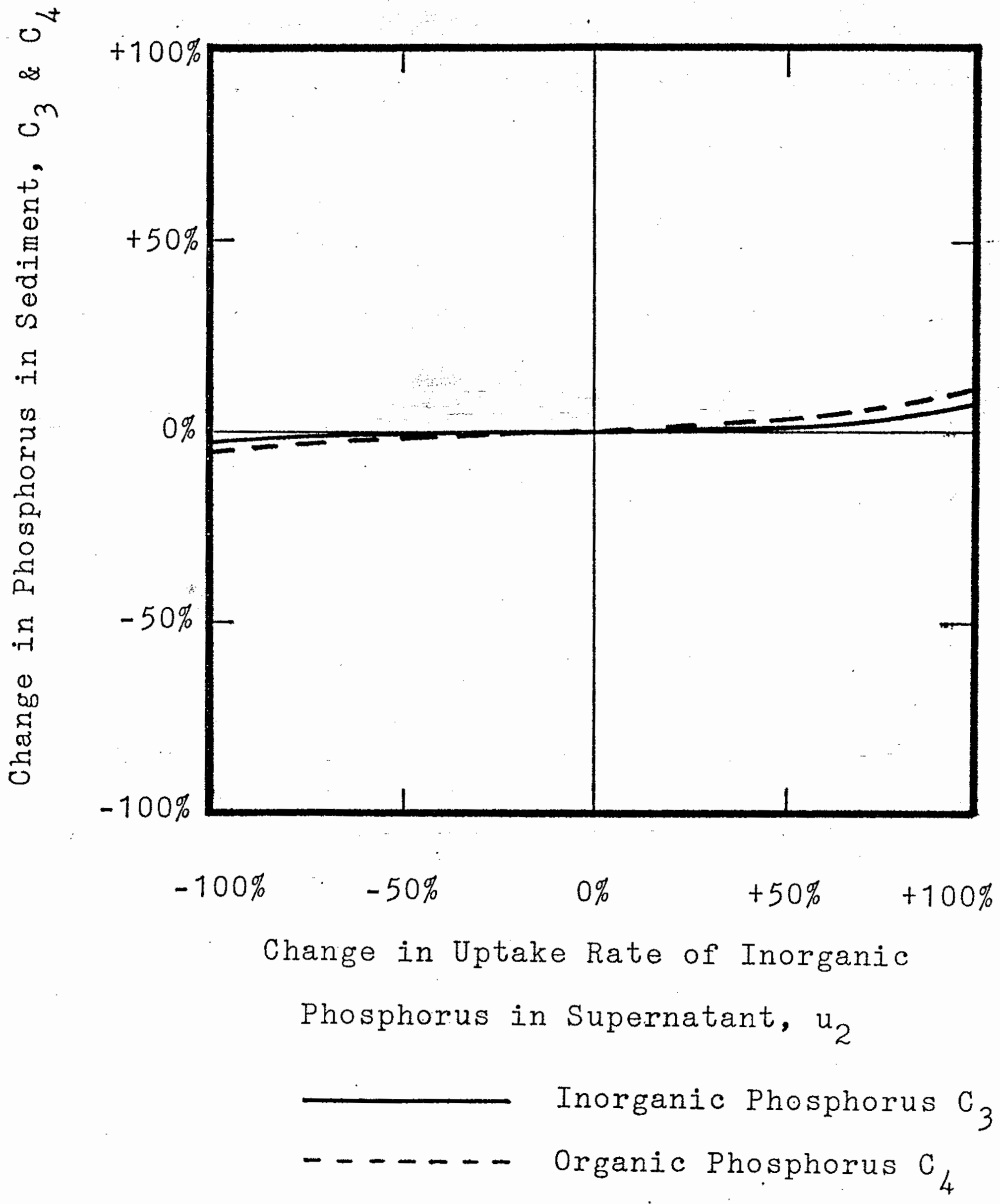


Figure 5-82 Sensitivity Analyses of C_3 & C_4 to u_2

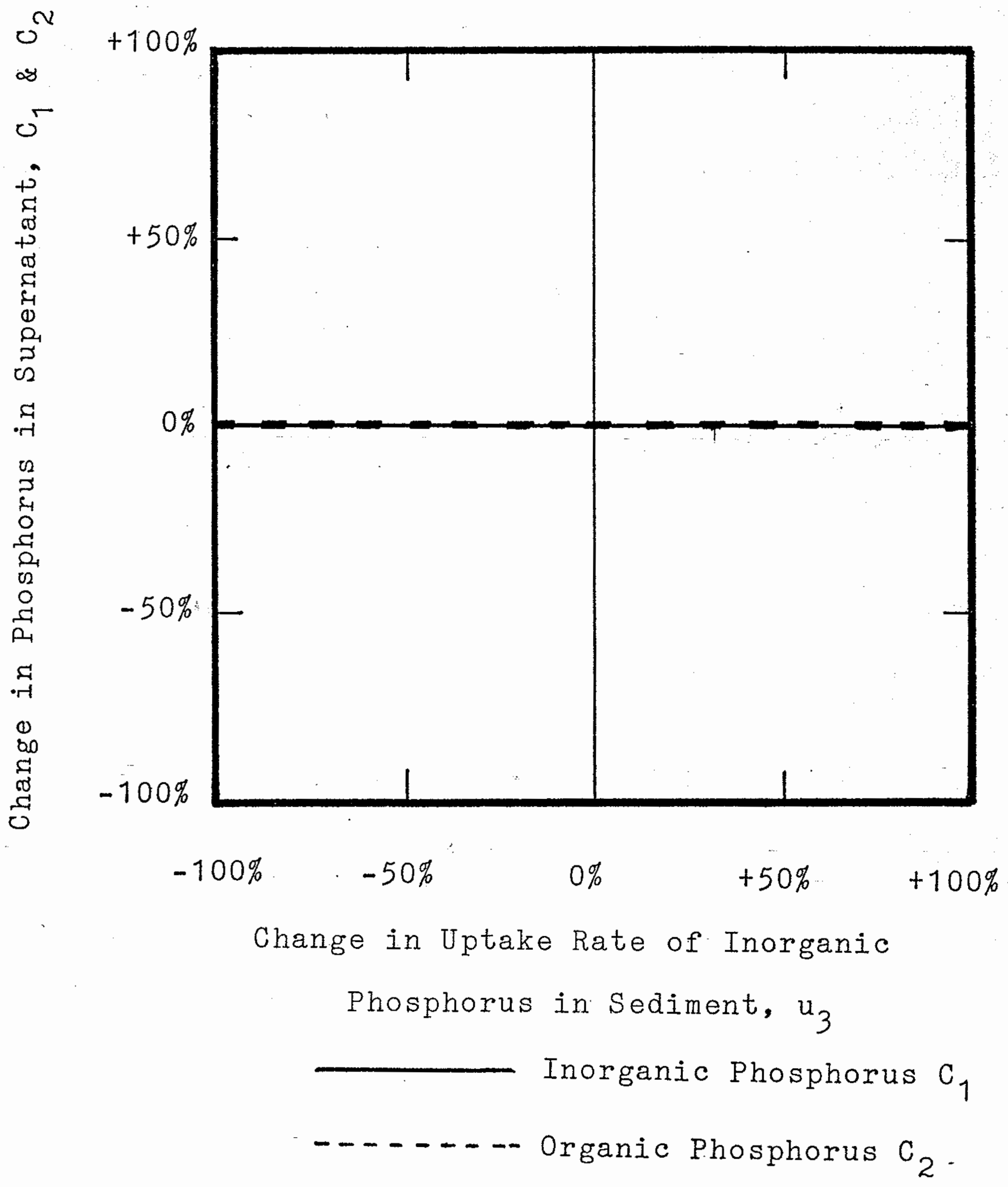


Figure 5-83 Sensitivity Analyses of C_1 & C_2 to u_3

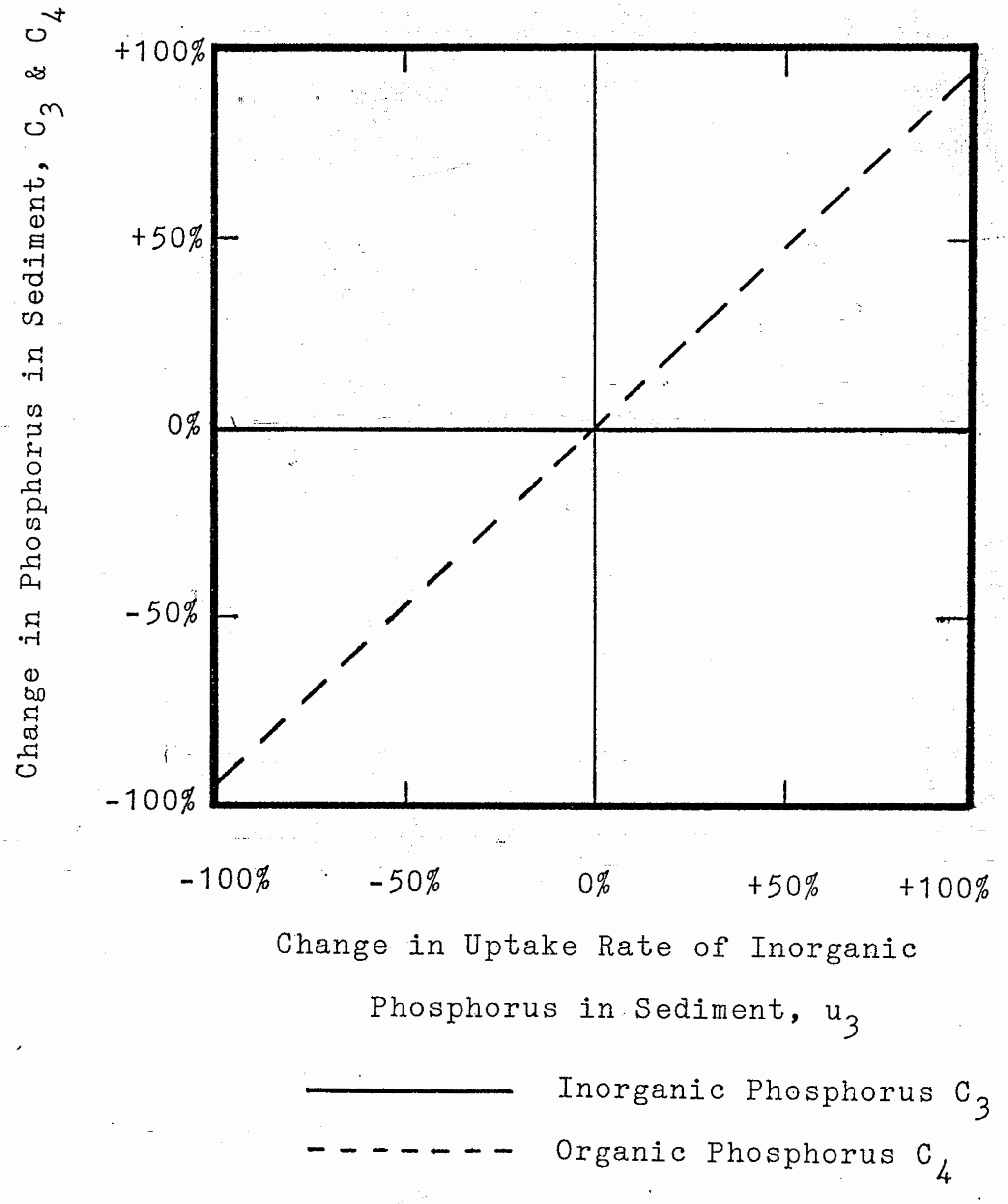


Figure 5-84 Sensitivity Analyses of C_3 & C_4 to u_3

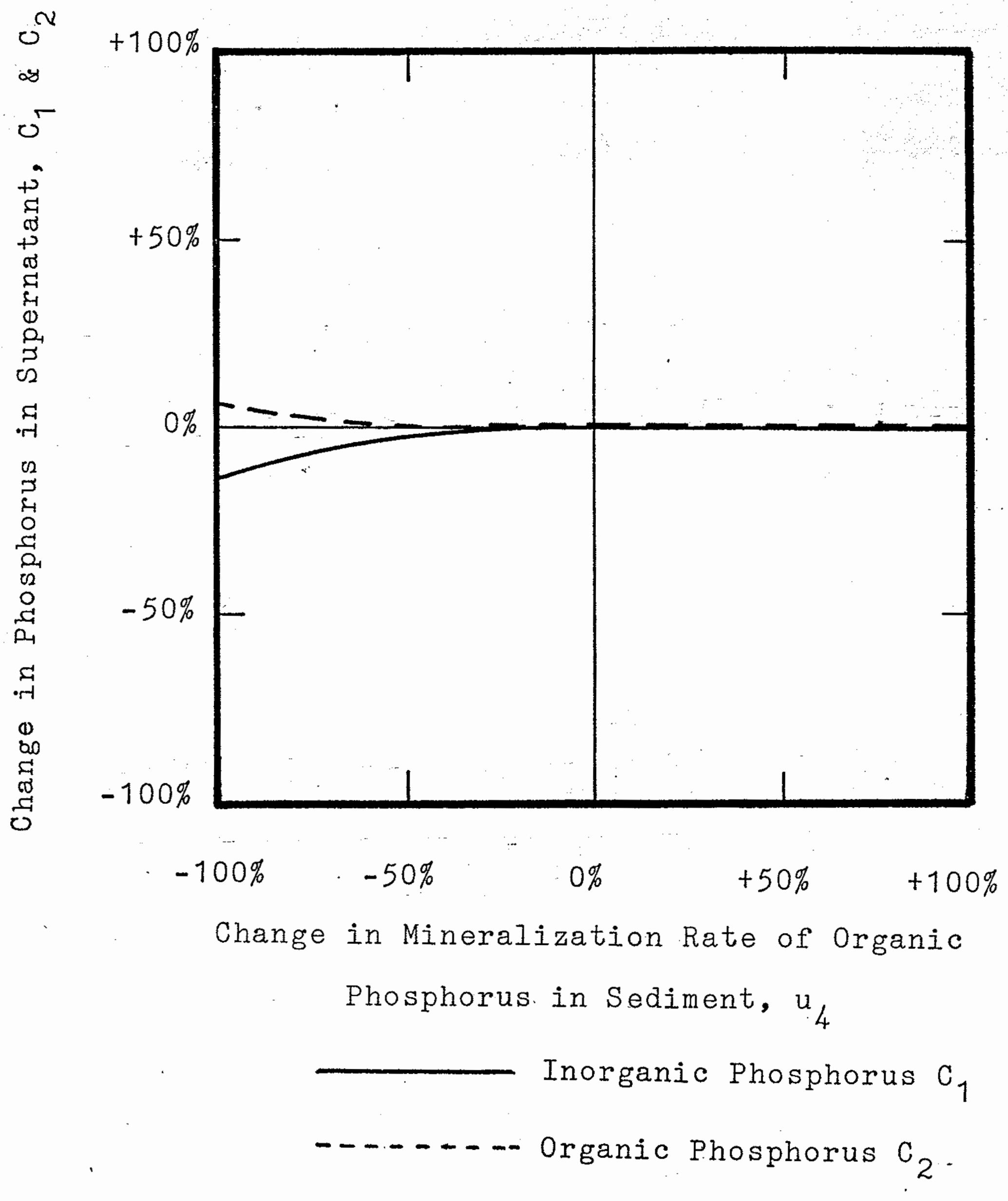


Figure 5-85 Sensitivity Analyses of C_1 & C_2 to u_4

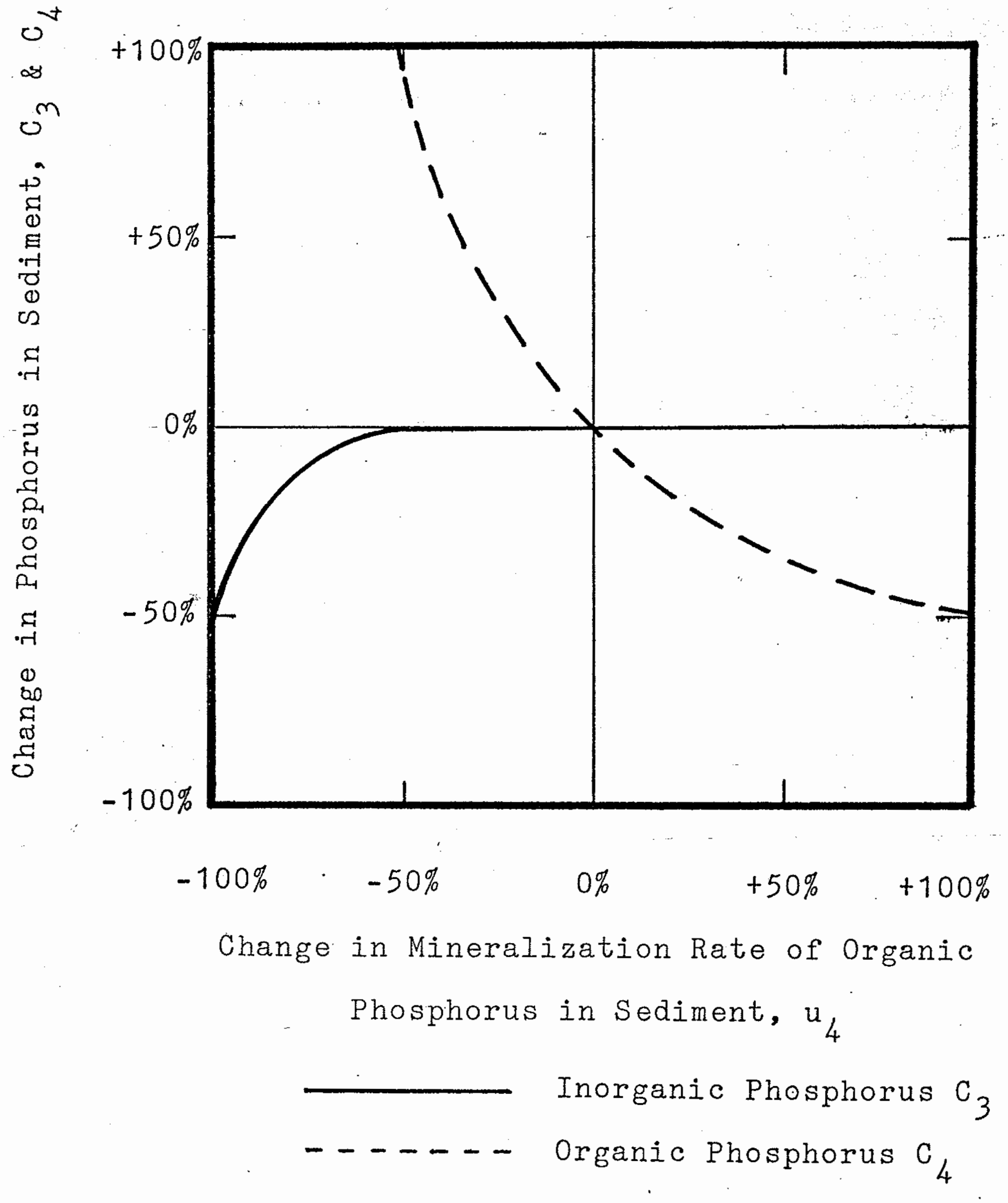


Figure 5-86 Sensitivity Analyses of C_3 & C_4 to u_4

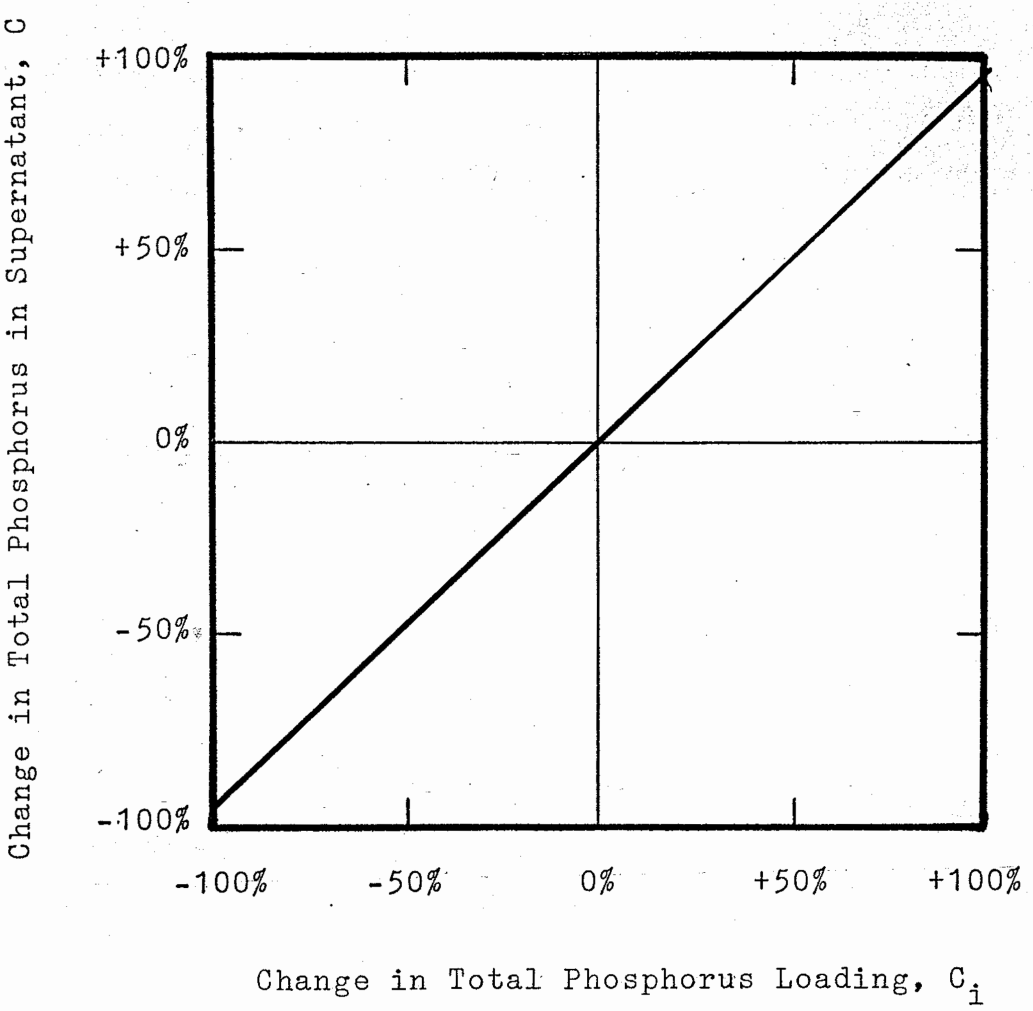


Figure 5-87 Sensitivity Analysis of C to C_i

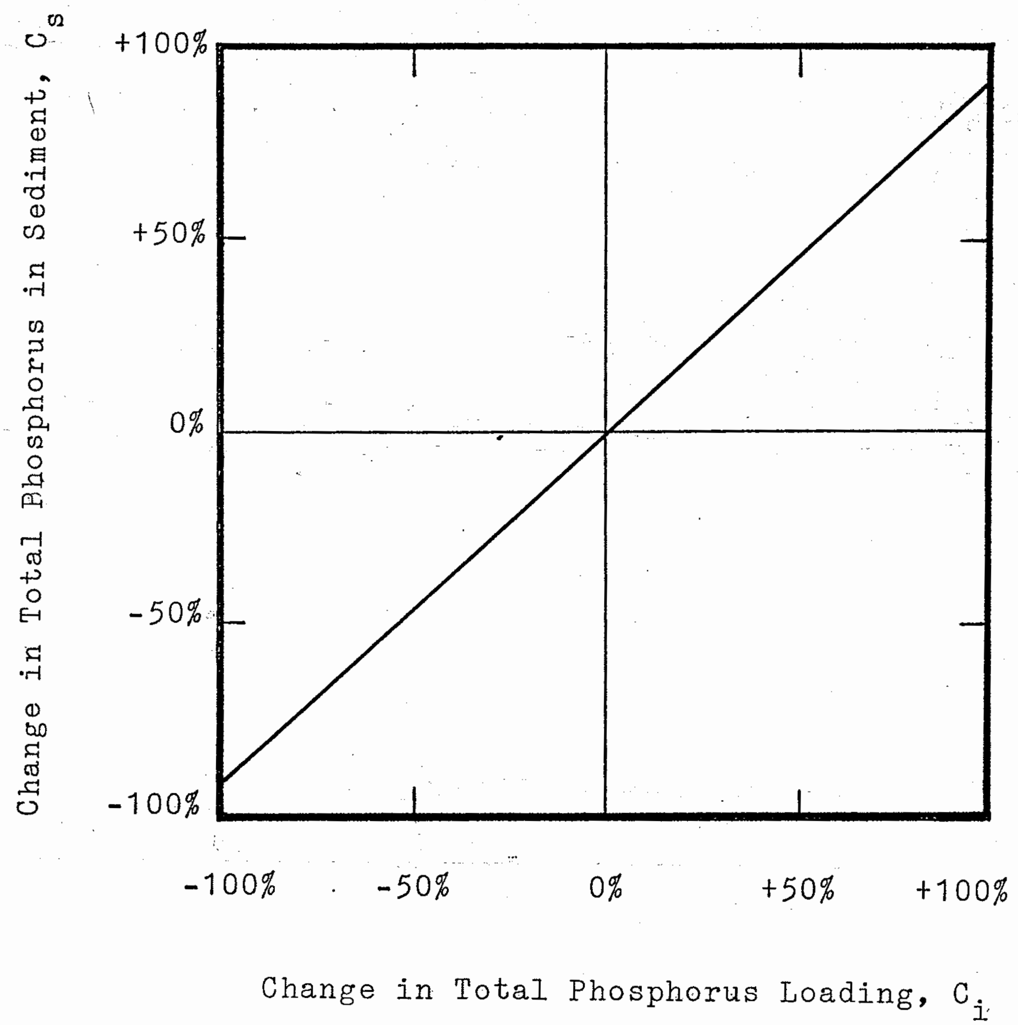


Figure 5-88 Sensitivity Analysis of C_s to C_i

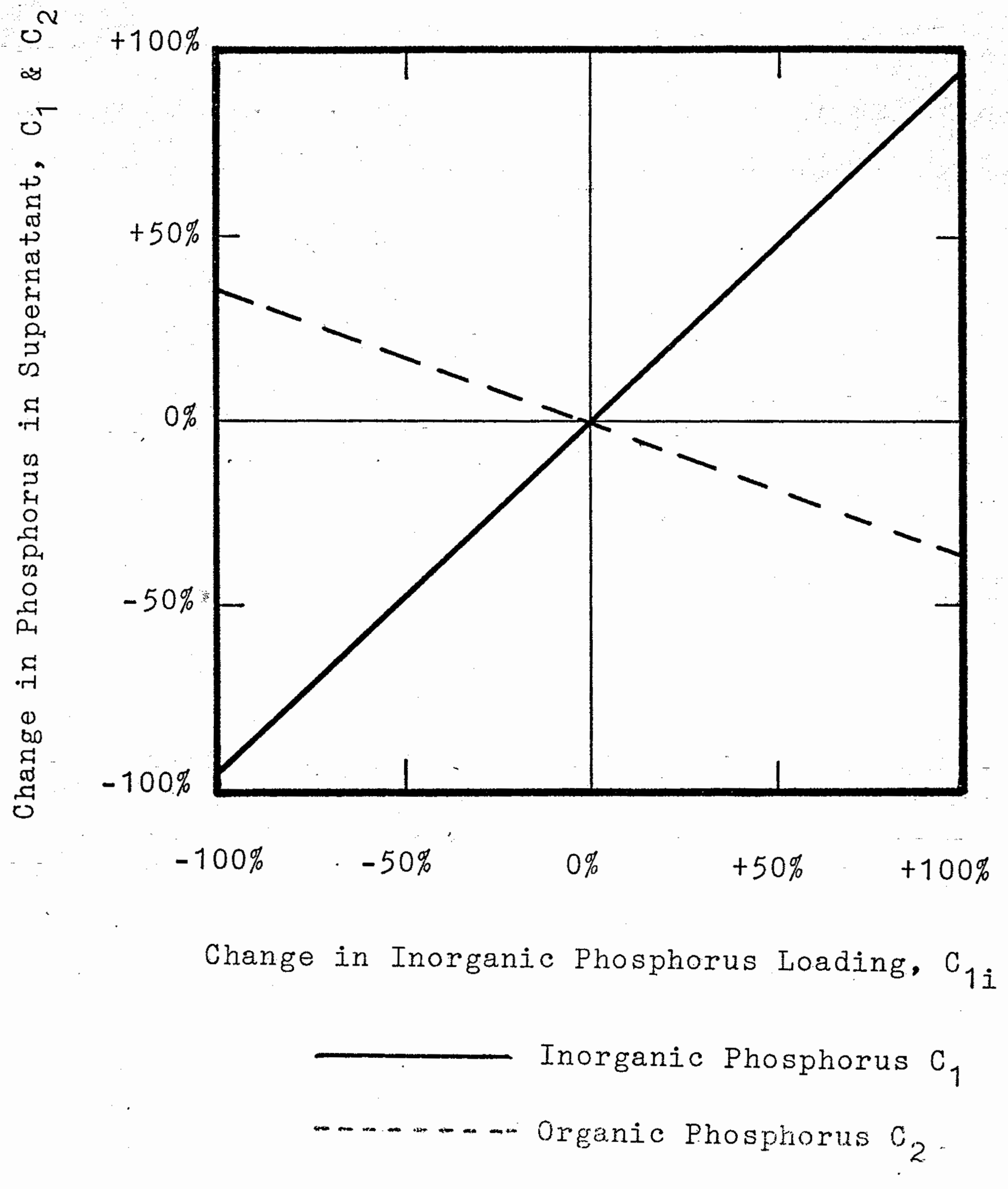


Figure 5-89 Sensitivity Analyses of C_1 & C_2 to C_{1i}

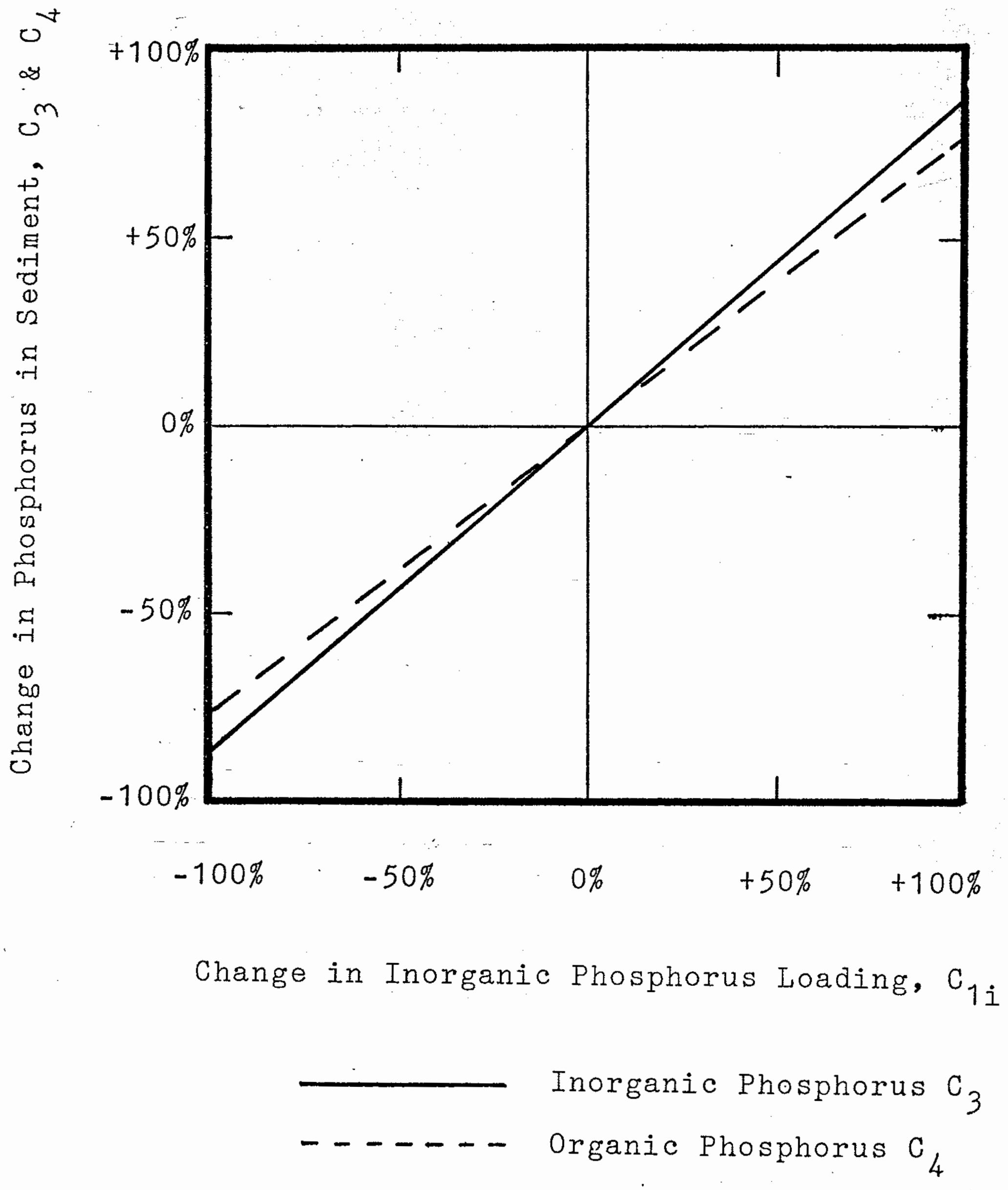


Figure 5-90 Sensitivity Analyses of C_3 & C_4 to C_{1i}

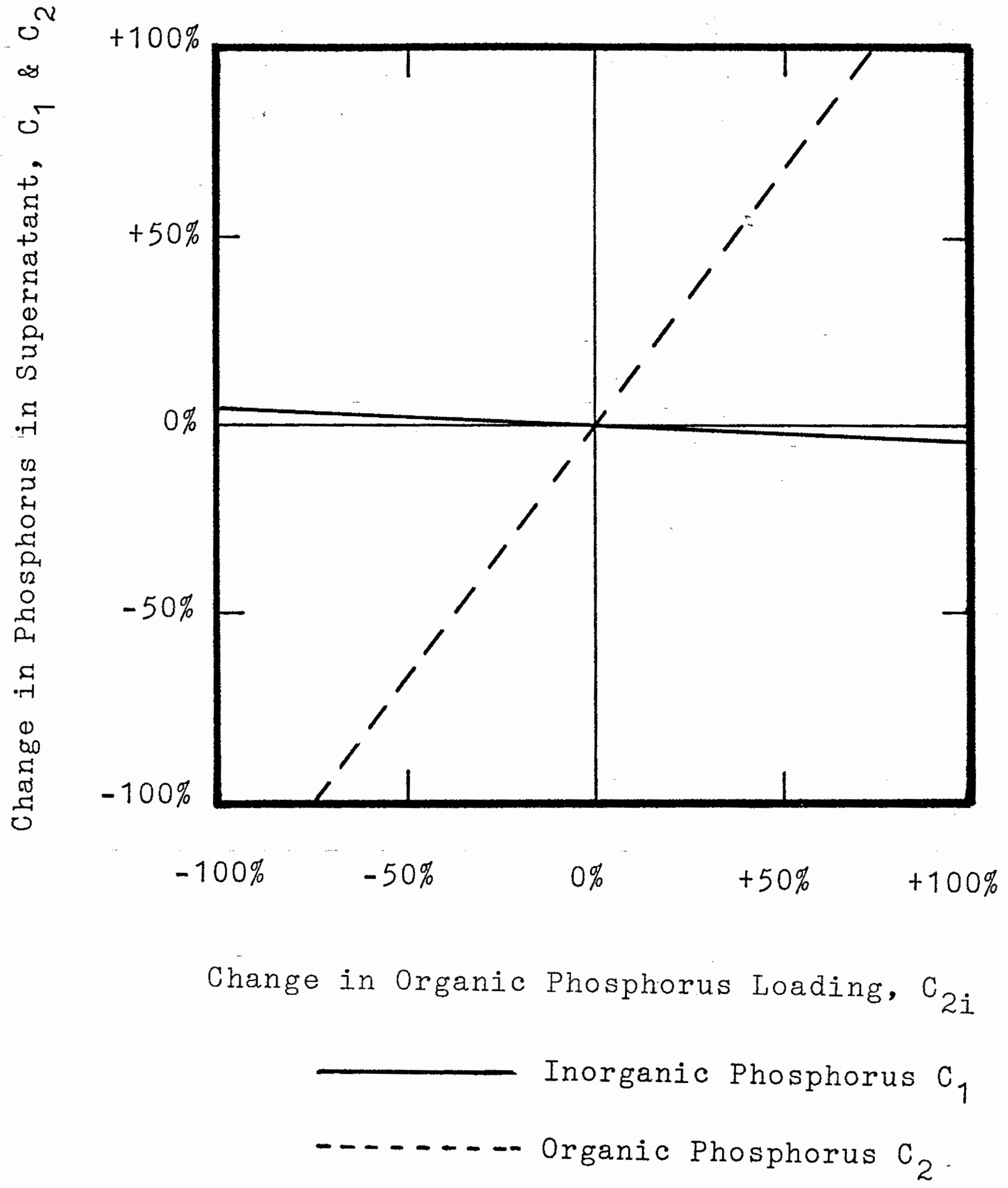


Figure 5-91 Sensitivity Analyses of C_1 & C_2 to C_{2i}

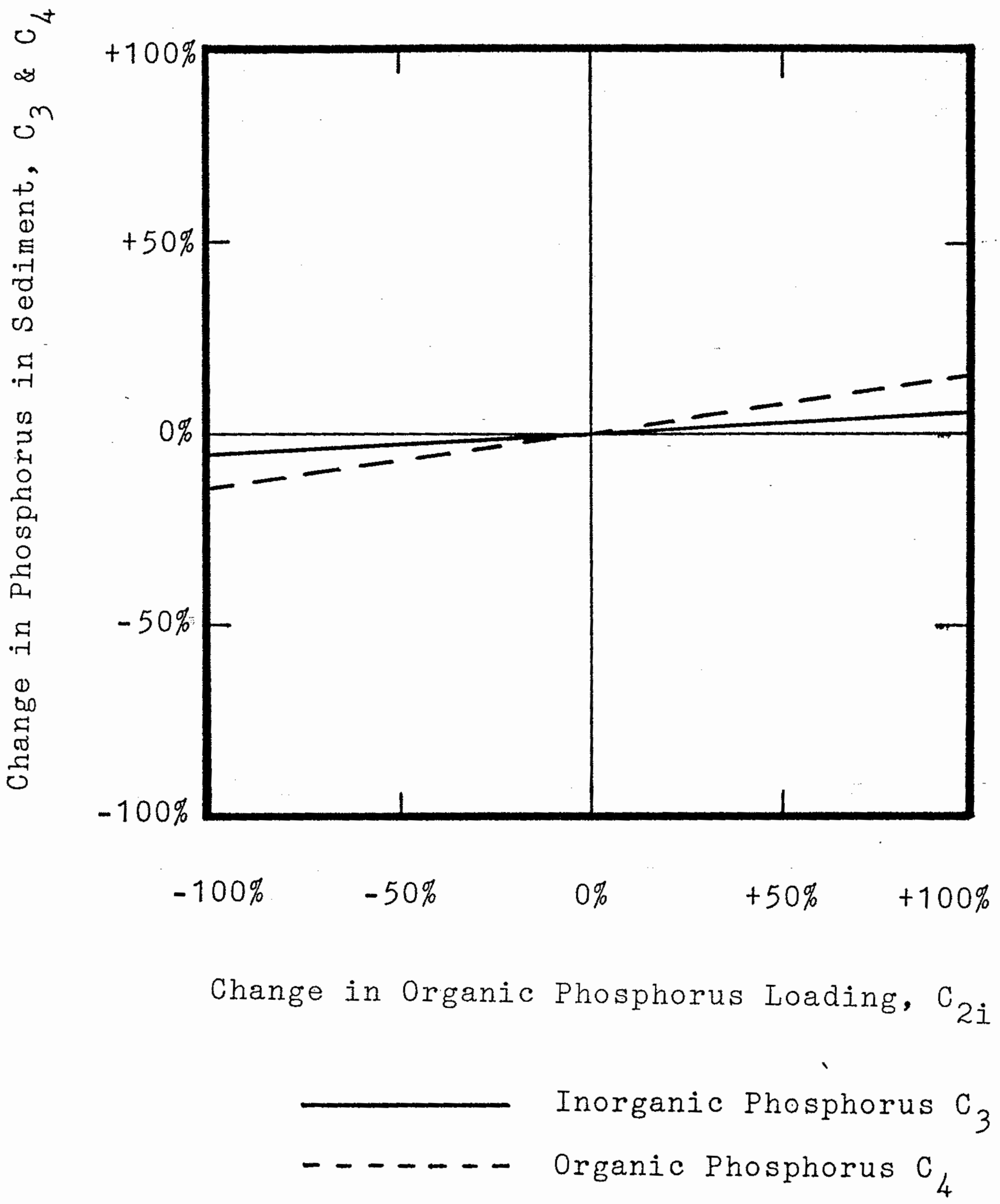


Figure 5-92 Sensitivity Analyses of C_3 & C_4 to C_{2i}

increase in K_1 or K_3 resulted in 23 percent decrease in C. An increase in K_2 may not cause C to increase greatly; however, a 100 percent decrease in the value of K_2 resulted in a decrease of 55 percent in C. The parameters, K_1, K_2, and K_3, had a significant influence on the total phosphorus in the sediment, C_s. A decrease in K_2 would make C_s increase dramatically. A 100 percent decrease in K_1 and K_2 resulted in a 90 percent decrease and a 75 percent increase in C_s; while only a 58 percent decrease in K_2 resulted in a 100 percent increase in C_s.

The relationships of the inorganic phosphorus in the supernatant (C_1), the organic phosphorus in the supernatant (C_2), the inorganic phosphorus in the sediment (C_3), and the organic phosphorus in the sediment (C_4) to the changes in the depostion rate of the inorganic phosphorus (k_1) were plotted in Figures 5-69 and 5-70. The responses of C_1, C_2, C_3, and C_4 to the changes in the release rate of inorganic phosphorus (k_2), the deposition rate of organic phosphorus (k_3), the unavailable release portion of inorganic phosphorus (k_4), and the unavailable release portion of organic phosphorus (k_5) are shown in Figures 5-71 through 5-78. The value of C_1 was affected by all the parameters k_1, k_2, k_3, k_4, and k_5, although a decrease in parameter k_2 seemed to influence the value of C_1 more significantly. A 100 percent increase in k_1, k_3, k_4, and k_5, respectively, resulted in 18 percent decrease, 2 percent increase, 18 percent decrease, and 3 percent increase in C_1; while a 100 percent decrease in k_2 resulted in a 62 percent decrease in C_1. Only minor change in C_2 resulted from variations in the parameters k_1, k_2, k_4, and k_5. However, as k_3 decreased, C_2 increased dramatically. A 77 percent decrease in k_3 resulted in a 100 percent increase in C_2. Variations in k_3 and k_5 did not materially influence C_3 and C_4. A 100 percent increase in the value of k_3 resulted in a four percent increase in C_3 and a six percent increase in C_4. A 100 percent increase in k_5 resulted in a nine percent decrease in C_3 and a 12 percent increase in C_4. It is interesting that changes in the parameters k_1, k_2, k_3, k_4 and k_5 create similar changes in C_3 and C_4. As shown in Figures 5-77 and 5-78, it is obvious that not only C_3 and C_4 but also C_1 and C_2 were only slightly influenced by variations in k_5. A 100 percent increase or decrease in k_5 only resulted in a two percent decrease or increase in C_1 and no change in C_2. Therefore, a constant k_5 value may be used without appreciably affecting the model results.

Figures 5-79 through 5-86 illustrate the effects of C_1, C_2, C_3, and C_4 to changes in the biological coefficients u_1, u_2, u_3, and u_4. Each percent decrease in u_1, u_2, and u_4 resulted in 0.02, 0.05, and 0.05 percent decrease in C_1. There was no effect on C_1 as u_3 changed. As shown in Figure 5-81, the value of C_2 was highly influenced by an increase in u_2, and this effect was much greater in comparison with other coefficients such as u_1, u_3, and u_4. An 89 percent increase in u_2 resulted in a 100 percent increase in C_2. Variations in u_2 produced changes in C_1, C_3, and C_4, although these effects were not as significant as those exhibited by C_2.

Changes in u_3 and u_4 significantly influenced C_3. There were no changes in C_1, C_2, and C_3 as u_3 was varied; however, a change in C_4 was almost proportional to the change in u_3. The relationship between C_4 and u_3 is linear with a slope of 0.93, i.e., each percent change in u_3 may result in a 0.93 percent change in C_4. Therefore, the choice of u_3 is critical if an accurate C_4 value is desired.

The inorganic and organic phosphorus concentrations in the supernatant (C_1 and C_2) did not appear to be changes by the sediment coefficients u_3 and u_r. Similarly, the inorganic and organic phosphorus concentrations in the sediment (C_3 and C_4) were not influenced greatly by the biological coefficients associated with the supernatant (u_1 and u_2).

The total phosphorus concentration (C_i) in the influent was varied in the total phosphorus model to test the sensitivity with respect to C and C_s. The results are shown in Figures 5-87 and 5-88. The lines in Figures 5-87 and 5-88 are linear, with slopes of 0.95 and 0.92, respectively. The results reflected that C_i dominated the determinaton of C and C_s. Each percent increase or decrease of C_i resulted in an average increase or decrease of 0.95 in C and 0.92 in C_s.

The impacts on C_1, C_2, C_3 and C_4 by varying inorganic phosphorus (C_{1i}) and organic phosphorus (C_{2i}), as found in the influent of the FWSP, were observed. These results are found in Figures 5-89 through 5-92. Figures 5-89 through 5-92 show these relationships to be linear. A change in C_{1i} produced positive slopes of 0.95, 0.85, and 0.75. Figure 5-89 illustrates a negative relationship between C_{1i} and C_2 with a slope of -0.33, i.e., each percent increase in C_{1i} results in a 0.33 percent decrease in C_2. Though an increase in C_{2i} caused a dramatic change in C_2, the output values of C_1, C_3 and C_4 were not appreciably affected by changes in C_{2i}. A 100 percent increase or decrease in C_{2i} exhibited no influence on C_1 and resulted in only seven and 16 percent variations, respectively, in C_3 and C_4. However, a 75 percent variation in C_{2i} resulted in a 100 percent variation in C_2.

5.5 MODEL APPLICATION

The phosphorus models developed in this study were based on idealized completely mixed systems. However, even with wind and thermal influences, waste stabilization ponds can not attain completely mixed conditions. The idealized flow pattern, plug flow, or completely mixed flow, may not be able to represent the actual flow pattern of field systems. The actual flow pattern for a real pond is governed by the entrainment, width of influent jet, outlet configuration, mixing due to dispersion (non-uniformities in velocity), diffusion, and other mixing processes (e.g., wind). Therefore, in most cases, deviation caused by short-circuiting of fluid, recycling of fluid, or creation of stagnant regions in the field ponds should be considered.

The problem of nonideal flow is intimately tied in with the scale-up problem. Often the uncontrollable factors differ widely between large and small units. Therefore, ignoring these factors and their influences may lead to gross errors in design and prediction.

A tanks-in-series (Levenspiel 1972) is widely used to present nonideal flow. The fluid flows through a series of equally-sized and ideally stirred tanks. The number of tanks in the series model is defined as N (Figure 5-93). If N equals one, the series model approaches an ideal completely mixed reactor; when N equals infinity, the series model becomes an ideal plug flow system. As long as N is determined for an operational waste stabilization pond, the phosphorus models must be applied to a N-series, completely mixed tank.

In order to determine N for each individual waste stabilization pond, the residence time distribution (RTD) approach has to be employed. Elements of fluid taking different routes through a reactor results in different times of passage through the reactor. The distribution of retention times for the fluid leaving the reactor is called the RTD of the fluid.

Pulse injection of dye, tracer studies, are used to determine RTD. The technique involves instantaneous injection of a conservative dye to the influent and continuous measurement of the effluent dye concentration beginning at the time of the injection. A non-dimensionalized plot of L versus M, Figure 5-94, results from such tracer experiments. The non-dimensionalized L and M are defined as follows:

$$L = C_e/C_o \tag{5-2}$$

$$M = t'/t \tag{5-3}$$

where

C_e = the effluent dye concentration, mg/l
C_o = the mass of dye injected divided by the total pond volume, mg/l
t' = actual time of measurement, minute
t = mean detention time, minute.

N can be obtained by comparing the measured RTD curve with Figure 5-94. The solution of N can also be obtained from Equation 5.4.

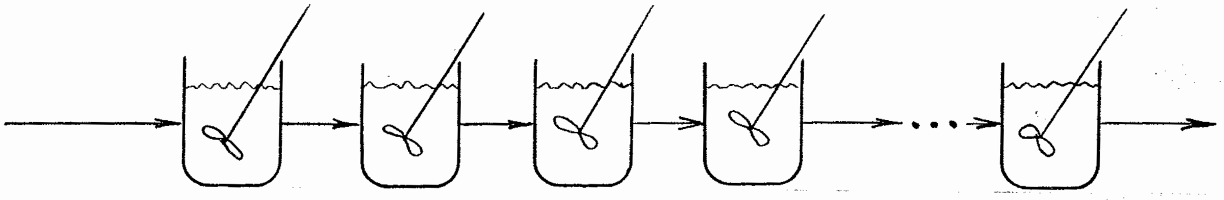


Figure 5-93 Tanks-in-Series Model

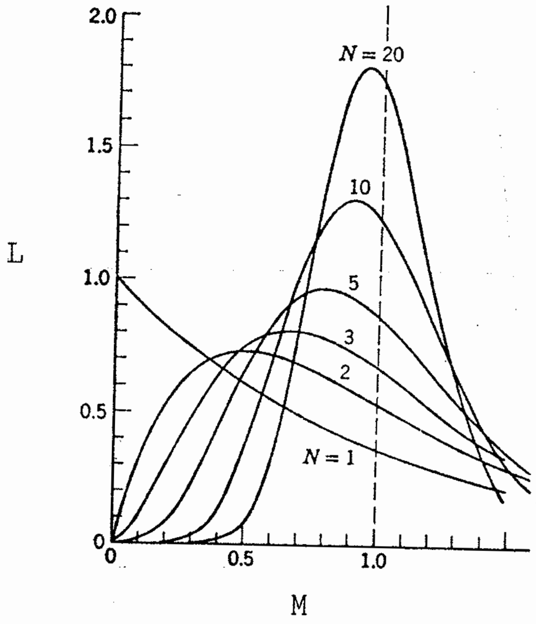


Figure 5-94 RTD Curves for the Tanks-in-Series Model Eq. 5-1 (Levenspiel, 1972)

$$L = \frac{N(MN)^{N-1}}{(N-1)!} \exp(-MN) \qquad (5\text{-}4)$$

where

N = the number of equally-sized, completely mixed tanks.

Figures 5-95 through 5-98, illustrate the relationships between phosphorus concentration and the number of equally-sized, completely-mixed tanks, N. The analysis is based on a FWSP, a flow of 3×10^3 m^3/d, and a phosphorus concentration of 8.0 mg/l (5.0 mg/l inorganic and 3.0 mg/l organic phosphorus). The FWSP was assigned a volume of 1.06×10^5 m^3 and an area of 6.2×10^4 m^2, and initial values of $C_o = 2.4$ mg/l and $C_{so} = 150$ mg/l. The sediment volume, V_s, was equal to 6.2×10^3 m^3 based on an assumption depth of 10 cm.

Assumming a completely mixed FWSP, i.e., N = 1, the value of C and C_s were calculated to be 7.4 mg/l and 130 mg/l. For N = 2, C and C_s became 4.5 and 78.5 mg/l. As N increased to three, C and C_s reduced to 4.4 and 77 mg/l. As shown in Figures 5-95 and 5-96, when N was equal to or greater than three, C and C_s remained at 4.4 and 77 mg/l.

When the tanks-in-series model was applied to the organic-inorganic phosphorus model, the result was consistent with that obtained above. As N was made equal to one, the values of C_1, C_2, C_3, and C_4 were 3.4, 4.0, 54, and 76 mg/l, respectively. However, as N was made equal to or greater than three, C_1, C_2, C_3 and C_4, respectively, remained at 2.8, 1.6, 40, and 37 mg/l.

As a result, it is important to determine the flow pattern to achieve an accurate prediction. If a completely mixed system is used in place of plug flow, the prediction will tend to be conservative. The observed phosphorus concentrations will be less than the predicted ones. If a plug flow system is assumed, the observed value will be greater than the expected value.

Since waste stabilization ponds generally perform in a plug flow manner, the completely mixed situation with N=1 is difficult to achieve. Modification of the phosphorus models becomes necessary in most cases. However, as N is equal to or greater than three, the predicted values will not change. Therefore, a value of N=3 may be used for predicting organic and inorganic phosphorus concentration in both the supernatant and sediment of waste stabilization ponds.

5.6 DESIGN EXAMPLE

A hypothetical example was selected for analysis in this section. To use the phosphorus models in improving the effluent quality, the physical, chemical, and

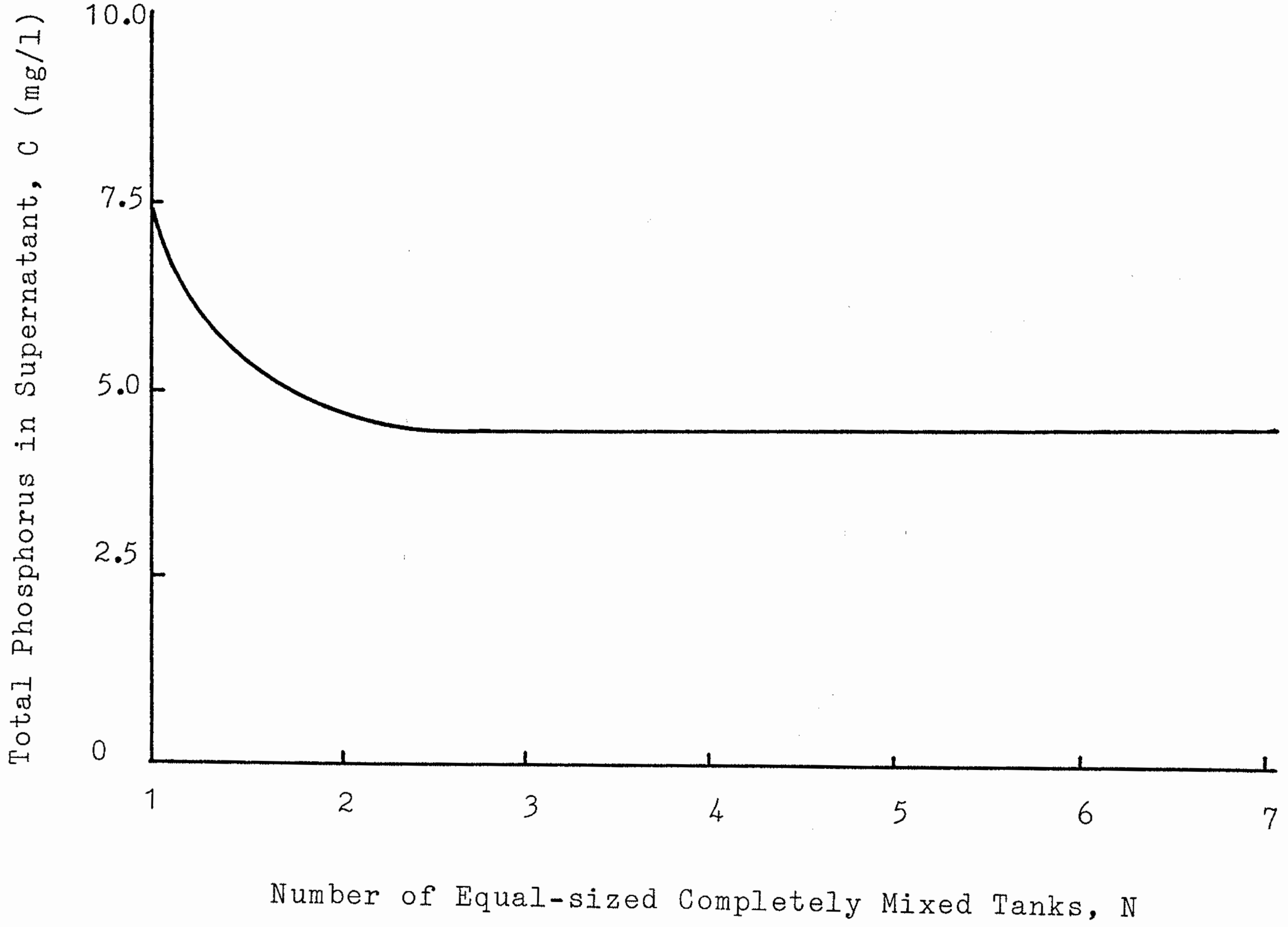


Figure 5-95 Model Application of C to N

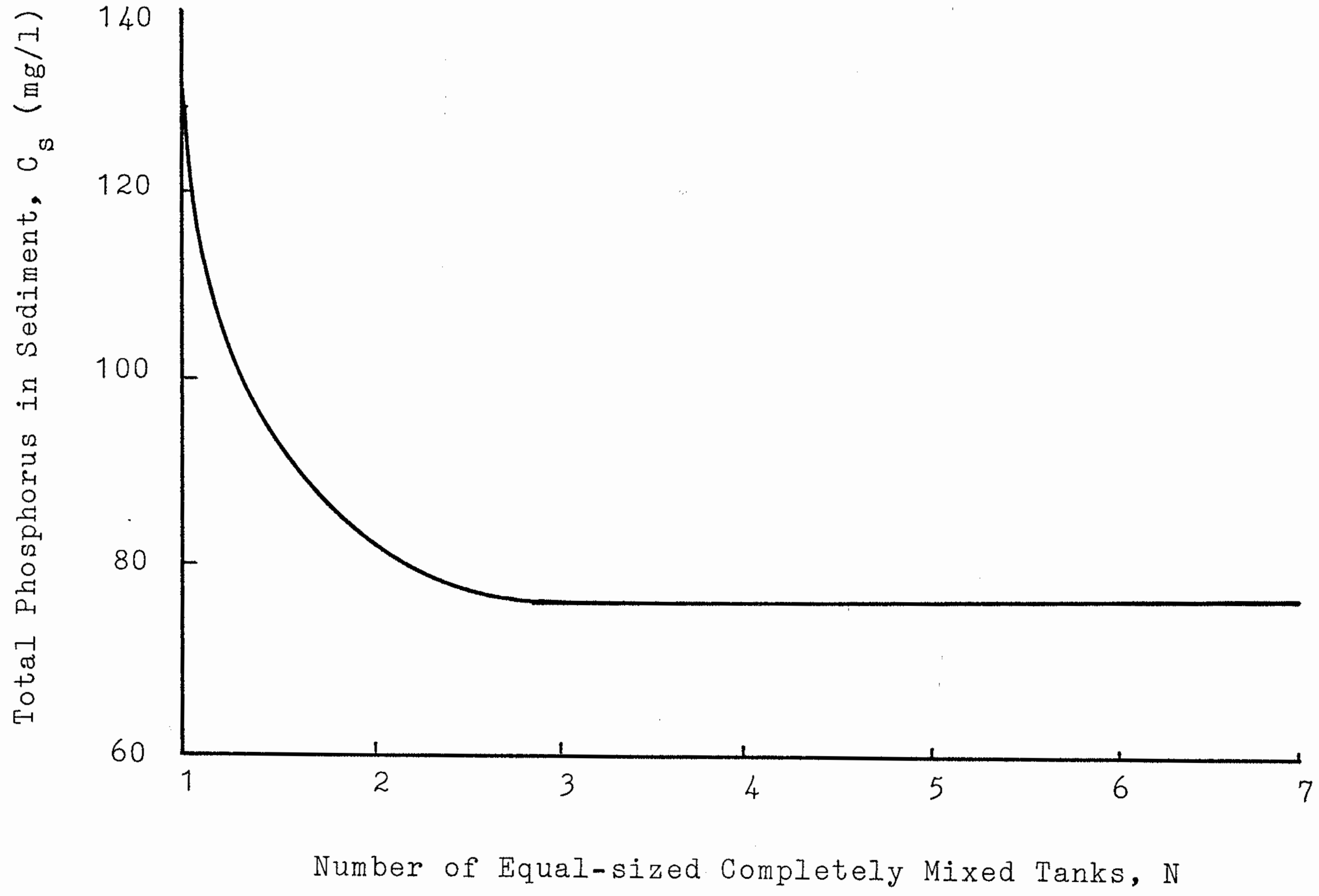


Figure 5-96 Model Application of C_s to N

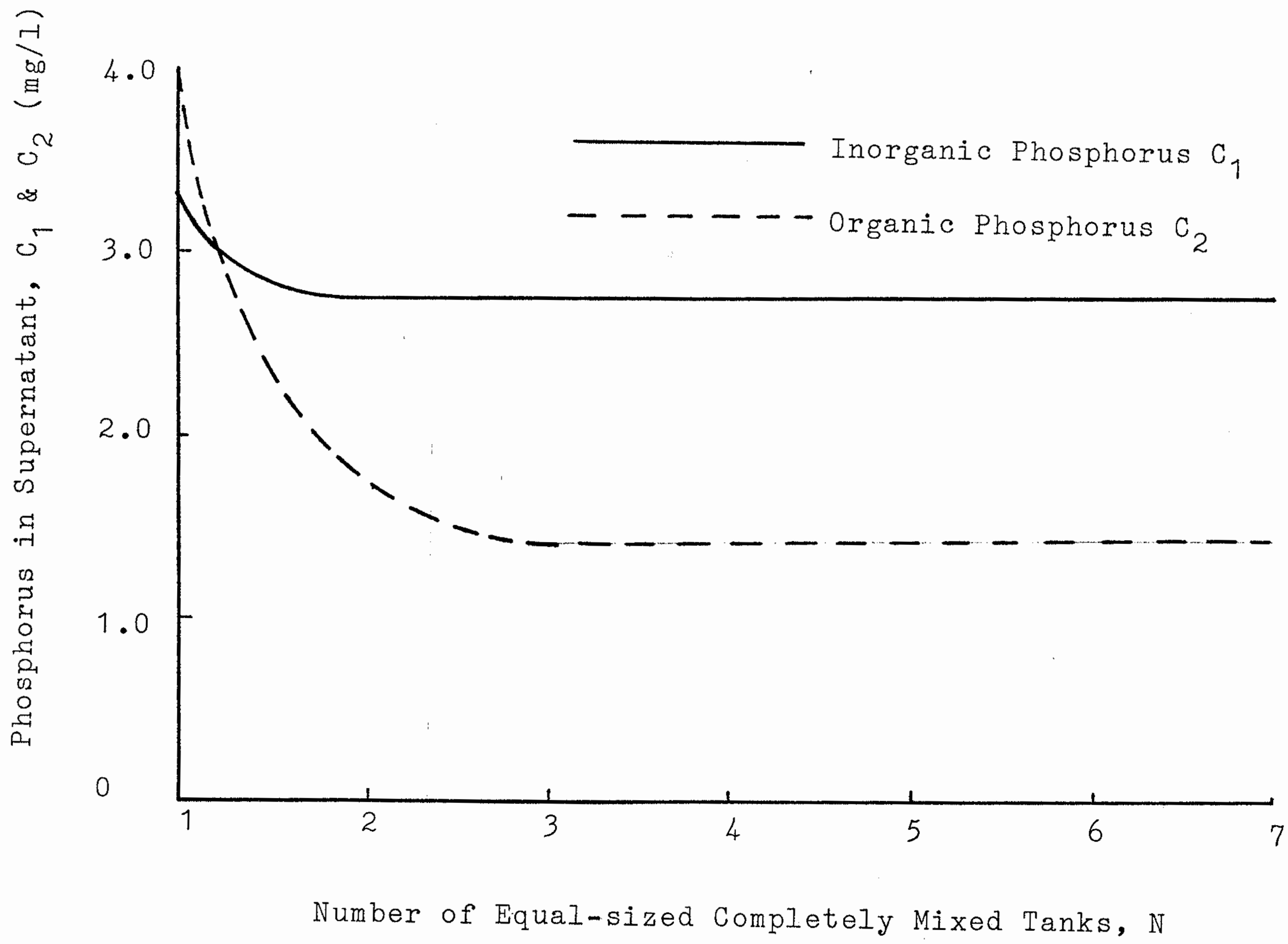


Figure 5-97 Model Application of C_1 & C_2 to N

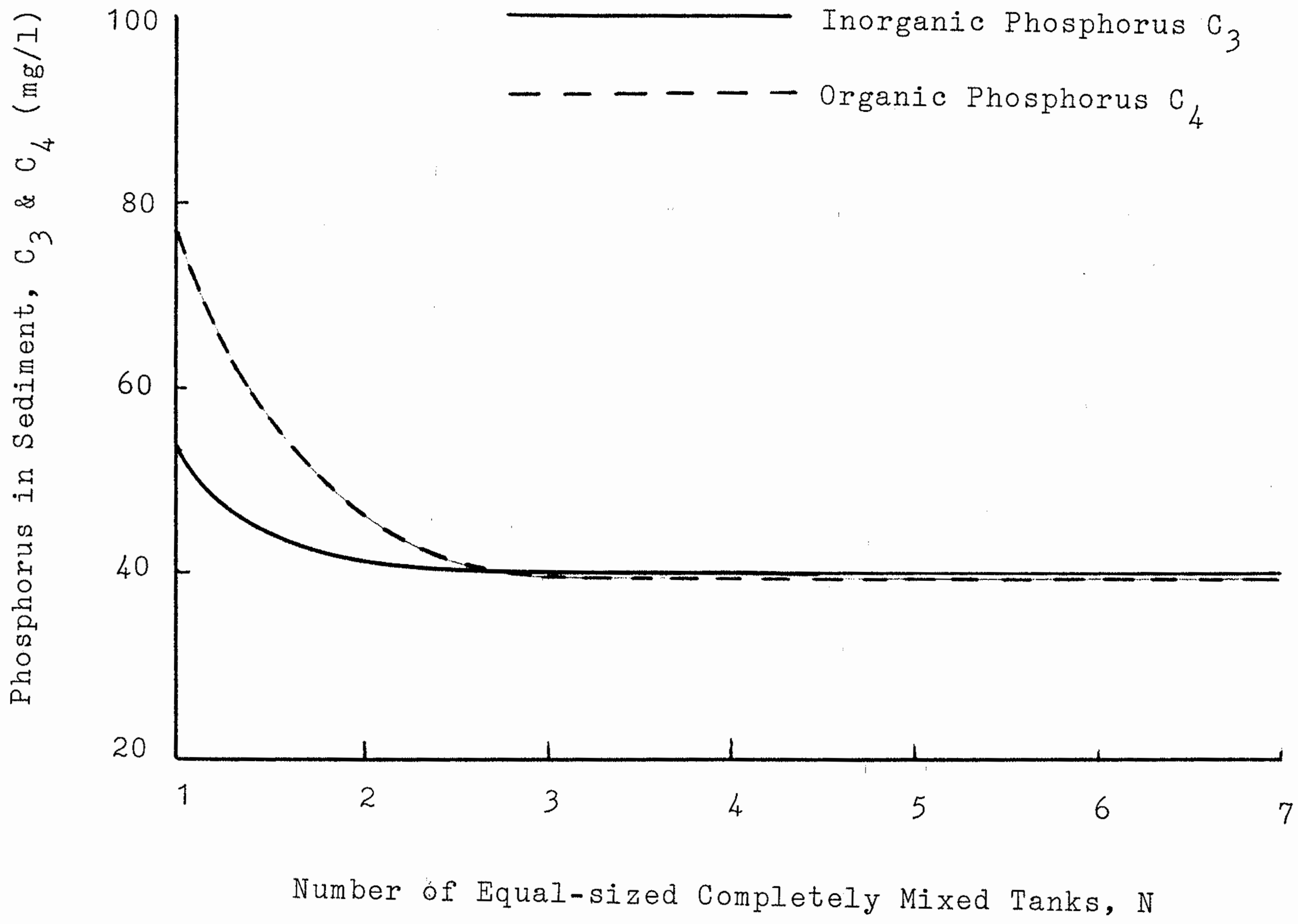


Figure 5-98 Model Application of C_3 & C_4 to N

biological constants must be available. The surface area and the volume of the pond also must be calculated or measured.

For this example, a city with a population of 20,000 was assumed to generate 500,000 gal/d (1900 cu. m/d) of raw sewage, 0.17 lb BOD_5/caput/d (0.08 kg/caput/d). The wastewater characteristics and environmental factors are listed in Table 5-13. Seepage from the FWSP was assumed to be zero, and the amount of precipitation was equal to the amount of evaporation. The wastewater temperature was assumed to be at 20^oC. By using the previously described procedure (Gloyna 1971), the pond volume was calculated to be 1.06×10^5 m^3. Using a depth of 1.75 m, the required surface area was 0.619×10^5 m^2.

The total phosphorus, inorganic phosphorus, and organic phosphorus concentrations in the effluent, calculated by the phosphorus models using the fourth-order Runge-Kutta method, are shown in Figure 5-99 to Figure 5-102. The total phosphorus in the influent with 8.0 mg/l, will be reduced to 4.4 mg/l in the effluent after the system has reached a steady state. The inorganic phosphorus will be reduced from 5.0 mg/l in the influent to 2.8 mg/l in the effluent. Similarly, the organic phosphorus will be reduced from 3.0 mg/l to 1.6 mg/l. The latter value includes the phosphorus in the algae. If the calculated phosphorus concentration for the effluent does not meet the discharge criteria, additional ponds can be added to the treatment train and the model can be applied again.

The procedure would be similar if the phosphorus models were applied to a AWSP or a MWSP. However, appropriate physical, chemical, and biological parameters must be developed. Any changes in the parameters may significantly affect the predicted phosphorus concentrations.

Table 5-14 Constants for Hypothetical Waste Stabilization Pond Design

	Characteristics	units	values
K_1	Deposition Rate of TP	cm/day	2.0
K_2	Release Rate of TP from Sediment	cm/day	0.11
K_3	Unavailable Release Portion of TP	%	22
k_1	Deposition Rate of IP	cm/day	2.0
k_2	Release Rate of IP from Sediment	cm/day	0.20
k_3	Deposition Rate of OP	cm/day	2.0
k_4	Unavailable Release Portion of IP	%	22
k_5	Unavailable Release Portion of OP	%	22
u_1	Mineralization Rate of OP in Supernatant	day^{-1}	0.0014
u_2	Uptake Rate of IP in Supernatant	day^{-1}	0.050
u_3	Uptake Rate of IP in Sediment	day^{-1}	0.005
u_4	Mineralization Rate of OP in Sediment	day^{-1}	0.010
N	Number of Tank-in-Series		3

TP = Totoal Phosphorus
IP = Inorganic Phosphorus
OP = Organic Phosphorus

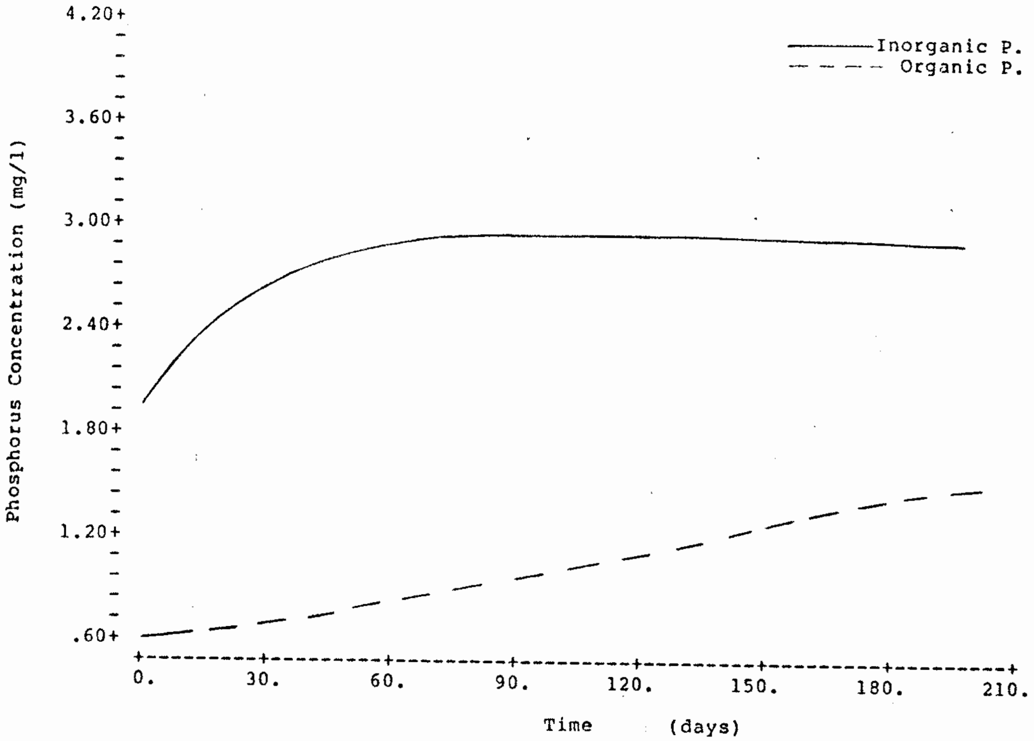


Figure 5-99 Phosphorus Concentration in Hypothetical FWSP Supernatant

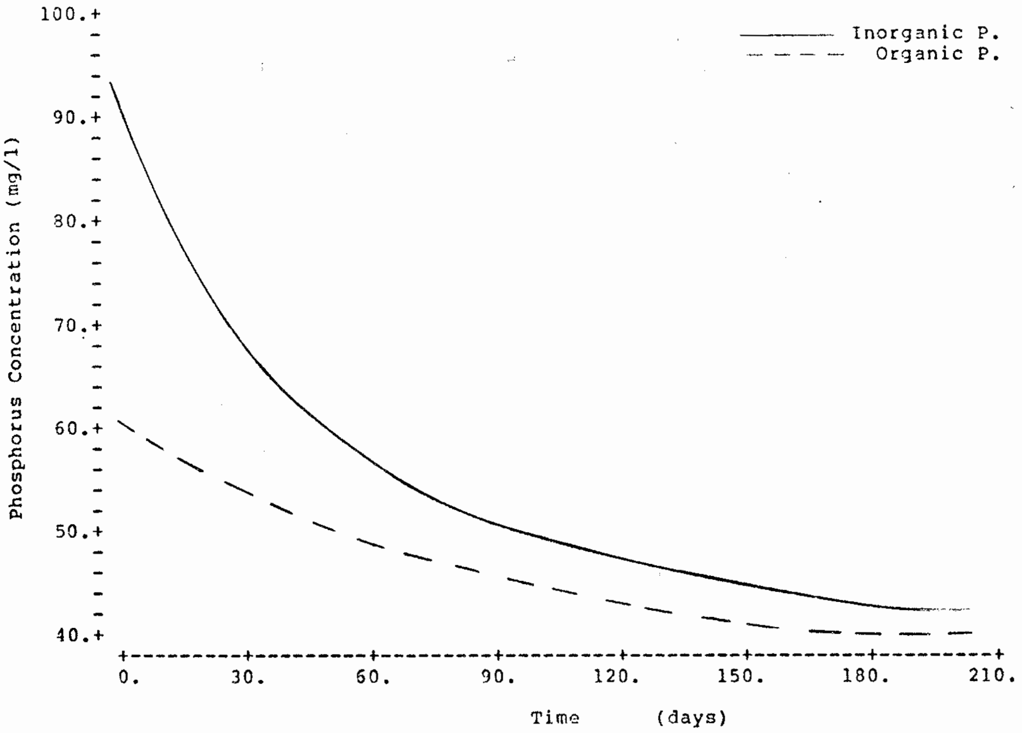


Figure 5-100 Phosphorus Concentration in Hypothetical FWSP Sediment

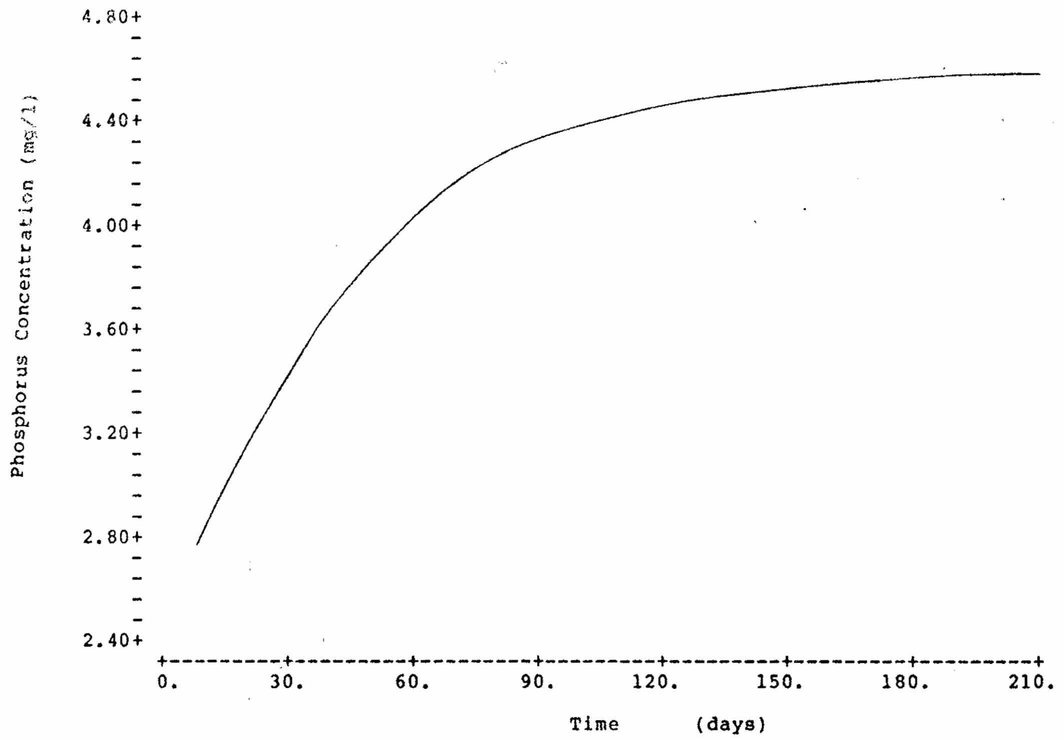


Figure 5-101 Total Phosphorus Concentration in Hypothetical FWSP Supernatant

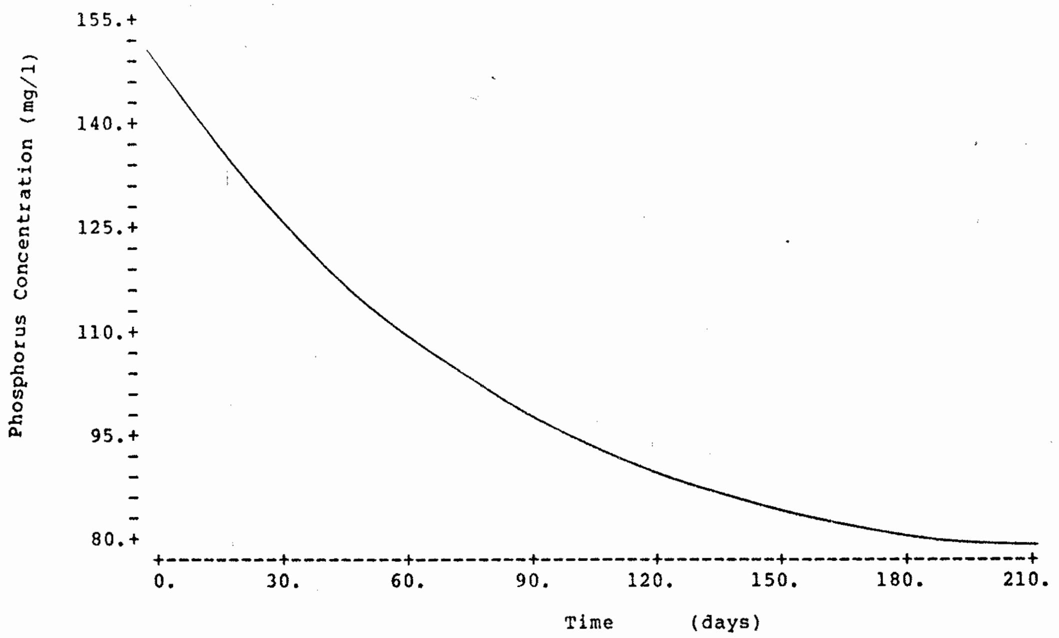


Figure 5-102 Total Phosphorus Concentration in Hypothetical FWSP Sediment

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