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A Study of Differences in Vertical Phosphorus Profiles Within the Sediments of Selected Florida Lakes as Related to Trophic Dynamics

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A STUDY OF DIFFERENCES IN VERTICAL PHOSPHORUS PROFILES WITHIN THE SEDIMENTS OF SELECTED FLORIDA LAKES AS RELATED TO TROPHIC DYNAMICS

BY

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B.S., University of Florida, 1971

THESIS

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ABSTRACT

Several Florida lakes with different documented trophic state indices were selected for sediment analysis. Vertical sections of the sediment were taken at depths of .1, .5, 1, 2, 3, 4, 5, 6, 10 and 15 centimenters below the surface of the sediment-water interface. Total Phosphorus analysis was done on each section. The profile presented was then evaluated and was found that the profiles best fit the equation $Y = \frac{X}{A + BX}$, where Y is the Phosphorus Concentration in ppm and X is the sediment depth in cm. Correlation between the trophic state and the profiles characteristics are presented.

A hypothesis as to how the sediment profile changes as the lake experiences increased Phosphorus loading is presented, and is used to evaluate the lake studied. This discussion expresses phosphorus dynamics within the sediments in terms of adsorption, chemical changes, biological activity, and molecular and eddy diffusion.

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ACKNOWLEDGMENTS

I would like to thank all of the instructors at Florida Technological University who have made this a learning experience of considerable value. In particular, I would like to thank the professors on my graduate committee, Dr. W. M. McLellon, Dr. M. P. Wanielista, and Dr. Y. A. Yousef. I must certainly express great respect for Dr. Yousef's patience and understanding, which fortunately was usually to formidable an adversary for my stubborness and naivity.

There is no doubt that this study would not have been possible if it had not been for the help in the field, in the laboratory, and on the drawing board by my good friend Herb Zebuth. To him I want to give my special thanks.

I would also like to thank Ted Penland for his help in designing field sampling devices.

To my wife Glennda, and my six year old son Tommy, I want to express my thanks for tolerating someone who at times was something less than tolerable.

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CHAPTER I

Introduction

Increased awareness of the need for good water quality management has recently stimulated research towards understanding the dynamics of the eutrophication process. From these efforts have emerged certain indices that correlate pollutant loading to accelerated maturation of aquatic systems. To date, all of these indices are related to phytoplankton activity, which is a representation of the trophic state of the lake.

Because the assessment of trophic state is somewhat subjective, there has been considerable confusion in some of the environmental sciences as to how such terms as eutrophic, oligotrophic, mesotrophic, and succession should be defined. In Florida for example, the rate of primary production in an "oligotrophic" lake may be greater than that of an "eutrophic" Northern lake. The reason, of course, is that there is a great variability in the factors that determine the rate of photosynthesis. In this case, the great variability in the temperature and solar influx may be held responsible for the differences in productivity.

It is apparent then that perhaps a new parameter which assesses the efficiency of energy utilization within lake systems is needed to replace or supplement those parameters such as Chlorophyll, Nutrient concentrations and rate of primary production which are actually related to the rate of Carbon fixation into organic molecules and tell very little about the total energy flow within all energy levels of the ecosystem. To date, the only studies that attempt to determine the energy flows within aquatic systems are extensive "budget" investigations that are not always practical as they require considerable time and effort.

The mechanisms of nutrient transfer between bottom sediments and the overlying water may prove to be of considerable value in evaluating the trophic state of the lake, since sediments play a significant role in regulating energy flow within lacustrine systems. If lake systems are to be viewed macroscopically, it can be seen that certain biological, chemical and physical phenomenon serve to maintain relatively uniform conditions within the lake and its related watershed. The capacity of sediments for nutrient retention is high, and this fact accounts for their homeostatic role as a nutrient sink and regulator. This transfer of nutrients from the sediments to the overlying water is an area needing much investigation at this time.

Scope and Objectives

This study deals with Phosphorus profiles within the sediments of Central Florida lakes in an attempt to better understand the trophic dynamics concept in lakes. Phosphorus is selected because it is so often considered the limiting nutrient and is not complicated by such phenomenon as fixation from the atmosphere as in the case of nitrogen. Its distribution within the sediments from lakes of different trophic levels is being investigated during the course of this study.

Sediment samples were collected from various lakes of different trophic states in an attempt to determine if any correlation exists between the trend in vertical distribution of phosphorus within the lake sediment and their trophic state. In addition, the investigation is designed to examine the role of the sediments as a nutrient regulator and to look more closely at phosphorus movements within the sediments in hopes of finding an indicator that would assist in understanding the dynamics of the entire lacustrine ecosystem.

In terms of energy flows, it might be possible to determine whether a lake is in equilibrium, steady state, quasi-steady state, or in positive balance (organic accumulation) by investigating the phosphorus distribution throughout the sediments. Although it is somewhat theoretical to talk about trophic dynamics in terms of entropy, enthalpy and free energy, they are utilized throughout the discussion in hopes of clarifying some of the phenomenon that occur within the aquatic ecosystem which serve to maintain rather constant conditions. These phenomenon will be called homeostatic mechanisms throughout the discussion although some might be in disagreement with the usage of this term.

CHAPTER II

LITERATURE REVIEW

Ecosystems

Prior to the time when it was revealed that technological activities could have permanent devastating effects upon natural systems, Ecology was more or less concerned with plant and animal species, and their distributions and behavioral patterns. However, during the first half of this century, it became evident that a unit existed in nature that was a result of interactions of organisms between themselves and their physical environment. This unit, although it appeared to be equipped with a certain buffering capacity when meeting the natural fluctuations of its environment, did show vulnerability when attempting to deal with the huge burdens planced upon it by human technological societies. This basic ecological unit was called the "ecosystem" by Tansley (1) in 1935 and was defined as a system composed of physical-chemical-biological processes active within a space-time unit of any magnitude. Recognition of such a unit as the subject of primary ecological concern led logical thinkers to realize that energetics, that is the transfer of energy within the system, was the cohesive factor that maintained the system. Thieneman (2) used the term biosystem rather than ecosystem, and was one of the first to realize that solar energy captured by the plant "producers" was the source of the total energy that became available to the many carnivorous and herbivorous organisms known as "consumers".

Hutchinson (3) as a leader in energetics, recognized that each energy level, which he symbolized by Λ_N, has an energy content somewhat higher than the level below it, that is to say that the total energy contained within the producers would be higher than that held by the herbivorous organisms, while the carnivores would be at an even lower level. Lindeman (4) used these thoughts to develop his trophic-dynamic concept, which approaches the ecosystem in terms of bio-energetics. Figure 1 is a representation of this idea applied to lacustrine ecosystems.

In conjunction with the bio-energetics approach is the observation made by Prigonine (5) that a steady state is one in which entropy is at a minimum, and that a steady state system will not leave this state by a spontaneous irreversible change. This is in accordance with Le Chatelier's principle which states that a system tends to change so as to minimize any external stress. This helps explain why ecosystems which are close to a steady state tend to be stable, and the relative abundance of biological and chemical material rather constant. As has been noted, most ecosystems will tend to evolve towards a steady state condition (4).

Succession Of Aquatic Systems

In aquatic systems, the energy flow may be expressed by $I + P = R + E$ at steady state, where I and E are the input and output of organic matter, respectively, and P and R are the rate of photosynthesis and respiration, respectively. As both P and R are

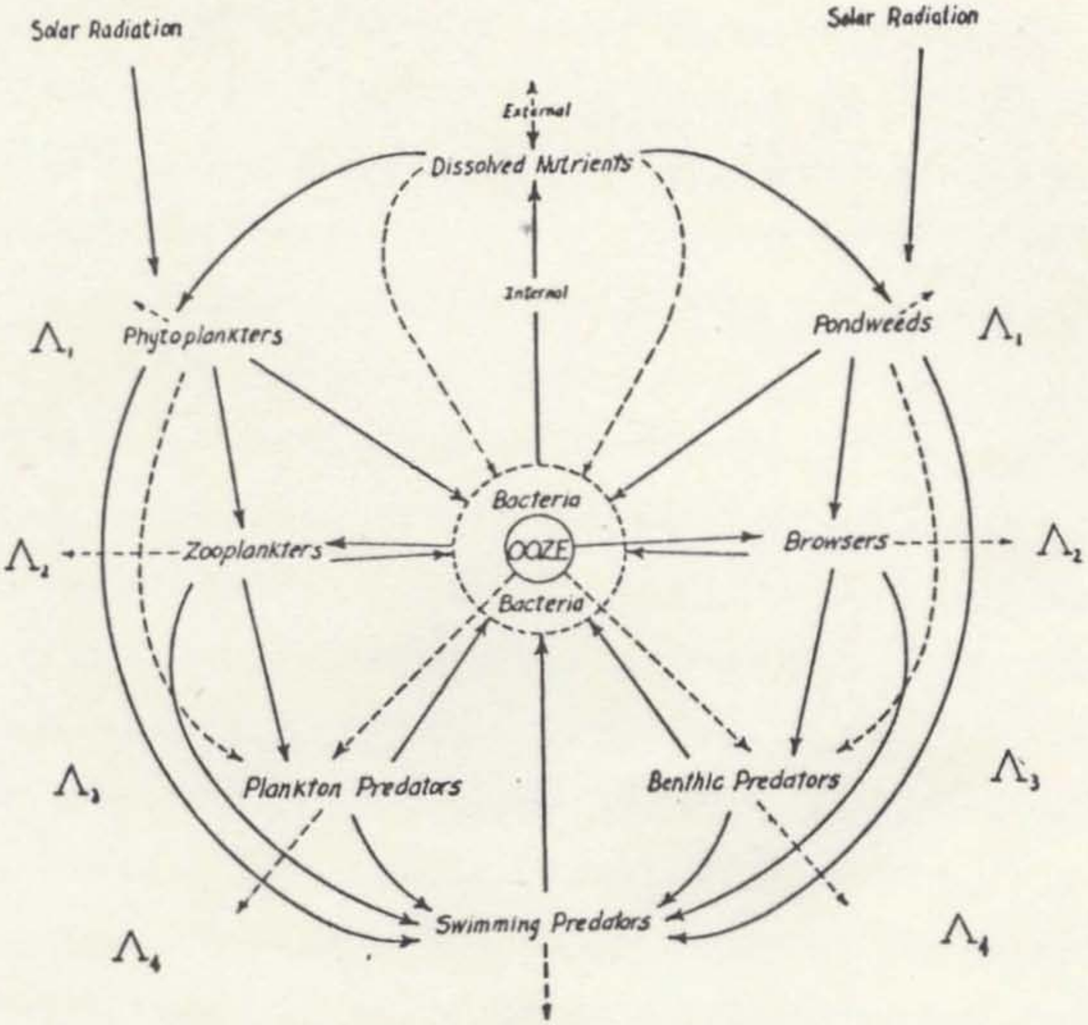


Fig. 1. Generalized Lacustrine Food Cycle Relationships

SOURCE: R. L. Lindeman, "The Trophic-Dynamic Aspect of Ecology," <u>Ecology</u> 23 (1942): 4406.

interrelated, and both may be functions of nutrient availability, it becomes evident that nutrient cycles play an important part in the energetics of aquatic systems. This is emphasized further when Liebig's law of limiting factors is considered, for it is often one of the nutrients that limit the rate at which solar energy is captured. It is feasible then that energy flow within the system might be expressed in terms of the limiting nutrient, at least as long as that nutrient remains limiting.

As stated previously, natural systems tend to evolve towards a steady state. It does this through a series of changes over time, a process called succession. In ecological terms, the system will reach a climax state, and will at this time retain its compliment of different species and operate as a steady state, or near steady state. This was demonstrated by Odum (6) who found that energy influx nearly equalled energy export and storage in Silver Springs. Lindeman (4), in his discussion presents two views on the mode of succession in lacustrine systems. First, the concept of Thieneman (2), is that a lake begins as an oligotrophic (low production) system, and that at this time efficiency is high. As influx of nutrients from the watershed begins, productivity increases and the lake begins to fill with organic surplus and a eutrophic (high production) condition prevails. As organic matter begins to accumulate, an oxygen depletion is noted on the bottom, and anaerobic conditions predominate. This means a collapse of the benthic community as it had existed, and a take over by anaerobic and facultative bacteria. These tend to be rather slow decomposers, and there tends to be a greater rate of accumulation of organic material because of this. As the lake fills it becomes a march or bog, and eventually becomes a terrestial system. Hutchinson (3) tends to look at natural lake succession as a process that approaches a terrestial state in a much slower and more orderly fashion. It does this while in some "ideotrophic" state whose rate of production is dependent upon the availability of the many variables that affect photosynthesis such as temperature, nutrient influx, and morphometric characteristics. It then approaches a quasi-steady state condition. This is called by Lindeman (4) the eutrophic-stage equilibrium. It is suggested that during this period there is an accumulation of organic material in the sediment, but the process is slow and controlled, and is regulated by the external influx and export of material, primary production rate, rate of sedimentation, and the rate of nutrient regeneration from the sediments. The implication then is that the lake does appraoch a terrestial climax, but it does so as a stable system which is evolving at a relatively slow rate under most natural conditions. This concept of lake succession is seen schematically in Figure 2.

The Hutchinson-Lindeman idea is in line with Odum (7) and others who feel that succession culminates in a stabilized ecosystem in which maximum biomass and symbiotic functions between organisms are maintained per unit of available energy flow. This is seen in Figure 3, which is taken from an article by Stumm and Zollinger (8) on the homeostatic capabilities of aquatic ecosystems. As can be

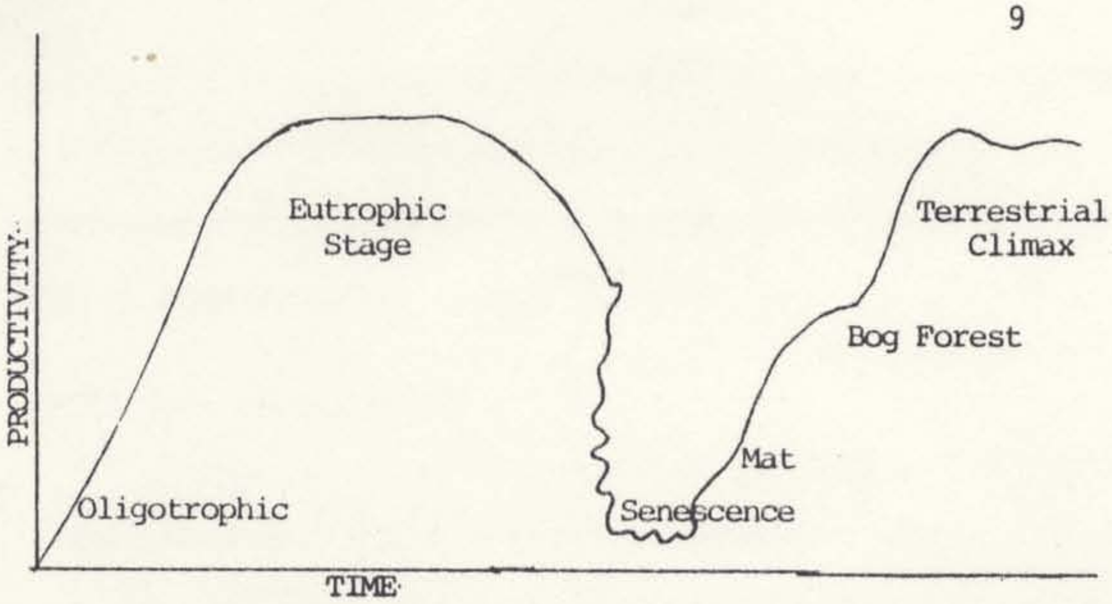


Fig. 2. Lake Succession Showing the Eutrophic State Equilibrium

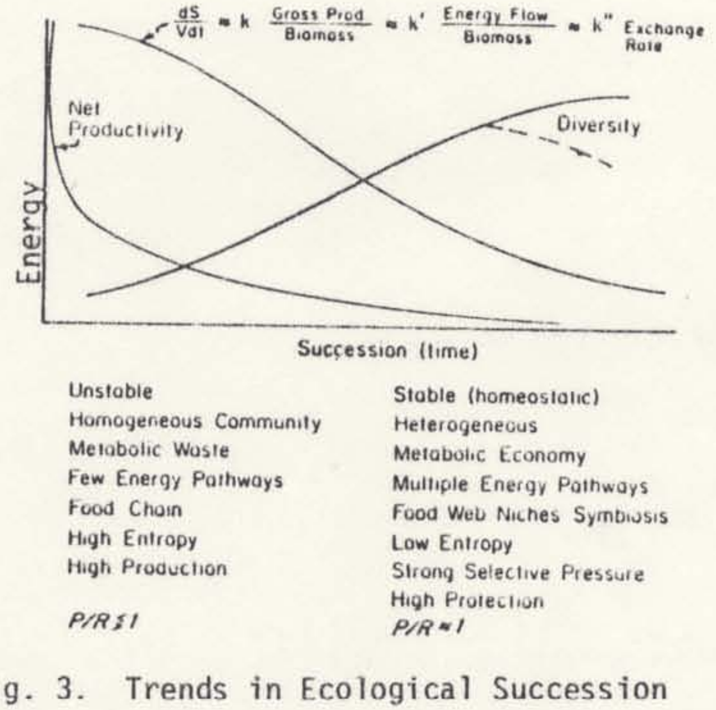


Fig. 3. Trends in Ecological Succession

SOURCE: W. Stumm and E. Stumm-Zollinger, "Chemostasis and Homeostasis in Aquatic Ecosystems: Principles of Water Pollution Control," in Nonequilibrium Systems in Natural Water Chemistry, ed. R. F. Gould (Washington, D.C.: American Chemical Society, 1971), p. 20.

seen by this figure, succession leads to an increase in diversity, with a reduction in the rate of productivity and entropy change. In accordance with Le Chatelier's principle, succession is maximization of self organization.

Energy Flow and Succession

Patten (9), in an application of the laws of thermodynamics to the energetics within an ecosystem, considers energy flow and succession and how they are interrelated. He begins by noting that the ecosystem as well as living organisms are highly improbable aggregates of energy. He then views the mature ecosystem as a steady state in which energy enters and is then stored or degraded. In the degradation process, entropy is created, which corresponds with the second law of thermodynamics, in which it is stated that there is an increase in entropy with any energy transformation. This entropy may be considered as a measure of disorder within the system. If "I" is considered negative entropy, that is a measure of order within the system, (negentropy), then $I_{organism} = I_{food} - I_{waste}$, or I_{waste} can be considered the entropy gain.

This can be represented in terms of the free energy, ΔF, which can be considered analogous to the energy output, and the enthalpy change, ΔH, which corresponds to the energy input, to obtain the familiar equation:

$$\Delta F = \Delta H + T\Delta S$$

As entropy (S) represents disorder, it is paramount that it is dissipated away from the living system which is of course highly ordered. The mode by which this entropy is dissipated is by excretion of waste products, and of heat from respiration into the environment. The excreta of course, in a complex ecosystem, will be further broken down, and, in words of Patten (9), the negentropy extracted from it by the secondary (decomposer) food chain.

If H_1 is the solar energy converted by primary production to chemical energy within the system, then $\Delta H_1 = \sum_{i=1}^{n} \Delta F_i + \sum_{i=1}^{n} T\Delta S_i$; where i refers to the trophic level. Figure 4 reveals how the energy flow may be viewed in these terms. As can be seen, a fraction, $T\Delta S$ must always be lost, and this for all practical purposes in a quasi-steady state may be considered equivalent to the heat released during respiration.

In applying these thoughts to succession, Patten (9) notes that the stability of a system is related to the number of channels through which energy may move during its flow through the ecosystem. This is of course a function of the diversity (see Figure 3). These choices may be called information, and are related to negentropy. If the information increases with maturation, then negentropy increases. This implies a more organized ecosystem with more evolutionarily advanced organisms (specialists). Patten went further by developing the energy terms seen in Figure 4 into three equations.

1. $\Delta H_1/T + \sum_{i=1}^{n} \Delta H_i''/T = \sum_{i=1}^{n} (\Delta F_i'''/T + \Delta S_i)$
2. $\Delta H_1/T + \sum_{i=1}^{n} \Delta H_i''/T > \sum_{i=1}^{n} (\Delta F_i'''/T + \Delta S_i)$
3. $\Delta H_1/T + \sum_{i=1}^{n} \Delta H_i''/T < \sum_{i=1}^{n} (\Delta F_i'''/T + \Delta S_i)$

Fig. 4. Energy Flows in Lacustrine Systems

SOURCE: B. C. Patten, "An Introduction to the Cybernetics of the Ecosystem: the Trophic-Dynamic Concept," *Ecology* 40 (1959): 228.

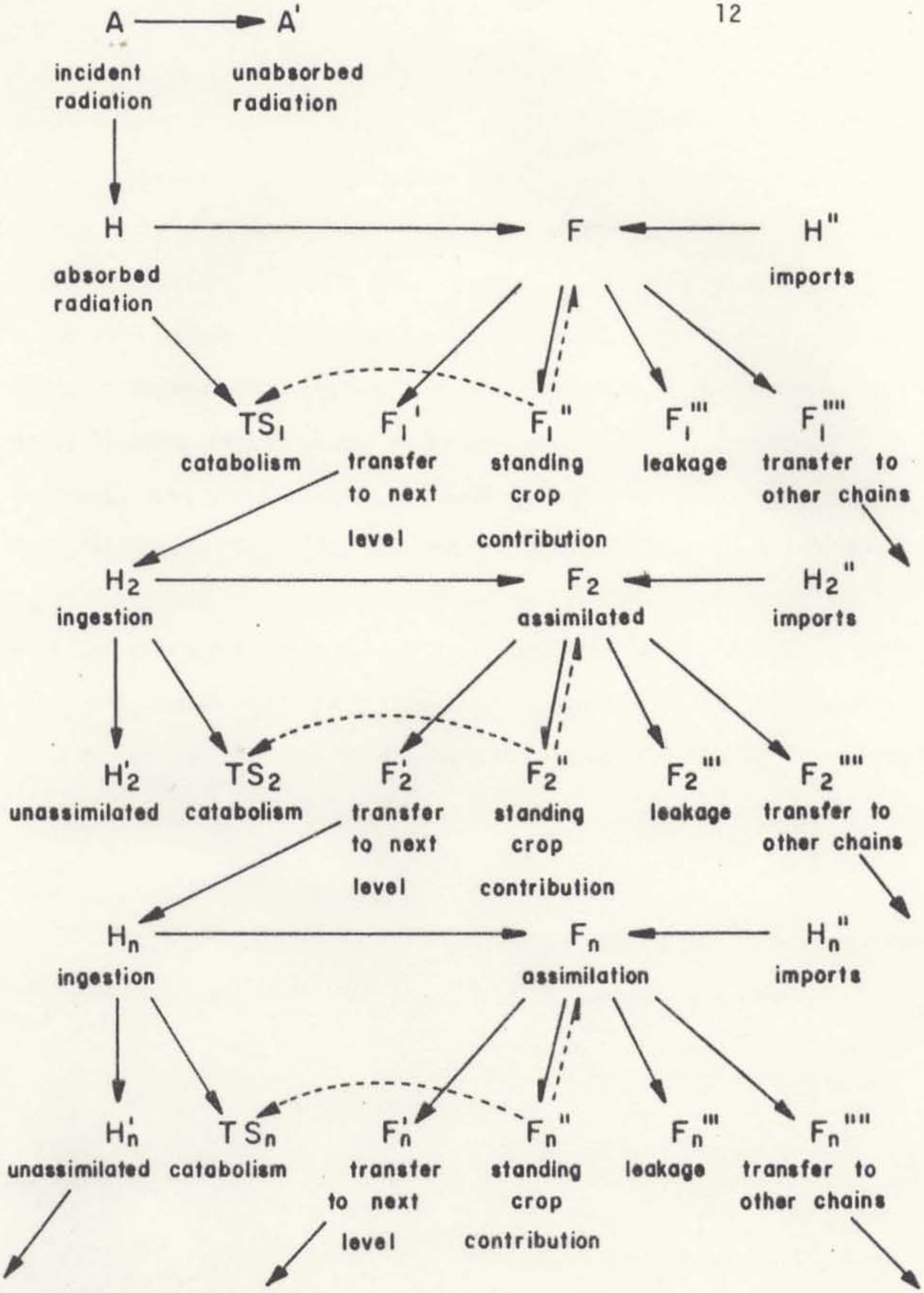


Fig. 4. Energy Flows in Lacustrine Systems

$\sum_{i=1}^{n} \Delta H_i''$ here represents the input of energy other than that derived from solar radiation. $\sum_{i=1}^{n} \Delta F_i'''$ is that free energy which is lost (leached) from the system, and $\sum_{i=1}^{n} \Delta S_i$ is of course the entropy which is the heat energy lost from the system via respiration.

Equation 1 shows a true steady state condition, equation 2 is a positive balance condition. In terms of succession, equation 1 is a climax representation (although a true steady state condition may actually never exist, as was noted by Lindeman(4)). Equation 2 indicates that succession is proceeding, and equation 3 represents senescence (see Figure 2). Lindeman's eutrophic-stage equilibrium might be thought of in terms of equation 2, with the ratio of the two sides of the equation remaining rather constant over time, and tending to approach one. This is not what Thieneman (2) implies. He would tend to believe that the ratio would change rather rapidly or fluctuate greatly as it approaches one.

Nutrient Loading and Succession

Lindeman (4), in 1944, realized the importance of the surrounding drainage areas upon the nutrient dynamics within a lake.

> "Lake succession is internally complicated by a rather considerable influx of nutritive material from the drainage basin surrounding the lake."

Lately, some attention has been given to the rate of nutrient loading from natural, rural, and urban areas. This material, which may be called allochthonous, may come from a controlled point source such as a wastewater treatment facility, or may originate from an uncontrolled nonpoint source, such as stormwater runoff. Only in the last ten years or so has the real significance of nonpoint allochthonous material been recognized by those in the engineering and planning fields.

Weibel, et al. (10) investigated the quality of runoff from cultivated land and found that it was high in both phosphorus and nitrogen. Total phosphorus was found to be as high as 3.3 mg/l and was mostly as insoluble ferric, aluminum or calcium phosphate which was formed upon the application of fertilizer. Loehr (11) noted that only 5-10% of the phosphorus applied as fertilizer was taken up by crops and the balance remains as the insoluble forms until resolubilization occurs, usually through microbial action. Phosphorus transport through runoff is usually caused by erosion. Runoff from forest areas was reported by Cooper (12) to be considerably lower in nitrogen and phosphorus than agricultural areas. Total phosphorus ranged from 0.015 mg/l to 0.115 mg/l.

Urban runoff was found to vary considerably in phosphorus content, but the loading in all cases is considerably higher than that found from unmolested watersheds. Wanielista (13), in a study on nonpoint source effects in Central Florida, found that phosphorus loading from urban runoff in downtown Orlando, Florida ranged from 2.0-3.5 K_g/ha-yr. Loadings from the U.S. urban areas varied from 1.0-5.0 kg/ha-yr.

The Eutrophication Survey Branch of the Environmental Protection Agency (14) has accumulated much of the data obtained from various nonpoint source pollution studies done in the United States. Figures 5 and 6 show their findings of the average loading rates of ortho and total phosphorus from runoff of various land uses.

Predictive Models

Nutrient influx in lakes is related to increased nuisance algae blooms and other signs of disrupted energy flows, such as a decrease in species diversity, collapse of the benthic community, and a high degree of anaerobiosis. A relationship between nutrient loading from allochthonous sources and the trophic state of the lake has been established. Several models have been designed to check the mass balance of the limiting nutrients as related to trophic state. Phosphorus was found to be the limiting nutrient in 67% of the 812 lakes studied by EPA (14). The Eutrophication Survey Branch has applied three models to the information it has received on various lakes throughout the U.S.

Vollenweider's model (15) makes use of several assumptions in developing a mass balance equation. The primary assumption is that the lake being evaluated is in a steady state, i.e., $dP/dt = 0$, where P is the phosphorus content within the lake. Also, it is assumed that the lake is completely mixed, that the loading rate is constant over time as is the flushing and sedimentation rate, that the phosphorus concentration of the outflowing water is equal to the average concentration within the lake, and that the rate of phosphorus sedimentation is dependent solely upon the phosphorus concentration within the lake. The basic equation used for the model then is:

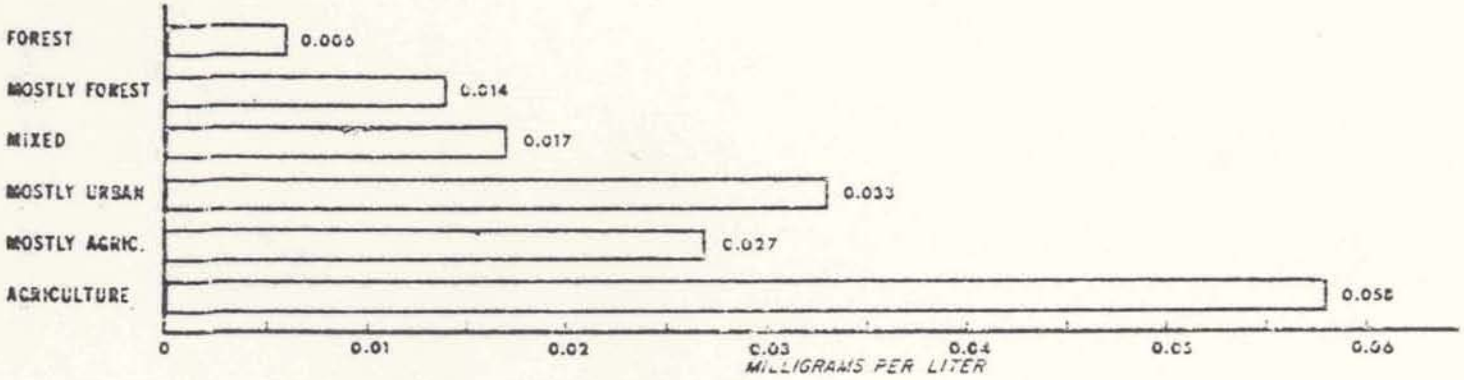


Fig. 5. Orthophosphate Concentrations in Runoff From various land uses in the U. S.

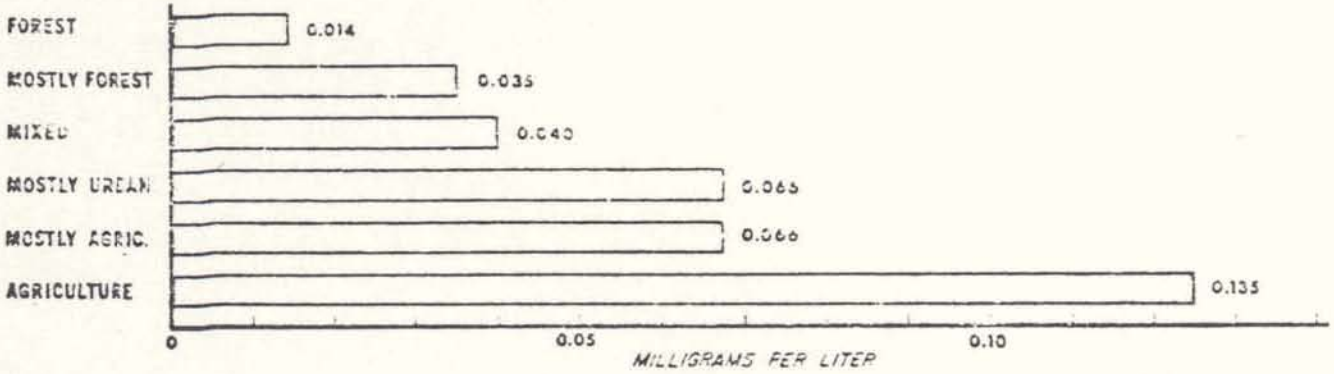


Fig. 6. Total Phosphorus Concentration in Runoff from various land uses in the U. S.

SOURCE: U. S. Environmental Protection Agency, Eutrophication Workshop, Region IV, Atlanta, Georgia, December 3, 1975. (Corvallis, Oregon: National Eutrophication Survey) (mimeographed).

$$d(m_w)/dt = (1-S)J/V - \sigma(m_w)$$

where:

m_w = the concentration of the total phosphorus in the lake

$(1-S)J/V$ = the supply of phosphorus to the lake per unit volume after correction is made for the outflow of phosphorus

$\sigma(m_w)$ = the phosphorus lost to the sediments

The solution to the differential equation at steady state is:

$$\bar{z} = (1-S)J/A(m_w) \text{ (Vollenweider (15))}$$

where:

$\bar{z}$ = the mean depth of the lake

A = the surface area

As can be seen, the mean depth and loading are related, and it is these two variables that Vollenweider utilizes in establishing trophic state nutrient-loading relationships. Figure 7 shows how this model classified several lakes investigated by EPA (14).

Dillon (16) noted that some of Vollenweider's assumptions weakened the viability of the model. He expounded upon the complexities involved in the sedimentation process, pointing out that the concentration of phosphorus within the lake does not necessarily control sedimentation, but rather such cations as Fe^{+3}, Al^{+3}, and Ca^{+2}, as well as adsorptive phenomenon, may serve as regulators. From these considerations, Dillon (17) developed a model which utilizes a parameter that incorporates the phosphorus loading rate, L, the hydraulic flushing rate, ρ (reciprocal of the hydraulic retention time in years),

Fig. 7. SOURCE: U. S. Environmental Protection Agency, Eutrophication Workshop, Region IV, Atlanta, Georgia, December 3, 1975. (Corvallis, Oregon: National Eutrophication Survey) (mimeographed).

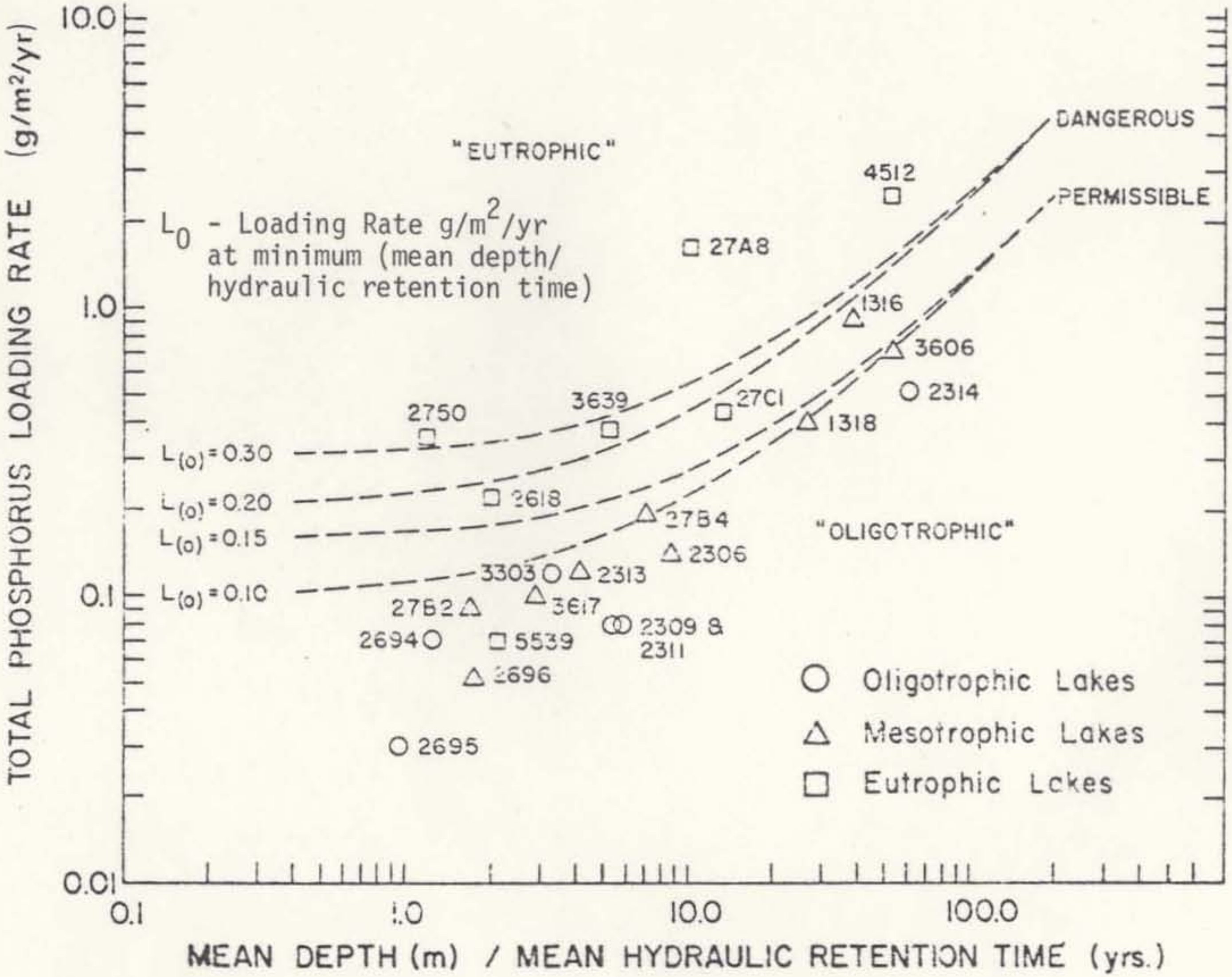


Fig. 7. The Vollenweider Relationship Applied to a Number of Eastern U. S. Lakes and Reservoirs Sampled by EPA.

the phosphorus retention coefficient, R, (the ratio of the phosphorus remaining in the system, (input-output), and the incoming load). The parameter, $L(1-R)/\rho$, is plotted on the Y axis, rather than just loading rate as in Vollenweider's model. Mean depth remains the parameter represented by the X axis. Figure 8 shows the EPA (14) results using this model which indicates a linear relationship on a log-log scale.

The third model utilized by EPA was one developed by Larsen and Mercier (18) under EPA sponsorship. They also used the phosphorus retention time, but rather than integrating it into loading rate, they used it as the independent variable, while a loading parameter, $(L/\bar{z}p)$, was used as the dependent variable. Because with both Dillon and Larsen's models loading is compared with the concentration of phosphorus within the lake, the vertical distance from a given point to a transition line is somewhat of an indicator of the degree of eutrophication. The Larsen-Mercier plot, as done by EPA (14), is seen in Figure 9.

The question must now arise as to the actual value of these predictive models. There is no doubt that through Vollenweider's efforts, the significance of loading upon the trophic state of the Great Lakes was recognized. Also, these models can predict, to a degree, the effects of loading upon lake systems, and this prediction can be used in planning and management, as well as restoration. However, continued refinement of these models and better understanding of the eutrophication process are needed.

Phosphorus Regulation By Bottom Sediments

Patten (19) notes that any model that attempts to adequately

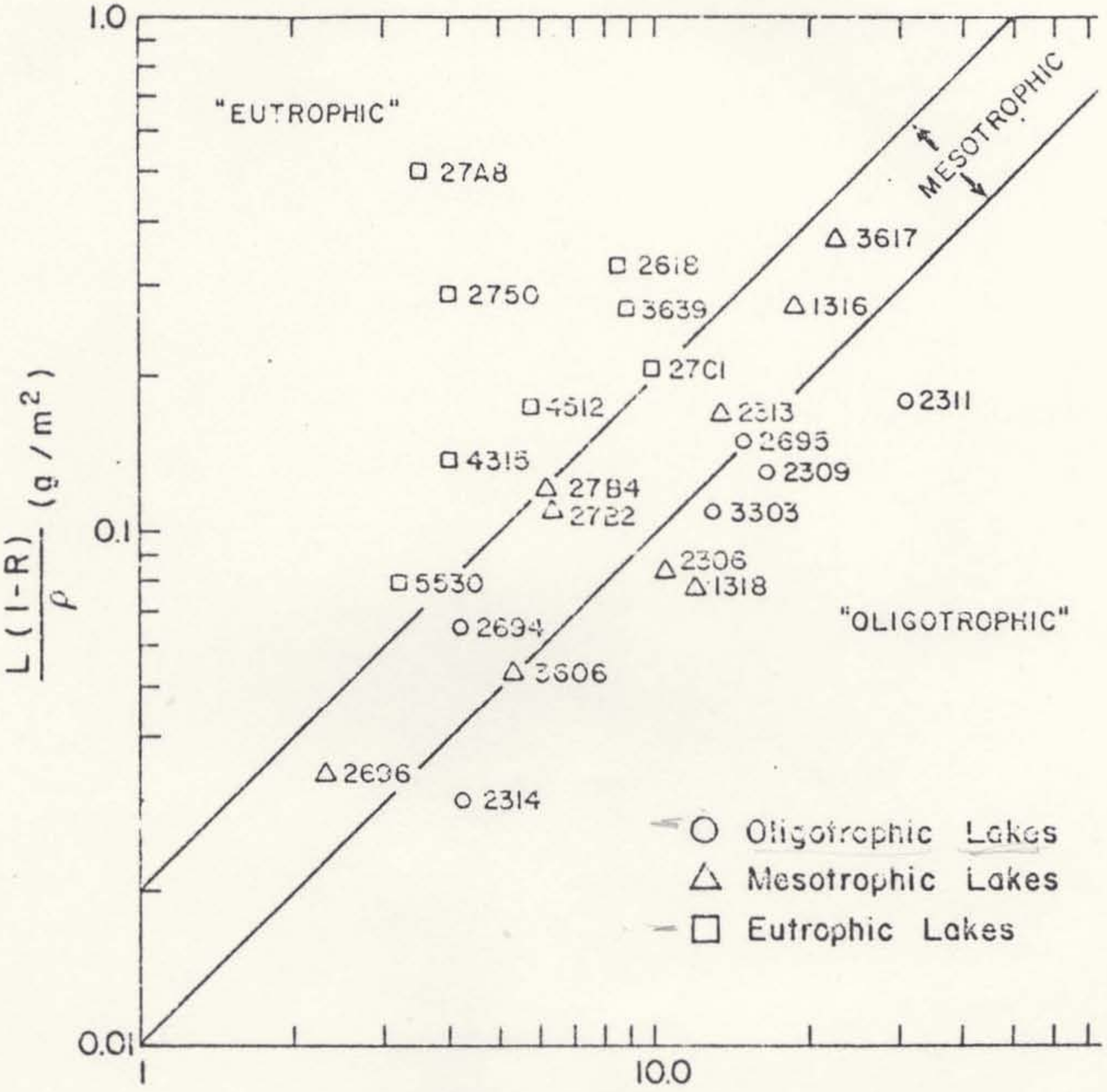
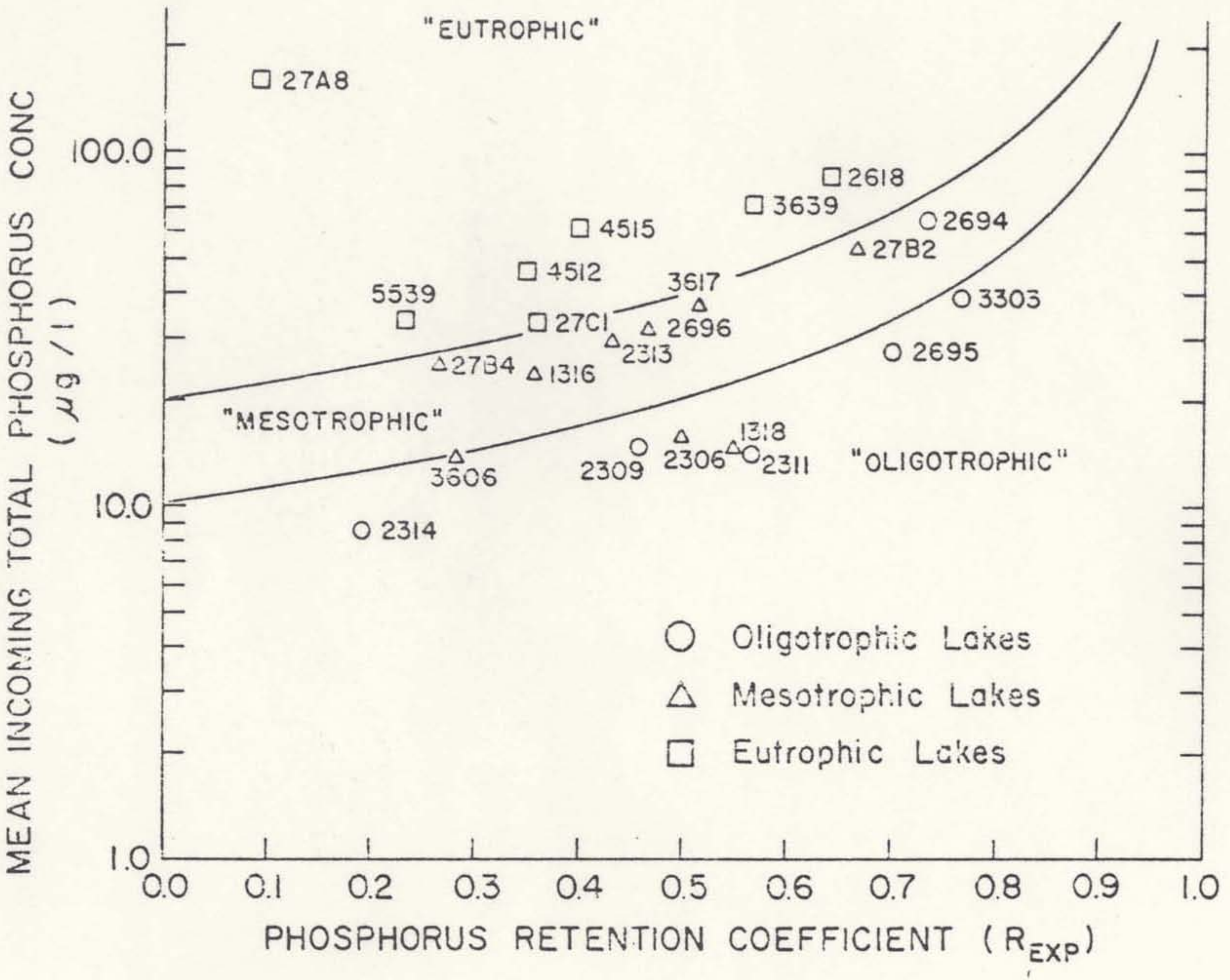


Fig. 8. The Dillon Relationship Applied to A Number of Eastern U. S. Lakes and Resevoirs Sampled by EPA.

SOURCE: U. S. Environmental Protection Agency, Eutrophication Workshop, Region IV, Atlanta, Georgia, December 3, 1975. (Corvallis, Oregon: National Eutrophication Survey) (mimeographed).

Fig. 9. The Larsen-Mercier Relationship Applied to a Number of Eastern U. S. Lakes and Resevoirs Samples by EPA.

SOURCE: U. S. Environmental Protection Agency, Eutrophication Workshop, Region IV, Atlanta, Georgia, December 3, 1975. (Corvallis, Oregon: National Eutrophication Survey) (mimeographed).


"EUTROPHIC"
27A8
100.0
2618
3639
2694
4515
27B2
4512
3617
5539
3303
27C1
2696
2313
2695
27B4
1316
"MESOTROPHIC"
1318
2309
2306
2311
"OLIGOTROPHIC"
3606
10.0
2314
Oligotrophic Lakes
Mesotrophic Lakes
Eutrophic Lakes
1.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
MEAN INCOMING TOTAL PHOSPHORUS CONC (μg/l)
PHOSPHORUS RETENTION COEFFICIENT (R_{EXP})

describe eutrophication must use the whole ecosystem as its basic conceptual unit; "Control points for attacking eutrophication exists everywhere in the ecosystem, not just in the producer and nutrient parameters".

Perhaps some of the best examples of the limitations of these models is their inability to cope with the sediment "control point" or regulatory point. Larsen and Mercier (20) in attempts to model Lake Shagawa in Minnesota, noted that the sediments supplied significant amounts of phosphorus to the lake, and that this could cause a delay in the restoration following diversion of a significant portion of the allochthonous phosphorus. This phenomenon was demonstrated by Welch, et al (21) when nutrients were diverted from Lake Sammamish in Washington. They found that, unlike Lake Washington which had been studied by Edmondson (22), a decrease in primary production did not follow. They determined that sediment nutrient supply was probably the cause. It was emphasized that Lake Sammamish is much shallower than Lake Washington, and that the hypolimnion goes anaerobic during the summer. It is hypothesized that phosphorus incoming is complexed with iron before uptake with algae can occur, and that production is limited by internal (autochthonous) loading.

Cooke, et al. (23) studied phosphorus dynamics in the Twin Lakes in Ohio. They noted that for small lakes, the rates of certain processes, such as sedimentation, are anything but constant when watershed morphology is changing, and that a "steady state" assumption is not acceptable. They view lake recovery as a successional process, i.e. it is seeking a new steady state.

Lorenzen (24) studied several models that attempted to cope with the internal loading phenomenon by modeling sediment dynamics. Some difficulty seems to have been encountered when terms such as sediment volume and concentration are presented. The input data which would be needed for these models also appears to be difficult to obtain, and may not be reliable unless considerable care, time and money are used to gather it. Also, these models give no consideration as to what phosphorus is permanently lost from the aquatic system. The evidence then seems to indicate that these models would be high in cost, while giving data that is suspect.

Perhaps, then, for evaluation of the sediments and their role in determining the trophic state and stability of lake systems additional research is needed before mathematical modeling is justifiable. Such research may seek development of some indicator parameter, or a series of such parameters. These might be biological, chemical-physical or a combination of both. Also methods for monitoring changes within the sediments with time might be helpful.

Loss of phosphorus from a lake system may occur by direct exportation, such as insect emergence, external grazing and predation or by sediment fixation. Phosphorus in the top layer of sediments may on the other hand be returned to the overlying water. This layer is constantly being redistributed by the benthic community. Below this layer at some depth microbial activity becomes insignificant and phosphorus becomes fixed. This was suggested by Nauman (25) who estimated the depth of this top layer to be about 10 cm. However, variations in the biologically active layer of sediments are certainly to be expected not only from lake to lake, but from different areas in the same lake, and probably within the same area with time.

When phosphorus influx within a lake is increased significantly over a short period of time, the system may experience a stress or shock. Depending upon the nature of the system, the phosphorus will either be taken up by the sediments or will be used for production by the phytoplankton and/or macrophytic plants. As the system reacts to the stress, there will be either an increase in entropy or sedimentation. If fixation by sediments predominates, perhaps little change will be noted within the system and no recognized increase in phosphorus influx will be noted. The ability of phosphorus to be taken up by the sediments has been demonstrated by Shannon, et al. (26) during an artificial fertilization experiment in Florida. The lake studied did not respond as expected with an immediate increase in primary production. Unfortunately, detailed sediment monitoring was not done, and there is some question whether the nutrients were captured in the sediments or taken up by submerged macrophytes.

Uptake of phosphorus by plankton and/or macrophytes has been demonstrated by Schindler (27) from artificial fertilization studies done in Canada. He observed a rather rapid rise in primary production with an increased phosphorus influx. The morphological and biological characteristic of the lakes used, however, differed greatly from Florida lakes.

Phosphorus Transfer

In an early study on sediments, Hutchinson and Bowen (28) showed that in Linsley Pond, Connecticut, a small eutrophic thermally stratified lake, that regeneration of phosphorus from the sediments occurred when the hypolimnion became oxygen depleted (anoxic). It was noted that there was a rapid uptake of phosphorus initially by phytoplankton, with sedimentation following. This cycle was seen to go from the littoral areas into the epilimnion, with a subsequent loss to the sediments, with some regeneration of phosphorus after stratification. The regenerated nutrients became available when turnover (mixing of hypolimnion into the eiplimnion waters) occurred. It was observed that sedimentation of phosphorus took place at such a rate that there was a net loss of phosphorus from the system, meaning that this process served as a phosphorus sink, and maintained the phosphorus limited condition. The nature of the sediments had also been investigated by Hutchinson and Wollack (29) who mentioned the importance of phosphorus precipitation with trivalent iron. Reduction occurring under anaerobic conditions permitted resolubilization of ferrous phosphate. They also recognized the possibility of phosphorus regeneration as a result of the activities of benthic organisms. It was felt, however, that allochthonous phosphorus was much more important as a regulating factor than sediment regenerated phosphorus in Linsley Pond.

Hayes, et al. (30), using P^{32} in a study of Phosphorus cycling in aquatic systems, explained the flux of phosphorus from the water to the biological solids (phytoplankton, macrophytes, epiphytic algae, etc.) by the differential equation:

$$dN/dt = -N(\lambda+\mu) + \mu N_o$$

where:

λ & μ = the percent phosphorus removed daily from the water and sediments, respectively

N = the concentration at time t in mg/L

μN_o = the concentration at time t_o in mg/L

From this equation and the use of P^{32}, it was found that there occurred a turnover time of 5.4 days for soluble phosphorus within the water. It was suggested that eutrophication could occur only when the phosphorus influx could not be equilibrated with the biological units within the system. The inference is that cessation of phosphorus influx would result in a return to an oligotrophic state, meaning that the rate of phosphorus regeneration from the sediments is a rather constant phenomenon, not being affected by the concentration in the bottom muds or the over-lying water.

Mortimer (31) studied mechanisms of ion exchange between mud-water interface, emphasizing the importance of oxidation-reduction potential and its effects upon the rate of nutrient release from the sediments. He revealed that eddy currents are responsible for accelerated diffusion within the hypolimnion, whereas molecular diffusion allowed movements within the pore water. It was noted that the reduction in the mud surface following oxygen depletion converted the trivalent iron to the reduced ferrous ion, which because of its higher solubility allowed a release of phosphorus associated with iron. Diffusion through the sediments follows this phenomenon as a concentration gradient is created, and the phosphate is eventually released into the hypolimnion waters. Adsorption was also noted to be an important factor in phosphorus regulation, with oxidized sediments having a greater adsorptive potential. A Ferri-Silico-Humic complex was suspected as the main adsorptive agent, although trivalent manganese was also noted as being an effective adsorptive agent. The rate of removal of ions from the mud seemed to be a function of the eddy diffusion coefficient and the concentration gradient between the mud and water. The role of wind speed in setting up the structure of the thermocline and the nature of the eddy currents also was noted. For phosphorus, aside from these factors, the thickness of the oxidized layer has to be considered also, as adsorption and precipitation may act as barriers against diffusion. This thickness is a function of the oxygen absorbing power of the muds and the oxygen concentration of the overlying waters.

These early studies on phosphorus in aquatic systems have inspired much work on the interplay between water and sediments and the role this interplay has in phosphorus dynamics. Some of the questions developed during these investigations are: 1) What is the role of the sediments in supplying phosphorus to the ecosystem?

2) What is the importance of adsorption-desorption in phosphorus dynamics? 3) Are there any correlations between sediment characteristics, such as adsorptive ability, iron concentration, density, grain size, carbon content, etc. and the trophic state of the lake? 4) Can the sediments supply enough phosphorus to the system to maintain an eutrophic state even after external loads are diverted, and if so, to what extent? 5) What segment of the sediment phosphorus may be considered as available for algal growth? 6) At what sediment depth is the phosphorus lost from the ecosystem? 7) How important is diffusion? 8) What is the role of mixing, and at what rate can mixed sediments release phosphorus when oxidized? 9) How much mixing is needed before it can be considered a significant factor in nutrient dynamics? 10) What is the relationship between bacterial action and phosphorus release in the sediments? 11) Is sedimentation of phosphorus controlled by chemical or biological activities?

Most of the work that has been done to date in attempts to answer these questions has been done in the Great Lakes, in certain Wisconsin lakes, and in Linsley Pond, Connecticut. Sediment studies are lacking in Florida, although Brezonik (32) recently has done considerable work on the sediments of Lakes Harney, Monroe and Jessup. Because of the peculiarity of the sub-tropical lakes found in Florida, certainly much more work is needed.

Sediment Characteristics

The actual characteristics of lake sediments were studied by Kemp, et al. (33) in Lakes Erie, Huron and Ontario. An attempt was made to determine the rate of sedimentation of organic material and nutrients as related to technological growth, i.e. cultural eutrophication. This is somewhat similar to the objectives of Hutchinson and Wollack (29) at Linsley Pond. Kemp, et al. (33) used the Ambrosia pollen horizon as a chronological benchmark, this coinciding with the clearing activities of early settlers. The dates were set at 1830 for Lakes Ontario and Erie, and 1870 for Lake Huron. Lake Huron represented a control area, being surrounded by a relatively unmolested watershed. As might be expected, it showed the slowest rate of sedimentation, about 148 gm/m^2-yr as opposed to 320 and 540 for Erie and Ontario, respectively. Figures 10, 11 and 12 show the variation with depth of various parameters within the sediments of these three lakes.

Phosphorus Distribution Through Sediments

A trend of decreasing phosphorus with depth is noted in all lakes. The Lake Huron sediments tend to stabilize at a shallower depth. Although the Lake Huron rate of phosphorus deposition appears to be increasing; the author notes that this may be due to the natural phenomenon of release in deeper areas with a lower oxidation-reduction potential, (Eh), with a subsequent migration to the higher Eh levels, where entrapment via precipitation, adsorption, and bacterial uptake occurs. The unevenness of the percent phosphorus for Lakes Erie and Ontario as seen in Figure 13 may be due to a variation in phosphorus loss from the sediments. It is stated that 25% of the settled

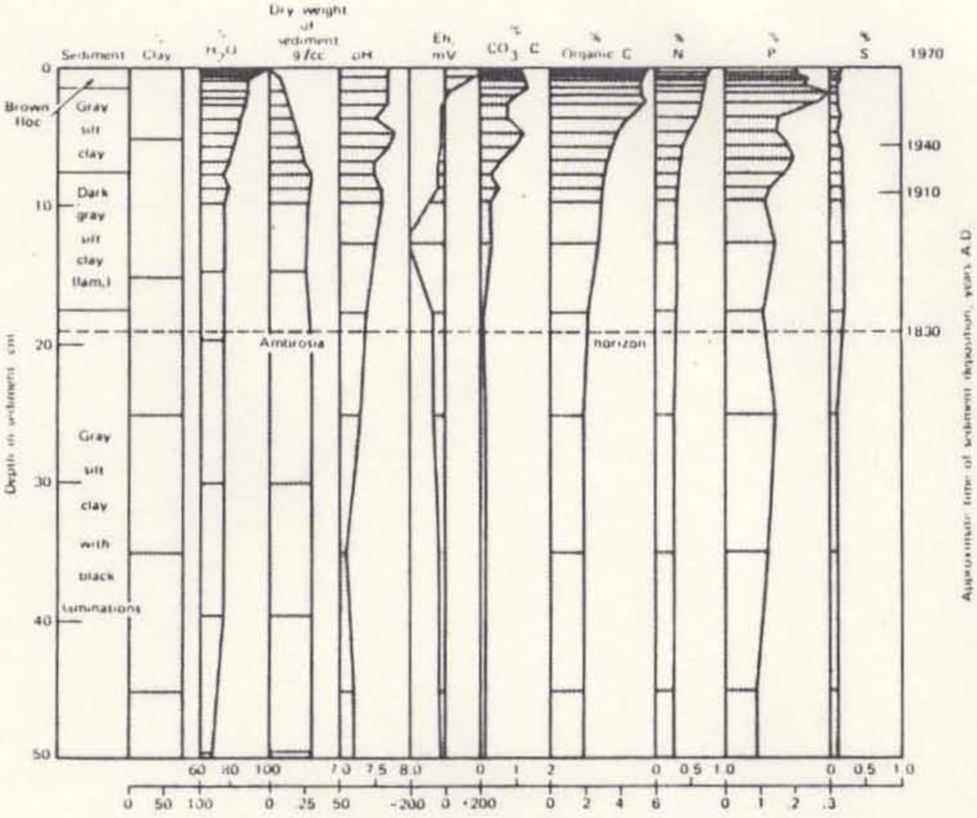


Fig. 10. Sample Locations and General Sediment Characteristics of Lake Ontario.

SOURCE: A. L. Kemp, C. B. J. Gray, and A. Mudrochova, "Changes in C, N, P and S in the Last 140 Years in Three Cores from Lakes Ontario, Erie and Huron," in Nutrients in Natural Waters, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons, 1972), p. 256.

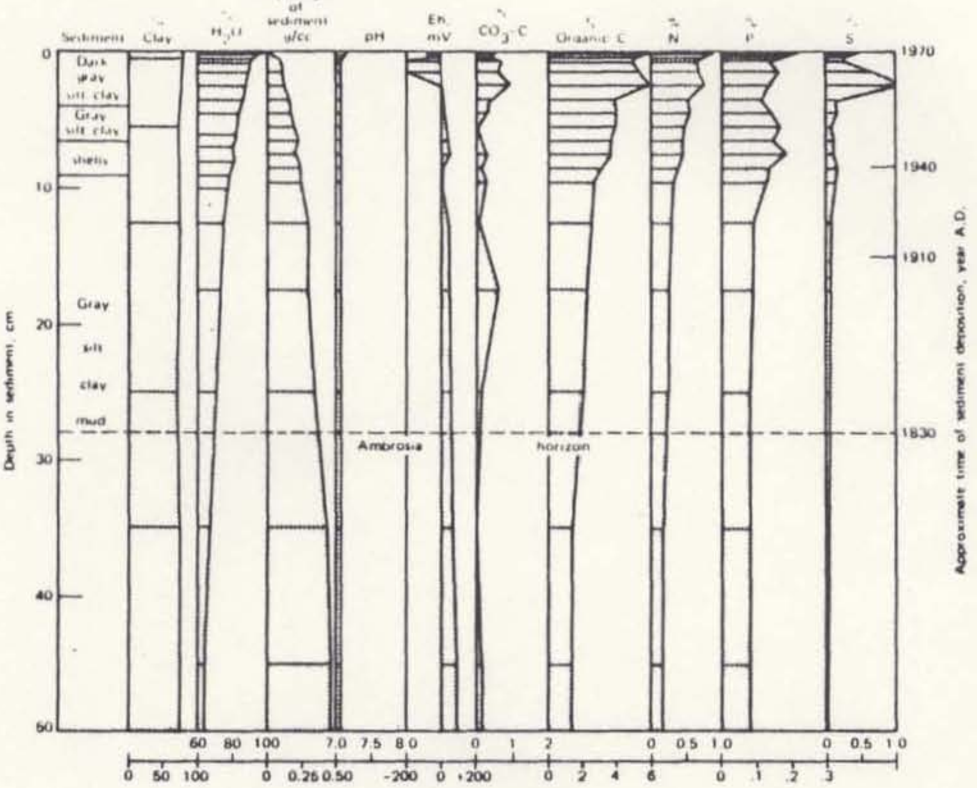


Fig. 11. Sample Locations and General Sediment Characteristics of Lake Erie

SOURCE: A. L. Kemp, C. B. J. Gray, and A. Mudrochova, "Changes in C, N, P and S in the Last 140 Years in Three Cores from Lakes Ontario, Erie and Huron," in Nutrients in Natural Waters, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons, 1972), p. 257.

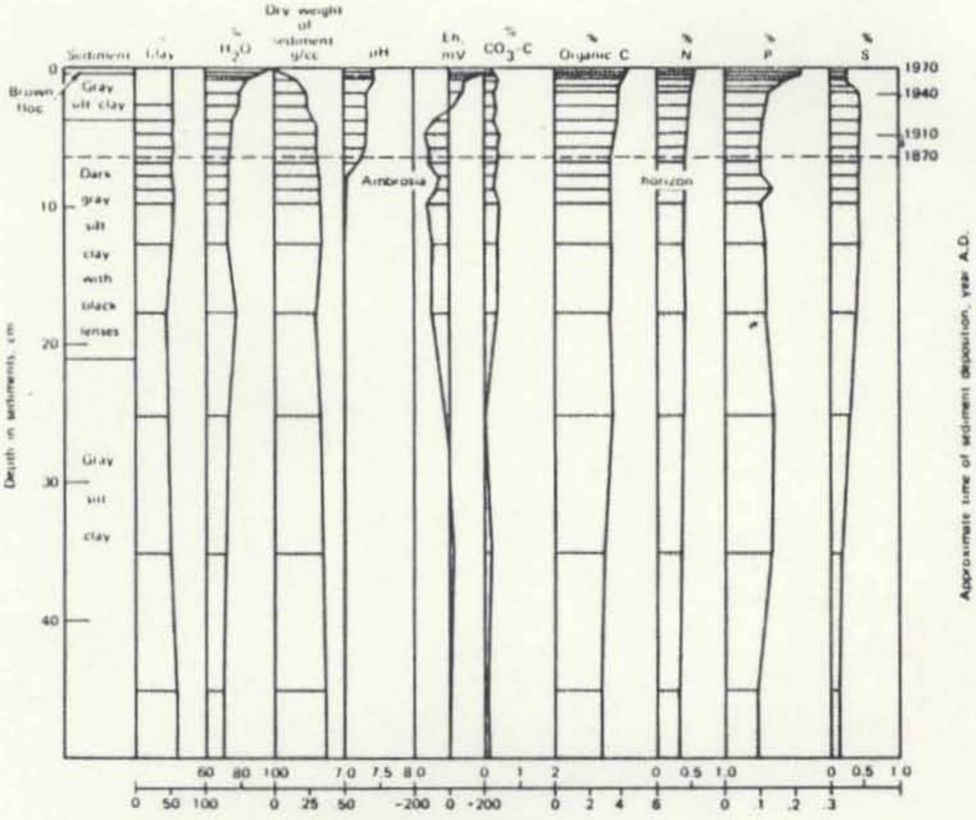


Fig. 12. Sample Locations and General Sediment Characteristics of Lake Huron.

SOURCE: A. L. Kemp, C. B. J. Gray, and A. Mudrochova, "Changes in C, N, P and S in the Last 140 Years in Three Cores from Lakes Ontario, Erie and Huron," in <u>Nutrients in Natural Waters</u>, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons, 1972), p. 258.

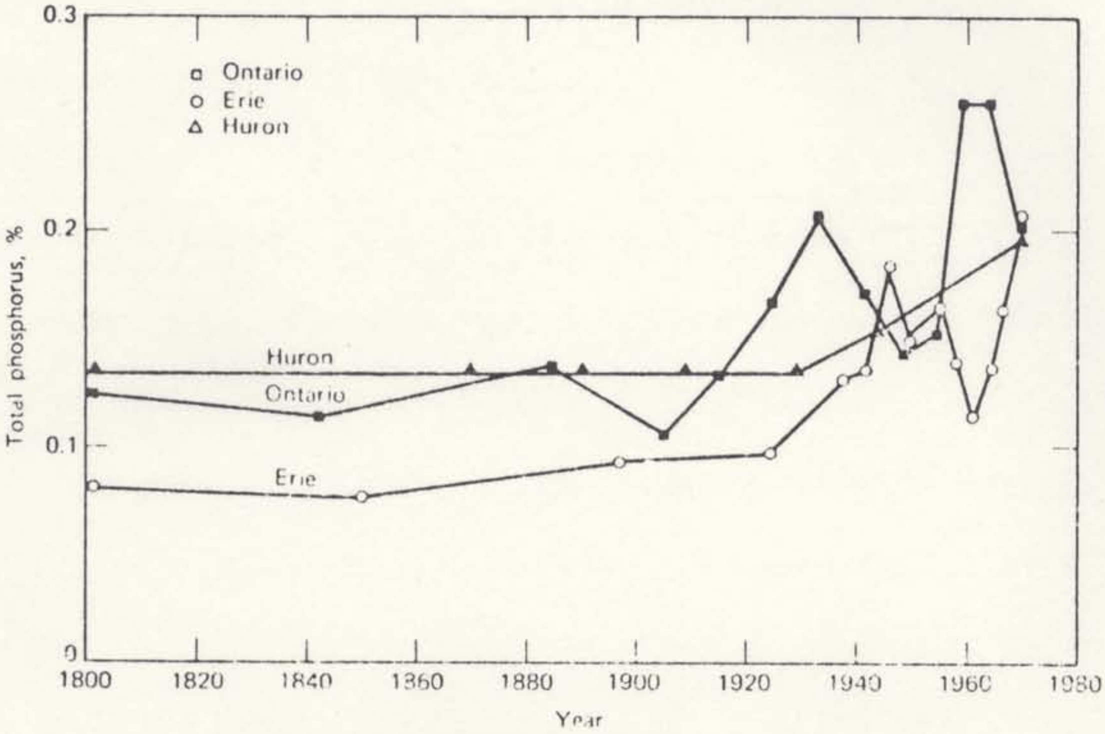


Fig. 13. Changes in Total Phosphorus Versus Approximate Time of Deposition (Lakes Ontario, Erie and Huron).

SOURCE: A. L. Kemp, C. B. J. Gray, and A. Mudrochova, "Changes in C, N, P and S in the Last 140 Years in Three Cores from Lakes Ontario, Erie and Huron," in Nutrients in Natural Waters, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons, 1972), p. 266.

phosphorus may be regenerated back into solution from the lakes. These see-saw type fluctuations as seen in Lake Erie and noted also in Lake Wauberg in this study, might well indicate periods of high productivity with a following increase in sedimentation, which increases the degree of anaerobiosis in the hypolimnion, this in turn allowing an increase in the amount of phosphorus released when stratification occurs. These vertical patterns of phosphorus concentration are interesting, and are the inspiration for this paper, for there indeed appears to be considerable difference in this pattern among different types of lakes. The work done here by Kemp, et. al. (33) appears to have confirmed the feeling that fluctuation within the sediments of phosphorus at various depths is more than a historical phenomenon.

Wentz and Lee (34) like many others, viewed phosphorus in the sediments as rather static. This may be valid if relatively great depths (30-100 cm) are considered, and large sections (5-20 cm) are investigated. They correlated changes in phosphorus at various depths with changes in land use activity around the watershed at that time, although they apparently ignored movements of phosphorus within the sediment itself. They attempted to determine the "available" phosphorus with depth rather than total phosphorus. "Available" phosphorus had previously been defined by Wentz and Lee (35) as that which can be extracted by a dilute HCl-H_2SO_4 solution. Unfortunately, it was noted that the "available" phosphorus not only consisted of adsorbed phosphorus, but also some fluoroapatite and calcium phytate, the availability of which is certainly questionable, although it can be degraded slowly by some microorganisms. Their results show a greater concentration of available phosphorus in the top sediments (0-35 cm) than in the lower sediments (35-100 cm) with evidence again of varying rates of sedimentation. The assumption here is that there is little diagenesis or diffusion within the sediments, and that regeneration is not significant. The validity of these assumptions is questionable in light of the work by Kemp, et al. (33), and of Williams and Mayer (36) who investigated diagenesis and regeneration of phosphorus within the sediments of Lake Erie, and the role of these two processes in determining water quality. The work previously mentioned that was done at Lakes Sammamish (21), Shagawa (20), and Twin Lakes (23) also seem to question the validity of their assumptions. Williams and Mayer (36) state that the net sedimentation may reduce the time needed for re-establishing a steady state (quasi-steady state), while net regeneration will prolong the time.

Sedimentation is believed to predominate in the Great Lakes and it is felt that 75-85% removal of inflowing phosphorus by sedimentation occurs. Two factors, however, were mentioned that may allow the phosphorus in the sediments to become available at a greater rate than predicted. First of all, the amount of sorbed phosphorus may be greater than before technological interference, as suggested by Wentz and Lee (34), and secondly, the desorption rate may depend upon the total adsorbed concentration within the sediments. Williams, Syers and Harris (37) found, however, that little correlation could be made between the trophic state and the adsorptive-desorptive capacities of the sediments of several Wisconsin lakes. It was noted, however, that non-calcareous deposits were much more effective adsorbers. Bortelson (38) demonstrated the effect of iron concentrations on the adsorption capacity of phosphorus, as seen in Figure 14, and noted that the concentration of phosphorus within the sediments does not appear to be correlated with trophic state. However, Livingstone (39) indicated, by his studies on Linsley Pond, that the trophic state could possibly be regulated by the adsorptive potential of the sediments. He found that periods of oligotrophic conditions in the pond's history revealed more adsorptive sediments. Fitzgerald (40), in studying the availability of adsorbed phosphorus to certain algae species, found that adsorption could render the phosphorus unavailable to many algal species, but it could be extracted by most macrophytes.

3

Williams and Mayers (36), also discussed the manner in which phosphorus is regenerated and precipitated under conditions of constant sedimentation. This idealized situation is seen in Figure 15. The area $E_1' D_1' C_1' C_1 D_1$ is that phosphorus which has migrated upward through the interstitial water, while $F_1 E_1 E_1' F_1'$ is the amount obtained from sedimentation. This idealized pattern is not unlike that seen in Lake Huron, (Figure 12) although it varies considerably from Lakes Erie (Figure 10), Ontario (Figure 11), Apopka (Figure 24) and Griffin (Figure 25). The authors state that

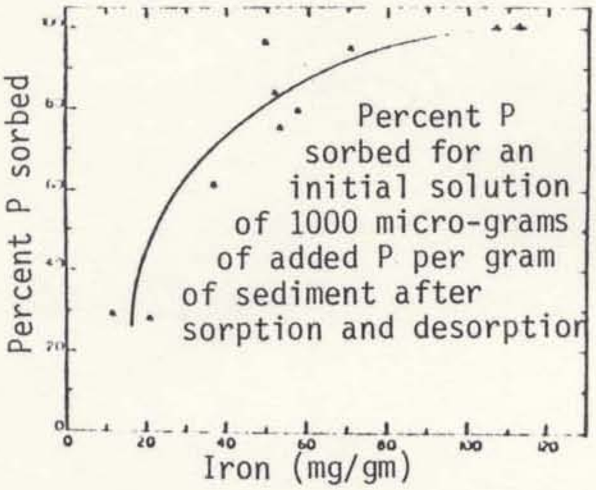


Fig. 14. Effects of Iron on Phosphorus Sorption in Lake Sediments

SOURCE: G. C. Bortelson and G. F. Lee, "Phosphorus, Iron and Manganese Distribution in Sediment Cores of Six Wisconsin Lakes," Limnology and Oceanography 19 (1974): 798.

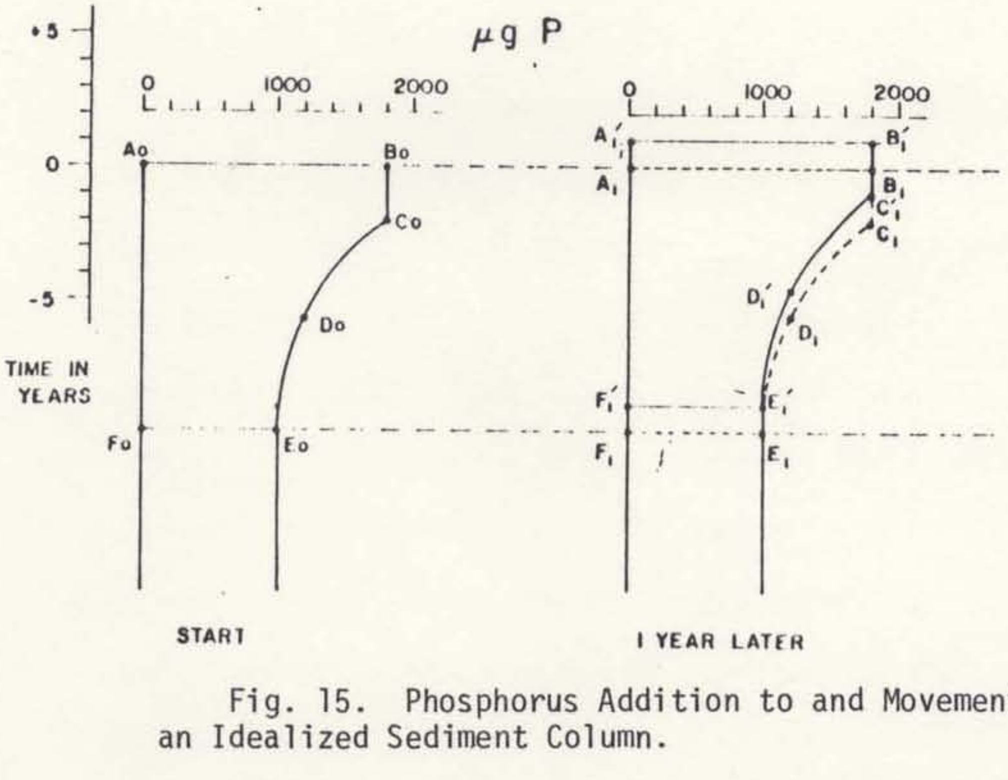


Fig. 15. Phosphorus Addition to and Movement within an Idealized Sediment Column.

SOURCE: J. D. H. Williams and T. Mayer, "Effects of Sediment Diagenesis and Regeneration of Phosphorus with Special Reference to Lakes Erie and Ontario," in Nutrients in Natural Waters, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons), p. 285.

mixing of the sediments by thermal and wind induced currents, or biological activity may disturb this steady state condition and increase the rate of regeneration. Schultz (41) notes that in Lake Shagawa, mixing of even oxidized sediments may contribute significant phosphorus to the water column. Shannon, et al. (26) notes that in shallow sub-tropical Florida lakes, such as those seen in Florida, mixing, may be a prime factor in nutrient regulation. Yousef (42) in a preliminary study on the impact of motor boating upon water quality, implies that mixing by boats may serve to induce eutrophic conditions by redistribution of sediment held nutrients. Shannon et al. (26), went on to demonstrate in the laboratory a very significant increase in soluble phosphorus in lake water following a period of agitation of the sediments. Brezonik (32) recently has shown that there exists an equilibrium phosphorus concentration at which the sediments neither desorb nor adsorb phosphorus. This is demonstrated in Figure 16 and must be considered an important indicator of the lakes homeostatic abilities.

The role of diffusion as a factor in nutrient regeneration has led to several studies on pore water (interstitial water). Weiler (45) revealed that this water is very high in soluble phosphorus as compared to the overlying water. It is stated that this gradient enables the sediment to be a source of phosphorus, in correlation with Fick's Law:

$$(dC/dx)D = F$$

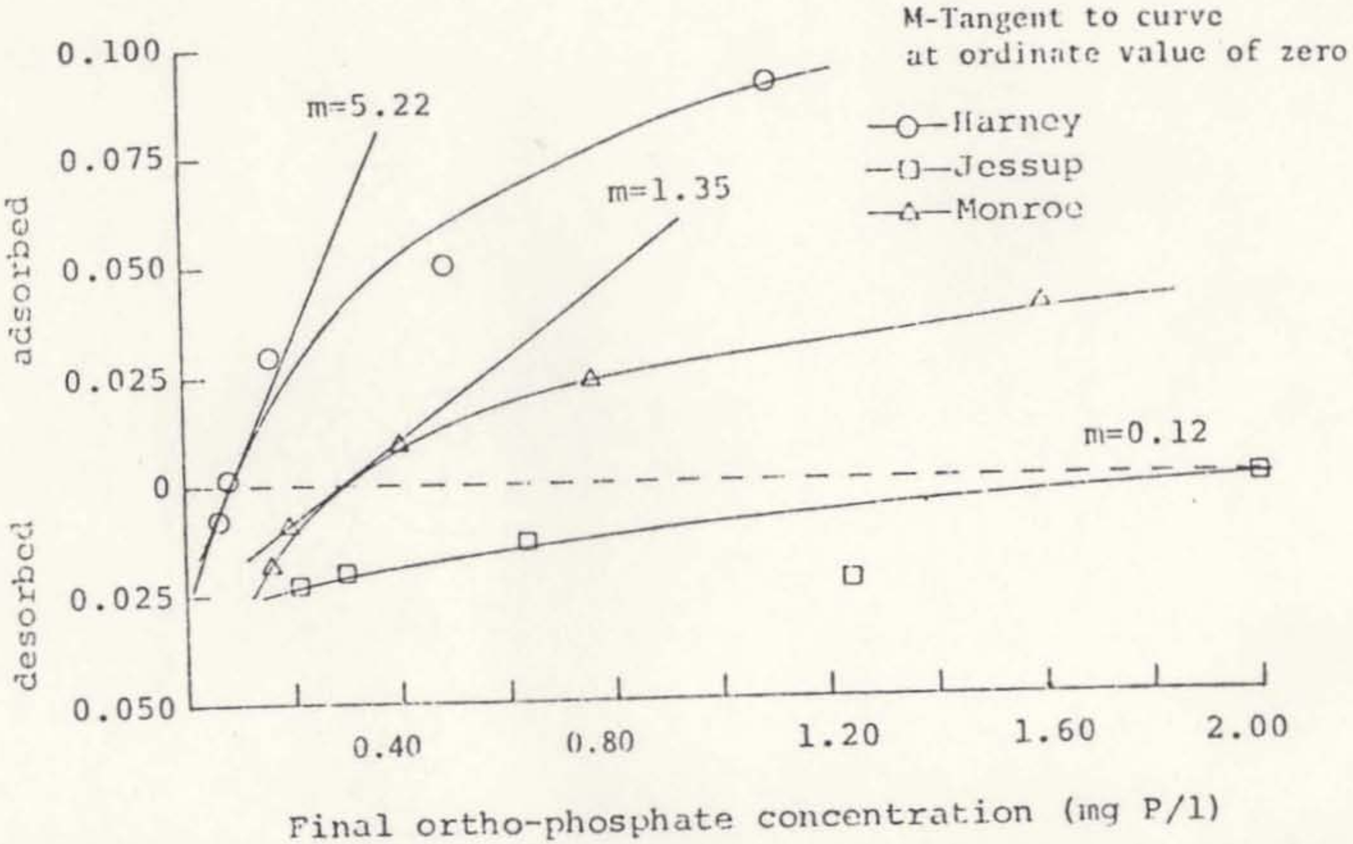


Fig. 16. Phosphate Taken up or released by Sediments After Equilibrium with Solution of Varying Initial Phosphate Concentrations versus Final Phosphate Concentrations. Intersection of Isothorms with Dashed Line is the Equilibrium Phosphate Concentration (EPC)

SOURCE: P. L. Brezonik, "Nutrient Exchange Studies on SEdiments of the Middle St. John's Lakes," (awaiting publication by the Florida Department of Environmental Regulation).

where:

D = the diffusion coefficient in cm^2/sec

dC/dx = the diffusion gradient in mg/cm^4

F = the flux in mg/cm^2-sec.

As stated earlier, barriers against phosphorus release may exist to work against the concentration gradient. Surruya and Edelstein (43) attempted to demonstrate fluctuations in nutrient concentrations in pore water in stratified lakes. Variables considered were horizontal currents created thermally or by wind action, temperature, and benthic flora. Again, a large gradient was noted between the concentration of the pore water and the lake water. Inflowing water was noted to be high in calcium, thereby encouraging the precipitation of hydroxyapatite, which in this particular lake (Lake Kinneret) appeared to regulate the rate of phosphorus regeneration. Fluctuations, then, in the solubility product of hydroxyapatite allowed fluctuations of available phosphorus in the lake water. A cycle was noted with changes in the solubility product allowing release of phosphorus into the water column. Productivity then increased with eventual increase in the alkalinity, indicating an increase in OH^- concentration which stimulated precipitation of hydroxyapatite. Williams and Mayer (36) also demonstrated this type of phenomenon in Lake Erie. They showed a decline in sorbed and organic phosphorus with increasing sediment depth, as seen in Figure 17. It is calculated that the rate of apatite fixation is considerably greater than the rate of regeneration, and that at least for Lake Erie, it

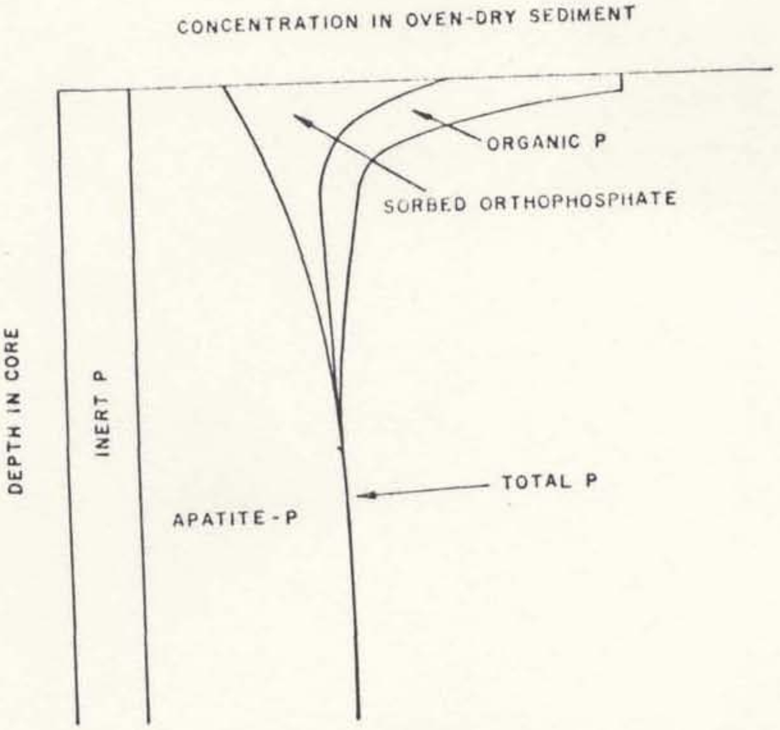


Fig. 17. Variations with Depth of Forms of P in an Idealized Great Lakes Core, Assuming Uniform Conditions Throughout the Period of Accumulation.

SOURCE: J. D. H. Williams and T. Mayer, "Effects of Sediment Diagenesis and Regeneration of Phosphorus with Special Reference to Lakes Erie and Ontario," in _Nutrients in Natural Waters_, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons), p. 308.

appears that a reduction of allochthonous phosphorus would allow the lake to eventually return to an oligotrophic state. Figure 18 shows how phosphorus is seen to be transformed within the Great Lakes sediments.

Florida Lakes

Shannon, et al. (26) in a study of eutrophication in North Central Florida lakes realized the need for discriminating between sub-tropical and temperate lakes. Table 1 shows some of the more obvious differences.

TABLE 1

DIFFERENCES IN NORTH TEMPERATE AND SEMITROPICAL LAKES WHICH MAY BEAR ON EUTROPHICATION PROCESS

Northern Lakes	Semitropical Florida Lakes
1. Defined shoreline usually with beach	1. Shore-water interface ill-defined
2. Thermally stratified, usually dimictic	2. Little or no thermal stratification
3. Usually calcareous	3. Soft, acid water
4. Ice covered	4. Always ice free
5. Runoff from meltwater	5. No spring runoff
6. Winter solar radiation and temperature limit primary production	6. Low temperature and solar energy not evident; longer periods for optimum plant growth. Sustained yields of standing crop throughout year.

Only one study of the phosphorus content of the sediments was made, and this involved preliminary studies on Anderson-Cue Lake which was the subject of an artificial fertilization experiment.

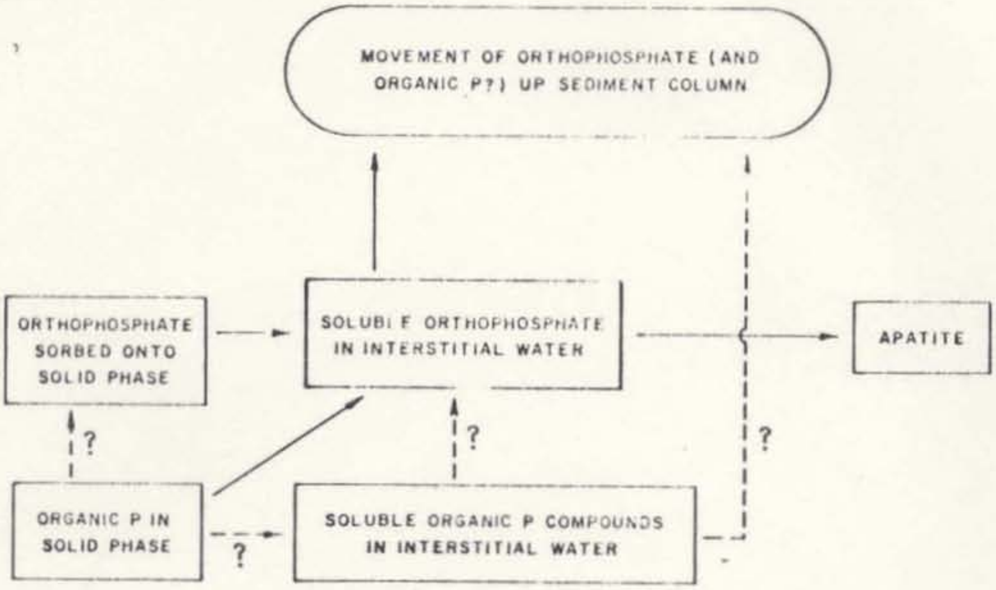


Fig. 18. Transformation of P within Great Lakes Sediments.

SOURCE: J. D. H. Williams and T. Mayer, "Effects of Sediment Diagenesis and Regeneration of Phosphorus with Special Reference to Lakes Erie and Ontario," in Nutrients in Natural Waters, ed. J. R. Kramer and H. E. Allen (New York: John Wiley and Sons), p. 307.

Unfortunately, no reference was made as to the depth at which the sediments were taken. It may be that the rate of sedimentation, if it had been monitored during this experiment, would have allowed analysis of the results easier.

A study done on the hypereutrophic Lake Apopka and its sediments by Schneider and Little (44), revealed an unconsolidated mud covering 90% of the bottom, with an average depth of 5 feet and a maximum depth of this mud layer of 40 feet. This lake has been the victim of cultural eutrophication, and its plight is well documented. The need for understanding sediment regeneration of nutrients is obvious in this case, for the sediments are high in nutrients, the lake is shallow, so mixing by the wind is probably complete, and the oxygen demand of the sediments is high so that anaerobiosis often predominated. It may be safe to say that regeneration of nutrients from the bottom would probably maintain the eutrophic state of this lake long after external loading had been diverted. For this reason, any restoration program should include some way of removing or permanently immobilizing the sediment held nutrients. The Lake Apopka sediments were shown to be comprised of 32-77% volatile solids, with a corresponding high COD average of 1100 mg/kg of sediments. Phosphorus content ranged from 200-2000 ppm, which is consistent with sediments in other Florida lakes. Also consistent is the fact that phosphorus decreased with sediment depth, although again only historical intervals were investigated.

Another study done on Florida Lakes by Brezonik and Shannon

(45) attempted to correlate trophic state to nitrogen and phosphorus loading. Most lakes showed a good correlation between trophic state index (TSI) which is a function of total phosphorus, total nitrogen, primary production, Pearsall's Cation ratio, Secchi disk, specific conductivity, chlorophyll, and the surface loading rates. The equation, as developed, is: $TSI = .919(1/secchi) + .800(SpCond) + .896(TON) + .728(TP) + .942(PP) + .862(Chlo) + .635(Cation\ ratio)$. The model failed, however, when macrophytes predominated, as their production rate was not monitored. It also showed a poor correlation in Lake Wauberg, which is highly eutrophic, even though loading from the watershed appeared to be low. The significance of mixing from recreational activities would be interesting to study in Lake Wauberg, as the lake has received intense recreational activity in the past. It appears that sediments may play a significant part in loading the lake with phosphorus.

Another study by Brezonik and Shannon (46) on the limnological characteristics of 55 North Central Florida lakes found only eight under the influence of stable stratification with the characteristic low bottom oxygen levels. None of the lakes were meromictic, that is, they all mix vertically at some time. The tendency to stratify is seen to decrease as the surface area increases. In general, complete mixing occurs in most lakes at a much greater frequency than in temperate lakes. Sediment analysis was not considered.

Research Needs

The need for understanding nutrient interchange between sediments and water was realized at the Uppsala Symposium (47) in 1968. In their list of areas needing research was included the need to find a way to render sediment held nutrients unavailable to plankton, need for better monitoring of nutrient flows, investigation of the depth of sediment that influences overlying water, and the effects of such factors as mixing upon algal growth. Experiments dealing with the rate and nature of sedimentation would be valuable. Unfortunately, problems have been encountered in attempts to determine the rate of sedimentation. This problem was realized by Golterman (48) who pointed out that devices used usually decrease the turbulence of the water in the region, thereby increasing the rate of sedimentation. Also, organisms caught in the traps, such as benthic invertebrates seeking cover, could often destroy the validity of the data. Whit and Wetzel (49) have recently proposed a trap that allows correction for non-sedimenting material, such as periphytic organisms. It appears to be useful, although it does not detect some of the material that falls at less than a 90^o angle. It also fails to measure horizontally moved or redistributed sediments. Also, it interrupts turbulence. Fuhs (50) also developed a sediment trap with a control section, although several areas were noted to cause error, the most significant being the inability to discriminate between redistributed and new sediments. He notes that without measurement of sedimentation rate, the extent of nutrient cycling, including the effects of increases and decreases in phosphorus loading on plankton production, cannot be measured with any degree of reliability. Fuhs' method was applied to Lake Canadarago in New York. An average sedimentation rate of 453 grams of material/ha-day was observed during summer stratification. It was stated by the author that the work may have been made more meaningful if rates had been measured in the more productive littoral areas.

In a summarization, then, it appears that in Florida lakes, studies on sediment-water interchanges could be very informative in understanding the mechanisms of accelerated eutrophication. Much needed is a means of monitoring the rate of phosphorus deposition throughout the lake as a whole, with attention being given to all limnological zones. Effects of mixing in Florida lakes need to be evaluated in such a study, also, which would almost demand a constant monitoring of phosphorus and other parameters as they flow through the system. Again, the success of such a project would depend upon the accuracy at which rates of deposition could be measured.

CHAPTER III

FIELD INVESTIGATIONS AND LABORATORY PROCEDURES

Vertical distribution of phosphorus through bottom sediment cores collected from Florida lakes of various trophic states were studied. The cores were sectioned to measure phosphorus concentration and volatile solids content in each layer. Selected lakes for this study had previously received attention from Shannon and Brezonik (4) in their study of trophic state determination. This made it possible to investigate the correlation between the trophic state index developed by Shannon and Brezonik (48) with phosphorus profiles through the sediment cores.

Description of Study Areas

The study area included lakes with different trophic levels and located in Central Florida. These lakes are:

1. Lake Claire

Lake Claire is considered to be an oligotrophic-colored lake. It is relatively small, about 28 acres, with a very small littoral area. The mean depth is about 8 feet. Because of the proximity of the lake to FTU, it was used for much of the preliminary work. Also, considerable background information has been collected on this area .

2. Lake Apopka

The study of the degradation of Lake Apopka is well documented. Nonetheless, the actual cause has not been completely determined. This lake is a hardwater lake, originating from artesian flow. It is the head lake of a chain of lakes which feed the Oklawaha River. The water quality of all the lakes within this chain has been jeopardized by Lake Apopka, and technological development within their watersheds. Lake Apopka lends itself as a representation of a highly culturally eutrophic system in which the rate of organic accumulation is extremely high.

3. Lake Griffin

This lake also belongs to the Oklawaha chain, being the last lake before the river is developed. It is considered to be eutrophic, and recent water quality degradation has been noted.

4. Lake Weir

This lake also lies within the Oklawaha basin, but is not connected to the chain directly. Its watershed contains large numbers of citrus groves. It is classified mesotrophic by Shannon and Brezonik (44).

5. Lake Swan

This lake, classified as ultraoligotrophic by Shannon and Brezonik (45) lies within a relatively natural watershed. A few homes surround the lake.

6. Lake Geneva

This lake is similar to Lake Swan, although it is larger and receives more boat traffic. It is also classified ultra-oligotrophic.

7. Lake Altho

Unlike Swan and Geneva, Lake Altho is highly colored, being surrounded by cypress hammocks. It is classified as oligotrophic.

8. Lake Wauberg

This lake was selected because it is somewhat of an enigma. Although it appears not to receive large amounts of nutrients from its watershed, it is highly eutrophic. The sediments of this lake are now receiving considerable attention from the University of Florida's Environmental Engineering Sciences Department.

9. Lake Eola

Recently, Lake Eola, which has suffered from excessive urban runoff, was subjected to a restoration effort. As loading was not diverted after restoration by drawdown, it appeared that the eutrophic condition might be manifested again. It was decided that viewing the sediments might reveal how the lake is responding to the nutrient load.

Sampling Procedure

Considerable difficulty was encountered in attempts to procure undisturbed sediment cores which could be sectioned at vertical intervals of 1 cm or less. After much experimentation, a plunge type device, Figure 19, was developed. The device consists of a 2" diameter plexiglass column, with a rubber plunger which moves easily within the column. The plunger stabilizes the sample, preventing disturbance by any water that otherwise would be above the sample. It appears that the sampler works adequately in firm sediment, however, very loose sediments were displaced instead of offering adequate resistance to move the plunger upward. For this reason, it was decided that only those sediments which could move the plunger would be seriously considered. The upper loose sediments were assumed to represent a fairly homogeneous mass because of the high water content which allows rapid diffusion. To verify this assumption, two samples were taken from Lake Apopka and one from Lake Griffin of this loose sediment, and then analyzed for phosphorus with depth. Of these samples a standard deviation of 160 mg/kg and 271 mg/Kg were found respectively, which indicates even after adjustment for lab variability that this assumption is not totally correct. This collection error is addressed further throughout this paper. Only in Lakes Griffin, Apopka, and Wauberg were the sediments so loose that a large amount of floc had to be displaced before a sample was obtained. Lee (52) notes that complete mixing in the top sediments should not be assumed. Brezonik (32) noted that the homogeneity of the top loose sediments is not due to mixing but rather to more rapid diffusion because of the poor consolidation.

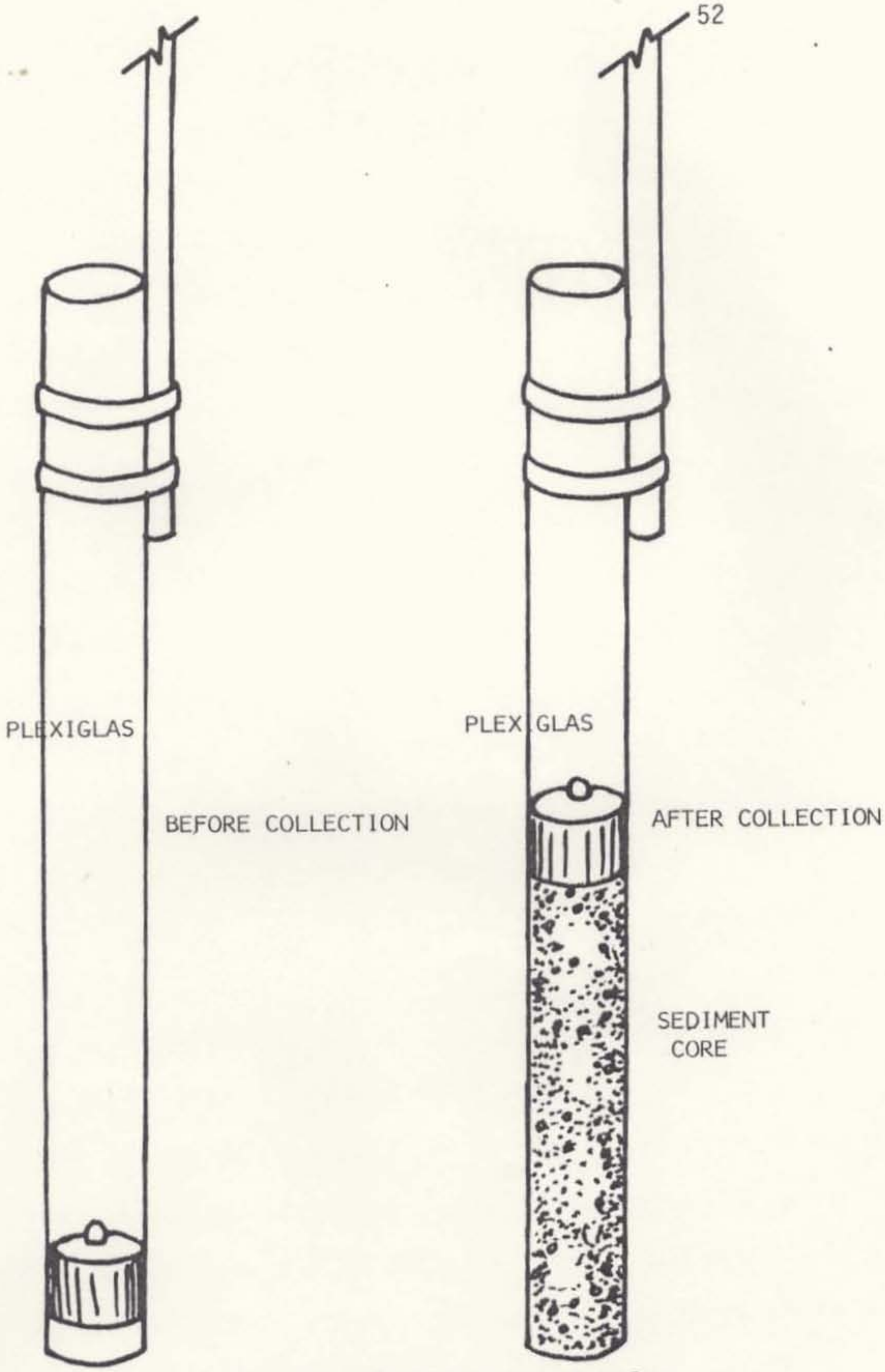


Fig. 19. Sediment Core Sampler Developed For Collecting Vertical Sections

It appears, then, that even though mixing may not predominate, these loose sediments are probably active enough that those more consolidated unerlying sediments may better represent the true sediment, with the loose sediments acting as a transitional area which perhaps needs to be investigated as a separate entity all together.

Samples collected without difficulty were extruded carefully so that sections could be cut at intervals beginning with 15cm, then 10cm, 6cm, 5cm, 4cm, 3cm, 2cm, 1cm, 0.5cm and 0.1cm. Total phosphorus and volatile solids were determined on each sample. In addition, water samples were collected just above the sediment. They were analyzed for total phosphorus. Percent water was determined on some of the samples, although often too much time elapsed between collection and weighing in the laboratory for this measurement to be reliable.

Field samples were placed in preweighed crucibles, which were held in a carrying box, as seen in Figure 20, and brought to the laboratory for analysis. It was attempted to keep samples between 0.05 and 0.300 gram weight in the field to facilitiate digestion of sediments for phosphorus determination as specified in the EPA Laboratory Manual (52) and by Schneider and Little (44).

After weighing, the samples were dried at 105°C for 24 hours. These were then cooled and weighed again to obtain the dry weight. The samples were then burned at 550°C for 1 hour, cooled and weighed. The weight of volatile and non-volatile solids were determined from this data in accordance with Standard Methods (53).

Determination of total phosphorus was done by modifying the

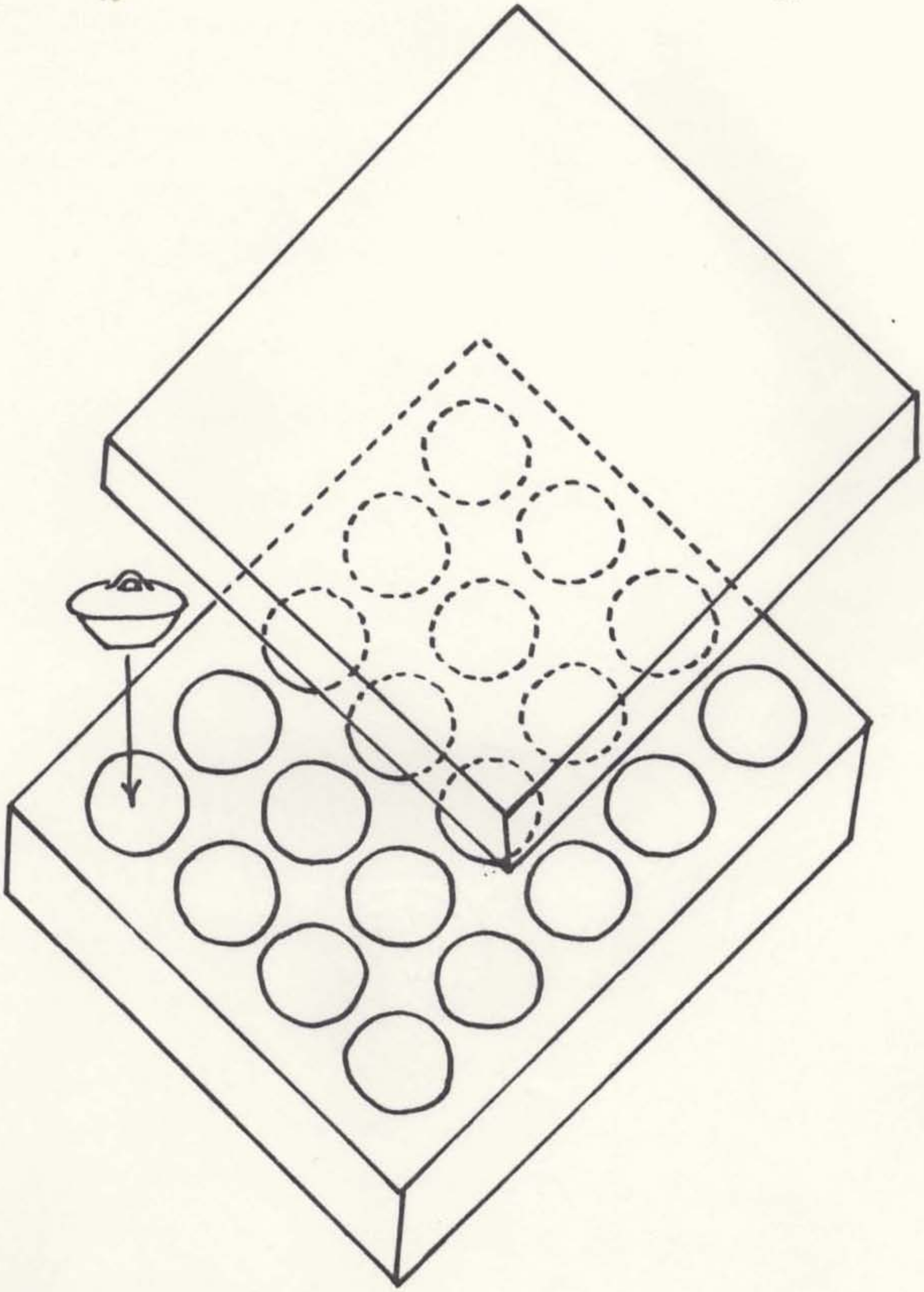


Fig. 20. Field Crucible Carrier

digestion process described by Schneider and Little (44) utilizing colorimetric determination by the ascorbic acid-combined reagent method, as described by EPA (52). A step by step process of the procedure follows:

1. To the crucible add 3 ml H_2SO_4 and 5 ml HNO_3
2. Heat in a hood at 100° C for one hour
3. Add 5 ml more HNO_3 and heat for 15 more minutes
4. Remove and cool
5. Filter through a vacuum filter using a glass fiber filter. Care must be taken to prevent contamination with extraneous phosphorus.
6. Transfer quantitatively to a 100 ml volumetric flask
7. Add 2 drops of phenolpthalein
8. Add slowly saturated NaOH until the solution turns pink
9. Add 5 N H_2SO_4 dropwise until the pink color disappears
10. Bring the volume up to 100 ml
11. This solution may now be used for determination of phosphorus by the ascorbic acid method, as described by EPA.
12. The total phosphorus in ppm of dry weight can be determined by the formula:

    $$TP = \frac{\text{concentration in mg/L x dilution factor x 0.1 liters}}{\text{sample dry wt. in kg.}}$$

13. Read at 710 nm on Beckman Spectrophotometer

The precision of this procedure was measured by running three sets of five portions from three different grab samples. The results are presented in Table 2.

TABLE 2

PRECISION OF PHOSPHORUS DETERMINATION FOR FOR SEDIMENTS SAMPLES USING THE ASCORBIC ACID METHOD

Sample #	Mean (ppm)	SD (ppm)
1	281	24
2	200	18
3	1032	93

Although the precision is not great with this procedure, it is sufficient when the variation is considered. Figure 21 shows the calibration curve.

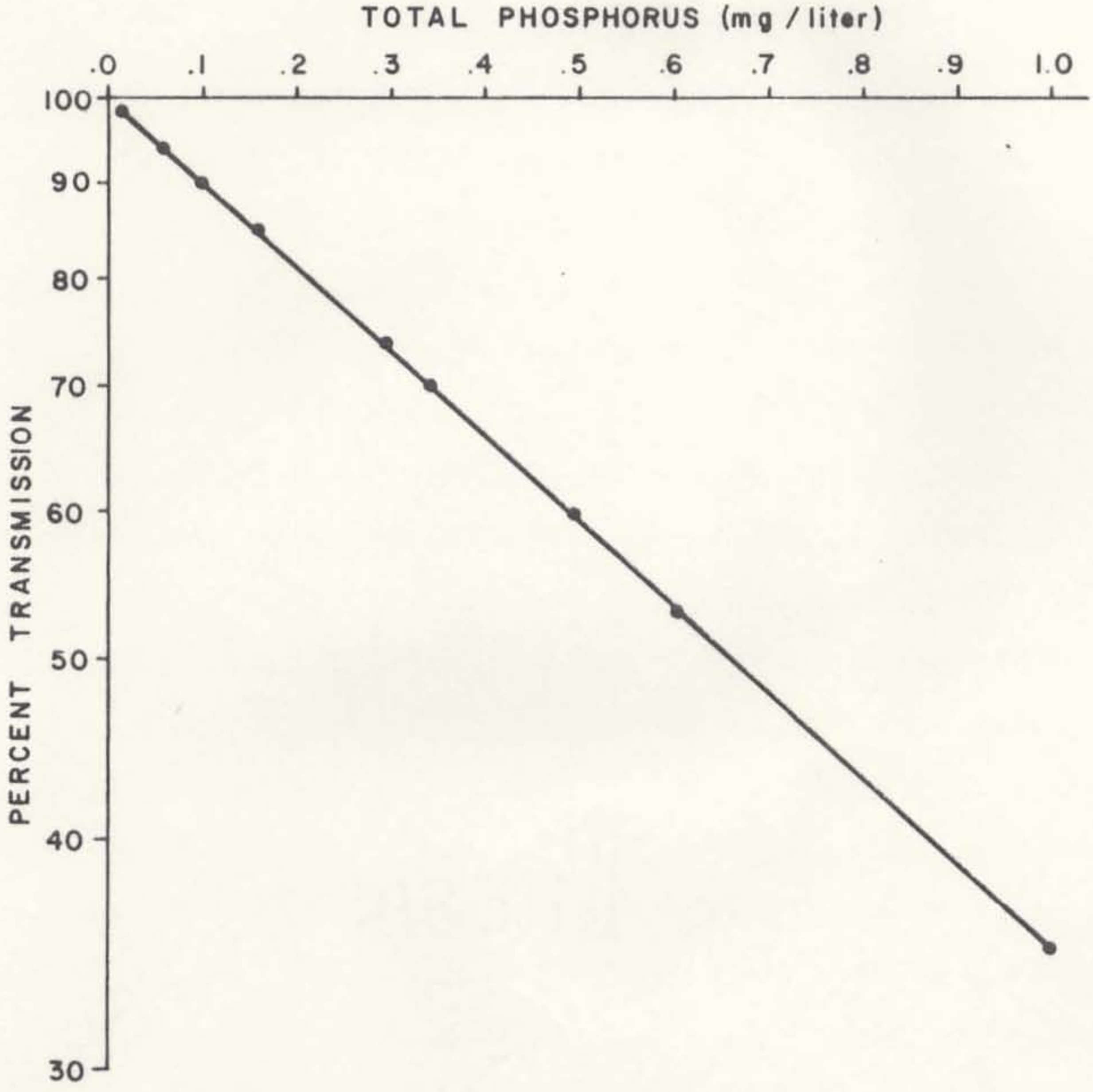


Fig. 21. Total Phosphorus Standard Curve

CHAPTER IV

RESULTS AND ANALYSIS

Sample Description and Field Data

1. APOPKA #1: This sample was collected on the southeast side of the lake on January 26, 1976. The water temperature at the time was 17^{0}C. The water depth was 4.5 feet (1.37 meters). The lake water was noted to be very turbid, as the wind was mixing the water with considerable force. The sediment sample was collected in an area about 200 feet from the shore. This region of the lake historically was overgrown with emergent type plants such as Pontederria sp. These plants, however, had been destroyed by hurricanes and by the degraded water quality. These plants are now represented as a compact peat layer on the lake bottom. This sample taken in this area was 15 cm in depth, and consisted of a homogeneous layer of peat.

2. APOPKA #2: This sample and the following sample represent the type sediment that is most commonly found in Lake Apopka. The water temperature at the time of collection (March 8, 1976) was 20^{0}C. The water depth was approximately 5.5 feet (1.68 meters). The water was very turbid as it appeared there was an excess of phytoplankton growth. The area in which the samples were taken was located in the southern region of the lake, about 1/2 mile from the Winter Garden shoreline. Some difficulty was encountered in obtaining a sediment sample, as the top layer was very loose and flocculant. This loose

material resembled sludge that might be found in an aerobic digestor. In fact, the similarity is probably more than coincidental, as this sediment consists mostly of heterotrophic bacteria which are working on deposited algae cells. The fact that this material appears to be relatively unconsolidated seems to indicate mixing occurs periodically with the overlying water. With considerable difficulty, some of this material was obtained and sampled at various depths. This group of samples were labeled Apopka #4 (floc). This loose sediments extended to about 3.0 feet (0.91 meters) deep. Apopka #2 represents a sediment sample which underlies this floc, and is characterized by a black, organic layer of two cm. thickness, consisting of a silty material, below which a dark layer intermingled with shells was noted. This probably represents the original bottom before accelered autrophication began. The shells became more prevalent with increasing sediment depth.

3. APOPKA #3: This sample was taken in an area similar to Apopka #2. The black organic layer, however, was somewhat thicker, being about 5 cm. The shells became evident at about 6 cm. Flocculent material overlay this sample also. It was sampled and labeled Apopka #5 (floc).

4. CLAIRE #1: This sample was collected on December 15, 1975 in about 2.5 feet (0.76 meters) of water. The area was covered with maiden hair grass, and was representative of what might be called a sublittoral zone. The water temperature at this time was 15^{o}C. The core taken was 7 cm in depth. The top 3 cm consisted of

a peat like material. Below this, sand became more prevalent, although it appeared to be mixed with some organic material. The bottom here was characterized by underlying gas pockets, indicating a rather biologically active area.

5. CLAIRE #2: This sample was taken in the deep region of the lake at about 12 feet. There was no indication of a thermocline at this time (January 8, 1976) although a slight temperature gradient was noted from top to bottom. The top temperature was 15.6^{0}C and the bottom was 14.7^{0}C. The dissolved oxygen level was at saturation throughout. The water of this lake is highly colored, although the turbidity is low. The sediment core consisted of 9.4 cm of a black soft silty material. It appeared to be homogeneous throughout.

6. CLAIRE #3 is essentially a duplicate of Claire #1, taken at the same time in a similar area.

7. CLAIRE #4 is a duplicate of Claire #2, with the sediment's characteristics essentially the same.

8. WEIR: This sample represents sediment underlying 10 feet (3.05 meters) of water on the south side of the lake. This sample was taken on February 16, 1976. The water temperature was 16^{0}C and no thermocline existed at this time. The water was very clear, having very little color or turbidity. The sediment core itself consisted of a top thin layer about 1 cm thick of dark organic material mixed with sand. Below this, the sediment consisted almost completely of sand.

9. GRIFFIN: This sample was also taken on February 16,

1976 in an area about 100 yards from a cypress stand on the west shore of the lake near Leesburg, Florida. The water temperature at this time was about 16^{0}C, and the depth was 7.5 feet. The oxygen level was noted to decline considerably with depth, reaching zero at the sediment-water interface. Like Lake Apopka, the Lake Griffin sediment was characterized by a loose flocculent top layer. Its thickness, however, was only about one foot. A rather consolidated sample was collected below this. It consisted of a black-brown mud which was characterized by the odor of hydrogen sulfide. At about 3 cm sand was noted to be mixed with this material. The sand became more prevalent at four to ten centimeters depth. At a depth of 15 cm, a layer of peaty material was noted.

10. EOLA: This sample was taken on January 26, 1976 in 9 feet of water. The water tempearture was 16^{0}C. No thermocline was noted. The oxygen level varied from saturation at the surface to 60% saturation at the bottom. The top centimeter of the sediment core was a black organic mud. The remaining portion of the sample consisted mostly of sand, becoming lighter in color as the depth increased.

11. SWANN: This sediment collected February 23, 1976 came from a sublittoral region of about five foot depth. The water was very clear in the lake and it could be seen that the bottom was covered with a thin layer of black organic material. The core revealed this layer to be about 1.5 cm with sand underlying to a depth of 10 cm followed by a dark layer of peat like material.

12. GENEVA: This sample was taken on the same day, February 23, 1976, and its characteristics were similar to the Lake Swann sample. The peat layer, however, was not noted.

13. WAUBERG: Like Lakes Griffin and Apopka, the sediments of Lake Wauberg were very loose and flocculent and it was difficult to obtain a core sample. A relatively well consolidated sample was finally obtained on February 22, 1976 from the west side of the lake just north of a recreational area. This sample consisted of a brown organic mud with sand becoming more abundant with depth and was taken at a water depth of 8 feet (2.44 meters).

14. ALTHO: This sample was taken in six feet (1.83 meters) of water on the east side of the lake. This lake is surrounded by cypress stands which give the water alot of color. The sediment sample was characterized by a dark organic layer one centimeter thick, below which sand mixed with dark organic material was noted, to a depth of 10 cm. A peat layer was noted below 10 cm.

Laboratory Results

Data on phosphorus content and percent volatile solids at various sections of sediment cores are presented in Table 3. Also, moisture content and phosphorus of the overlying water for selected samples are presented in this table. Change in phosphorus content with core depth from the water sediment interface for various lakes are shown in Figures 22-25. The trophic state index (TSI) as calculated by Shannon and Brezonik (45) is given on these figures when available.

TABLE 3

ANALYSIS OF SEDIMENT CORE SAMPLES COLLECTED FROM SELECTED FLORIDA LAKES

Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments			TP of Overlying Water mg/l	Trophic State Index
		Total Phosphorus mg/Kg	% Volatile Solids	% Water Content		
LAKE GRIFFIN	.1	915	56	95	.25	13.7
	.5	264	90	76		
	1.0	4620	45	96		
	2.0	492	49	94		
	3.0	533	53	94		
	4.0	531	77	96		
	5.0	556	43	92		
	6.0	370	49	90		
	10.0	231	44	90		
	15.0	1475	47	89		
GRIFFIN (FLOC)	.5	2031	78	96		
	1.0	1596	85	98		
	2.0	1801	90	99		
	4.0	2251	86	96		
	6.0	1662	79	96		
WAUBERG	.1	4301	13		.24	7.4
	.5	1979	3			
	1.0	5166	12			
	2.0	1226	2			
	3.0	2137	3			
	4.0	2983	3			

Table 3—Continued

Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments			TP of Overlying Water mg/l	Trophic State Index
		Total Phosphorus mg/Kg	% Volatile Solids	% Water Content		
WAUBERG (cont.)	5.0	3882	3			
	6.0	1516	3			
	10.0	510	1			
	15.0	2598	9			
ALTHO	.1	2773	26		.065	2.5
	.5	2497	26			
	1.0	3467	39			
	2.0	422	9			
	3.0	619	6			
	4.0	337	7			
	5.0	768	11			
	6.0	850	31			
	10.0	1606	40			
	15.0	1458	29			
GENEVA	.1	1163	5		.05	1.8
	.5	909	4			
	1.0	668	2			
	2.0	341	2			
	3.0	507	3			
	4.0	604	5			
	5.0	713	2			
	6.0	508	1			
	10.0	315	1			
	15.0	253	2			

Table 3—Continued

Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments			TP of Overlying Water mg/l	Trophic State Index
		Total Phosphorus mg/Kg	% Volatile Solids	% Water Content		
SWANN	.1	608	3		.050	1.5
	.5	558	1			
	1.0	775	2			
	2.0	328	1			
	3.0	213	<1			
	4.0	261	<1			
	5.0	240	2			
	6.0	333	<1			
	10.0	1227	12			
	15.0	929	5			
EOLA	.1	2583	57		.22	
	.5	2143	15			
	1.0	601	6			
	2.0	661	6			
	3.0					
	4.0	303	5			
	5.0	192	2			
	6.0	439	3			
	10.0	109	2			
	15.0	44	1			
LAKE CLAIRE #1	.1	2030	83		.069	
	.5	1571	53			
	1.0	1375	46			
	2.0	2683	59			

Table 3—Continued

Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments			TP of Overlying Water mg/l	Trophic State Index
		Total Phosphorus mg/Kg	% Volatile Solids	% Water Content		
LAKE CLAIRE #1 (continued)	3.0	1188	51			
	4.0	296	16			
	5.0	210	8			
	6.0	55	4			
	7.0	34	3			
LAKE CLAIRE #2	.5	2041	47		.055	
	1.0	3108	35			
	2.5	2586	50			
	5.2	1831	40			
	6.5	1087	31			
	8.0	920	28			
	9.4	1080	42			
LAKE CLAIRE #3	.1	5013	59		.04	
	.5	3145	53			
	1.0	1845	33			
	2.0	1411	43			
	3.0	1034	46			
	4.0	628	35			
	5.0	351	17			
	6.0	95	7			
	7.0	87	7			
LAKE CLAIRE #4	.5	1429	32		.025	
	1.0	1818	31			
	2.5	1549	38			

Table 3—Continued

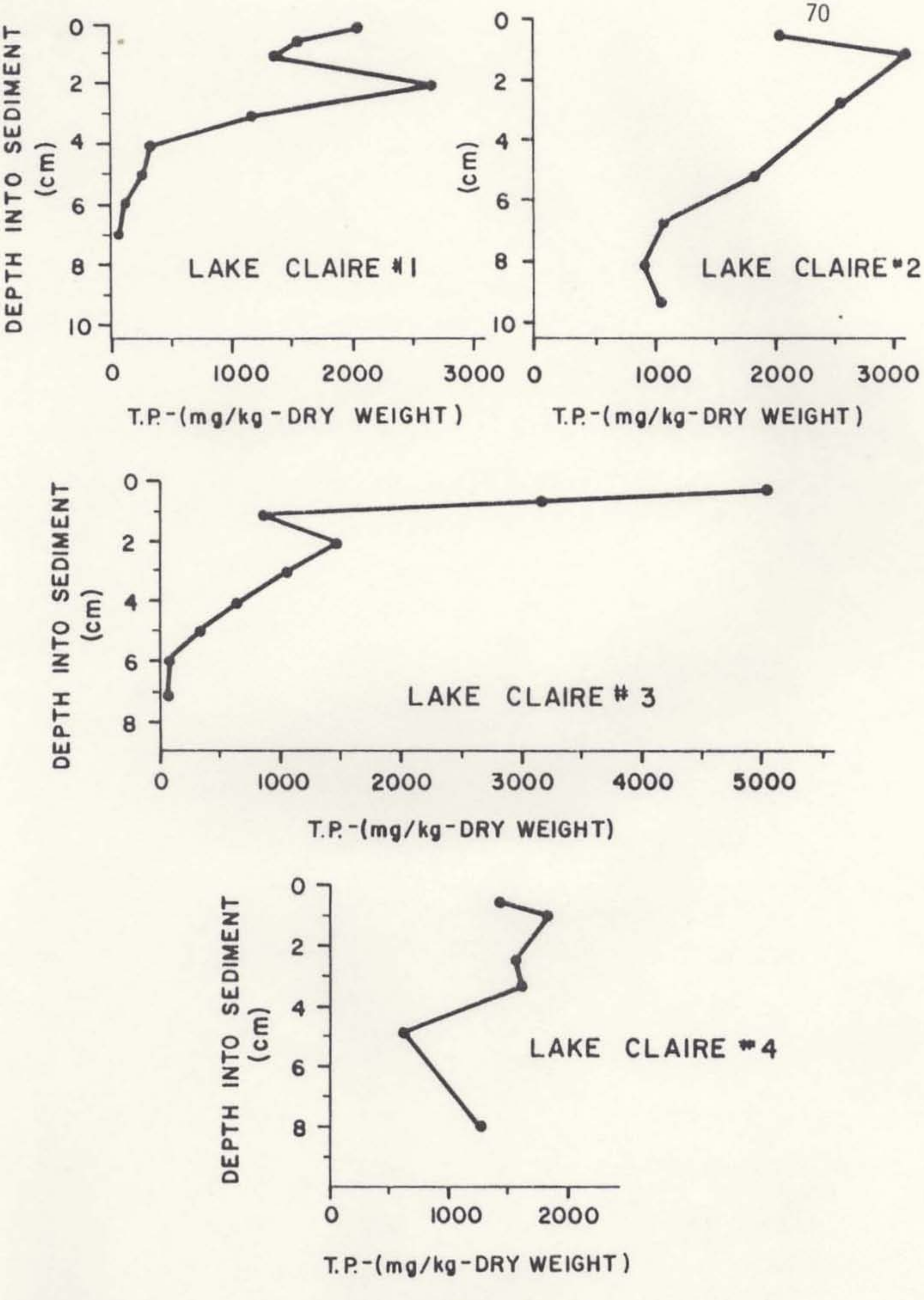
Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments			TP of Overlying Water mg/l	Trophic State Index
		Total Phosphorus mg/Kg	% Volatile Solids	% Water Content		
LAKE CLAIRE #4 (continued)	3.5	1627	46			
	5.0	620	3			
	8.0	1284	47			
APOPKA #1	.1	315	91	91	.17	22.1
	.5	151	96	93		
	1.0	425	94	92		
	2.0	363	99	91		
	3.0	627	58	85		
	4.0	1193	99	88		
	5.0	7002	62	79		
	6.0	711	99	80		
	10.0	1075	78	82		
	15.0	1511	47	86		
APOPKA #2	.1	881	87			
	.5	1156	49			
	1.0	1417	46			
	2.0	702	14			
	3.0	232				
	4.0	462	18			
	5.0	318	4			
APOPKA #3	.5	504	39		.18	
	1.0	584	66			
	3.0	575	51			
	4.0	1006	6			

Table 3—Continued

Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments: Total Phosphorus mg/Kg	Analysis of Bottom Sediments: % Volatile Solids	Analysis of Bottom Sediments: % Water Content	TP of Overlying Water mg/l	Trophic State Index
APOPKA #3 (continued)	5.0	106	8			
	10.0	118	3			
APOPKA #4 (Floc)	.5	682	70			
	1.0	550	66			
	2.0	701	67			
	3.0	843	60			
	4.0	626	65			
	5.0	967	62			
APOPKA #5 (Floc)	.1	2101	63			
	.5	1582	88			
	1.0	1316	70			
	2.0	1625	75			
	3.0	2319	90			
	4.0	1201	71			
	5.0	2230	59			
LAKE WEIR	.1	111	3	25	..10	3.3
	.5	45	2	11		

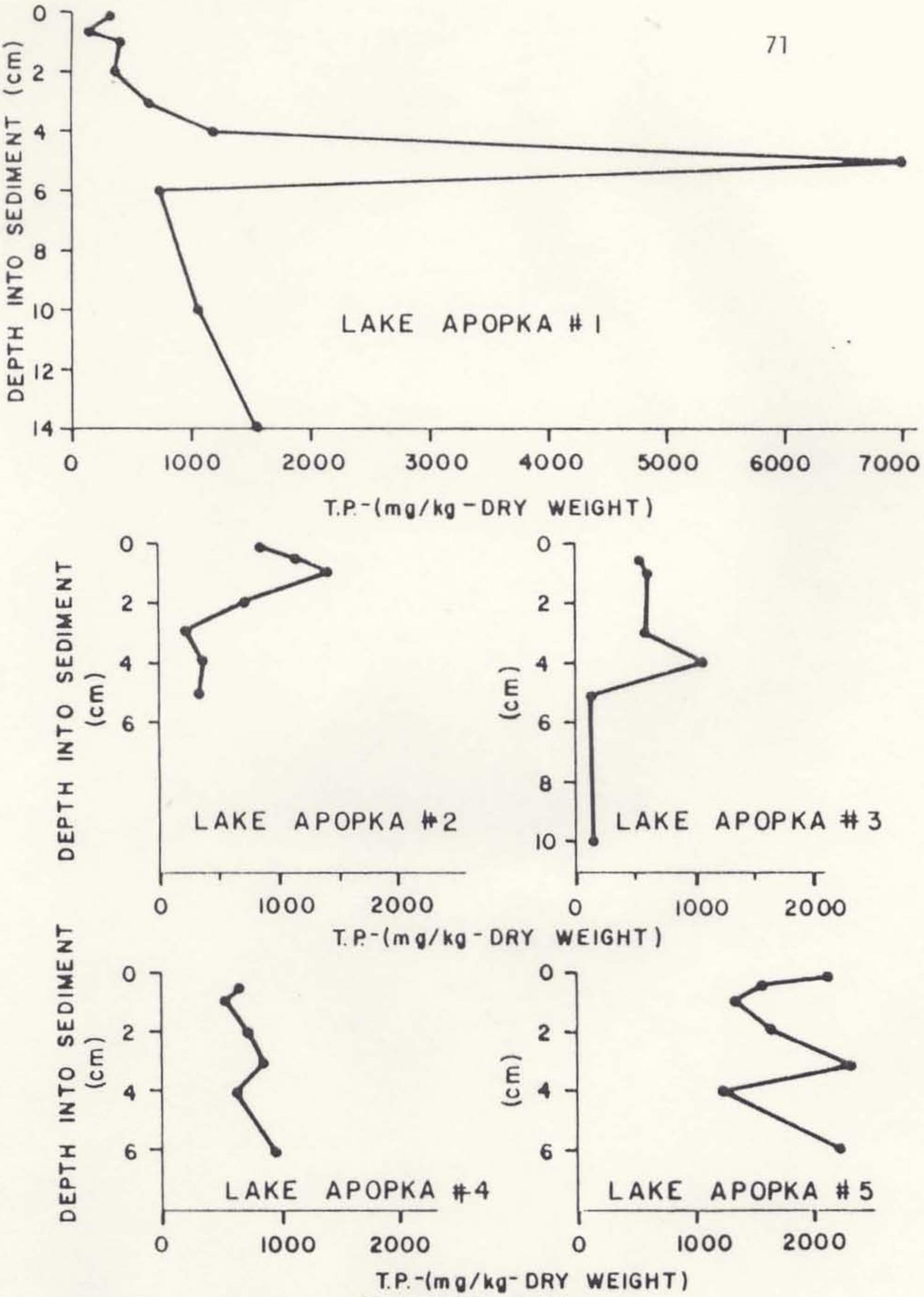
Table 3—Continued

Sediment Sample Identification	Core Depth into Sediment "cm"	Analysis of Bottom Sediments			TP of Overlying Water mg/l	Trophic State Index
		Total Phosphorus mg/Kg	Volatile Solids	Water Content		
LAKE WEIR (continued)	1.0		1.5	7		
	2.0	56	1.0	15		
	3.0	42	1.0	9		
	4.0	20	< 1.0	16		
	5.0	41	< 1.0	13		
	6.0	30	< 1.0	28		
	10.0	22	< 1.0	18		
	15.0	25	< 1.0	27		



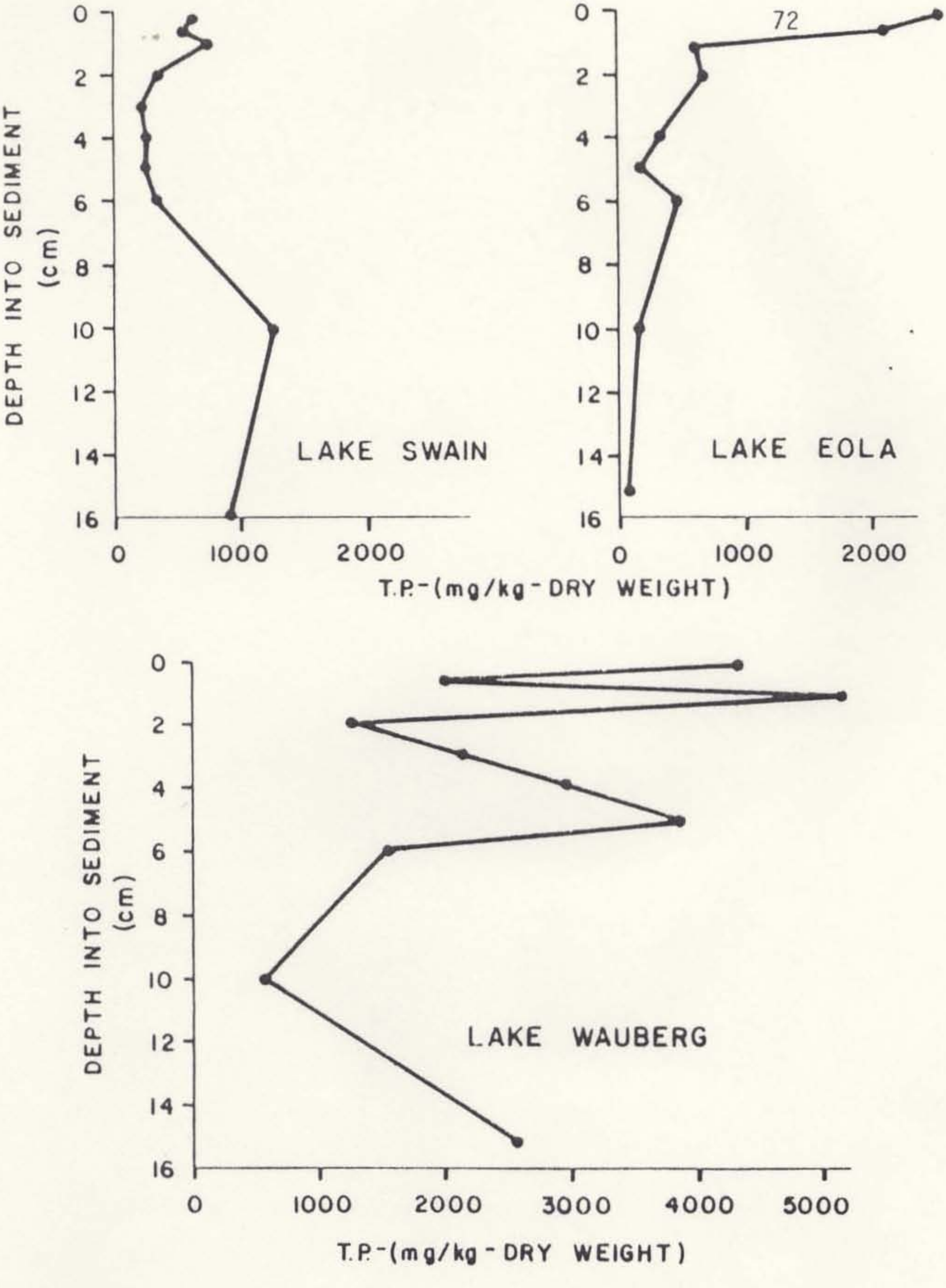
(FIGURE 22)

SEDIMENT - PHOSPHORUS PROFILES



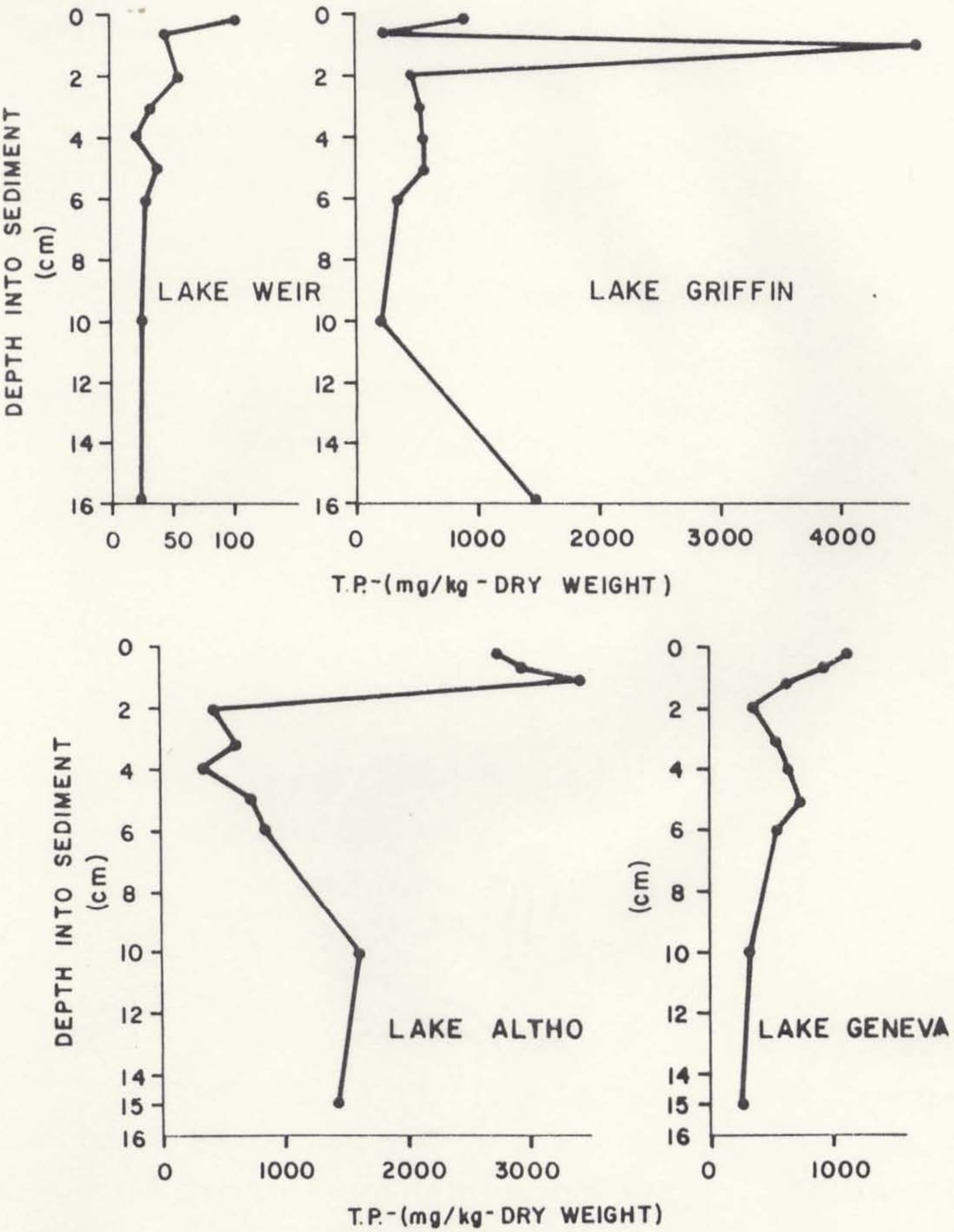
(FIGURE 23)

SEDIMENT-PHOSPHORUS PROFILES



(FIGURE 24)

SEDIMENT - PHOSPHORUS PROFILES



(FIGURE 25)

SEDIMENT - PHOSPHORUS PROFILES

Statistical Analysis

In an attempt to analyze this data, regression analysis was done on each data set as well as on the Williams and Mayer (36) idealized sediment profile as seen in Figure 15. The depth was set as the independent variable, while the phosphorus concentration was used as the dependent variable. Five equation types were investigated with the aid of an IBM 360 computer. The general formula for these equations follows:

$$Y = A + Bx$$

$$Y = Ae^{Bx}$$

$$Y = Ax^{B}x$$

$$Y = A + B/x$$

$$Y = \frac{x}{A + Bx}$$

where:

A = intercept of straight line

B = slope of straight line

Y = phosphorus content mg/Kg of dry sediment

x = core depth in centimeters

The results of the statistical analysis are shown in Table 4. The A and B values and correlation coefficients, R, are presented with each set of data. From this table, it can be seen that the best correlations are found to follow the equation $Y = \frac{x}{A + Bx}$ in most cases. The idealized pattern of Williams and Mayer (36) also follows this pattern. This equation is obviously the best fit for idealized situations as well as for many of the selected Florida lakes.

TABLE 4

CORRELATION BETWEEN PHOSPHORUS CONCENTRATION WITH SEDIMENT DEPTH FOR CORE SAMPLES FROM SELECTED FLORIDA LAKES

LAKE	NO. OF OBSERVATIONS	$Y = A + Bx$			$Y = Ae^{Bx}$			$Y = Ax^{B}$			$Y = A + \frac{B}{x}$			$Y + \frac{x}{A+Bx}$		
		A	B	R	A	B	R	A	B	R	A	B	R	A	B	R
Ideal Distribution Williams & Mayer (9)		1133	- 67	54	1049	6.00	52	1062	-0.26	88	634	389	94	-.00052	.00153	99
APOPKA 1	(10)	909	92	4	413	0.12	30	492	0.46	44	1568	-.00016	6	.0021	.00058	62
APOPKA 2	(6)	667	- 51	33	731	-.186	49	551	-0.47	32	409	-87	4	- .013	.0094	86
APOPKA 3	(7)	1162	-190	80	1187	-0.29	81	671	-.322	66	669	34	28	-.0013	.0032	92
CLAIRE 1	(9)	2074	-322	70	3430	-.612	88	8215	-.841	52	824	139	21	- .034	.023	65
CLAIRE 2	(7)	2792	-207	75	2925	-.121	80	2397	-.326	60	1468	598	25	-.00108	.00106	94
CLAIRE 3	(9)	3311	-566	74	4574	-.568	96	1305	4.896	76	769	458	80	-.0142	.0104	71
CLAIRE 4	(6)	1651	- 77	26	1636	-.063	20	1523	-.169	20	1266	183	10	-.00017	.00097	71
GRIFFIN	(10)	1180	- 43	12	695	-.062	65	642	-.344	18	964	9.8	10	-.00481	.0091	81
EOLA	(9)	1390	-125	45	1313	-.245	85	755	-0.76	85	402	242	71	-. 043	.020	80
ALTHO	(10)	1785	- 66	8	1208	-.015	1	1401	-0.26	23	1208	186	27	..0024	.00061	48
GENEVA	(10)	796	- 42	50	784	-.070	61	676	-0.26	67	491	73	63	-.0048	.0038	93
SWANN	(10)	375	37	26	361	.052	16	464	-.0054	0	537	6.7	0	.0058	.00092	31
WEIR	(8)	67	-5.9	44	61	-0.12	52	48	-0.32	76	31	..081	88	- .017	.042	93
WAUBERG	(10)	3139	-113	13	2831	-.054	14	2623	-0.20	20	2334	202	18	-.00021	.00081	41

Regression Analysis Depth (cm), X vs. Phosphorus (ppm), Y

It can be seen from Figure 15 that profiles for this idealized situation may be legitimately divided into three zones; a top zone in which the phosphorus concentration is rather constant, a middle zone in which the phosphorus concentration decreases geometrically, and a lower zone in which the phosphorus concentration tends to remain constant. These zones will be referred to, from top to bottom, as the interchange, migratory, and historical zones. It may be unrealistic to expect idealized patterns in field situations because of the variability in many phenomenon, such as mixing by currents or benthic invertegrates, which can disturb the profile. On the other hand, it seems reasonable to compare existing field profiles in lake sediments with idealized profiles for better understanding conditions and mechanisms that cause this deviation.

As previously mentioned, the top region of loose flocculent sediments which is poorly consolidated must be thought of as part of the interchange area. It may not be possible at this time to adequately address these sediments, although they must play an important part in the dynamics of phosphorus cycling within hypereutrophic lakes.

Within the interchange zone, the phosphorus concentration may decrease, remain constant, or increase with depth. From logical deduction, it would seem that the slope of this linear transfer segment might reflect the effects of phosphorus regeneration and deposition within the sediment. A negative slope may indicate a high rate of phosphorus regeneration from the sediments to the water, while a positive slope may show that sedimentation is dominant.

Using the data that is represented graphically in Figures 22-25, an attempt was made to separate each profile into the three zones. This is shown in Table 5. Using this table, and the available data on sediment depth and phosphorus concentration within the interchange zones, straight line relationships were developed, and the slopes of these lines in mg-P/kg dry sediment per centimeter of depth into the sediment determined. These slopes and the trophic state indices for the selected lakes are shown in Table 6. A further analysis was made to determine the correlation between these slopes and the trophic state index (TSI). The relationship was represented by the equation $Y = -.0021x - 11.6$, with Y as the TSI and the slope as x. The relationship showed a very poor correlation, with the correlation coefficient, R, equal to -.18. It must be realized that the slopes examined were determined from a limited number of data points within the interchange zone, and they varied considerably between different samples in the same lake. This is partly due to collecting and sampling error and partly to the differences between the sampling sites. For example, in Lake Claire, the slopes from the sediments taken from the deep areas were negative, while the sublittoral samples showed positive slopes. Indeed, this type of variability is expected, as the whole lake cannot be treated as a homogeneous entity. With this attempt good correlations between trophic state and phosphorus profiles are far from being established, however, the possibility of relationships between

TABLE 5

HYPOTHETICAL ZONES ESTIMATED FOR EACH DATA SET FROM SEDIMENT CORES FOR SELECTED FLORIDA LAKES

Sample Identification	Depth in Centimeters		
	Interchange Zone	Migratory Zone	Historical Zone
APOPKA #1	0-3	3-5	>6
APOPKA #2	0-1	1-3	>3
APOPKA #3	0-3	3-5	>5
CLAIRE #1	0-1	1-4	>4
CLAIRE #2	0-1	1-8	>8
CLAIRE #3	0-1	1-6	>6
CLAIRE #4	0-1	1-5	>5
WEIR	0-1	1-4	>4
GRIFFIN	0-1	1-2	>2
WAUBERG	?	?	?
ALTHO	0-1	1-2	>2
GENEVA	0-1	1-4	>4
SWANN	0-1	1-4	>4
EOLA	0-1	1-5	>5

TABLE 6

CORRELATION BETWEEN SLOPES OF LINEAR INTERCHANGE SEGEMENTS AND TROPHIC STATE INDEX FOR THE LAKES

LAKE	SLOPE** (mg/kg · cm)	TSI *
APOPKA #1	- 156	22.1
APOPKA #2	- 500	22.1
APOPKA #3	- 83	22.1
APOPKA #4 Floc	- 125	22.1
CLAIRE #1	+ 700	---
CLAIRE #2	- 500	---
CLAIRE #3	+3000	---
CLAIRE #4	- 700	---
WEIR	+ 100	3.3
GRIFFIN	-2500	13.7
ALTHO	- 500	2.5
GENEVA	+ 500	1.8
SWANN	- 63	1.5
EOLA	+1400	---

*TSI after Shannon and Brezonik (43)

**mg total phosphorus per kg sediments times cm. Sediment depth within the interchange zone.

these profiles and trophic state may still exist. Therefore, it was decided to try a different phosphorus profile indicator as the independent variable.

It seems logical to assume in lieu of the literature review, that dynamic relationships exist between the migratory and the interchange zones. Therefore, a ratio between the highest concentration in the migratory zone and the lowest value in the interchange zone might prove to be a good trophic state indicator. The reasoning behind this selection is made clearer in the following chapter. In essence, it has to do with the theory that the highest level of phosphorus in the migratory zone represents the summation of the phosphorus contributed by sedimentation and molecular diffusion, while the minimum interchange value represents the same value minus that phosphorus regenerated to the overlying water. A ratio then of these two values would be a function of the rate at which the lake is loaded with phosphorus by the sediments, which, it would seem, is related to the trophic state, at least in a phosphorus limited lake. These ratios for the lakes studied are seen in Table 7. A correlation between this ratio as X and the TSI as Y revealed the linear equation:

$$Y = 1.07X - 4.63 \quad R = .49$$

This correlation was improved to $R = .97$ when samples Apopka #2 and Apopka #3 were deleted. This adjustment seemed reasonable in light of the trouble involved in the collection of those two samples. The variability in sediments within the same lake again may be considered here as before. The fact may be that those sediments represented by Apopka #2 and #3 may not be as active in phosphorus dynamics as the sediments represented by Apopka #1.

TABLE 7

RATIO OF THE MAXIMUM PHOSPHORUS MIGRATORY VALUE TO THE MINIMUM CONCENTRATION IN THE INTERCHANGE ZONE

LAKE	RATIO	TSI
APOPKA #1	46	22.1
APOPKA #2	2.6	22.1
APOPKA #3	2.0	22.1
WEIR	1.2	3.3
GRIFFIN	18	13.7
SWANN	1.4	1.5
GENEVA	1.8	1.8
ALTHO	1.4	2.5
CLAIRE #1	1.9	no data
CLAIRE #2	1.3	no data
CLAIRE #3	1.7	no data
CLAIRE #4	1.1	no data
EOLA	.31	no data

Although considerable time and effort could be spent investigating multivariate relationships between trophic state index and other parameters relating to the vertical distribution of phosphorus in the sediments, it must be noted that such an effort not only would probably over-estimate the quality of the data presented here, but it would also probably reveal that the correlation between these parameters and trophic state is limited. This is readily seen again by the great amount of variation in sediment characteristics within the same lake. Indeed, the assumption that all portions of the sediments within the same lake are homogeneous or even similar would be absurd. It may be specified then that only in certain regions can the sediment be related to trophic state, for it may be that only certain portions are contributing enough nutrients to have an impact upon the trophic dynamics within the lake while other sediments are relatively inactive. The improvement of the correlation between the maximum migratory minimum interchange ratio to TSI when Apopka #2 and #3 are ignored may demonstrate this. The problem then of sediment analysis needs further discussion before definitive statements can be made about certain ratios, slopes, etc., of the vertical phosphorus profile within the sediment. Logical, realistic observations however, do seem in order at this time, as long as it is recognized that considerable theorizing is involved.

CHAPTER V

DISCUSSION

Phosphorus profiles for sediment core samples from selected Florida lakes were analyzed for possible relationships that might be useful as indicators of the trophic state. However, the variability of phosphorus profiles within the same lake, limited data collected, and limited availability of the Trophic State Index (TSI) for the lakes prevented conclusive results. The study adds to the current knowledge on phosphorus profiles in lake sediments of Central Florida and presents hypothetical approaches to explain the variation between these profiles.

Phosphorus-Sediment Depth Relationships

The phosphorus concentration through the sediment core with depth for an idealized profile as shown in Figure 15 followed the generalized equation:

$$Y = \frac{X}{A + BX}$$

where:

Y = phosphorus concentration in mg/Kg dry sediment

X = depth into the sediment in Cm.

The correlation coefficient for this profile fit to the equation above was $R = .99$.

Florida lakes exhibited various phosphorus-depth profiles as seen in Figure 23-26. Most of these profiles followed the same equation type as the idealized profile. From the lakes tested, Apopka #1, Apopka #2, Apopka #3, Claire #2, Claire #4, Griffin, Altho, Geneva, Swann, Weir, and Wauberg followed the idealized equation with correlation coefficients, R, of .62, .86, .92, .71, .81, .48, .93, .31, .93, and .41 respectively.

The three remaining samples showed better correlation coefficients with the equation type:

$$Y = Ae^{BX}$$

The correlation coefficients were .88, .96, and .85 for Claire #1, Claire #3 and Lake Eola respectively. This equation resembles that used for describing molecular diffusion by Fick's law. It seems reasonable to assume that molecular diffusion may be the dominant factor in phosphorus dynamics within these sediments. The interchange zone is noticably poorly defined in these samples, meaning the migratory zone predominates. These sediments are addressed further in the discussion.

Patterns of Phosphorus Distribution in Lakes

Available data is insufficient to conclude that distribution of phosphorus within lake sediments is a useful tool as a trophic state indicator. However there is evidence that shows it may be helpful in evaluating phosphorus dynamics within Florida lakes.

The highly eutrophic lakes, Apopka (Apopka #1), Griffin, and Ontario (34) (Figure 10) reveal similar phosphorus profiles within the sediment. It appears that from these similarities that perhaps the sediments react in a somewhat predictable manner to large external phosphorus loads, and that the net result is a unique pattern that may be helpful in evaluating lacustrine dynamics. With the data presented in this study and with the information gathered from available literature, it seems reasonable to present a hypothesis which attempts to explain these and other patterns of vertical phosphorus distribution within Florida lake sediments as follows.

Oligotrophic-Ideotrophic Lakes

These type lakes will ideally demonstrate a vertical pattern of phosphorus within the sediments as shown in Figure 15. This pattern is closely followed by Lake Huron (34) (Figure 12), Lake Weir (Figure 25), Lake Swan (Figure 24), and Lake Geneva (Figure 25). This profile may be considered to be the resultant of an equilibrium situation caused by the interaction of three phenomenon; diffusion through the pore water of the sediments, sorption and regeneration of phosphorus by the sediments, and sedimentation onto the sediments from the overlying water.

Diffusion, regeneration and sedimentation of phosphorus are related to several other variables as was noted in the literature review. Diffusion through the pore water for example is related to the ortho-phosphate concentration gradient throughout the pore water and may follow Fick's law. Regeneration of phosphorus to the overlying water is dependent upon the adsorptive capacity of the sediment as well as molecular and eddy diffusion phenomenon. Sedimentation may result from chemical precipitation or settling of dead algae cells. It is therefore dependent upon such factors as net productivity, pH, and ionic activity. There is a complex interdependency of these factors among themselves and with other variables such as temperature and Eh.

If D is the phosphorus contributed by diffusion through the interstitial water to the sediment at the water interface, R is that lost to the water by regeneration, and S is that phosphorus which is gained from settling and precipitation, then the rate of change of phosphorus concentration at the sediment surface, dS/dt, may be equated as:

$$dP/dt = dD/dt + dS/st - dR/dt$$

When the lake approaches an equilibrium situation, dP/dt approaches zero. The ideal profile then represents the net result of this equilibrium situation.

Cultural Eutrophication of Lakes

Consider now a hypothetical oligotrophic lake which reveals the ideal phosphorus profile through its sediments as seen in Figure 26a. Suppose that the phosphorus loading to this lake is suddenly increased significantly. This will result in an increase in dS/dt. This will in turn increase dP/dt at the sediment surface, resulting in a change in the profile as seen in Figure 26b. If this loading were to stop at this time then this excess phosphorus might be fixed into the sediment and homeostasis within the lake maintained. This peak in phosphorus concentration would eventually become buried by

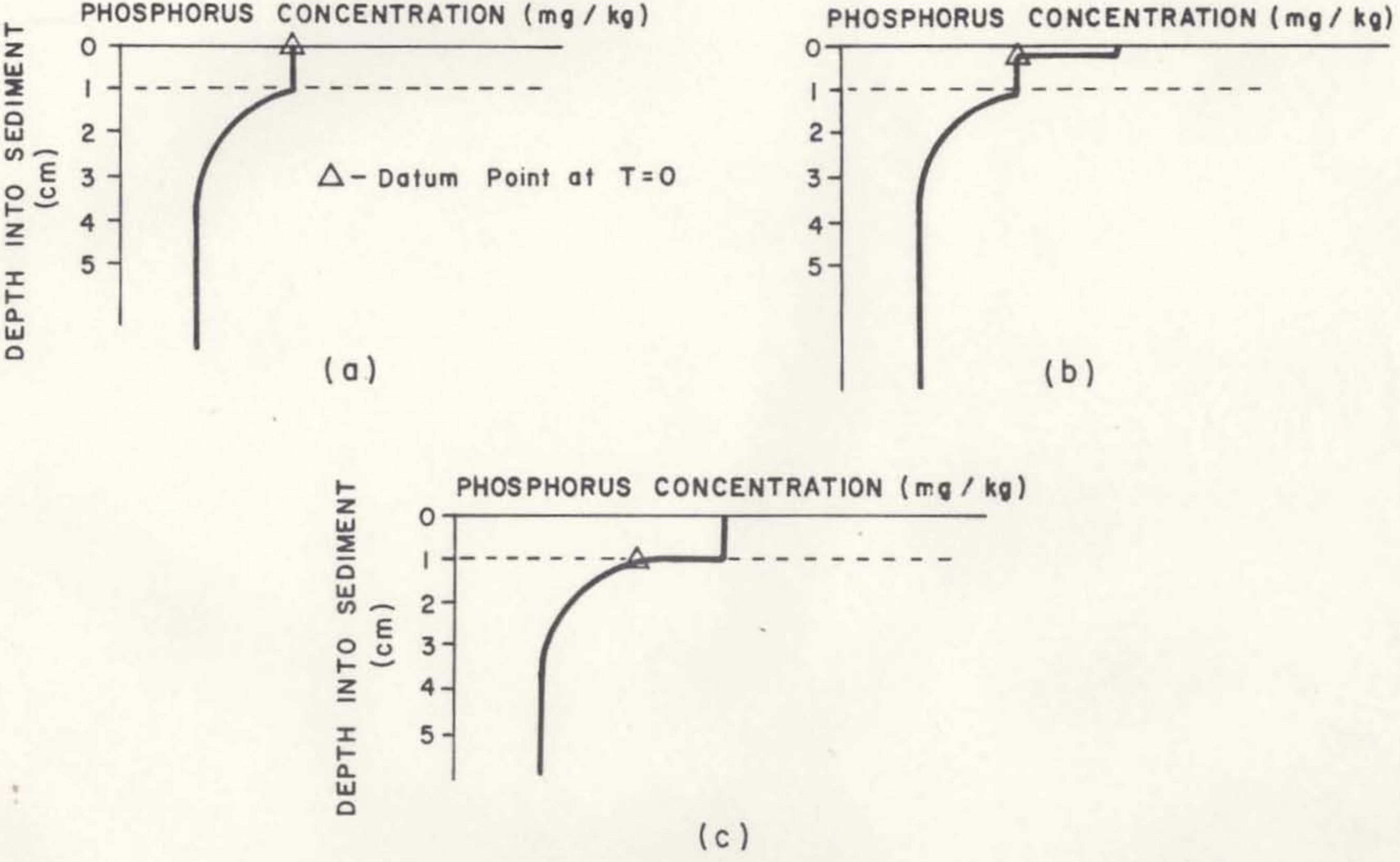


FIGURE 26

SCHEMATIC REPRESENTATION OF PHOSPHORUS DYNAMICS IN LAKE SEDIMENTS (continued)

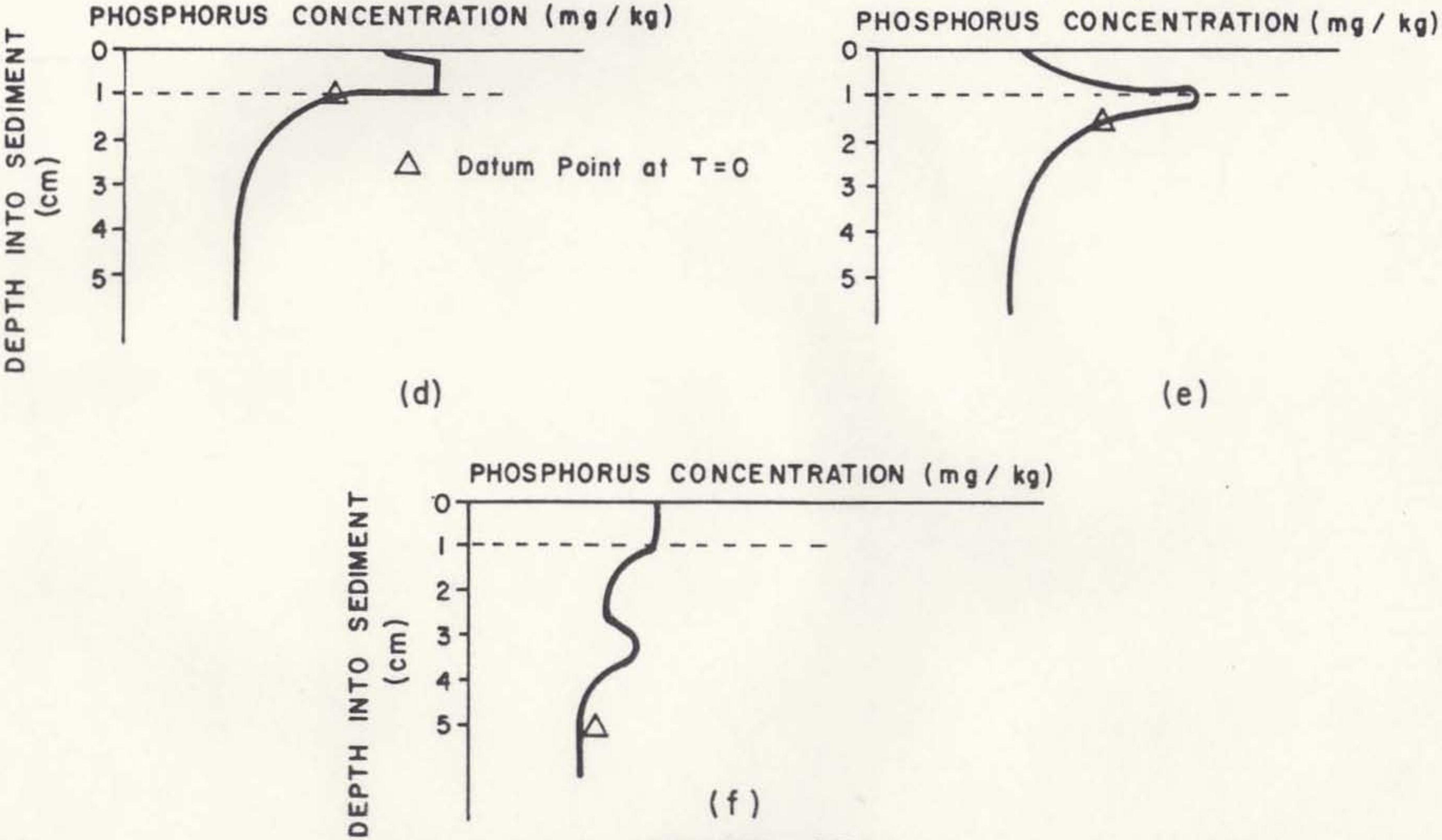


FIGURE 27

SCHEMATIC REPRESENTATION OF PHOSPHORUS DYNAMICS IN LAKE SEDIMENTS (continued) following sedimentation and become part of the historical zone. This peak, if discovered at some time later would give evidence of the event that resulted in this brief overloading of phosphorus. Such a natural event could be a hurricane, flooding, or fire. All of these could cause temporary excessive nutrient loading. In Lakes Altho and Swann such an increase is observed at about 10 cm. into the sediment. This layer may indeed represent one such past natural event. An attempt to chronologically label this event was not made, although, using the sedimentation rate calculated by Kemp et al. (34) for Lake Huron, it probably occurred well over one hundred years ago.

If the hypothetical phosphorus loading is not ended, but is rather allowed to continue, then dP/dt may be expected to continue increasing. Net productivity within the lake may also increase. Dead algae cells will eventually begin to settle at a higher rate, placing a large Oxygen demand upon the sediments, which may create anaerobic conditions at the water-sediment interface. These anaerobic conditions cause a reduction in the redox potential at the sediment surface. Brezonik (32) and others note that the redox potential at the sediment surface is lower usually in lakes with high trophic states as seen by the comparison of the redox potentials with sediment depth between mesotrophic Lake Monroe to hypereutrophic Lake Jessup in Figure 28 (32).

With a reducing environment at the sediment surface, several changes may occur. First of all, ferric compounds are reduced to ferrous compounds, which may enable some resolubilization of

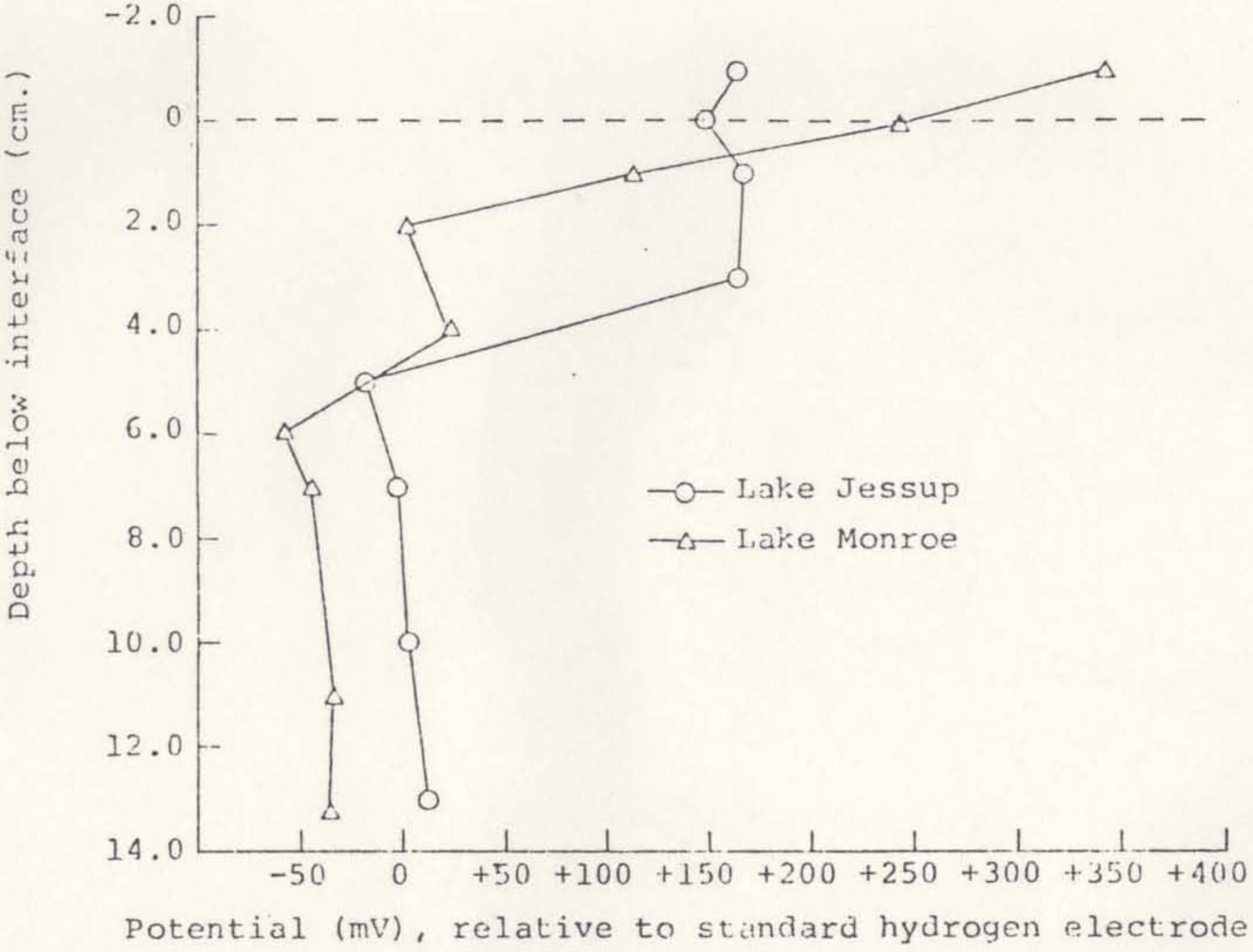


Fig. 28. Redox Potential at Various Depths in Sediments of Lakes Jessup and Monroe

SOURCE: P. L. Brezonik, "Nutrient Exchange Studies on Sediments of the Middle St. John's Lakes," (awaiting publication by the Florida Department of Environmental Regulation).

phosphate. This may create an increased concentration gradient within the pore water, and between the pore water and the overlying water. Also, anaerobic conditions tend to be correlated with the production of organic acids and a corresponding drop in pH. Adsorption efficiency decreases with low pH and Eh values. This means that the adsorptive capacities of the sediments decrease while at the same time additional burdens are placed upon the adsorption sites by increased phosphorus loading. At some time then, the rate of regeneration must increase, causing a change in the profile as seen in Figure 27d.

As the regeneration rate of phosphorus from sediments to the water column increases, a negative slope throughout the interchange zone will develop as seen in Figure 27e. With the increase in phosphorus regeneration, a corresponding increase in total phosphorus concentration within the overlying water would be expected with a corresponding change in the trophic state. The significant point here is that at no time does the sediment cease to be a phosphorus sink, for there is always a net loss of phosphorus to the sediments, as can be seen by following the original surface reference through Figure 27. What does occur is an increase in the amount of phosphorus returned to the water (dR/dt). This increase is more or less represented by the difference between the point A on Figure 29 and point B on the same figure. Hypothetically, the area under this curve (Figure 29), which is indicated by the shaded area, might represent that phosphorus which has been transferred to

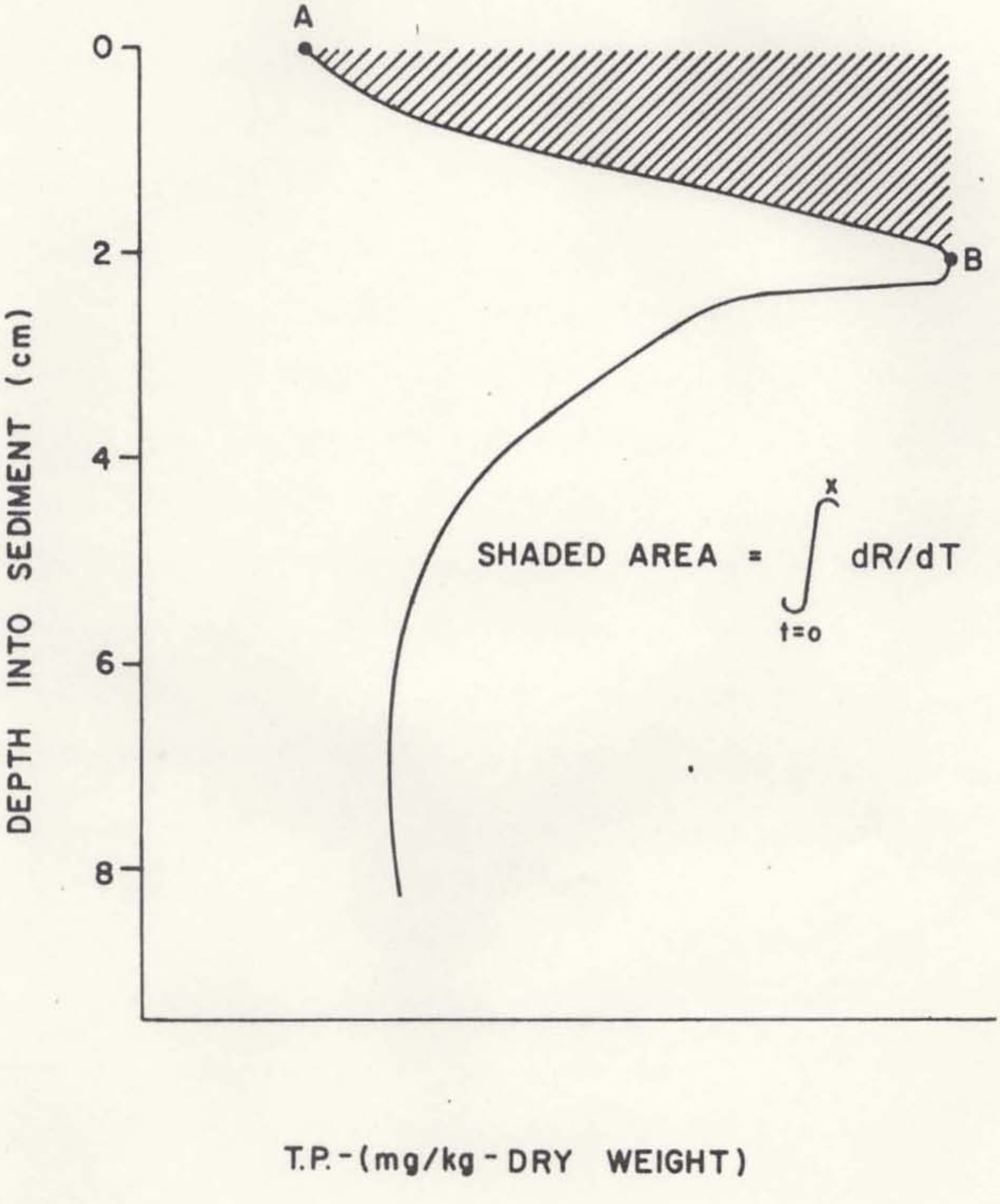


FIGURE 29

HYPOTHETICAL PHOSPHORUS LOADING FROM LAKE SEDIMENT the water column in excess of the preloading regeneration. This may be mathematically represented simple as $\int_{t=0}^{x} dR/dt$ or $R_{t=x}-R_{t=0}$ where t=x is represented by figure 27e, and t=0 is represented by figure 26a. Figure 30 shows how each factor involved in phosphorus dynamics within the sediment (diffusion, regeneration and sedimentation) may change with time following increased phosphorus loading.

This brings up the question as to what happens if the allochthonous loading decreases after the sediment profile has progressed to the stage represented by figure 27e. First of all, a decrease in dS/dt will occur. Although dR/dt may now decrease, it may be maintained at a higher level than before external loading began. It can be seen then that return to the original trophic state cannot always be expected, at least not until certain environmental conditions within the sediment changes. It must also be remembered that the great increase in the gross amount of phosphorus in the lake may have created conditions in which phosphorus is no longer limiting. Nitrogen usually accompanies heavy phosphorus loading, so it could be that nitrogen also is not limiting at this time. In actuality, light or even space may become the limiting factor. This is to say that algae growth is not controlled by nutrients, but rather by the antagonistic interactions of algae cells (toxin production, creation of light blocking turbidity, or even competition for oxygen during respiration). The implication then is that regeneration of nutrients from the sediments no longer is as

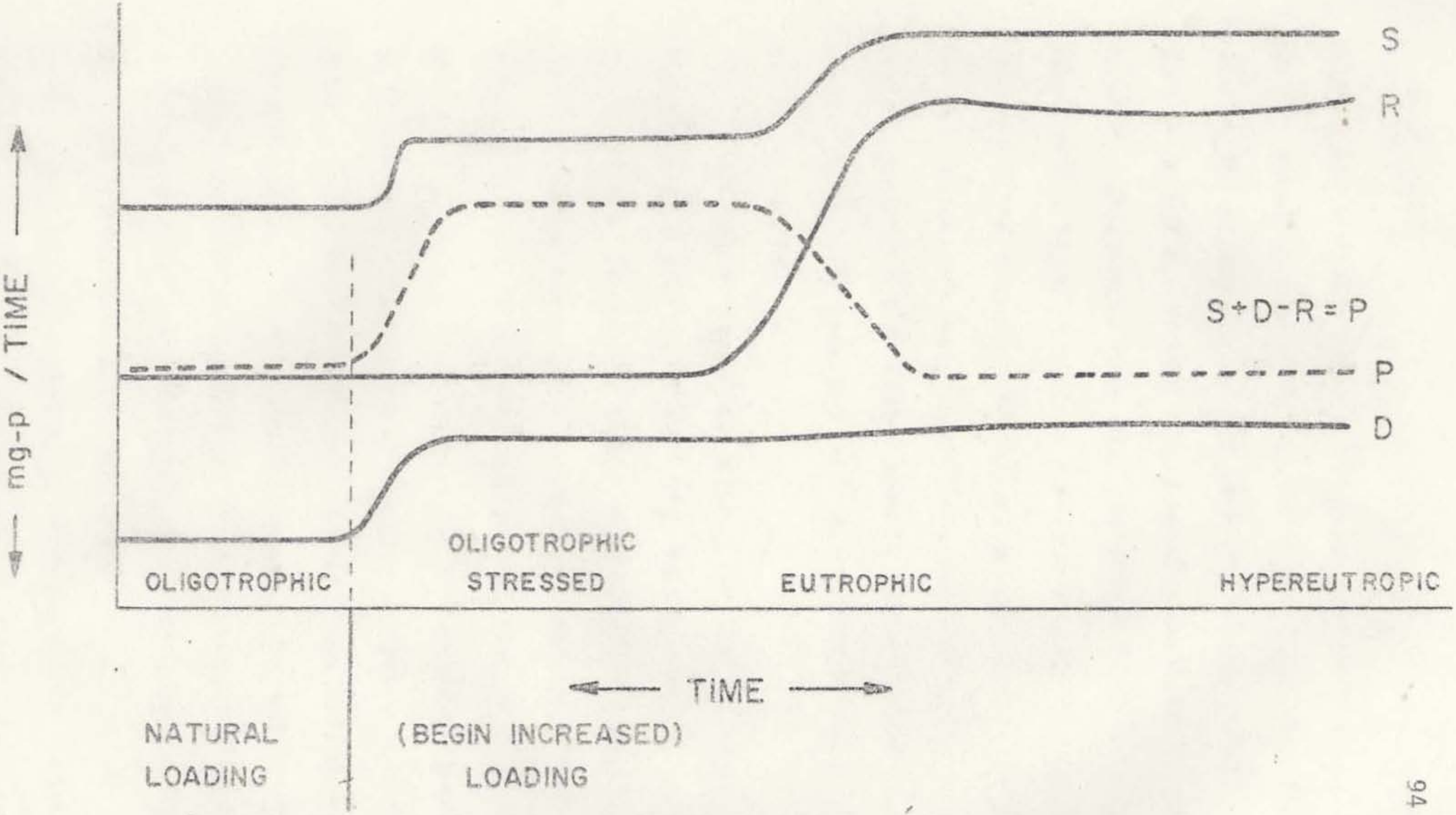


Fig. 30. Hypothesized Reaction of Phenomenon Involved in Sediment Dynamics to increased Phosphorus Loading (D - molecular diffusion, S - sedimentation, R - regeneration, P - phosphorus concentration at sediment surface)

important. Recycling within the water maintains the high nutrient levels needed for the high rate of growth. The lake then may be heading for a senescent stage, with the bottom filling rapidly with dead algae cells. It may not be totally accurate to think that diverting phosphorus loads will not affect trophic dynamics, but with Florida lakes it must be considered naive to expect total recovery after a short time following such diversion. Because of the shallowness of lakes in Florida, sediment water interchanges are probably more significant than in deeper Northern lakes. Water quality management programs must consider such interchanges if they are to be successful.

A final question now arises, and that is, what happens to the phosphorus profile if this high loading rate is continued indefinitely? It must be though that if dP/dt stabilizes, that a new equilibrium condition will develop eventually. The original increase in phosphorus concentration may become represented historically by a slight increase in the deeper sediments as seen in Figure 27f. This historical increase represents that phosphorus which escaped resolubilization and subsequent diffusion through the pore water. As the lake approaches a terrestrial stage, i.e. as the water volume diminishes, it can be expected that regeneration will decrease so that the profile will demonstrate a highest phosphorus concentration at the interface. It must be remembered however that with invasion by macrophytic plants redistribution of phosphorus within the saturated soil may cause some distortion of the profile.

Phosphorus Profiles and Trophic Dynamics

From the previous presentation it can be seen why the vertical phosphorus profile within the sediment does not always serve as a good indicator of trophic state. The dynamics within the sediments are not always coordinated in time with trophic changes in the lake. This is because of the homeostatic properties of the sediments. This "compartment" within the system may be thought of as an entropy diversion area, as described by Patten (9). This is to say that any materials which might create disorder within the biological community of the lake are delivered to the sediments, where they are stored and, if possible, rendered unavailable for phytoplankton growth, or at least allocated in controllable quantities by regeneration.

Looking now at the lakes presented in this study, several observations may be made which might demonstate the value of studying phosphorus levels within lake sediments. The first observation pertains to the Lake Claire profiles. As noted previously, two areas of this lake were sampled. The profiles of each of these areas reflect their differences. First of all, the phosphorus from the sublittoral areas, Claire #1 and #3, appears to be mostly correlated with organic material. This was made evident after a linear regression was made using phosphorus in mg/sample as the independent variable and volatile solids as grams/sample as the dependent variable. The correlation coefficient was R = .97. When the nonvolatile solids were used as the dependent variable, a very poor correlation was noted, R = .08. This suggests that most of the phosphorus is organic, or at least aligned with organic material, perhaps through adsorption. It would appear, looking at Figure 22 that these sediments are accumulating phosphorus at a high rate near the water sediment interface. This accumulation may be occurring because of an increase in external loading, or perhaps because of the high biological activity in the upper sediments. The sediment profile from the deeper regions of the lake present a different situation. First of all, there is an excellent correlation between organic and inorganic material (grams/sample) with phosphorus concentration (mg/sample), R = .96 and .97 respectively. This indicates that adsorption as suggested by Mortimer (31) perhaps by a Ferri-Silico-Humic complex may be the predominate factor in the phosphorus dynamics of these sediments. Attempts were made, and were unsuccessful, to extract phosphorus from these sediments with a slightly acidic solution. This indicates that adsorption has probably rendered the phosphorus within these sediments biologically unavailable, or nearly so. The profiles themselves, Figure 22, Claire #2 and #4, give hint that some release to the water is occurring, and that the ratio between sedimentation, S, and regeneration, R, is decreasing. This tends to support any thoughts that Lake Claire may be experiencing a trophic change due to increased external loading. Although this lake is currently considered oligotrophic, it may be progressing more rapidly towards mesotrophic or eutrophic conditions. Clearing and recreational activities within the watershed may be responsible for the additional loading.

Lake Altho, in appearance, is very similar to Lake Claire. Its vertical phosphorus profile through the sediment appears similar also, as seen in Figure 25. The indication is then that perhaps Lake Altho is also experiencing increased phosphorus loading, and that a trophic change from oligotrophic to mesotrophic or eutrophic conditions may follow. Trailor parks and development within the watershed may be responsible for this loading.

As noted earlier, Lake Eola has recently been the subject of a restoration project. This project utilized a drawdown which enabled some oxidation of the underlying sediments which had imposed a large oxygen demand upon the system. Also, considerable amounts of sand were deposited on the lake bottom during this restoration. The sediment sample from this lake, whose profile is seen in Figure 24, seems to demonstrate what has transpired since this restoration effort was completed. The large slope seen in the interchange zone gives some indication that considerable phosphorus loading is continuing in this lake, and that an eventual return to eutrophic conditions might be expected. This prediction is easily made without the use of sediment profile studies, but the profile that is seen does seem to support the discussion which was previously presented on the mode of development of phosphorus profiles within the sediments.

Lake Wauberg is an enigma, for it is not at all clear why it is eutrophic. It certainly does not appear to be receiving large amount of allochthonous phosphorus, for the watershed is almost completely natural, and yet the phosphorus content of the sediments in this lake was the highest of those studied. The profile as seen in Figure 24 does not seem to follow any usual pattern. What may be the case in Lake Wauberg is the presence of some natural phosphorus deposit which through bacterial action has been rendered biologically available in recent years. This is of course only speculation, and only after extensive sediments studies have been completed can the true source of these nutrients be determined.

The one discernible characteristic of the Lake Wauberg sediment phosphorus profile is the almost systematic fluctuation in the phosphorus concentration with depth. This may be an indication of some sort of cycling phenomenon which allows the maintenance of a consistent fluctuation with time of the sedimentation to regeneration ratio. Whether this is set up by algae blooms followed by deposition, which is in turn followed by regeneration and a subsequent algae bloom, or by another type of cycle is not known. This lake presents itself as an interesting subject for further research.

Lake Apopka has been subjected to intensive phosphorus loading for several years, and therefore it might not be unusual to find some of the sediments approaching a new equilibrium, as has been hypothesized (Figure 27f). This seems to be most evident in the sediments from Apopka #2 and #3, Figure 24. These are the loose flocculant type sediments as previously mentioned. They tend to present a profile which is a hybrid between Figure 27e and Figure 27f. Again, the difficulty in collecting samples confuses this analysis considerably. The profile seen in Figure 24 of Apopka #1 presents an entirely different sediment profile. It appears to be behind the others in its evolution, clearly presenting a profile like that seen in Figure 27e.

The various types of phosphorus profiles through the sediment cores found in the Florida lakes investigated may be found to fit the patterns presented in Figures 26 and 27, which is presented to show one hypothesis on how the sediments react to changes in phosphorus loading. Which patterns these lakes fit may serve to detect changes in the allochthonous phosphorus being received by the lake before trophic changes become evident, as well as giving hints as to the degree in which the sediments are loading the lake with phosphorus through regeneration. Table 8 shows how the lakes studied have been evaluated.

TABLE 8

CATEGORIZATION OF LAKES STUDIED ACCORDING TO THE PHOSPHORUS PROFILES THROUGH THE SEDIMENT

LAKE	PROFILE TYPE	DESCRIPTION
GRIFFIN	FIGURE 27e	HYPEREUTROPHIC - non-equilibrium
APOPKA #1	FIGURE 27e	HYPEREUTROPHIC - non-equilibrium
APOPKA #2, #3	FIGURE 27e & f	HYPEREUTROPHIC - near equilibrium
WAUBERG	CYCLIC PATTERN	EUTROPHIC - reason unclear
ALTHO	FIGURE 26b	OLIGOTROPHIC - non-equilibrium. Experiencing stress from excessive phosphorus loading?
CLAIRE #1, #3	FIGURE 26b	OLIGOTROPHIC, non-equilibrium. Experiencing stress from excessive phosphorus loading?
CLAIRE #2, #4	FIGURE 26c or FIGURE 27e	OLIGOTROPHIC, non-equilibrium. May be increasing regeneration rate. May be a normal profile for these deeper sediments. Regeneration may be naturally higher here, serving to regulate phosphorus within the lake.
SWANN	FIGURE 26a	OLIGOTROPHIC-equilibrium
GENEVA	FIGURE 26a	OLIGOTROPHIC-equilibrium
WEIR	FIGURE 26a	OLIGOTROPHIC-equilibrium
EOLA	FIGURE 26b	ALTERED EUTROPHIC - non-equilibrium. Experiencing stress from excessive phosphorus loading.

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CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

Conclusions

During the course of this study much information on phosphorus distribution through sediment cores from selected Florida lakes has been generated. Also attempts have been made to correlate the phosphorus sediment profiles with the trophic state levels that have been derived from previous studies on these lakes. From this study the following conclusions were made:

1) Phosphorus distributions throughout the sediments from most of the lakes under investigation followed the generalized equation

$$Y = \frac{X}{A + Bx}$$

where:

Y = the phosphorus concentration in mg/kg dry sediment

X = sediment depth from the water-sediment interface in cm.

2) The correlation coefficients, R, values for the representative equation varied between 0.31 and 0.99.

3) Only three samples followed the generalized equation $Y = Ae^{BX}$ and R values varied from 0.85 to 0.96.

4) The phosphorus distribution for lake sediments reflects the dominant mechanisms involved in the dynamics of phosphorus within

the sediments, as well as serving as a benchmark for historical events which affected the external phosphorus loading rate.

5) Existing evidence from the results suggests that phosphorus distribution through the sediments may be a useful tool as an indicator of trophic changes within Florida lakes. However there may not always be a direct correlation between phosphorus profile and the current trophic state because of the buffering ability of the sediments.

6) Sediment profiles vary greatly for different areas within the same lake. However, one trophic state is assigned to each lake. Therefore correclation between different samples and trophic state would be different unless enough samples of sediment cores were collected from various sections of the lake for statistical analysis.

7) Representative core samples should be collected for analysis, therefore careful consideration should be given to the type of bottom sediments being sampled and the devices to be used for this sampling. Loose flocculent sediments are difficult to handle and do not lend themselves well to collection and analysis.

8) Hypothetical analysis to explain variations in phosphorus profiles from various lakes was possible and was presented in the discussion section of this study.

Recommendations

The study showed that inadequacies exist with methods used for field collection, laboratory analysis, and evaluation of lake sediments. Therefore the following recommendations should be considered:

1) A research need exists for development of techniques to study the feasibility of using the sediment dynamics as a tool for describing and controlling trophic changes within Florida lakes.

2) The role of the sediments in lacustrine dynamics is not well understood, therefore, further studies are recommended that would investigate the mechanisms involved and to quantify the contributions from these mechanisms.

3) The role of the sediments from each limnological zone needs to be evaluated.

4) The available methods for sampling various types of sediments from lakes are limited and often unsatisfactory. Therefore, methods for collecting undisturbed samples which allows reliable vertical sectioning of the sediment should be further developed.

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