Working Paper

A REVIEW OF MATHEMATICAL MODELS
OF PHOSPHORUS RELEASE FROM SEDIMENTS

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November 1981
WP-81-153

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PREFACE

The effect of sediments as a potential nutrient source is
often taken into account in water quality models. In many cases
however, the sediment nutrient load, or internal load, is very
significant and it may even be higher than the external one.
Therefore the problem of the influence of sediment on the quality
of water resources should be carefully studied, in order to have
a distinctive picture of the role of sediment in the nutrient
balance of water bodies, as well as on the mechanisms regulating
the nutrient exchange through the sediment-water interface.
This problem is considered especially important when studying
water body eutrophication as a consequence of the excess input
of phosphorus (or sometimes nitrogen) compounds. The major
objectives of this study are to review the literature on this
topic and to discuss the approaches in the mathematical descrip-
tion of phosphorus exchange in water quality models of different
complexity. This paper contributes to the Task on Environmental
Quality Control and Management in IIASA's Resources and Environ-
ment Area.

ABSTRACT

This report summarizes the data available on the role of the sediments as an internal source of phosphorus and reviews the literature on the phosphorus exchange processes in the sediment-water interface. Data on the sediment phosphorus release rates is presented. The role of individual processes such as mixing and diffusion as well as important environmental characteristics (oxygen and organic matter concentrations in sediment, temperature, pH and sediment oxidative state and bacterial activity) are discussed. Specific attention is given to analyzing the available information on the mechanisms of phosphorus transformations in the sediment-water interface because it is considered important in choosing the approaches when modeling the phosphorus exchange reactions in the sediment-water layer. The report also includes: models of phosphorus adsorption which are used in calculations of phosphorus removal by sediments. In addition, this report discusses 31 different models that are used for estimations of phosphorus release from the sediment as well as for the simulation of phosphorus transformations in the sediment-water interface. The report summarizes the rate coefficients and model parameters used in the simulation runs.

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PHOSPHORUS RELEASE FROM SEDIMENTS

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1. INTRODUCTION

The processes of phosphorus exchange between sediment and
water are important for the nutrient balance and particularly
for the phosphorus cycle in natural waters. These processes
also play an important role in the water quality and the develop-
ment of eutrophication. Sometimes in eutrophication studies
by mathematical modeling techniques (Orlob, 1968), the effect
of sediments is ignored and as Jorgensen et al., (1975)
indicated, this may give a false prognosis of the trophic state
of water bodies. Because the exchange processes have been
extensively studied in the last few years, the possible effects
of sediment on the nutrient balance may be taken into account
in the models describing nutrient cycling and eutrophication in
water. As Imboden and Emerson (1977) had shown in the case of
Greifensee, the phosphate contents in the sediment with informa-
tion on the values of vertical eddy diffusion, give the magnitudes
of phosphorus flux from the sediment within reasonable limits.

However, a better understanding of mass transport across the sediment-water interface, especially with respect to the impact on shallow lakes and reservoirs where nutrient-rich sediment may greatly hamper attempts at improving water quality which could be effected by reducing the external load (Gregor and Johnson, 1980), is one of the important purposes of eutrophication and phosphorus transformation studies (Imboden and Gachter, 1978).

Therefore, emphasis in this report is given to reviewing the existing information on the role of sediments on the mechanisms of phosphorus transformation in the sediment-water interface and the interrelationships of nutrient fluxes with factors that regulate the intensities of exchange processes through the sediment-water boundary as well as to models used for the estimation of sediment influence on the phosphorus balance and its cycling within water bodies.

2. CHARACTERISTICS OF THE SEDIMENT-WATER INTERFACE WITH RESPECT TO PHOSPHORUS EXCHANGE

Many studies have been made to clarify the role of sediments as nutrient sources in different water bodies. It is recognized that phosphorus in sediments is present in the form of minerals (primarily apatite), sorbed by the surfaces of other minerals, in solution in interstitial water, as organic phosphorus and as "nonapatite inorganic phosphorus" (Porcella et al., 1970; Williams et al., 1976). Apatite phosphorus consists of orthophosphate present in the crystal lattices of apatite grains, while nonapatite inorganic phosphorus includes all remaining PO_4-P ions in sediment pore water. Organic phosphorus consists of organic phosphorus compounds in sediment, including

all phosphorus association with carbon atoms via C-O-P or C-P bonds (Williams et al., 1976).

It was noted that in the unproductive lakes, the sediment behaved mainly as a sink for phosphorus, while in productive lakes, the sediment may consitute a considerable reservoir of phosphate (Webster and Schofield, 1971) and they act as a phosphate buffer, keeping the phosphate concentration in the overlying water constant (Harter, 1968). The direct availability of sediment-derived phosphate as a nutrient source for phyto-plankton is determined by the type of sediments. Golterman (1977) indicated that iron-bound phosphate and phosphate freshly adsorbed into the clay were available for algae uptake while the avail-ability of apatite was dependent upon the size of the crystals. In studies of sediment effect upon the nutrient exchange in tropical lakes, Viner (1977) concluded that compared to the water column, the sediment was much less important for the recycling of nutrients.

Stumm and Leckie (1971) noted that the processes of nutrient exchange in the sediment-water interface are important factors of primary production. The sediments may act as significant nutrient sources, because the concentration of dissolved chemical compounds in interstitial water is considerably higher than in the upper layers of water (Glass and Podolski, 1975).

The net phosphorus release from the sediment in shallow polluted water bodies may be compared to external loading (Ryding and Forsberg, 1977). Ulen (1978b) found that internal phosphorus loading or phosphorus release from the sediment was a more impor-tant phosphorus source for Lake Norrviken than the present exter-nal loading and the latter was about 17-35 percent of the internal

load from the sediment. Even for large lakes, for example, Lake Ontario, the sediment-derived phosphorus load is estimated to be essential and equal to 10 percent of the stream load (Bannerman et al., 1975).

Ku et al., (1978) showed that a significant amount of phosphorus is available for exchange in the sediment-water inter-face. Li et al., (1972) found that exchangeable phosphorus comprised from 19 to 43 percent of the total native phosphorus of the sediments. The dominant role of sediments in the phospho-rus cycle has been shown by Holden and Caines (1974), Andersen (1975), Bengtson (1975), and Stevens and Gibson (1977).

Intensity of phosphorus release from the sediment varies seasonally as results of changes in oxic conditions, macrofauna biomass, pH, temperature and dissolved phosphorus content in the water (Wildung and Schmidt, 1973; Neame 1977; Ku et al., 1978). Holdren et al., (1977) assumed that seasonal changes in inter-stitial phosphorus and sediment phosphorus release may be explained by temperature and oxygen penetration from the upper layers of water.

Essential seasonal variations in the rates of nutrient release from sediment were observed by Kamp-Nielsen (1975a). It was found that in winter the release of phosphorus does not take place under the ice (Gahler, 1969). As Golterman (1975) indicated, in shallow lakes it is possible that the phosphorus will accumulate in the sediment during the winter and release from sediment in summer. Kozerski (1981) found that phosphorus losses to sediment dominated in winter and spring time in the shallow, eutrophic lake, Mugelsee. Gahler (1969) has shown that exchange of nutrients including phosphorus between sediment and water was the most

active in June and September 1968 in Upper Klamath lake. For

Lake Moosø, Riemann (1977) found a binding of phosphate to sediment

all over the bottom of the lake amounting to 0.2-1.6 mgP/m^2-day

during January-February, while during the summer the release of

phosphorus from sediment was observed with maximum rates of 4.5-8.6

mg P/m^2-day in July. The study results of Hutchinson (1957),

Andersen (1974), Ryding and Forsberg (1977), Theis and McCabe

(1978) show that a substantial amount of phosphorus is released

from the sediment during the summer. It was also found that the

interstitial water may be enriched with phosphorus by a factor

of 5-20 compared to overlying water in the summer (Holdren et

al., 1977). Sometimes the increased release of nutrients from

the sediments during summer is explained by intensive decomposi-

tion of particulate matter, both living and dead (Ryding and

Forsberg, 1977). As Moss (1980) concluded, the sediments in

effect only temporarily store nutrients during the spring and

early summer before the release can begin. Simm (1977) found

that phosphate concentration in the interstitial water was

especially high in winter and early spring, and during these

seasons the phosphate content in interstitial water was from 10

to 30 times higher than in the lake water. However, Serruya

(1977) indicated that Lake Kinneret sediment acted as a phospho-

rus trap, except in winter when it supplied phosphorus to the

upper layers. Ahlgren (1977) found that there was a considerable

net release of phosphorus both in winter and summer and net

deposits occurred only in May, after diatom bloom in Lake Norrviken,

1971. However in 1974-75 there was a net release only during the

summer months.

The "nutrient excess" and mixed layer depth of the sediment are the important characteristics which determine the amount of nutrient available for exchange in the sediment-water interface (Bengtsson, 1978). For example, in Lake Södra Berqundajön, the mixed layer depth is estimated to be equal to be about 20 cm and phosphorus concentration in interstitial water of sediment is about 10 times that of prepollution. It was estimated that the time required for phosphorus concentration in the mixed layer to decrease to prepollution levels is about 20 years.

Information available in literature about the phosphorus-sediment exchange shows that the net flux of phosphorus through this interface or the resultant phosphorus accumulation in and release from sediment has always been measured as positive. This means that accumulation is larger than release (Porcella et al., 1971). As Schindler et al., (1977) have estimated, about 81 percent of phosphorus was deposited in sediment and only 1 percent appeared by resuspension in a water column. In Lake Balaton, about 75-83 percent of total phosphorus entering the lake from the watershed settled into the sediment (Leonov, 1980). Over 80 percent of phosphorus entering Lake Erie is sedimented within the lake basin (International Joint Commission, 1969). In discussion of the water ecological problems, Moss (1980) concluded that in most lakes, the net flux of phosphorus tends strongly toward the sediments.

The ability of sediments to adsorb the phosphorus may be estimated in special experiments (Wildung and Schmidt, 1973; Collins, 1977; Jacobsen, 1977, 1978), and as a rule, on the basis of experiments, the models of phosphorus adsorption by sediments are formulated. Some of the models used for evaluating

sediment phosphorus adsorption are presented in Table 1. As Jacobsen (1977) indicated, values of model parameters may be quite varied for sediments in different lakes. He also found that applying the hyperbola-like Langmuir isotherm (equation 3 in Table 1) gave the best agreement for experiments with oxidized mud, while for reduced mud, the best fit was obtained by the Freundlich isotherm (equation 4 in Table 1). Hwang et al. (1976) noted that adsorption characteristics of lake sediments with various size fractions are significant for both colloidal and noncolloidal fractions and the best adsorption efficiency was obtained at size fractions of 5 to 2 μ. Green et al.(1978) found a positive correlation between total phosphorus of suspended sediment and calcite content of sediment and concluded that calcite contributes to the phosphorus adsorption capacity of suspended sediments.

The study results show that the sediments within a lake are not uniform in respect of phosphorus release as well as in the composition of phosphorus compounds. For example for Lake Constance, Müller and Tiets (1966) found that sediment phosphorus concentrations depend primarily on the mud particle size and increases with clay content. Williams et al. (1971) and Shukla et al. (1971) obtained lower values for phosphate adsorption by calciferous sediments in comparison with noncalciferous muds. Riemann (1977) found considerably horizontal differences in the structure of the sediment and its ability to release and bind phosphate in spite of the phosphorus content (at the various stations) in the upper sediment layer being nearly the same. To a large degree, this is defined by chemical features of sediments and conditions in phosphorus transformations in sediments.

Table 1. Models for Phosphorus Adsorption by Sediments

NN	Equations	Symbols	Reference
1	$X = K \cdot P_o \cdot t^{1/m}$	X is amount of phosphorus adsorbed per unit weight of sediment; P_o is initial phosphorus concentration in water; t is reaction time; K and m are constants.	Kuo and Loste (1974)
2	$X = k \cdot P^n$	P is actual phosphate concentration in water; k and n are constants equal to 0.205 and 0.618 respectively;	Hwang et al. (1976)
3	$X = PSC \cdot \dfrac{P_e}{k' + P_e} - NAP$	P_e is equilibrium phosphate concentration; k' is half-saturation constant; PSC is highest phosphate sorption capacity of sediment;	Jacobsen (1977)
4	$X = K_e \cdot (P_e)^p - NAP$	NAP is native adsorbed phosphate; K_e and p are constants.	
5	$\dfrac{P_e}{X} = \dfrac{1}{X_m \cdot b} + \dfrac{1}{X_m} \cdot P$	X_m is equilibrium capacity of sediments; b is constant related to the energy of adsorption.	Ku et al. (1978) Green et al. (1978)
6	$\dfrac{P_{ads}}{Fe} = 0.298 - 0.0316 \cdot pH + 0.201 \sqrt{[P]}$	Fe is iron concentration in water; P_{ads} is phosphorus concentration adsorbed by sediment	Lijklema and Hieltjes (1979)

In any case, the sediments are intimately involved in the phosphorus cycle of the lakes and it is noted that low reactivity of the phosphate retaining phase of the sediments is a key factor in this cycle, allowing it to operate with reasonable efficiency and minimal loss through the formation of stabile phosphate. The rates of organic phosphorus mineralization is the major limiting factor in this cycle (Webster and Schofield, 1971).

However the situation strongly depends on the type of lake. Schindler et al. (1977) found that almost all phosphorus in the sediment of eutrophic lakes was bound to the particulate fractions. Ulen (1978b) showed that 40 percent of phosphorus in sediment was in the organic P-fraction, 30 percent in the sorbed P-fraction, 15 percent in the apatite P-fraction and 15 percent in stable P-minerals. Porcella et al. (1971) also revealed that almost all sediment phosphorus in eutrophic Lake Huron was organically bound and the cycling of available inorganic phosphorus would be more rapid than organic. Therefore in the eutrophic lake, the mineral phosphorus release from the sediment should be dominant. This fact is confirmed by the experimental results of Banoub (1975) that phosphorus release from the sediment was mostly inorganic. Wildung and Schmidt (1973) also found that algae growth response to the phosphorus release from the sediment was approximately equivalent to the response to orthophosphate.

Webster and Schofield (1971) concluded that sediments in productive lakes were dominantly autochthonous with low contents of Fe and Al and had a low phosphate retention capacity. Phosphate mineralization in eutrophic lake sediments is readily available for phytoplankton because the inorganic phosphate retaining phase is nearly saturated, resulting in the formation of a pool of highly labile phosphate on the sediment surface.

In oligotrophic lake sediments, the rates of organic phosphorus mineralization is low and partly inhibited by low substrate availability (Webster and Schofield, 1971). This fact may be attributed to the high retention capacity of an iron dominated retaining phase in the sediment.

Some of the information available in literature on the rates of phosphorus release from sediments is summarized in Table 2. The rates presented in Table 2 were estimated by methods of analysis of phosphorus balance in water bodies on the basis of field studies as well as analysis of conditions in the phosphorus release in special laboratory experiments with sediment cores and muds. However as Riemann (1977) indicated, the rates of phosphorus release from sediments calculated on the basis of mass balance considerations are considerably in excess of those obtained in laboratory experiments. He assumed that differences in these rates may be due to the constant movements of the upper sediment layer, accelerating the nutrient release from sediment, as well as by anaerobic conditions at the sediment surface. The gross fluxes of nutrients across the sediment-water interface are estimated in practice by multiplying the maximum nutrient gradients by the diffusion coefficients. Ulen (1978b) estimated the phosphorus release rates from the sediments by three different methods: (i) on the basis of diffusion laws; (ii) from laboratory experiments and (iii) from net phosphorus increase in the hypolimnion during stagnant conditions. He obtained the following values of rates: 7, 3.6-4.7 and 7.9-9.3 mgP/m^2-day respectively and concluded that the first two methods probably gave low estimates, because the effects of some important processes on phosphorus cycling was not taken into account in these calculations, while the third method gave the upper limit of phosphorus release rates.

Table 2. Review of Phosphorus Release Rates from Sediments

NN	Phosphorus release rates	Oxic conditions	Temperature or season	Reference
1	9.7 mgP/m^2-day	anaerobic	-	Vollenweider(1968)
2	3.0 mgP/m^2-day	aerobic	-	Fillos and Molof(1970)
	30.0 - " - " -	anaerobic	-	
3	0.11-0.73 mg DIP/m^2-day	-	-	Porcella et al(1971)
	7.3-49.0 mg TP/m^2-day	-	-	
	0.1 mg POP/m^2-day	-	-	
4	0.27 mgP/m^2-day	-	-	Stumm and Leckie(1971)
5	0.22·10^{-4} molP/m^2-day	aerobic	Winter	Burns and Ross(1972)
	0.24·10^{-3} -.",- " -	anaerobic	Summer	
6	0.597-1.22 mgP/g-hour	aerobic	-	Armstrong et al(1972)
	1.43-3.02 - " - " -	anaerobic	-	
7	4.0 mgP/m^2-day	anaerobic	-	Welch and Spyridakis(1972)
8	1.2 gP/m^2-month	aerobic	-	Andersen(1974)
	0.1-0.75 mgP/l-month	- " - " -	-	
	2.5-8.0 mgP/m^2-day	- " - " -	-	
9	17.3 ± 4.6 mgP/m^2-day	anaerobic	-	Kamp-Nielsen(1974)
	12.3 ± 3.6 - " - " -	- " - " -	-	
	1.2 ± 0.2 - " - " -	- " - " -	-	
	0.8 ± 0.2 - " - " -	- " ,- " -	-	
10	8.0-10.0 mgP/m^2-day	anaerobic	Summer	Zonzogni(1974)
11	0.0008-0.01 mgP/l-day	-	-	Shidharan and Lee(1974)
12	0.8 mgP/m^2-day	aerobic	-	Serruya et al(1974)
13	16.1-16.2 mg DIP/m^2-day	-	-	Kamp-Nielsen(1975)
14	1.0-16.0 mgP/m^2-day	anaerobic	-	Jørgensen et al(1975)
15	0 - 50.0 μg-atP/m^2-hour	-	-	Nixon et al(1975)
16	0.27 mgP/m^2-day	aerobic	-	Bannerman et al(1975)
17	1.2 mgP/m^2-day	anaerobic	4	Banoub(1975)
	2.2 - " - " -	- " - " -	10	
	3.5 - " - " -	- " - " -	15	
	9.4 - " - " -	- " - " -	25	
18	1.2 mgP/m^2-day	aerobic	-	Fillos and Swanson(1975)
	26.0 - " - " -	anaerobic	-	
19	22.0-49.0 mgP/m^2-day	-	8	Bengtsson(1975)
20	3.0 mgP/m^2-day	anaerobic	20	Fillos and Biswas(1976)
21	9.0-47.0 mgP/m^2-day	aerobic	-	Ryding and Forsberg(1976)
22	0.65 mgP/m^2-day	-	-	Neame(1976)
23	3.0 mgP/m^2-day	anaerobic	-	Fillos(1976)
24	13.0 mgP/m^2-day	-	-	Burns(1976)

. . . .

Table 2.   (contd..)

NN	Phosphorus release rates	Oxic conditions	Temperature or season	References
25	0.02 mgP/1-day	-	Spring	Lung et al(1976)
	0.08-0.12 - " - " -	-	Summer	
	0.02-0.05 - " - " -	-	Autumn	
26	2.8-7.1 mgP/m^2-day	-	-	Ahlgren(1977)
27	20.0-440.0 gP/m^2-hour	aerobic	-	Poon(1977)
28	25.1 mg DIP/m^2-day	-	-	Freedman and Canale(1977)
	38.0 mg TP/m^2-day	-	-	
29	2.9 mgP/m^2-day	-	Summer	Holdren et al(1977)
	1.3 - " - " -	-	Winter	
30	10.4 mgP/m^2-day	-	-	Rippey(1977)
31	14.0-38.0 mgP/m^2-day	-	-	Stevens and Gibson(1977)
32	4.5-8.6 mgP/m^2-day(in experi- ments)	-	Summer	Rieman(1977)
	9.0-15.0 - " - " -(by balance calculations)	-	Summer	
33	4.0-10.8 mgP/m^2-day	anaerobic	-	Zonzogni et al(1977)
34	10.0-20.0 mgP/m^2-day	aerobic	11-19(Autumn)	Theis and McCabe(1978)
	10.0-80.0 - " - " -	anaerobic	6-23(Summer)	
35	68.0 mgP/m^2-day	-	Autumn	Ulen(1978a)
36	1.7-3.0 mgP/m^2-day	aerobic	4	Ulen(1978b)
	3.0-4.6 - " - " -	anaerobic	- " -	
	2.4-6.7 - " - " -	aerobic	10	
	4.0-7.3	anaerobic	- " -	
37	1.5 gP/m^2-year	-	-	Bengtsson(1978)
38	5.0-138.0 mgP/m^2-day	-	-	Chiaro and Burke(1980)

However, it may be noted that the calculated rates of phosphorus release from sediment obtained by Ulen (1978b) have the same order of magnitude and he used them for estimating the importance of the sediments as an external source in the nutrient loading of Lake Norrviken.

3. EFFECTS OF ENVIRONMENTAL FACTORS AND PHYSICAL-CHEMICAL AND BIOLOGICAL PROCESSES ON PHOSPHORUS EXCHANGE IN THE SEDIMENT-WATER INTERFACE

Sediments have the ability to support certain levels of phosphate in the water. This fact may be important in the phosphorus cycle in water bodies (Kuffel, 1977). The degree of sediment influence on the water through the release rate is recognized as a complicated function of physical, chemical and biological processes which interact with each other (Fillos and Swanson, 1975). Moss (1980) noted that the reason for substances becoming trapped in sediment is largely both physical and chemical and the importance of sediment chemistry is apparent in exchange processes in the sediment-water interface. Sridharan and Lee (1974) suggested that the release rate of phosphorus is the result of chemical reactions and this process is most likely abiotic. Golterman (1977) concluded that potential availability of sediment phosphorus in lakes will strongly depend on the hydrodynamic processes. The release rate is considered to be dependent on mechanisms which lead to solubilization of phosphorus (decomposition, anaerobic condition) or benthic uptake and transport from the sediment (Porcella et al. 1971).

As Moore and Silver (1972) concluded, one weakness of the existing literature on phosphorus transformation and exchange in the sediment-water interface is a failure to carefully consider the individual and combined effects of a variety of parameters

that might influence the mechanisms. Because the identification
of the active mechanisms in the regulation of nutrient release
from the sediment by budget calculation is not possible (Ryding
and Forsberg, 1977), in the given study it is assumed to be
useful to analyze the available information on factors that
regulate the exchange processes in the sediment-water interface.
The effects of some physical factors (such as mixing, diffusion
and temperature) and chemical factors (such as oxygen and organic
matter levels, oxidative state of sediment, pH and redox condi-
tions) and biological factors (such as bacterial activity) on the
process of phosphorus release from the sediment is discussed in
this section of the report based on data available from literature.
These factors are considered to be the most important in under-
standing and explaining the conditions and trends in the phos-
phorus cycle and the transformation of phosphorus compounds in
water bodies. It is also assumed that information presented in
this section may be useful for the formulation of certain
approaches to the simulation of phosphorus transformation in
water quality models considering the eutrophication and phosphorus
transformations in water environments.

3.1 Mixing

It is recognized that mixing by various physical processes
such as wind and wave action, currents, ebullition of gas, etc., is
one of the most important factors in the regulation of phosphorus
exchange in the sediment-water interface (Lee, 1970). Yousef
et al. (1981) estimated changes in phosphorus concentrations due
to the mixing caused by motorboats in shallow lakes. They found
that maximum phosphorus increase occurred in the shallowest lake

and the effect of mixing showed an increase in phosphorus content for lakes Clair (average depth 2.3 m), Mizell (4 m), and Jessup (1.8 m) varying from 39-43 percent, 16-28 percent and 59-73 percent respectively. The authors also estimated the amount of orthophosphate resuspended due to mixing in the same lakes to be equal to 46, 24 and 105 mgP/m^2 of the bottom sediments and these phosphorus amounts averaged 55, 41 and 42 percent of total phosphorus in similar lakes.

When the water-sediment system is completely mixed, relatively rapid release of phosphorus from sediment occurs in both aerobic and anaerobic conditions. Kramer et al. (1972) indicated that the degree of mixing and disturbance of sediment surface by agitation influenced the phosphorus exchange between sediment and water. Zicker et al. (1956) have shown that phosphorus release from sediment under dynamic or mixed conditions was almost twice the release under static conditions. Bates and Neafus (1980) indicated that mixing in all experimentally studied cases enhanced phosphorus release from the sediments. Rippey (1977) also found that the phosphorus release rate was sensitive to the stirring.

Under static conditions a slow release rate of phosphorus was observed (Lee, 1973). It is noted that the phosphate release was retarded when bottom water enriched by phosphate was not exchanged by hydrodynamic movements (Hallberg et al. 1976). The intensity at which the mixing redistributes the sedimented phosphorus in overlying water is more significant for shallow lakes and reservoirs. Porcella et al. (1971) indicated that nutrient cycling in shallow lakes is accelerated by mixing because of

greater effects on the bottom sediments due to wind, wave and current actions (Williams and Mayer, 1972). In western Lake Erie the top layer 5 to 7.5 cm of sediment was well mixed by wave action and currents (Skoch and Britt, 1969). Serruya (1977) found that the turbulent mixing of sediment was a mechanism explaining the increase of the total phosphorus storage of Lake Kinneret water in December-January.

Resuspension of particulate matter that defines the rates of phosphorus accumulation in the sediments (Ahlgren, 1977) is strongly stimulated by wind and this may accelerate the nutrient exchange and it is especially expressed in shallow water bodies (Andersen, 1974; Kamp-Nielsen, 1975b). Moss (1980) noted that in lakes, where turbulent mixing induced on the surface by wind is least, the sediment becomes dense and its effects on nutrient regulation in the lake water is not significant.

3.2 Diffusion

Diffusion is also one of the mechanisms of nutrient release from the sediment. It is the result of differences in concentrations of phosphorus in overlying and interstitial sediment water (Williams and Mayer, 1972). Lee (1970) and Wood (1975) noted that the effect of diffusion on exchange processes is smaller than the effect of mixing. However many authors found that processes of phosphorus release from sediment have been well correlated with gradients between phosphorus concentrations in interstitial water and overlying water and that these processes are diffusion controlled reactions (Mortimer, 1971; Stumm and Leckie, 1971; DiGiano, 1971; Fillos and Biswas, 1976). Ulen (1978b) indicated that the relationship between sediment

phosphorus release and the corresponding phosphorus gradients
was nonlinear. Viner (1977) suggested that the sediment contribu-
tion of nutrients was limited by the diffusion in tropical lakes.
Wildung and Schmidt (1973) and Kamp-Nielsen (1974, 1975b) con-
cluded that release rate is a function of phosphorus content in
the sediment and interstitial water and that the low phosphorus
content in overlying water stimulates the phosphorus release
from the sediment. Rippey (1977) found that the process of
phosphorus release from the sediment was sensitive to the super-
natant phosphorus concentration. The diffusion transfer of
phosphorus will be much influenced by its capacity to be
adsorbed (Gupta and Greenkorn, 1974).

Fleischer (1978) assumed that phosphorus transport from
interstitial water to overlying water seems to be a physical
process (diffusion or turbulence) controlled by earlier biological
processes. Hecky (1977) noted that diffusion of nutrients from
the sediment was maximized by high porosity of sediment, 90 percent
and high annual temperature $20^{o}C$ in the small Momela Lake. Viner
(1977) found that the effective diffusion gradients were actually
within the sediment and not at the undisturbed sediment-water
interface.

3.3 Temperature

The effect of temperature on the intensity of phosphorus
release from sediment to overlying water was studied by many
authors. The highest phosphorus release rates occurred when
water temperature near the bottom reached a maximum value (Theis
and McCabe, 1978). Similar trends have been reported by Schippel
et al. (1973), Wildung and Schmidt (1973), Andersen (1974),
Kamp-Nielsen (1975b), Banoub (1977), Holdren et al. (1977),

Ulen (1978b), Ku et al. (1978). This factor may partly explain the highest phosphorus release rates in summer months that is often observed in water bodies (Gahler, 1969; Ryding and Forsberg, 1977). Lee et al. (1977) noted that the rate of phosphorus release from sediment was markedly affected by temperature under oxic and anoxic conditions. In experimental studies of phosphorus release from sediments, Riemann (1977) found no significant differences in rates at 5°C and 15°C. According to Banoub (1975) and Kamp-Nielsen (1974) the sharp increase in the phosphorus release from sediment was observed at temperatures higher than 15°C.

The explanation for the temperature influence on the phosphorus release is that temperature has an indisputable influence on microbiological activity (Andersen, 1974). It can suppress the redox potential and stimulate greater dissolution of phosphorus from solid to solution (Theis and McCabe, 1978). Holdren et al. (1977) concluded that increasing the temperature will increase the rate of electron transfer from the organic carbon to oxygen and other electron acceptors resulting in the reduction of Fe^{+++} to Fe^{++} with concurrent releases of phosphorus from interstitial water of sediment.

As Wildung and Schmidt (1973) concluded, temperature alone cannot explain the variations in sediment phosphorus release but rather appeared to play an indirect role in influencing biological growth.

It is noted that temperature dependence of phosphorus release from the sediment may be described by exponential temperature function (Kamp-Nielsen, 1975b; Jacobsen and Jørgensen, 1975; Jørgensen et al. 1975; Kremer and Nixon, 1975).

The classical Arrenius equation was applied by Ku et al. (1978) for a description of temperature influence on the equilibrium between phosphorus contents in sediments and overlying water. The exponential temperature dependence was also obtained for nitrogen (Nixon et al. 1975) and silica (Andersen, 1974; Rippey, 1977) release from the sediments.

3.4 Oxygen

The oxygen level is considered to be important in the regulation of the phosphorus release from the sediment to overlying water (Fillos and Swanson, 1975). As Fillos and Molof (1970) experimentally showed, the rate of phosphorus release from the sediment increases with decreasing oxygen content in the surrounding water. A similar tendency was observed by Kuffel (1976), Banoub (1977), Stevens and Gibson (1977).

As oxygen in bottom water decreased from 7.6 to 2.9 mgO_2/ℓ the buffering level of phosphate increased from 0.1 $mgPO_4/\ell$ to about 0.75 mg PO_4/ℓ; in other lakes where oxygen depletion was observed the buffering level was considerably higher (Kuffel, 1976). The critical oxygen content in sediment is considered to be equal to 2 mgO_2/ℓ; the oxygen uptake in sediment above this level is independent of the oxygen concentration. Therefore the content of 2 mg O_2/ℓ may also be considered as a critical level for the phosphorus release from the sediment (Fillos, 1977). Stevens and Gibson (1977) found that phosphorus was being released from the sediment when the dissolved oxygen concentration in the water just above the sediment was apparently 50 percent saturated. Mortimer (1971) indicated that transfer of nutrients from the sediments may be expected when oxygen concentrations near the bottom are below 20 percent saturation.

In lakes which are too shallow for stratification the surface of the sediment may become anaerobic in summer if sufficient sedimentory organic matter is provided for rapid decomposition at higher summer temperatures (Moss, 1980). Because the oxygen is regulated by many processes, physical, chemical and biological, the factors defining the sediment oxygen levels should be of major importance in determining the observed interstitial phosphorus level. Among these factors, mixing and diffusion are considered to be the major factors controlling the oxygen transfer to sediment (Holdren et al. 1977).

As Table 1 shows the release of phosphorus from the sediments takes place in anaerobic as well as aerobic condition in overlying water. Bates and Neafus (1980) showed that aerobic phosphorus release began much later in the experimental period than the anaerobic release and lower values were obtained for the aerobic system in comparison with corresponding anaerobic units. Stevens and Gibson (1977) found that the phosphorus release occurred when the water overlying the sediment was oxygen depleted but not anoxic. Sridharan and Lee (1974) and Lee et al. (1977) noted that the release of phosphorus under anoxic conditions was higher in many respects than that found in oxic release. The data in Table 1 confirms this conclusion.

Lee et al. (1977) also showed that phosphorus release under oxic conditions over extended periods of time was equal to that obtained under anoxic conditions. They suggested that oxic release of phosphorus was primarily related to mineralization of organic matter and it plays a much more important role in lake self-purification than generally thought.

3.5 Oxidative State of the Sediment

Oxygen conditions define the oxidative state of the sediment influencing the release rate of phosphorus. The aerobic layer of the sediment possesses a certain capacity to adsorb the nutrients including phosphorus from overlying water (Fillos, 1977). It is noted that phosphorus adsorption by oxidized sediment is larger than by reduced sediments (Golterman, 1975). It was found that in the reduced state, the sediments showed a release of phosphorus only when the phosphorus content in the surrounding water was below the relatively high value equal to 2 mg/ℓ (Golterman, 1973b). The aerobic layer may not be more than a few millimeters deep. Therefore the changes in oxygen content in the bottom water will seriously affect the phosphorus release conditions in the sediment-water interface. The aerobic oxidized layer of sediment is considered a diffusion barrier (Mortimer, 1942; Lee, 1970) and this layer quickly disappears when oxygen in overlying water is reduced to zero. During summer when the temperature is high the oxidized sediment layer is broken down and as a rule completely disappears. As a result of its disturbance, the molecular diffusion or turbulent dispersion of the nutrients from sediments to overlying water may become effective (Serruya et al. 1974; Kamp-Nielsen, 1975b). As Golterman (1975) concluded, the reduction condition in the sediment-water interface stimulates the phosphorus release from the sediment. A similar tendency was observed by Schippel et al. (1973). Fillos (1977) also found that in anaerobic conditions the destruction of the nutrient adsorption capacity of the sediment and increased nutrient release from sediment takes place.

Kamp-Nielsen (1975b) noted that the gradual breakdown or perforation of the oxidized sediment layer can explain the exponential temperature relationship and a gradual transition from adsorption to diffusion as dominating processes of nutrient exchange in the sediment-water interface.

An oxidized sediment layer is often found in non-stratified lakes with high oxygen content (Andersen, 1974). It is noted that in these lakes the oxidized zone of sediment may be broken when the oxygen consumption of sedimented material is larger than the oxygen transfer to the sediment from the overlying water (Gorham, 1958). Oxygen consumption affecting the oxidative state of the sediment, changes with the supply of available organic matter, bacterial activity and temperature (Holdren et al. 1977).

Release of the substances of which the solubility is in part determined by the oxidative state of the Fe, Mn, PO_4 and others in sediment, occurs when the overlying water becomes depleted of oxygen though not necessarily completely anaerobic (Moss, 1980). Holdren et al. (1977) concluded that phosphorus content in interstitial water should be controlled largely by the oxidative state of sediment iron which is a function of the relative availability of electron donors (primarily organic C) and alternative electron acceptors, such as oxygen, in the sediment. They noted that the level of interstitial phosphorus should increase when sediment oxygen becomes depleted and Fe^{+++} becomes reduced. Rippey (1977) found that phosphorus release from the sediment in the eutrophic Lake Lough Neagh had been in association with ferric oxides rather than with calcium carbonate. Nriagu and Dell (1974) found that phosphorus regenerated under

anoxic conditions in Lake Erie sediments was associated with non-apatite inorganic phosphorus fractions.

In fertilized shallow lakes with a heavy nutrient load the sedimented organic material reaches the bottom surface in a relatively labile state because of the shallowness of the water column. The intensive decomposition at the sediment surface then not only breaks down the oxidized sediment layer but may reduce the redox potential. When this happens Fe^{++} is precipitated and nutrients, including phosphate, are excreted into the overlying water even in oxygenated waters. This mechanism of phosphorus release from the sediment is typical for summer periods in shallow lakes, when there is an intensive supply of labile organic matter to the sediment surface and it occurs when large external phosphorus supplies exist (Moss, 1980).

Sometimes the compositon of minerals in the oxidized layer of sediment is considered a factor regulating the nutrient exchange in the sediment-water interface. Stumm (1964) had suggested that hydroapatite is a mineral that controls the orthophosphate contents in lakes resulting in concentrations of 0.03 mg P/ℓ at the equilibrium. In analyzing the factors affecting the transfer of nutrients from the sediment, Lee (1970) assumed that the kinetics of hydroapatite formation in sediment controls the phosphorus release because the phosphorus concentration in many lakes is more than 0.03 mg P/ℓ. However Porcella et al. (1971) concluded that this may only be applicable not to eutrophic lakes but only to oligotrophic lakes, where concentrations of phosphorus compounds change seasonally, decrease in phytoplankton blooms and increase only after blooms, as a result of phosphorus turnover and cycling by chemical-biological transformations.

3.6 Redox and pH Conditions

The oxidative state of the sediment may be characterized by pH and redox potential. The influence of these state variables on the phosphorus release from the sediment were studied by many authors. Andersen (1974) found that release of phosphorus from the sediment is a result of increase in pH and change in redox conditions. This is confirmed by results obtained by Kramer et al. (1972), Kamp-Nielsen (1974), and Ku et al. (1978). The change in pH may shift an equilibrium concentration of compounds in the sediment-water interface. Andersen (1974) obtained the increasing phosphorus release rate from 20 to 100 mg P/m^2-day at increasing pH from 8 to 9.5, but this rate was rapidly decreased at the further pH increase from 9.5 to 11.0. He assumed that the general influence of pH on the phosphorus release can be released at high pH as a result of changes of surface charge of colloids and clay particles and when pH values are larger than 9.0 the dissolution of $A\ell(OH_3)$ as $A\ell(OH_4)^-$ occurs.

When phosphate phosphorus is present in sediments in sorbed and bounded states with Ca, Fe and $A\ell$ it has a high sorption ability. Golterman (1973b) indicated the ability of phosphorus anions to be sorbed into clays, organic particulates, Fe and $A\ell$ hydrooxides as well as calcium carbonate. Figure 1 shows the change of phosphorus adsorption by clays as a function of pH (Edzwald, 1977). The maximum adsorption of phosphate by kaolinite and illite is observed at pH varying between 4 and 5. Ku et al. (1978) and Kuffel (1976) studied the phosphorus adsorption in the eutrophic lake sediments in the range of pH 4.8-7.0 and they also found the most active phosphate sorption at the lowest pH.
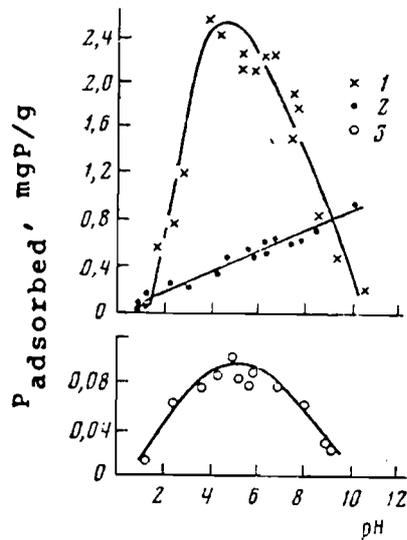
Figure 1. Phosphorus Adsorption by Clays as a Function
of pH after Edzwald (1977)
1 - illite; 2 - montmorillonite; 3 - kaolinite

During the adsorption of phosphate by clays, the interactions
of phosphate with metal ions on the clay surfaces is quite impor-
tant. This fact explains the different character of phosphate
adsorption which is dependent on pH for kaolinite, illite and
montmorillonite as shown in Figure 1. Stumm and Leckie (1971)
indicated that adsorption of phosphate to clays, as well as the
solubility of some minerals such as $A\ell PO_4$ (variscite), $FePO_4$
(strengite) and $Ca_{10}(PO_4)_6(OH)_2$ (hydroapatite) determine the
heterogeneous equilibrium in phosphate concentrations in the
aqueous phase and solid phase in sediments. According to
Figure 2, showing the solubility of phosphate relations in solid
phases (Stumm and Leckie, 1971), the concentration of phosphate
in the aqueous phase is mainly determined by the solubility of
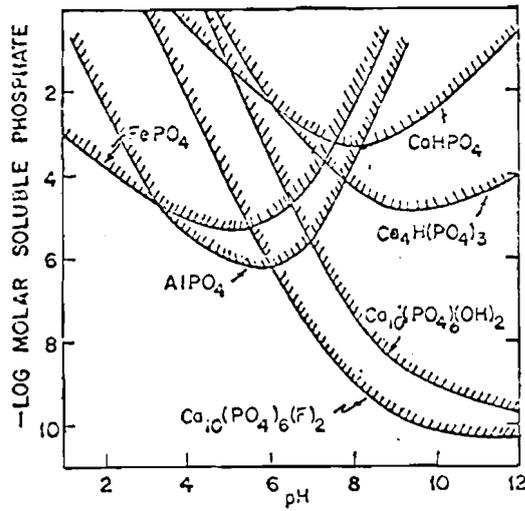
Figure 2. Diagram of Solubility for Solid Phosphate
Phases after Stumm and Leckie (1971)

phosphate relations with iron until pH is about 6.0, while at

pH higher than 6.0 it will depend on the solubility of phosphate

relations with calcium. Hepher (1958) presented a graph for the

calculation of the amounts of phosphate and calcium existing

together in the solution at various pH values. Figure 3 illus-

trates the relationship between the negative logarithm of the

calcium concentration, pCa, at saturation against pH in the

ternary system Ca $(OH)_2$-H_3PO_4-H_2O at 25°C (Brown, 1973). Using

this plot, the relative solubility of the salts at a given pH

may be found. Thus Figure 3 shows that $CaHPO_4 \cdot 2\ H_2O$ is more

stable than $Ca_5(PO_4)_3OH$ at pH lower than 4.3. The broken ver-

tical lines in Figure 3 define the pH values for various singular

points in the ternary system (Brown, 1973). The influence of
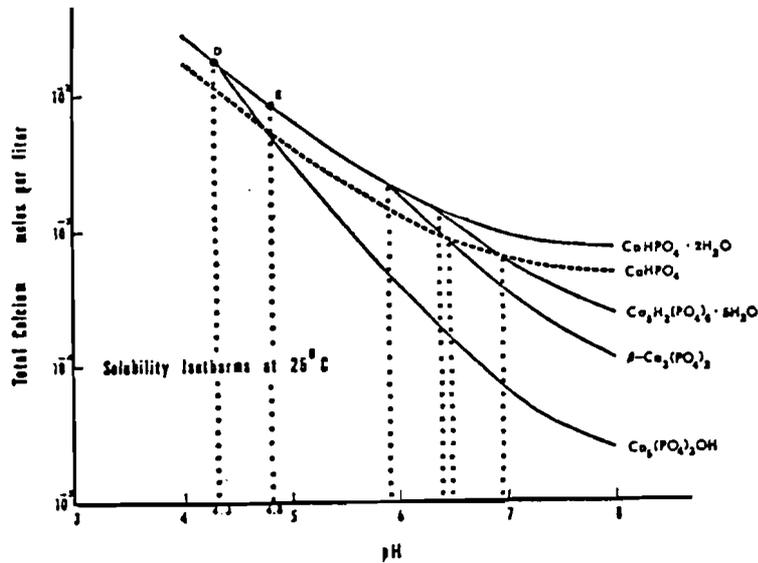
Figure 3.   Relationship between Calcium Concentration and pH
            Values of Solutions saturated with respect to
            Various Calcium Phosphates in the Ternary System
            $Ca(OH)_2$-H_3PO_4-H_2O at 25oC (after Brown, 1973)

Ca content and pH values on the behavior of the Ca-CO_3-PO_4 system

is discussed by Golterman (1973b). As Brown (1973) and Morse

and Berner (1979) showed, the mechanisms for solubility of the

calcium phosphates may be explained by physical-chemical laws.

Rippey (1977) found the experimental dependence between the

phosphorus release rate and pH in the range of pH 7.9-9.0. He

suggested that the increase of the phosphorus release rate with

pH depending on iron- or clay-bound P, rather than Ca-P, con-

trols the phosphorus solubility. The phosphorus solubility

minimum is between pH 5 and 8 increasing above and below this

pH range (Rippey, 1977). Helfrish and Kevern (1973) found that

at pH 8.0 and higher, the phosphate precipitation was enhanced

and the release into the water of two orthophosphates, H_2PO_4

and HPO_4, occurred at pH < 6.5. Stabel and Münster (1977) obtained the influence of pH on the composition of interstitial soluble organic matter and found that the amount of organic matter released was closely correlated with increasing pH in a range of 7.4-10.3. Lee et al. (1977) maintain that changing the pH from 8 to 7 had no effect on the orthophosphate concentration in solution but that it affected the concentration of iron present in the solution. Gumerman (1970) obtained a maximum phosphorus release from sediment within the pH range 4.5 to 5.5 and it was relatively constant in the pH range from 6.5 to 9.0. Macpherson et al. (1958) found the maximum release of phosphate by sediment in the pH range 5 to 7.

Lijklema (1977) concluded that pH in overlying water may regulate the binding capacity of the oxygenated sediment layer while the rate of photosynthesis, alkalinity, water depth and carbon dioxide exchange rate at the surface control the pH in overlying water. It is noted also that the temperature and temperature dependent biological and chemical processes have a considerable effect on the phosphate content in interstitial water and therefore on sediment phosphorus release through their effect on redox conditions in the sediment (Holdren et al. 1977).

3.7 Bacterial Activity

The sediment-water interface is important as potential nutrient sources or as sites of potential accumulation of nutrients or for the permanent lodging of microorganisms (Marshall, 1978), therefore bacterial activity is also considered one of the possible factors which regulate the nutrient exchange between sediment and water. Paerl (1977) noted that many studies have revealed an

interaction between suspended sediments and bacteria in a variety of lakes. The role of the bacteria is to decompose the organic matter coming from the production in the upper water layers which in turn depend on the maintenance of pools of necessary nutrients by external loading (Moss, 1980).

Collins (1977) concluded that the types and counts of bacteria in the surface of sediments and in the depth of the sediments may be a reflection of the availability of organic matter supplied from the decomposition of algae for utilization of bacteria. Therefore the bacteria are responsible for mineralization and for putting the inorganic compounds back into circulation (Petr, 1977). It is noted that in eutrophic lakes the biological transformation of compounds within sediments is probably most important in the regulation of nutrient transfer between sediment and overlying water (Porcella et al. 1971; Petr, 1977).

The importance of biological processes in sediment was confirmed by special experiments (Hallberg et al. 1973, 1976). Bates and Neafus (1980) indicated in an experimental study that phosphorus release from non-sterile sediment was more than twice the release obtained from the sterile system. Rodel et al.(1977) experimentally found that sediment microorganisms are responsible for the hydrolysis of organic phosphorus in sediment. However, Fillos (1977) in studies on the effect of bacterial activity on the release rate of phosphorus from sediment found that bacterial activity played a small role in nutrient release from the sediment and that this process was probably governed by desorption. Kuffel (1977) concluded that microorganisms do not influence the exchange process directly but they may affect the rate of exchange processes by regulating pH and redox potential.

It is obviously that bacterial activity may greatly depend
on environmental factors such as temperature and nutrient con-
centration in sediment. Boylen and Brock (1973) found that
rates of bacterial metabolism in Lake Wingra sediments at 4^oC
was about fivefold lower than at 25^oC, and that heterotrophic
bacteria do not adopt to the low temperature $(1-1.5^oC)$ which
prevails during winter. Kamp-Nielsen (1975b) noted the sig-
nificant role of biological degradation in phosphorus release
in the sediment-water interface in Lake Esrøm when the bottom
temperature was high. Holdren et al. (1977) showed the dependence
of bacterial activity on temperature and available organic matter.

Collins (1977) found that there was a tendency toward
higher bacterial counts on the surface of the sediment and in
the sediment-water interface at the initial stage of stratifica-
tion in a number of lakes. He assumed that the high bacterial
counts in the sediment-water interface, obtained for the shallow
eutrophic lake Estwaiter Water during winter and spring, may
well be a reflection of the type and quantity of particulate
matter circulating within the lake. The high bacterial counts
found during summer and autumn in the sediment surface of
Bassenthwaite Lake, that is about 5.3 m deep, may be due to
considerable turbulence and resuspension of surface sediment
material by wind action (Collins, 1977).

3.8 Organic Matter

A number of studies show that the phosphorus release from
the sediment is stimulated by the content of organic matter
(Wildung et al. 1977; Hallberg et al. 1973; Banoub, 1977). In

all lakes any release of oxidative sensitive substances from the sediment is dependent on a ready supply of easily decomposable organic matter to the sediment surface where bacteria can decompose it (Moss, 1980). The decomposition of sedimented material increases the concentration of the available organic matter (Holdren et al. 1977). This may explain the increased release of phosphorus during summer when the temperature of surface sediment is high and decomposition of sedimented material on the bottom surface is rapid (Andersen, 1974). Intensive decomposition of organic matter on the sediment-water interface also explains the formation of anaerobic conditions on the bottom layers of lakes during summer (Kamp-Nielsen, 1974).

This fact is especially important in the disturbance of the oxidative zone of sediments that have an influence on the change of regulation mechanisms in phosphorus exchange from adsorption to diffusion at the anaerobic condition in sediment-water interface. Porcella et al. (1970) assumed that the possible effect of organic materials would be to increase the phosphorus release from sediments by serving as a substrate for anaerobic bacteria which in turn would cause a lowering of sediment pH and increased solubilization of phosphates.

Williams and Mayer (1972) suggested that mineralization of organic phosphorus in sediment is one way by which soluble orthophosphate may be released into interstitial water. Lee et al. (1977) noted that this process can especially explain the phosphorus release under oxic conditions. This fact was experimentally confirmed by Bates and Neafus (1980).

The trend and rate of organic matter mineralization in bottom sediments depend on the character and depth of the water body. Physical-chemical conditions of the overlying water and in sediment have a significant influence on the mineralization of organic matter in sediments (Petr, 1977). This agrees with results presented by Hargrave and Kamp-Nielsen (1977).

In tropical lakes, Viner (1977) found that the decomposition of organic substances was inefficient. Hargrave and Kamp-Nielsen (1977) suggested that differences in the organic content of sediments along steep bottom gradients can often be related to erosional features caused by water circulation and may reflect the origin of sedimented material. Stabel and Münster (1977) concluded that the different composition of interstitial dissolved organic matter is due to the variety of lake sediments and lake metabolisms.

3.9 Other Factors

In the literature it is possible to come across some of the other factors mentioned, which influence the rate of phosphorus release from the sediments. Manheim (1970) concluded that the rate of phosphorus release from the interstitial water of sediment is defined by the porosity of the mud. This fact is also mentioned by Williams and Mayer (1972) and Lerman (1977). It is obvious that also other physical properties of sediments such as sediment density, partial volumes of liquid and solids in sediments, may be considered rather important in regulating the nutrient fluxes across the sediment-water interface (Robbins, 1980).

In the kinetic study of phosphorus exchange through the sediment-water interface, Hayes et al. (1952) suggested that the rapid equilibrium of phosphorus content in overlying water and in sediment in shallow lakes is due to the relatively large sediment surface to lake volume ratio. The role of benthic fauna as one of the factors is also considered important in circulating nutrients from the sediment to the water (Petr, 1977; Neame, 1977). The study results of Davis et al. (1975) gave an indication of the role of Chiromomids and Oligochets in the nutrient release from sediments. Ulen (1978b) assumed that gas convection is the main mechanisms for the nutrient release from the sediment. Kuo and Lotse (1974) found that the phosphorus release from sediment was dependent on the anionic species present in solution.

4. PHOSPHORUS TRANSFORMATION IN SEDIMENT

Processes of phosphorus transformations in sediment have a significant effect on the dynamics of phosphorus exchange in the sediment-water interface. On the basis of the kinetic factors Williams and Mayer (1972) distinguished the two major stages in the phosphorus regeneration responsible for the phosphorus release from the Great Lakes sediments. The first one is related to the transformation of sedimented material into soluble phosphorus in the sediment-water interface without incorporation of the sedimented material into the core of the sediment column. Actually this process is the decomposition of sedimented detritus or algae remains. According to Burns and Ross (1972), about 25 percent of phosphorus may be excreted during the few months to the overlying water by decomposition of the algae remains, while the other part is retained by the sediments.

The second stage of phosphorus regeneration is the result of diagenetic processes within the sediment. A hypothetical scheme of phosphorus transformations in sediment according to Williams and Mayer (1972), is presented in Figure 4. They concluded that apatite is a major phosphorus form in the sediments and other phosphorus forms in sediment are ultimately transformed into apatite under the dominating environmental conditions.

The concentration of orthophosphate in interstitial water is defined by the mineralization of organic phosphorus, which is a slow process and the release of sorbed phosphate by chemical reactions. The phosphate concentration may also be reduced by the precipitation of apatite. Williams and Mayer (1972) noted that kinetic factors regulate the rate of phosphorus transformations in sediments.

The phosphate exchange in the sediment-water interface is strongly influenced by the chemistry of iron-phosphorus and calcium-phosphorus compounds. The solubility of these compounds depends on the redox potential and pH (Golterman, 1960). Lijklema (1977) indicated that solubility of iron and phosphate in the sediment will be increased by reducing conditions. Golterman (1960) proposed that phosphate may precipitate in the form of iron or calcium phosphate if its presence exceeds the solubility products of these compounds.

Some of the features of iron-phosphate interactions in stagnant water is presented in Figure 5 (Lijklema, 1977). Rippey (1977) found that the sediments exhibit the same pH behavior as the iron-phosphorus system (or the basic ferric phosphate). Nriagu and Dell (1974) noted that the basic ferric phosphate undergoes acid and basic hydrolysis at the lower and higher pH respectively.

```
┌─────────────────────────────────────┐
│ movement of orthophosphate(and      │
│ organic P) up sediment column       │
└─────────────────────────────────────┘
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┌──────────────────┐     ┌──────────────────────┐          ┌──────────────┐
│ orthophosphate   │     │ soluble orthophosphate│          │ apatite      │
│ sorbed onto      │ ──► │ in interstitial water │ ───────► │              │
│ solid phase      │     │                      │          └──────────────┘
└──────────────────┘     └──────────────────────┘

      (?)                    (?)         (?)

┌──────────────────┐     ┌──────────────────────┐
│ organic P in     │     │ soluble organic P    │
│ solid phase      │─ ─► │ compounds in interstitial│
└──────────────────┘ (?) │ water                │
                         └──────────────────────┘
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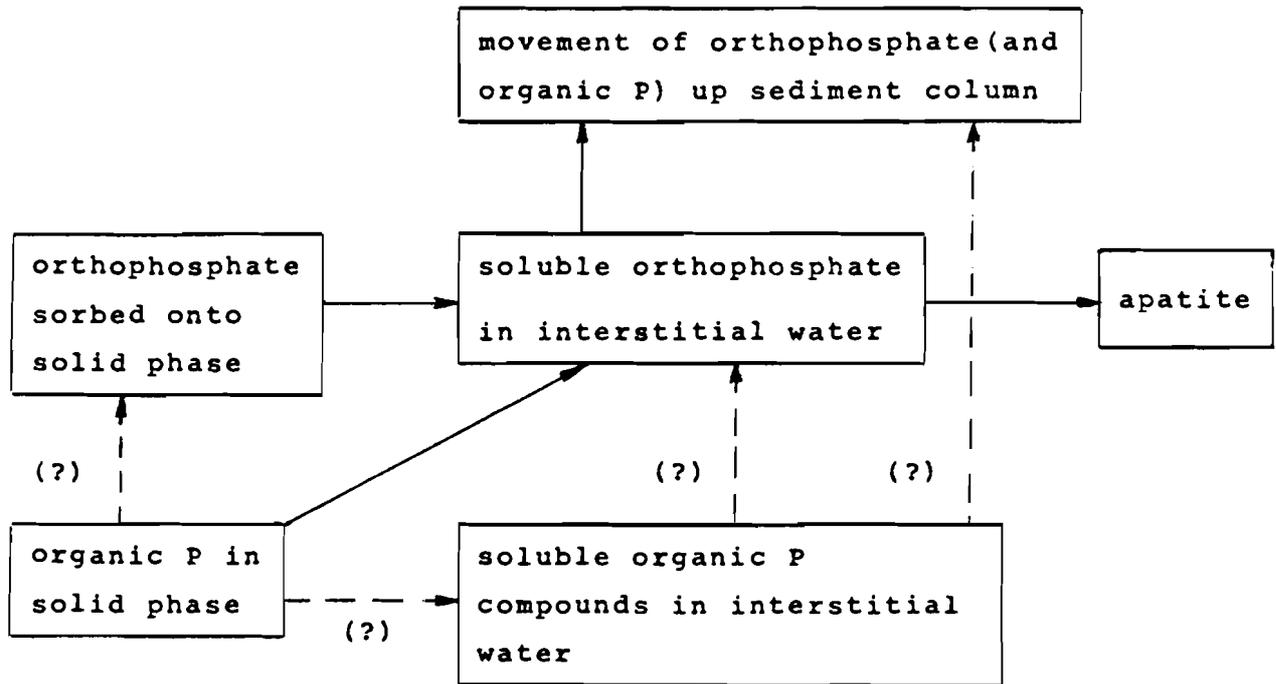
Figure 4. Hypothetical Phosphorus Transformations within
Great Lakes Sediments, after Williams and Mayer (1972)

Air

Algae

O_2 ─── Epilimnion

Fe(II)──►Fe(III)....P ⇌ o-PO_4

$[O_2]$

Hypolimnion

Fe(II) ──►Fe(III)....P ⇌ o-PO_4
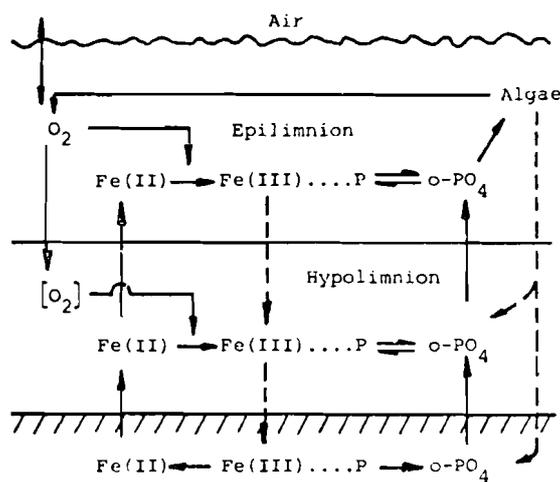
Fe(II)◄── Fe(III)....P ──► o-PO_4

Figure 5. Iron-Phosphate Interactions in Stagnant Water,
after Lijklema (1977)

Lijklema and Hieltjes (1979) proposed a scheme of phosphate cycling between the sediment and overlying water (Figure 6) suggesting that it includes all of the main processes with respect to the eutrophication problem. As a whole, Figure 6 demonstrates the relationships between some of the chemical and biological compounds in the water and sediments. Phytoplankton is considered a main component of the system in this case. The phytoplankton transforms the mineral phosphorus into particulate organic forms. Through the food chain, the particulate organic phosphorus is included in the biomass of the organisms of high trophic levels. In water, the quota of phosphate is regenerated by the activity of organisms or through decay and hydrolysis, while another part of phosphorus reaches the sediments. In aerobic and anaerobic conditions, the sedimented part of phosphate is bound with iron and calcium compounds in the sediment.

According to Lijklema and Hieltjes (1979), the seasonal variations of phosphorus release from sediment may be explained by the oxidative state of iron and redox conditions in the sediment-water interface.

Sridharan and Lee (1974) observed a concurrent release of iron with orthophosphate release in anoxic experiments, suggesting an association of phosphorus with iron. They proposed two possible ways in which iron-associated phosphorus release may occur under anoxic conditions. The first one takes place when ferric iron is reduced to ferrous iron and in this case, the phosphorus, in association with the former, is released to the overlying water. The second possible way pertains to the relationship of phosphorus to ferrous iron and considers the sorption of phosphorus by the ferrous compounds. In this case the phosphorus
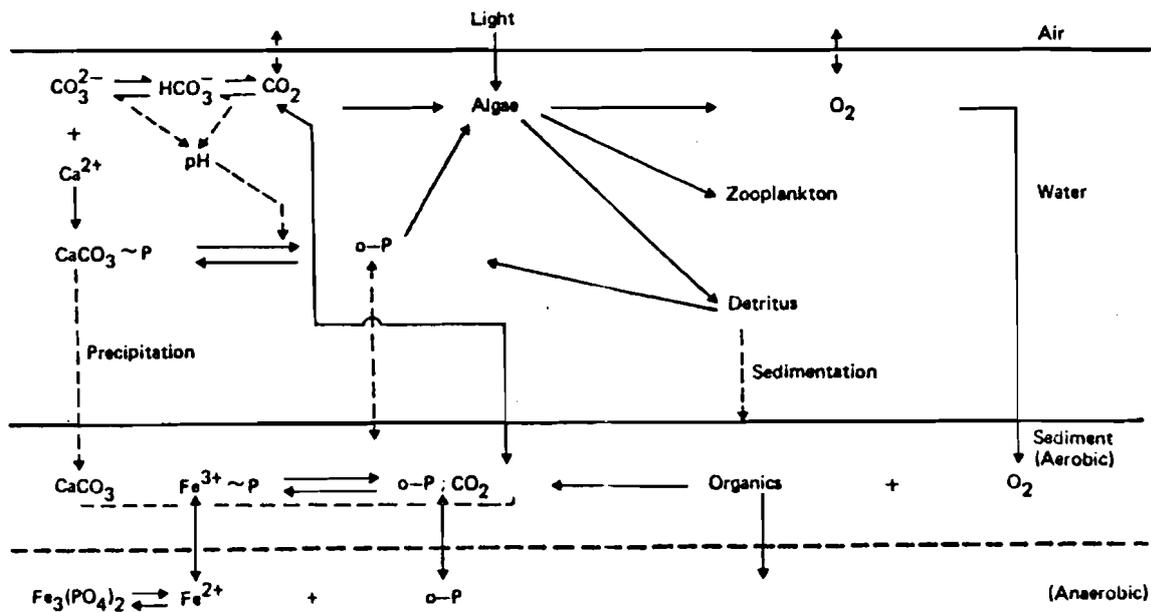
Figure 6. Scheme of Phosphate Cycling in the Sediment-Water Interface after Lijklema and Hieltjes (1979)

is desorbed when the sediment is in contact with a mild leaching solution under anoxic conditions (Sridharan and Lee, 1974). Lee et al. (1977) conducted special experiments for clarifying the behavior of iron and phosphorus with respect to release. They found that under anoxic conditions, the phosphorus release was independent of pH in neutral to slightly alkaline regions and the addition of air to the system caused the precipitation of ferric iron, with a corresponding removal of orthophosphate. Rippey (1977) explained the mechanisms of phosphorus release from the sediment due to pH increase as the ligand exchange of OH for phosphate in basic iron phosphate compounds.

Under oxic conditions about 60 percent of the total soluble
orthophosphate released in 30 days occurred within the first 10
days (Sridharan and Lee, 1974). They suggested that this high
percentage of phosphorus release in a relatively short time
indicated that the oxic release due to mineralization of organic
phosphorus is likely to be low in the oxic sediment. However,
it was suggested that the mineralization of sediment organic
phosphorus together with the chemical and biological desorption
of loosely bound phosphorus seems to be a mechanism of phosphorus
release under oxic conditions (Sridharan and Lee, 1974).

In calcium-rich waters, e.g., Lake Geneva (Golterman, 1973a)
phosphate may precipitate with $CaCO_3$ either being adsorbed or
included as a hydroapatite. As the precipitate moves to the
bottom, the low pH at the sediment-water interface may cause
the phosphate to dissolve although the rate of this reaction
may be slow. The secondary formation of hydroapatite may also
be in mud after sedimentation of particulate phosphorus. For
example, in Lake Erie all phosphates in sediment present in
this form (Williams and Mayer, 1972). Kuffel (1977) found that
the abundance of calciums in most of the lake waters facilitates
the permanent fixation and accumulation of phosphate in sediments.
Griffin and Jurinak (1974) indicated that the interaction of
phosphate and calcite may be described by two simultaneous
reactions: (i) second-order reaction of phosphate adsorption
on the calcite surface and (ii) first-order reaction of surface
arrangements of phosphate clusters into calcium phosphate
heteronuclei.

In the discussion of the exchange processes developed in the sediment-water interface, Lijklema (1980) indicated that a distinction can be made between the particulate and dissolved material as an exchangeable substance. The simplified scheme (Figure 7) for the phosphorus cycling in a shallow lake was suggested by Lijklema (1980) for the explanation of the phosphorus transformations in the water and of the different mechanisms controlling the phosphorus exchange processes in the sediment-water interface. The scheme in Figure 7 as well as the results reported elsewhere (Moore and Silver, 1972; Leonov, 1979, 1980) on the phosphorus cycling in waters, shows that the phosphorus transformations in water occurs as a complex interaction between microorganisms and chemical compounds of which the rates of change and character are quite dependent upon environmental factors. The important processes that regulate the phosphorus content in the water are diffusion, sedimentation and resuspension. Diffusion causes the transport of dissolved substances across the sediment-water interface in accordance with the concentration gradients in these environments. Sedimentation and resuspension are the processes defining the fluxes of particulate material to and out of the sediments respectively (Lijklema, 1980).

Thus in accordance with information available in the literature, the mechanisms of phosphorus conversion in the sediment may be identified. First of all there is a certain input of non-living particulate phosphorus from the water to sediment and then its transformation from the particulate form to dissolved
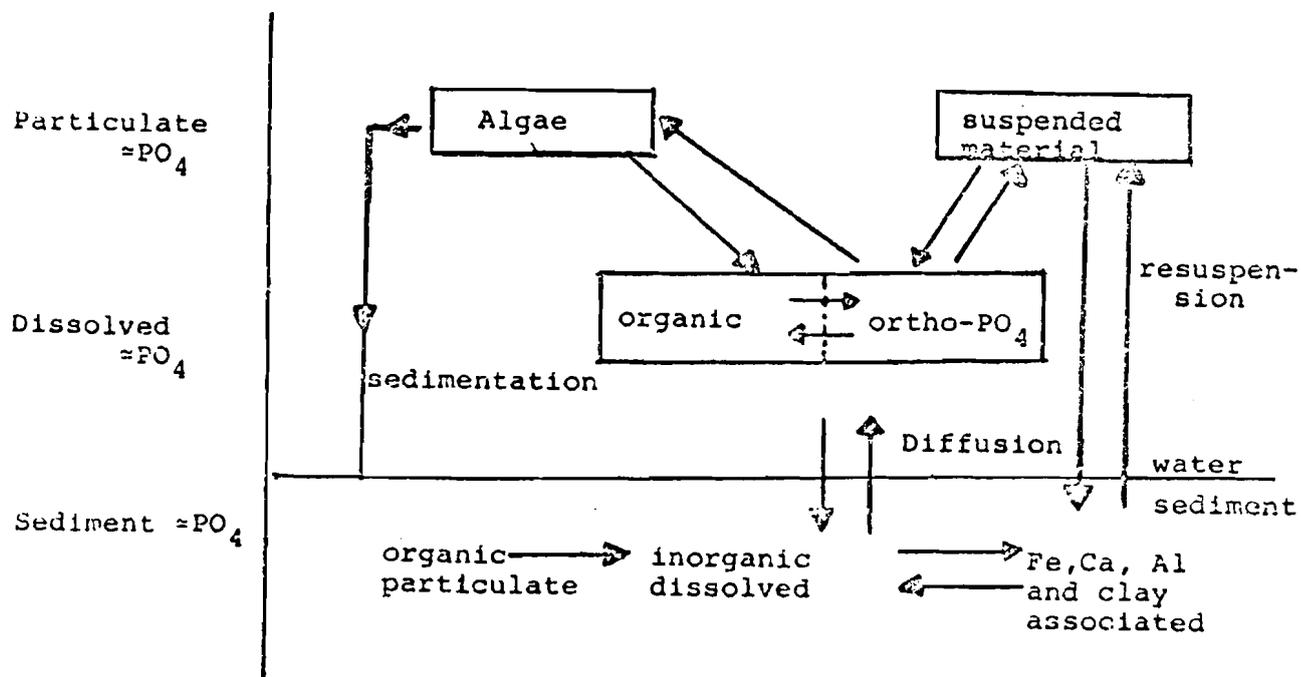
Figure 7. Main Pathways of Phosphate Cycling in
          Shallow Lakes, after Lijklema (1980)

forms. It is obviously during these subsequent transformations

that the dissolved organic phosphorus as well as dissolved

inorganic phosphorus would be formed in sediments. According

to Williams and Mayer (1972) the typical processes in consequent

conversion reactions are the biochemical oxidation and decomposi-

tion of sedimented particulate phosphorus, oxidation and reduc-

tion of associated inorganic compounds, chemical and physical

adsorption, precipitation and dissolution of phosphorus compounds

to and from mineral forms.

5. MODELS OF PHOSPHORUS RELEASE FROM SEDIMENTS

One of the problems of the modern water quality models of the phosphorus cycle or the transformation of its main compounds is in the description of dynamic interactions of phosphorus compounds or phosphorus exchange between sediments and water. In practice, many approaches are used to study the effect of sediment on the nutrient balance and phosphorus transformation in water bodies.

As a rule, in the simplest models used with limited information on phosphorus exchange through the sediment-water interface, the process of phosphorus release from sediment is parametrized as an external load, with a constant flux of phosphorus into the water body (Ahlgren 1973; Imboden, 1974; Macko et al., 1974). In an ecologically simple model of phosphorus dynamics, the individual rates of phosphorus sedimentation and phosphorus release from sediment are also used, but for simplification or because a reasonable amount of information on the P exchange is not available, the sediment P release is taken to be a constant (Welch et al., 1973).

Conceptual approaches to the study of processes in the sediment-water interface were formulated about ten years ago. To the present, various attempts to simulate the P exchange on the basis of mechanisms of phosphorus transformations in sediments and water, considering the influence of environmental factors on the rates of P conversion from one form to another, are already observed in literature. This section of the paper reviews the various models describing the sediment phosphorus release based on the physical and chemical-biological nature of phosphorus transformations, as well as on the empirical relationships

revealed in experimental studies with sediments or in considering the phosphorus mass balance in different water bodies.

5.1 Olsen's (1958,1964) Approach

The author showed in experiments that the phosphorus exchange in the sediment-water interface is a fast process and phosphate taken up by phytoplankton in the water may be replenished by phosphate release from the sediments with rates depending on the oxic conditions. On the basis of experiments with a coarse sediment, Olsen (1958, 1964) described a net quantity of phosphate adsorbed by sediment (a) as a difference between gross adsorbed quantity (A) and the sediment release (b):

$$a = A - b = K \cdot C^V - K_b \cdot C^{-V_b} , \qquad (7)$$

where A is amount of phosphate on dry sediment, 10^{-9} gP/g dry
     sediment;

  C is concentration of phosphate in water, 10^{-9} g P/ml
     solution;

  K, V and V_b are constants.

The first term in equation (7) is the Freundlich adsorption isotherm and the second one is the hyperbola-like P exchange function. This equation may be used for the description of phosphorus exchange in oxidized and reduced sediments. As Kramer et al., (1972) indicated, the major difference in phosphorus exchange in oxidizing and reducing sediment is due to the adsorption of phosphate, in particular by differences in the values of K.

5.2 Porcella et al. (1971) Approach

Porcella et al. (1971) considered a possible way to take into account the phosphorus balance in lakes under complete mixing conditions. The mass balance of phosphorus was described as

$$V\frac{dP}{dt} = (P_{in} \cdot F_{in}) + \begin{array}{c}\text{sediment}\\\text{release}\end{array} - \begin{array}{c}\text{sediment}\\\text{accumulation}\end{array} - (P_{res} \cdot F_{out})$$

(8)

where P_{in} and P_{res} are the phosphorus concentrations in the influent and in the reservoir ($\mu g/\ell$);

F_{in} and F_{out} are flow rates of input and output (day^{-1}),

t is time in days.

For steady-state conditions with respect to the phosphorus, the phosphorus balance will still exist, so that

$$(P_{in} \cdot F_{in}) - (P_{res} \cdot F_{out}) = \begin{array}{c}\text{sediment}\\\text{accumulation}\end{array} - \begin{array}{c}\text{sediment}\\\text{release}\end{array}$$

Therefore the net flux in sediment phosphorus over any period of time can be defined on an areal basis as:

$$P_b = \frac{(P_{in} \cdot F_{in}) - (P_{res} \cdot F_{out})}{SA}$$

(9)

where P_b is the flux of phosphorus ($\mu g/m^2$);

SA is the total surface area of sediment in a water body (m^2).

5.3 The Li et al. (1972) Approach

This model was formulated on the basis of experiments with sediment samples. Amounts of exchangeable phosphorus in the sediment were defined by adding carrier-free inorganic phosphate-^{32}P to the sediment-water system in steady state with respect to the levels of inorganic phosphate in the filtrate ($^{31}P_{soln}$), and measuring the levels of $^{31}P_{soln}$ and inorganic phosphate in solution ($^{32}P_{soln}$) after $^{32}P_{soln}$ had reached a constant level.

The general equilibrium state for the exchange phosphorus reaction is given by

$$Sed.Exch.^{31}P_i + {}^{32}P_{soln} \rightleftharpoons Sed.Exch.^{32}P + {}^{31}P_{soln} \qquad (10)$$
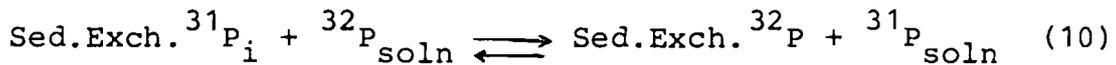
where Sed.Exch. $^{31}P_i$ is exchangeable sediment inorganic phosphorus expressed in µg/g sediment;

Sed.Exch.^{32}P is the ^{32}P in the sediment expressed in the percentage of added ^{32}P;

$^{31}P_{sol}$ is inorganic phosphate in filtrate (µg/g sediment);

$^{32}P_{soln}$ is inorganic phosphate in solution, expressed in the percentage of added ^{32}P.

When equilibrium is reached, the added ^{32}P is uniformly distributed between phosphate in solution and exchangeable sediment inorganic phosphate. The quantity of exchangeable sediment phosphate may be calculated as follows:

$$Sed.Exch.^{31}P_i = {}^{31}P_{soln} \cdot \frac{Sed.Exch.^{32}P}{^{32}P_{soln}} \qquad . \qquad (11)$$

The total exchangeable inorganic phosphate in the system that includes the sediment and solution P may be expressed as:

$$\text{Total Exch.P}_i = {}^{31}P_{soln} + \text{Sed.Exch.}{}^{31}P_i \ . \tag{12}$$

The rates of phosphorus exchange in the sediment-water interface can be defined for steady state conditions from the rate of ^{32}P transfer from the solution to the sediment phase using the following exchange reaction scheme:

$$ {}^{31}P_{soln} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Sed.Exch.}{}^{31}P_i \tag{13}$$

where k_1 and k_2 are the exchange rate constants. If ^{32}P is added to the solution phase, the net rate of ^{32}P removal from solution is given by

$$\frac{d^{32}P_{soln}}{dt} = k_2 \cdot (\text{Sed.Exch.}{}^{32}P) - k_1 \cdot {}^{32}P_{soln} \tag{14}$$

The solution of this equation by integration gives the next expression

$$ {}^{32}P_{soln} - {}^{32}P_{soln.inf} = ({}^{32}P_{total} - {}^{32}P_{soln.inf}) \cdot \exp(-k_1' \cdot t) \tag{15}$$

where inf is the time, required to reach the equilibrium state and

$$ k_1' = \frac{{}^{32}P_{soln} + \text{Sed.Exch.}{}^{32}P}{\text{Sed.Exch.}{}^{32}P} \cdot k_1 \ . \tag{16}$$

It was found that a plot of $\log({}^{32}P_{soln} - {}^{32}P_{soln.inf})$ against time is linear and it makes possible an evaluation of the exchange parameters.

Experimental results received by authors indicated that the exchange kinetics were the combined effects of several exchange reactions occurring at different rates due to differences in types of bounding or the position of sediments. The plot of equation (15) for each type of sediment was resolved into three separate reactions. The most rapid first reaction reached equilibrium in about 15 minutes, while periods of 2 to 4 hours and more than 24 hours were required for equilibrium in the intermediate second exchange reaction and slow third exchange reaction respectively. The authors concluded that the graphical resolution of the exchange process into three reactions with different rates do not constitute proof that three specific reactions are involved in the exchange process. Therefore, it was assumed that other reactions may also occur, but with rates not sufficiently different to allow resolution by the graphical approach.

5.4 Lorenzen's (1973) Approach

The author showed that predicted results in nutrient dynamics may significantly differ from each other, depending on the model structure. He considered the interaction of sedimentation and resuspension in the sediment-water interface as shown in Figure 8a. Lorenzen's model is presented by equations (17) and (18):

$$V \frac{dC}{dt} = M + K_2 \cdot C_s \cdot A - K_1 \cdot C \cdot A - C \cdot Q \tag{17}$$

$$V_s \frac{dC_s}{dt} = K_1 \cdot C \cdot A - K_2 \cdot C_s \cdot A \quad , \tag{18}$$

where M is mass flow in the system from all sources (g/year);

C is the average annual nutrient concentration (g/m^3);

K_1 is the specific rate of nutrient transfer to sediment (m/year);

Q is the lake volume (m^3);

A is surface area (m^2);

C_s is the nutrient concentration in the sediment (g/m^3);

V_s is the volume of sediment (m^3).

This model was improved (Lorenzen et al. 1976) to consider in the phosphorus budget model the fraction of the total phosphorus input to sediment that is unavailable for the exchange process. The structure of this model is presented in Figure 8b. Equation (18) in the improved model was modified and rewritten as

$$V_s \frac{dC_s}{dt} = K_1 \cdot C \cdot A - K_2 \cdot A \cdot C_s - K_1 \cdot K_3 \cdot A \cdot C \qquad (18a)$$

where K_3 is the fraction of total phosphorus input to sediment, unavailable for the exchange process (unitless).

5.5 The Wildung and Schmidt, 1973 Approach

The author's estimation of phosphorus release rate from the sediment were based on the regression analysis of the wide set of experiments designated to determine (i) the predominant inorganic and organic forms of phosphorus in sediments of the Upper Klamath Lake, Oregon; (ii) the effect of the environmental factors such as temperature, pH and water and sediment compound composition on the phosphorus release rate and (iii) the relationship of phosphorus release to algae growth requirements. A multiple correlation equation based on experimental data for
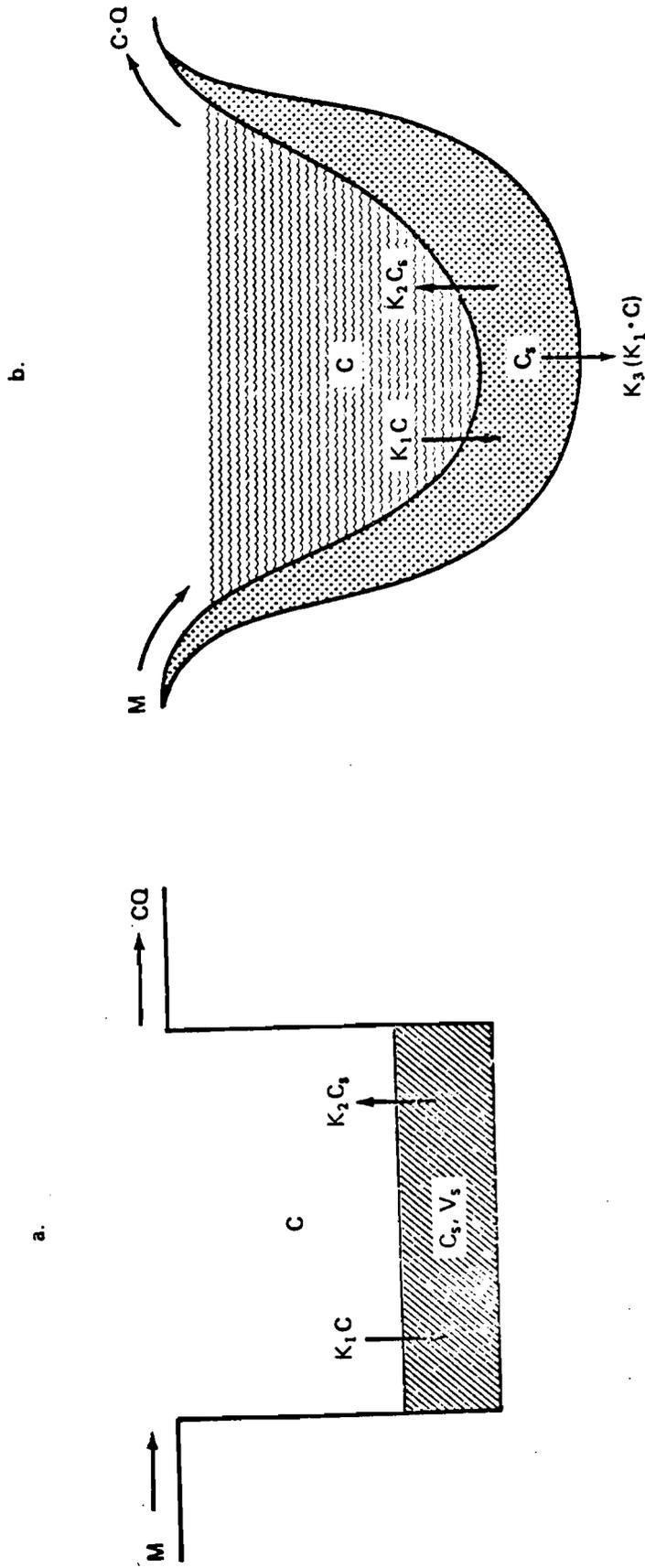
Figure 8. Models of Phosphorus Exchange Processes in the Sediment-Water
Interface. a) after Lorenzen (1973)
b) after Lorenzen et al. (1976)

description of phosphorus release from the sediment was presented, taking into account the effect of important variables on the processes considered in experiments. Thus the general form of the model equation is

$$Y = B_O + B_1 \cdot X_1 + B_2 \cdot X_4 + B_3 \cdot (X_1 \cdot X_4) + B_4 \cdot X_5 \qquad (19)$$

where Y is total phosphorus in solution μg P/g sediment;

B_O, B_1, B_2, B_3 and B_4 are partial regression coefficients;

X_1 is incubation temperature, ^{O}C;

X_4 is organic phosphorus concentration, μg P/100 g
sediment;

X_5 is total solid concentration, g/100 ml;

$(X_1 \cdot X_4)$ is temperature-organic phosphorus interaction.

This model was used to predict the phosphorus release to solution after 16 and 31 days at 10^{O}C and 23^{O}C. It was found that for both time periods the multiple regression coefficients (that are not listed in the report) indicated reasonable correlation (r=0.986-0.998) with good predictive capability and low variance.

5.6 Dahl-Madsen and Nielsen's (1974) Approach

The authors applied a simple first-order equation to describe the phosphorus exchange rate between sediment and water:

$$P_{rel} = K \cdot SP \qquad (20)$$

where P_{rel} has dimension mg/m^2-day; and K is rate constant, day^{-1} and SP is phosphorus concentration in sediment (mg P/m^2).

5.7 Berner's (1975) Approach

In studying the nutrient release from the sediment, Berner (1975) had suggested the equation to calculate the transport of dissolved substances from mud to water:

$$J_i = - D \cdot \phi \cdot \frac{dC_i}{dz} \tag{21}$$

where J_i is the diffusion flux of substance i $(mg/m^2\text{-day})$;

   D is effective diffusion coefficient (m^2/sec);

   C_i is the concentration of substance i (mg/ℓ);

   ϕ is porosity (unitless);

   z is the depth in sediment (m).

This model was used by Freedman and Canale (1977) to estimate the nutrient release from anaerobic sediment.

5.8 Gaume and Duke's (1975) Approach

Phosphorus release from organic sediment was described in the ecological model EPAECO (Gaume and Duke, 1975) as

$$P_{rel} = K_{4(20)} \cdot \theta^{(T-20)} \cdot \alpha_{sp} \cdot S \tag{22}$$

where S is sediment density expressed in grams per square meter;

   α_{sp} is the phosphorus fraction of organic sediment;

   $K_{4(20)}$ is the rate constant of sediment decay at 20°C
      (day^{-1});

   θ is the temperature coefficient;

   T is temperature in °C.

5.9 Kamp-Nielsen's (1974 and 1975b) Approach

Kamp-Nielsen (1974) proposed an empirical equation to describe the phosphorus release from the sediment:

$$P_{rel} = 1.21 \cdot (P_i - P_s) - 1.7 \tag{23}$$

where P_i is concentration of phosphorus in interstitial water

of sediment mg P/ℓ;

P_s is the concentration of soluble phosphorus in the

overlying water, mg P/ℓ.

In another empirical model, Kamp-Nielsen (1975b) considered the phosphorus release from the lake sediment as a result of desorption, diffusion and biological degradation in aerobic and anaerobic conditions. Aerobic phosphorus release at temperatures below 15°C for the profundal zone of the lake was described by

$$P_{rel} = 0.563 \cdot e^{0.203\ T} - 0.6\ \ln P_s - 2.27 \qquad (24)$$

while for the littoral zone of the lake equation (24) is transformed to

$$P_{rel} = 0.188 \cdot e^{0.203\ T} - 0.6\ \ln P_s - 2.27 \quad . \qquad (24a)$$

The phosphorus release at temperatures above 15°C for the aerobic and anaerobic conditions in the profundal lake zone was described by

$$P_{rel} = 0.563 \cdot e^{0.203\ T} + 0.6\ \ln P_s + 1.21 \cdot (P_i - P_s) - 3.97$$

$$(25)$$

In equations (24-25) T is water temperature in °C.

5.10 The Jørgensen et al.(1975) Approach

In Jørgensen et al.(1975) as well as Jørgensen (1980), equation (23) was used in the dynamical model of exchange processes in the sediment-water interface. This model shown in Figure 9 describes the temporary change of P_i. The model is as follows:

$$\frac{dP_e}{dt} = \alpha \cdot F \cdot PS_{net,s} - k \cdot P_e \cdot \theta^{(T-293)} \quad , \qquad (26)$$
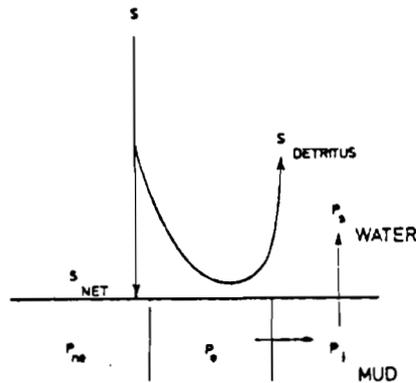
Symbols used are: S is total sedimented phosphorus subdivided into
fractions, S_{NET} and $S_{DETRITUS}$;

P_{ne} is nonexchangeable phosphorus in unstabilized
sediment;

P_e is exchangeable phosphorus in unstabilized
sediment;

P_i is phosphorus in interstitial water;

P_s is dissolved phosphorus in overlying water.

Figure 9.   Model of Phosphorus Exchange in Sediment-Water
Interface after Jørgensen et al.(1975) and
Jørgensen (1980)

$$\frac{dP_i}{dt} = k \cdot P_e \cdot \theta^{(T-293)} - \beta [1.21 \cdot (P_i - P_s) - 1.7] \cdot \frac{T}{280} \qquad (27)$$

where $PS_{net,s}$ is the phosphorus settling rate to the stabilized

sediment (mg/m^3-day);

α is the factor converting the phosphorus concentra-

tion in water to concentration units in sediment

(mg P/kg dry matter);

θ is the temperature coefficient;

k is the rate coefficient (day^{-1});

T is the absolute temperature;

β is the coefficient converting the concentration

units in the sediment to those in lake water;

P_e is the exchangeable phosphorus in upper layers

of sediment (mg P/l)

5.11 Kamp-Nielsen's (1977) Approach

The author developed a conceptual model of phosphorus exchange processes in the sediment-water interface which is shown in Figure 10. The model includes the differential equations:

$$\frac{dP_e}{dt} = PSDE - PSUM - PSEM - RESU_e \qquad (28)$$

$$\frac{dP_i}{dt} = PSEM - PDSP - RESU_i \text{ (for aerobic conditions)} \qquad (29)$$

$$\frac{dP_i}{dt} = PSEM - PDSP - RESU_i - PDIF \text{ (for anaerobic conditions)} \qquad (30)$$

where PSED is the rate of accumulation of the exchangeable fraction of sedimentary phosphorus that is described by

$$PSDE = PSED \left(\frac{F}{F + 1}\right) \qquad (31)$$

and PSED is the total phosphorus sedimentation in g P/m^2-day;

F is ratio of exchangeable/nonexchangeable phosphorus in total sedimented phosphorus (unitless);

PSUM is the rate of mineralization of exchangeable phosphorus on the sediment surface in g P/m^2-day, that is described as

$$PSUM = 0.56 \cdot e^{0.203\,T} \cdot \frac{PSED.10^{-3}}{PSED + 1} \cdot \qquad (32)$$

PSEM is the rate of mineralization of exchangeable phosphorus within the lake sediment in g P/m^2-day and this rate is regulated by temperature so that
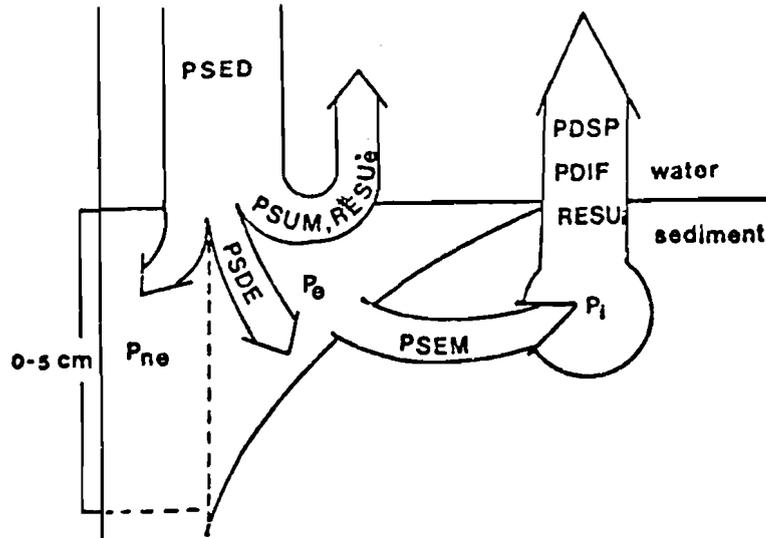
Symbols for phosphorus fractions are:

P_e is the exchangeable sedimentary phosphorus;

P_{ne} is nonexchangeable sedimentary phosphorus;

P_i is the interstitial and sorbed phosphate.

Figure 10. Conceptual Model of Phosphorus Pools and Exchange Processes in the Sediment-Water Interface after Kamp-Nielsen (1977).

$$PSEM = k \cdot P_e \cdot \theta^{(T-20)} \tag{33}$$

where k and θ are the rate constant and temperature coefficient respectively;

T is water tempeature in $^{\circ}C$;

$RESU_e$ is the rate of resuspension of the total sedimentary phosphorus in g P/m^2-day and it is calculated as

$$RESU_e = RESP \left(\frac{F}{F + 1}\right) \tag{34}$$

PDSP is the rate of desorption of interstitial and sorbed phosphate in g P/m^2-day and it is expressed by the empirical equation in form

$$PDSP = - (0.6 \ln P_s + 2.27) \cdot 10^{-3} \tag{35}$$

$RESU_i$ is the rate of removal of the interstitial and sorbed phosphate by resuspension in g P/m^2-day and this is a function of

$$RESU_i = RESP \cdot \frac{P_i}{P_e} \cdot (\frac{F}{F + 1}) \qquad (36)$$

PDIF is the rate of removal of the interstitial and sorbed phosphate by diffusion in g P/m^2-day and it is expressed by

$$PDIF = 1.21 \cdot (\frac{P_i - 0.004}{0.0157} - P_s) - 1.7 \; 10^{-3} \qquad . \qquad (37)$$

In this model the empirical equations (32), (35) and (37) were derived on the basis of experiments (Kamp-Nielsen, 1974; 1975b).

5.12 Jørgensen's (1976) Approach

On the basis of preliminary experimental studies of the sediment-water interface (Kamp-Nielsen, 1974; 1975b; 1977) and previous models (Kamp-Nielsen, 1975b; 1977; Jørgensen et al. 1975), the author considered the exchange processes of nutrients including phosphorus in a comprehensive eutrophication model. Interaction of phosphorus fractions in the sediment-water inter-face corresponding to Jørgensen's model is presented in Figure 11.

The dynamics of phosphorus in sediment and water, is de-scribed by the following differential equations:

$$\frac{dPI}{dt} = \frac{K_5 \cdot PE \cdot K_6^{(T-20)}}{1 - DMU} - \frac{1.2 \cdot (PI - PS) - 1.7}{LUL \; (1 - DMU)} \cdot \frac{T + 273}{280} \qquad (38)$$

$$\frac{dPE}{dt} = \frac{SA \cdot CA \cdot V \cdot 10^3}{f \cdot PP \cdot LUL \cdot S} - K_5 \cdot PE \cdot K_6^{(T-20)} + \frac{SA \cdot DP \cdot V \cdot 10^3}{f \cdot LUL \cdot S} \qquad (39)$$

$$\frac{dPS}{dt} = \frac{F_1 \cdot P_1 + F_2 \cdot P_2 + F_3 \cdot P_3 - F_4 \cdot PS}{365 \cdot V} + \frac{1.2 \cdot (PI-PS)-1.7}{1000}$$

$$\cdot \frac{T+273}{280} \cdot \frac{S}{V} + R \qquad (40)$$
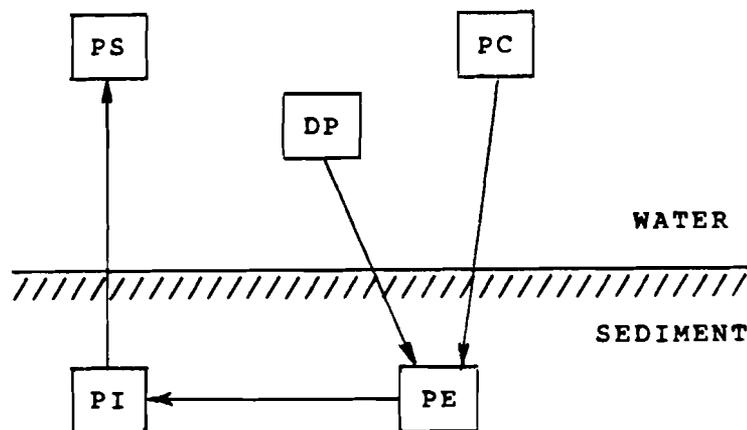
Symbols are: PS is soluble phosphorus in lake water (mg P/ℓ);

DP is detrital phosphorus in lake water (mg P/ℓ);

PC is phosphorus in phytoplankton (mg P/ℓ);

PE is exchangeable phosphorus in the upper layer of sediment (mg P/ℓ);

PI is phosphorus in interstitial water of sediment (mg P/ℓ).

Figure 11.   The Model of Phosphorus Exchange Processes in the Sediment-Water Interface after Jørgensen (1976).

where F_1, F_2, F_3 and F_4 are flow rates of the stream entering the lake, flow rate of waste load, precipitation and flow rate of stream leaving the lake respectively (all m^3/year);

P_1, P_2 and P_3 are phosphorus in the stream entering the lake in waste water and in rain water (all mg P/ℓ);

R is the rate of biochemical transformation of phosphorus in water which includes the effect of phytoplankton, zooplankton activities and detritus decomposition (mgP/ℓ-day);

S is surface area of the lake (m^2);

V is volume of the lake (m^3);

T is temperature in $^{\circ}$C;

LUL is upper unstabilized layer (100 mm);

DMU is dry matter of uppper layer in sediment (0.925 kg/kg);

SA is settling rate (day^{-1});

CA is phytoplankton concentration (mg/ℓ);

f is ratio of total phosphorus to exchangeable phosphorus in sediment (unitless);

PP is phosphorus content in phytoplankton (1/114);

K_5 is biodegradation rate of organic phosphorus in sediment (day^{-1});

K_6 is temperature coefficient for biodegradation.

These model equations of phosphorus exchange processes were also used in the specific study of the lake model examination (Jørgensen et al. 1978).

5.13 The Fillos and Biswas (1976) Approach

The authors proposed the formula below for calculating the phosphorus release rate from the sediment:

$$P_{rel} = \frac{Q}{A} \cdot \left(\frac{C_{n+1} + C_n}{2} - \frac{C_{o(n+1)} + C_{o(n)}}{2}\right) + \frac{V}{A \cdot t} \cdot (C_{n+1} - C_n) \quad (41)$$

where P_{rel} is in mg P/m^2-day; Q is flow rate in day^{-1}; A is surface area of sediment in m^2; C and C_o are concentrations in effluent and influent in mg/ℓ respectively; V is volume of over-lying water, ℓ; t is time interval from n to n+1 in days.

5.14 DiGiano's and Snow's (1977) Approach

The authors described the phosphorus release through the sediment-water interface by equation:

$$P_{rel} = \frac{\phi \cdot A}{V_L} \cdot K_1 \cdot (P_i - P_s) \quad (42)$$

where P_i is the phosphorus concentration in interstitial water (mg P/ℓ);

P_s is phosphorus concentration in overlying water (mg P/ℓ);

∅ is porisity (unitless);

A is sediment surface area (m^2);

V_L is volume of the lake (m^3);

K_1 is release rate (mg P/ℓ-day).

The authors indicated that the concentration gradient between the phosphorus concentrations in interstitial water and overlying water is the regulator of the mass transfer and that the rate of the change of P_s is directly influenced by the rate of change of P_i. As a whole the model of DiGiano and Snow (1977) includes the following equations:

$$V_L \cdot \frac{dP_s}{dt} = Q \cdot (P_o - P_s) + K_1 \cdot \emptyset \cdot A \cdot (P_i - P_s) - K_2 \cdot P_s \cdot V_L \quad (43)$$

$$V_S \cdot \frac{dP_i}{dt} = K_2 \cdot P_s \cdot V_L - \emptyset \cdot A \cdot K_1 \cdot (P_i - P_s) \quad (44)$$

where Q is flow rate through the lake (m^3/day);

P_o is input of phosphorus to lake (mg P/ℓ);

K_2 is the phosphorus sedimentation rate (day^{-1});

V_S is volume of sediment (m^3).

5.15 Lam and Jaquet's (1976) Approach

The authors proposed a formula which relates the regenerated amount of total phosphorus to wave oscillation and sediment mean grain size, on the basis of known concepts and data in wave theory, sedimentology and geochemistry. So upward flux of sediment J is given by

$$J = k_r \cdot \rho \cdot \left(\frac{\rho_s}{\rho_s - \rho}\right) \cdot \frac{u_a}{u_{cr}} \cdot (u_m - u_{cr}) \quad , \quad (45)$$

where k_r is dimensionless proportionality constant;

σ_s is sediment density (g/cm^3);

u_a is velocity (cm/sec);

u_{cr} is threshold velocity (cm/sec);

u_m is orbital velocity (cm/sec).

Equation (45) was used to estimate the upward flux of regenerated phosphorus (G) in µg/cm^2-sec with the help of the formula:

$$G = J \cdot \hat{P}_s \qquad (46)$$

where $\hat{P}_s$ is estimated regeneration-prone phosphorus (µg/g) and this parameter depends on the sediment mean grain size d (specific units):

$\hat{P}_s = 200$ when $d \leq 5.5$

$\hat{P}_s = 108 \cdot d - 394$ when $5.5 < d \leq 7.5$

$\hat{P}_s = 269 \, d - 1600$ when $7.5 < d$.

5.16 The Thibodenaus and Cheng (1976) Approach

The model of phosphorus flux from the sediment is given by

$$P_{rel} = 2 \cdot R \cdot \sqrt{\frac{D(t)}{\pi \cdot t}} \cdot (P_i - P_s) \qquad (47)$$

where R is the coefficient depending on thermic structure of the water body;

D(t) is the coefficient of turbulent diffusion of compounds in water;

t is time.

It is assumed that values of R and P_i may be found by cal-culations. The comparison of computed vertical profiles of

phosphorus concentration with observed profiles may be used for choosing the values of these parameters.

5.17 The Lung et al.(1976) Approach

Lung et al. (1976) and also Lung and Canale (1977) described the phosphorus transfer across the sediment-water interface in the phosphorus transformation model by diffusion mechanisms (Figure 12). The equation for the phosphorus release from the sediments by diffusion was written as:

$$P_{rel} = \frac{\emptyset \cdot D \cdot A}{L} \cdot (P_i - P_s) \tag{48}$$

where D is the diffusion coefficient (cm^2/sec);

    A is area size (m^2);

    L is characteristic length for diffusion process in m;

    $\emptyset$, P_i and P_s are mentioned above.

This model as a whole describes the dynamics of the phosphorus fractions (particulate and dissolved phosphorus) in epilimnion, hypolimnion and sediments in White Lake. In the given report, only equations that illustrate the phosphorus interactions in the sediment-water interface are presented.

The dynamics of particulate and dissolved phosphorus fractions in hypolimnion are described by the following equations:

$$V_2 \cdot \frac{dC_{p2}}{dt} = \frac{k \cdot A_{1,2}}{L_{1,2}} \cdot (C_{p1} - C_{p2}) + V_{s1} \cdot C_{p1} \cdot A_{1,2}$$

$$\underbrace{\hphantom{V_2 \cdot \frac{dC_{p2}}{dt}}}_{\text{eddy diffusion}} \quad \underbrace{\hphantom{V_{s1} \cdot C_{p1} \cdot A_{1,2}}}_{\substack{\text{settling from} \\ \text{epilimnion}}}$$

$$- V_{s2} \cdot C_{p2} \cdot A_{2,3} - \mu_2 \cdot C_{p2} \cdot V_2 \tag{49}$$

$$\underbrace{\hphantom{- V_{s2} \cdot C_{p2} \cdot A_{2,3}}}_{\substack{\text{settling to} \\ \text{sediment}}} \quad \underbrace{\hphantom{\mu_2 \cdot C_{p2} \cdot V_2}}_{\text{reaction}}$$
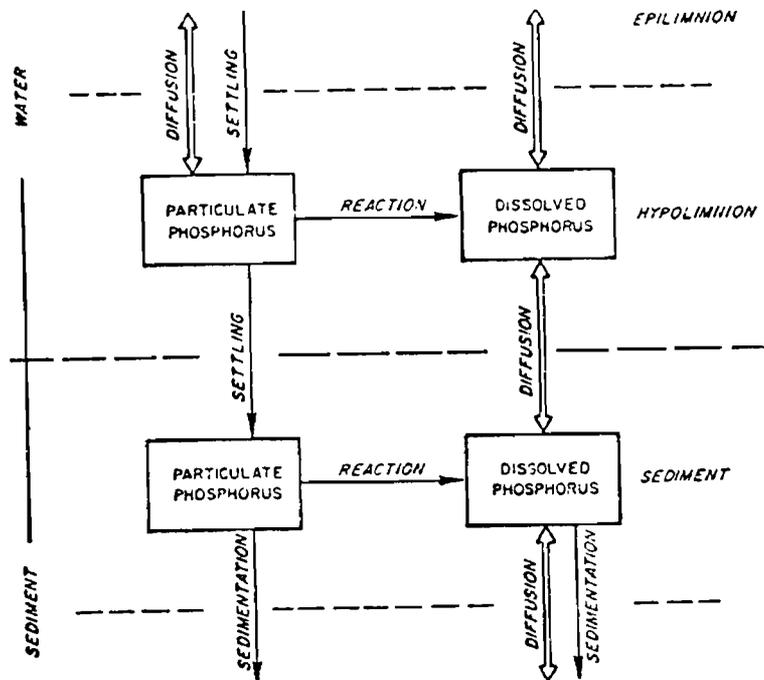
Figure 12. Part of Phosphorus Transformation Model showing the
Phosphorus Sediment-Water Interactions in White
Lake, after Lung et al.(1976) and Lung and
Canale (1977)

$$V_2 \cdot \frac{dC_{D2}}{dt} = \frac{k \cdot A_{1,2}}{L_{1,2}} \cdot (C_{D1} - C_{D2}) + \frac{\phi_{0,1} \cdot \bar{D} \cdot A_{2,3}}{L_{2,3}} \cdot (C_{D3} - C_{D2})$$

<center>eddy diffusion   diffusion across the interface</center>

$$+ \mu_2 \cdot C_{p2} \cdot V_2 - V_{ss} \cdot C_{D2} \cdot A_{2,3} \tag{50}$$

<center>reaction   loss due to moving</center>

The fluctuations of particulate phosphorus in sediment are
described by

$$V_n \cdot \frac{dC_{pn}}{dt} = V_{s_{n-1}} \cdot (\alpha_{n-1,n} \cdot C_{p_{n-1}} + \beta_{n-1,n} \cdot C_{p_n}) \cdot A_{n-1,n}$$

<center>sedimentation from the upper layer</center>

$$- V_{s_n} \cdot (\alpha_{n,n+1} \cdot C_{p_n} + \beta_{n,n+1} \cdot C_{p_{n+1}}) \cdot A_{n,n+1}$$

<center>sedimentation to lower layer</center>

$$- \mu_3 \cdot C_n \cdot V_n \tag{51}$$

and dissolved phosphorus are given as

$$\emptyset \cdot V_n \cdot \frac{dC_{D_n}}{dt} = \emptyset_{n-1,n} \cdot V_{s_{n-1}} \cdot (\alpha_{n-1,n} \cdot C_{D_{n-1}} + \beta_{n-1,n} \cdot C_{D_n}) \cdot A_{n-1,n}$$

<div align="center">sedimentation from the upper layer</div>

$$- \emptyset_{n,n+1} \cdot V_{s_n} \cdot (\alpha_{n,n+1} \cdot C_{D_n} + \beta_{n,n+1} \cdot C_{D_{n+1}}) \cdot A_{n,n+1}$$

<div align="center">sedimentation to the lower layer</div>

$$+ \frac{\emptyset_{n-1,n} \cdot \bar{D} \cdot A_{n-1,n}}{L_{n-1,n}} \cdot (C_{D_n} - C_{D_{n-1}})$$

<div align="center">diffusion</div>

$$+ \frac{\emptyset_{n,n+1} \cdot \bar{D} \cdot A_{n,n+1}}{L_{n,n+1}} \cdot (C_{D_{n+1}} - C_{D_n}) + \mu_3 \cdot C_{p_n} \cdot V_n \quad (52)$$

<div align="center">diffusion   reaction</div>

where k is vertical eddy diffusion coefficient (cm^2/sec);

$\bar{D}$ is diffusion coefficient in layer considered (cm^2/sec);

$A_{1,2}$; $A_{2,3}$; ... $A_{n-1,n}$ are contact areas between layer considered in m^2;

C_{p1}, C_{p2} ... C_{p_n} are concentrations of particulate phosphorus in mg/ℓ;

C_{D1}, C_{D2} ... C_{D_n} are concentrations of dissolved phosphorus in mg/ℓ;

$L_{1,2}$; $L_{2,3}$; ... $L_{n-1,n}$ are average characteristic length between layers in m;

V_2 and V_n are volumes of hypolimnion and sediment layer considered in m^3;

V_{s1}, V_{s2} ... V_{s_n} are sinking velocity or sedimentation rate in m/day or cm/year;

V_{ss} is accumulation rate at sediment-water interface in cm/year;

X_{p1} is phosphorus concentration in solid sediment particles in g P/g dry weight sediment;

α is weighting factor (unitless);

$\beta = 1 - \alpha$;

μ_2 and μ_3 are kinetic constants for conversion of particulate phosphorus to dissolved phosphorus in hypolimnion and upper layer of sediment respectively (both day^{-1});

β_1 is density of solid particles in top sediments in g dry weight/cm^3;

$\emptyset$ is porosity of sediment (unitless).

It was indicated that the rate of biochemical transformation of particulate phosphorus to dissolved phosphorus in the upper layer of sediment is one of the important factors that control the phosphorus sediment-water interactions in White Lake (Lung and Canale, 1977). The first-order rate constant of this process correlates well with the dissolved oxygen content at bottom water (Lung et al. 1976). The value of this rate constant for aerobic conditions was estimated to be equal $2 \cdot 10^{-5}$ day^{-1} and for anaerobic conditions $7.9 \cdot 10^{-4}$ day^{-1} with a difference of about 40 times.

5.18   The Spear and Hornberger (1978) Approach

Equation (48) used by Lung and Canale (1977) was also applied in the eutrophication model of Peel Inlet Basin in considering the interactions between plankton organisms, soluble phosphorus and sediment (Spear and Hornberger, 1978; Hornberger and Spear, 1980). The term "sediment" as assumed by the authors includes the layer of decomposed organic matter which underlies much of the actively photosynthesizing phytoplankton. Phosphorus release

from the sediment was presented as

$$P_{rel} = a_{43} \cdot (P_i - P_s) \tag{53}$$

where a_{43} is the coefficient showing the transport of phosphorus from the sediment to water (day^{-1}).

The dynamics of dissolved phosphorus (P_s) in the water is described in the given model as

$$V \cdot \frac{dP_s}{dt} = \begin{matrix} advection \\ term \end{matrix} - \begin{matrix} Cladophora \\ uptake \end{matrix} - \begin{matrix} Phytoplankton \\ uptake \end{matrix} + P_{rel} \tag{54}$$

where V is water volume in liters. The equation for sediment phosphorus (P_i) dynamics includes two terms:

$$V_s \cdot \frac{dP_i}{dt} + P_i \cdot \frac{dV_s}{dt} = [1 - (P_i/P_i^*)^3] \cdot \left(\begin{matrix} net\ inflow \\ rate \end{matrix} \right) + (P_i/P_i^*)^3$$

$$\cdot \left(\begin{matrix} net\ inflow \\ rate \end{matrix} \right) \tag{55}$$

where V_s is volume of sediment in liters;

P_i^* is maximum phosphorus concentration in interstitial
water in $\mu g/\ell$.

It was assumed that the terms in brackets in equation (55) (or concentration limiting function) allows a build-up to a maximum of P_i^* with further addition of phosphorus to sediment causing the expansion of the active layer. The equations for the separate

sediment compartments are written as

$$V_s \cdot \frac{dP_i}{dt} = [1 - (P_i/P_i^*)^3] \cdot \{ \begin{matrix} \text{river} \\ \text{deposition} \end{matrix} + \begin{matrix} \text{groundwater} \\ \text{through flow} \end{matrix}$$

<div style="text-align:center">concentration
limiting
function</div>

$$+ \begin{matrix} \text{phytoplankton} \\ \text{sedimentation} \end{matrix} + \begin{matrix} \text{Cladophora} \\ \text{loss to sediment} \end{matrix} - P_{rel}$$

$$- \begin{matrix} \text{Cladophora uptake from} \\ \text{interstitial water} \end{matrix} \} \tag{56}$$

and

$$P_i \cdot \frac{dV_s}{dt} = (P_i/P_i^*)^3 \cdot R(t) \tag{57}$$

where $R(t)$ is the expression $\{\}$ in equation (56).

The rates of processes such as phytoplankton sedimentation, Caldophora loss to sediment and Cladophora uptake from interstitial water, taken into account in equations (56) and (57), are considered as temperature dependent. Concentration limiting function $[1 - (P_i/P_i^*)^3]$, prevents P_i from exceeding P_i^* which may be considered as an arbitrary upper limit of phosphorus in sediment. When P_i increases from zero to P_i^*, increments in input to the sediment compartment cause a proportionately larger increase in sediment volume relative to changes in concentrations.

Although the above scheme is somewhat arbitrary, authors suggested that it is justified because the parametric uncertainty is relegated to P_i^* a value which can be interpreted on a physical basis. When phosphorus concentration near the bottom is increased, sharp gradients will appear in the downward migration of phosphorus. It may be interpreted as expansion of the "active sediment zone". Authors noted that the formation of the phosphorus concentration gradients near the bottom depends upon the rate of phosphorus

input to sediment and physical-chemical properties of sediment. All of these factors will result in an effective upper limit on the phosphorus content in the active sediment layer. Thus a number of unknown properties of sediment, such as sediment porosity, hydraulic conductivity, capacity for cation exchange, etc., are lumped in one parameter, P_i^*. Spear and Hornberger (1978) and Hornberger and Spear (1980) suggested that this semiempirical approach is satisfied because there is a good deal of information in literature about phosphorus concentration in the sediments of eutrophic water bodies.

5.19 Poon's (1977) Approach

On the basis of microcosms experiments, Poon (1977) proposed the following equation to calculate the phosphorus flux representing the uptake or release of total phosphorus from sediment as a function of time:

$$F(t) = (D^* - V \cdot K) \cdot (C_o - C_a) \cdot \exp(-K \cdot t) + D^* \cdot (C_a - C_i)$$

(58)

where $F(t)$ is phosphorus flux as function of time t;

D^* is flushing rate in day^{-1};

C_o is the initial phosphorus concentration in the water at t=0 in $\mu g\ P/\ell$;

C_a is asymptotic concentration of phosphorus for an infinitive period of time equal to ambient concentration 73.2 $\mu g\ P/\ell$ total phosphorus;

C_i is phosphorus input by water dilution in $\mu g\ P/\ell$;

V is volume of the water in microcosm equal in this case to liters;

K is rate constant or the rate of change of phosphorus concentration (day^{-1}).

5.20 The Dahl-Madsen (1978) Approach

Dahl-Madsen (1978) described the input of mineral phosphorus (P_{rel}) from the sediment in eutrophic coastal areas as a temperature-dependent process:

$$P_{rel} = K_{msp} \cdot P_{sed} \cdot \theta^{(T - 20)} \tag{59}$$

where K_{msp} is rate constant (day^{-1});

P_{sed} is phosphorus concentration in sediment which includes
the sedimented phytoplankton and detritus (mg P/ℓ);

θ is temperature coefficient;

T is water temperature in ^{o}C.

5.21 Nyholm's (1978) Approach

The author used the following formula to simulate the nutrient release from the sediment in a model of an eutrophic, shallow lake:

$$P_{rel} = K_{r(20^{o})} \cdot \theta^{(T - 20)} \cdot (\text{Sedimentation}) \tag{60}$$

where $K_{r(20^{o})}$ is rate constant at $20^{o}C$ (day^{-1});

P_{rel} is rate of nutrient release in g/m^2-day;

Sedimentation is the total amount of particular nutrient
sedimented;

θ and T are mentioned above.

5.22 The Theis and McCabe (1978) Approach

Theis and McCabe (1978) proposed a model of phosphorus sediment release for a hypertrophic lake on the basis of Fick's first law (Figure 13). The phosphorus release rate per unit area
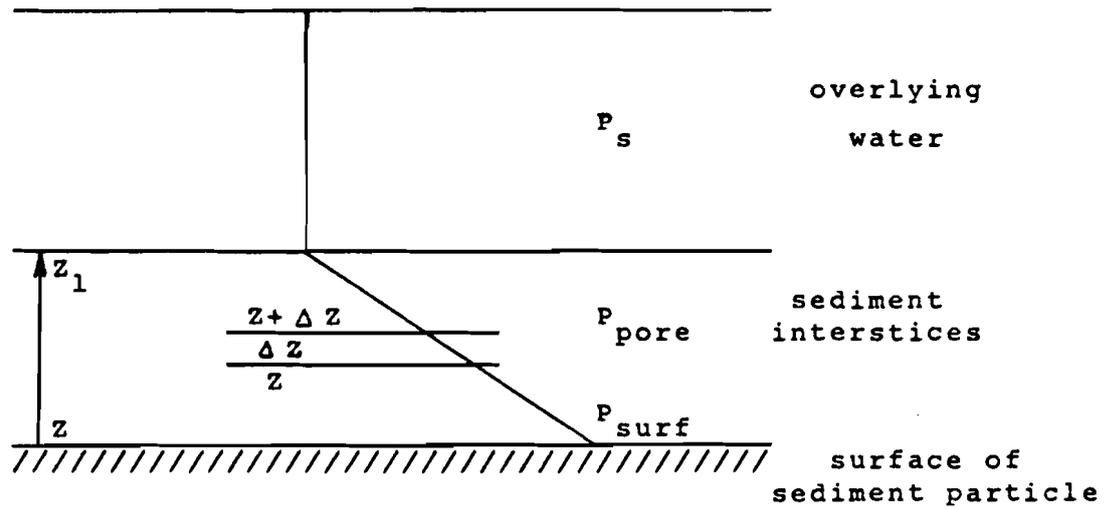
Figure 13. Sediment Phosphorus Release Model for Hypertrophic
Lake Sediment after Theis and McCabe (1978)

is given as

$$P_{rel} = \frac{D}{Z} \cdot (P_{surf} - P_s) \tag{61}$$

or

$$P_{rel} = \frac{D}{Z_1} \cdot (P_{surf} - P_{pore}) \tag{62}$$

where D is diffusion coefficient of phosphorus release from

sediment solid phase through the pore water to overlying

water;

P_{surf}, P_{pore} and P_s are concentrations of phosphorus at the

surface of sediment, in interstitial water and overlying

water respectively.

5.23 The Kremer and Nixon (1978) Approach

The authors considered the flux of phosphorus in the model of Narraganset Bay using the following equation:

$$\text{Flux P} = \frac{(\text{Flux P}_\text{O}) \cdot \exp(\text{Flux PT} \cdot \text{T})}{1000 \cdot \text{DEPTH}} \tag{63}$$

where Flux PT and Flux P_O are constants and T is water temperature in $^\text{O}$C.

5.24 Ulen's (1978b) Approach

For the description of phosphorus release from the sediment, the author used the expression:

$$P_\text{rel} = D \cdot \sqrt{\frac{K}{D}} \cdot (P_i^\text{S} - P_\text{S}) \tag{64}$$

where P_rel is calculated in µg P/cm^2-sec;

P_i^S is saturation concentration of phosphorus in inter-
stitial water of sediment $(µg/cm^3)$;

P_S is phosphorus concentration in free water $(µg/cm^3)$;

D is diffusion coefficient (cm^2/sec);

K is rate coefficient for dissolution (sec^{-1}).

This model was used for estimating the potential ability of sediment to release phosphorus and for comparing internal and external nutrient loading.

5.25 The Imboden and Gachter (1978) Approach

In predictive model calculations of the phosphorus dynamics and the future trophic state of Swiss lakes, the phosphate flux from the sediment in mg P/m^2-day was assumed to be proportional

to the primary production from May to the end of stagnation:

$$\text{Flux P} = 0.45 \cdot \Sigma P_p \qquad\qquad (65)$$

where P_p is rate of primary production in mg P/m^2-day.

5.26 Kamp-Nielsen's (1978) Approach

On the basis of previous theoretical and experimental studies of the sediment-water interface (Kamp-Nielsen, 1974; 1975a, b) the author created the model of the phosphorus exchange processes between the bottom water and sediments. The model structure is presented in Figure 14. Symbols used in this model are

SEDP and RESUP are processes of phosphorus sedimentation
and resuspension, respectively (both mg P/m^2-day);

$ADS_{(n)}$ is sorption of phosphorus in n-th layer (mg P/kg
dry matter-day);

$DIF_{(n)}$ is diffusion of phosphorus from n-th to (n+1)-th
layer (mg P/kg dry matter-day);

$DIFOX_{(n)}$ is diffusion of oxygen from n-th to (n+1)-th layer
(mg O_2/liter sediment-day);

$BIO_{(n)}$ is biological mineralization of phosphorus in n-th
layer (mg P/kg dry matter-day);

$BIOX_{(n)}$ is oxygen consumption in phosphorus mineralization
(mg O_2/liter sediment-day);

OXO and $OX_{(n)}$ are oxygen in bottom water and in n-th sediment
layer (mg O_2/ℓ);

$PA_{(n)}$ is sorbed phosphorus in n-th sediment layer (mg P/kg
dry matter);

$PI_{(n)}$ is interstitial phosphorus in n-th sediment layer
(mg P/ℓ);

Figure 14. Sediment Phosphorus Transformation Model after Kamp-Nielsen (1978)

$PE_{(n)}$ and $PNE_{(n)}$ are exchangeable and non-exchangeable phosphorus in n-th sediment layer respectively (both mg P/kg dry matter);

PS is soluble phosphorus in bottom water (mg P/ℓ);

This model considers the interaction between phosphorus fractions in the sediment-water interface as well in sediment layers.

The following assumptions were used by the author during the construction of the given model:

(i) mineralization of particulate phosphorus, sorption equilibrium between the dissolved and adsorbed phosphate and diffusion along the gradients between concentrations in an adjacent layer of sediment are considered a main processes regulating the intensity of phosphorus exchange in the sediment-water interface;

(ii) <u>temperature, oxygen</u> and <u>phosphate concentrations</u> and <u>ratio of exchangeable to non-exchangeable phosphorus</u> are the main driving characteristics in the given model;

(iii) <u>biochemical mineralization of phosphorus in sediment</u> was considered as a first order temperature-dependent reaction;

(iv) <u>diffusion of phosphate</u> and <u>oxygen</u> are described as ordinary Fick's diffusion process, corrected by a coefficient named "diffusion resistance parameter";

(v) <u>the kinetics of sorption processes</u> is regulated by oxygen concentration and the Freundlich and Langmuir equations are used for description of their rates in anaerobic and aerobic conditions respectively.

The main equations of this model are:

$$\frac{dPE_{(n)}}{dt} = S_o - BIO_{(n)}$$

(66)

$$\frac{dPI_{(n)}}{dt} = \frac{TS_{(n)} \cdot BIO_{(n)}}{100 - TS_{(n)}} + DIF_{(n-1)} - DIF_{(n)} \quad \cdot$$

$$
\begin{cases}
\dfrac{1}{1 + \dfrac{TS_{(n)} \cdot PAMX - KPS}{(100 - TS_{(n)})(KPS + PI_{(n)})^2}} & \text{when } OX_{(n)} > LOX \\[4ex]
\dfrac{1}{1 + \dfrac{TS_{(n)} \cdot KAPA}{100 - TS_{(n)}}} & \text{when } OX_{(n)} \leq LOX \\[4ex]
1 \qquad \text{when } PA_{(n)} = 0
\end{cases}
$$

(67)

$$\frac{dOX_{(n)}}{dt} = DIFOX_{(n-1)} - DIFOX_{(n)} - BIOX_{(n)}$$

(68)

where $TS_{(n)}$ is dry matter in n-th sediment layer

   (g/dry matter-100 mℓ);

S_o is "net" phosphorus sedimentation (mg P/m^2-day);

PAMX is maximum sorbed phosphorus in n-th sediment layer

   (mg P/kg dry matter);

KPS is half saturation constant (mg P/ℓ);

KAPA is anaerobic equilibrium constant for sorption

   (1/kg dry matter);

LOX is threshold oxygen level (mg O_2/ℓ).

The concentration of mobile phosphorus (PIAS) in the n-th
sediment layer is presented as

$$PIAS_{(n)} = \begin{cases} PA_{(n)} + PA_{(o)} + PI_{(1)} \cdot \dfrac{100 - TS_{(1)}}{TS_{(1)}} & \text{when } n = 1 \\[2ex] PA_{(n)} + PI_{(n)} \dfrac{100 - TS_{(n)}}{TS_{(n)}} & \text{when } n > 1 \end{cases} \qquad (69)$$

while the total phosphorus concentration (PTOT) is calculated
as the sum of all phosphorus forms:

$$PTOT_{(n)} = PE_{(n)} + PNE + PIAS_{(n)} \qquad (70)$$

The following equations are used in the given model for the
description of the processes defining the phosphorus exchange in
the sediment-water interface:

(i) <u>biological mineralization of phosphorus</u>:

$$BIO_{(n)} = \theta^T \cdot PE_{(n)} \cdot \begin{cases} KAE_{(n)} \cdot OX_{(n)} & \text{when } OX_{(n)} > LOX \\ KAN_{(n)} & \text{when } OX_{(n)} \leq LOX \end{cases} \qquad (71)$$

where $KAE_{(n)}$ and $KAN_{(n)}$ are constants of phosphorus mineralization

  in aerobic and anaerobic conditions respectively (both

  1/mg O_2-day);

  T and θ are temperature in ^oC and temperature coefficient.

(ii) <u>diffusion of phosphorus</u>

$$DIF_{(n)} = KDIF_{(n)} \cdot (PI_{(n)} - PI_{(n+1)}) \cdot \frac{273 + T}{293} ^{*} \qquad (72)$$

where $KDIF_{(n)}$ is a constant of phosphorus diffusion (day^{-1}) and it is calculated by

$$KDIF_{(n)} = KDIF \cdot t \cdot \frac{\dfrac{100 - TS_{(n)}}{100}}{D_{(n)} \cdot \left[\dfrac{D_{(n-1)} + D_{(n)}}{2}\right]} \qquad (73)$$

where t is diffusion resistance coefficient;

$D_{(n)}$ is thickness of n-th sediment layer in m and

$$D_{(n)} = \begin{cases} 10^{-3} & n \le 50 \\ 5.10^{-3} & n > 50 \end{cases}$$

(iii) <u>oxygen consumption in phosphorus mineralization</u>

$$BIOX_{(n)} = 118 \cdot BIO_{(n)} \cdot TS_{(n)} / (100 - TS_{(n)}) \qquad (74)$$

(iv) <u>diffusion of oxygen</u>

$$DIFOX_{(n)} = KDOX_{(n)} \cdot (OX_{(n)} - OX_{(n+1)}) \cdot \frac{273 - T}{293} ^{**} \qquad (75)$$

where $KDOX_{(n)}$ is constant of oxygen diffusion (day^{-1}) and it is calculated as:

$$KDOX_{(n)} = KDOX \cdot t \cdot \frac{\dfrac{100 - TS_{(n)}}{100}}{D_{(n)} \cdot \left[\dfrac{D_{(n-1)} + D_{(n)}}{2}\right]} \qquad (76)$$

---

[*]Condition is that $PI_{(o)} = PS$
[**]Condition is that $OX_{(o)} = OXO$

(v) "net" phosphorus sedimentation

$$S_O = \begin{cases} (\frac{F}{F+1} \cdot SEDP - RESUP) \cdot \frac{100}{TS_{(n)}} & \text{for } n = 1 \\ 0 & \text{for } n > 1 \end{cases} \quad (77)$$

where F is ratio of exchangeable phosphorus to non-exchangeable phosphorus.

(vi) sorption of phosphorus

a. in the sediment surface

$$PA_{(o)} = \begin{cases} \frac{PAMX \cdot (KPS + PS)}{PS} - NAP & \text{for } OX_{(o)} > LOX \\ 0 & \text{for } OX_{(n)} \leq LOX \end{cases} \quad (78)$$

b. in n-th sediment layer

$$PA_{(n)} = \begin{cases} \frac{PAMX \cdot PI_{(n)}}{KPS + PI_{(n)}} - NAP & \text{when } OX_{(n)} > LOX \\ KAPA \cdot PI_{(n)} - NAP & \text{when } OX_{(n)} \leq LOX \end{cases} \quad (79)$$

where NAP is native sorbed phosphorus (mg P/kg dry matter). The value of PAMX is dependent on the oxygen level:

$$PAMX = \begin{cases} PAMXAE & \text{when } OX_{(n)} > LOX \\ PAMXAN & \text{when } OX_{(n)} \leq LOX \end{cases} \quad (80)$$

This model considers 60 layers in the active zone of the sediment. The thickness of the sediment layers were considered to be equal to 1 mm for the upper 5 cm part of the sediment (50 layers) and 5 mm for the remaining sediment zone (10 layers). The model was applied for analysis of the seasonal dynamics of the phosphorus concentration in Lake Esrøm sediment.

5.27 The Wittman et al.(1980) Approach

Several models of phosphorus exchange processes in the sediment-water interface were suggested by the authors for Keszthely Bay of Lake Balaton. Figure 15 illustrates the relationships between phosphorus fractions in water and sediment in these models. The symbols used in Figure 15 are:

P   -   dissolved phosphorus in the water;

A   -   algae in the water;

SP   -   sediment phosphorus;

OM   -   organic matter in sediment;

OM1 -   aerobically decomposable organic matter;

OM2 -   anaerobically decomposable organic matter;

ADB -   adsorbed phosphorus

The numbers near the arrows in Figure 15 show the processes that are modeled. The following equations were used for modeling these processes which are important in phosphorus exchange:

(1) <u>biologically available part of the particulate phosphorus</u>

    <u>(PPIN)</u> entering the Lake Balaton with River Zala[*] discharge water:

$$PPIN = 0.04 \cdot \frac{(TPIN - OPIN) \cdot DEPTH}{d} \cdot \frac{Q}{V} \tag{81}$$

where TPIN and OPIN are total phosphorus and orthophosphate concentrations respectively in River Zala discharge water (g/m^3);

    DEPTH is average water depth (m);

    d is sediment thickness (cm);

    Q is River Zala discharge flow rate (m^3/day);

    V is volume of Keszthely Bay (m^3).

---

[*]River Zala is the main tributary of Lake Balaton
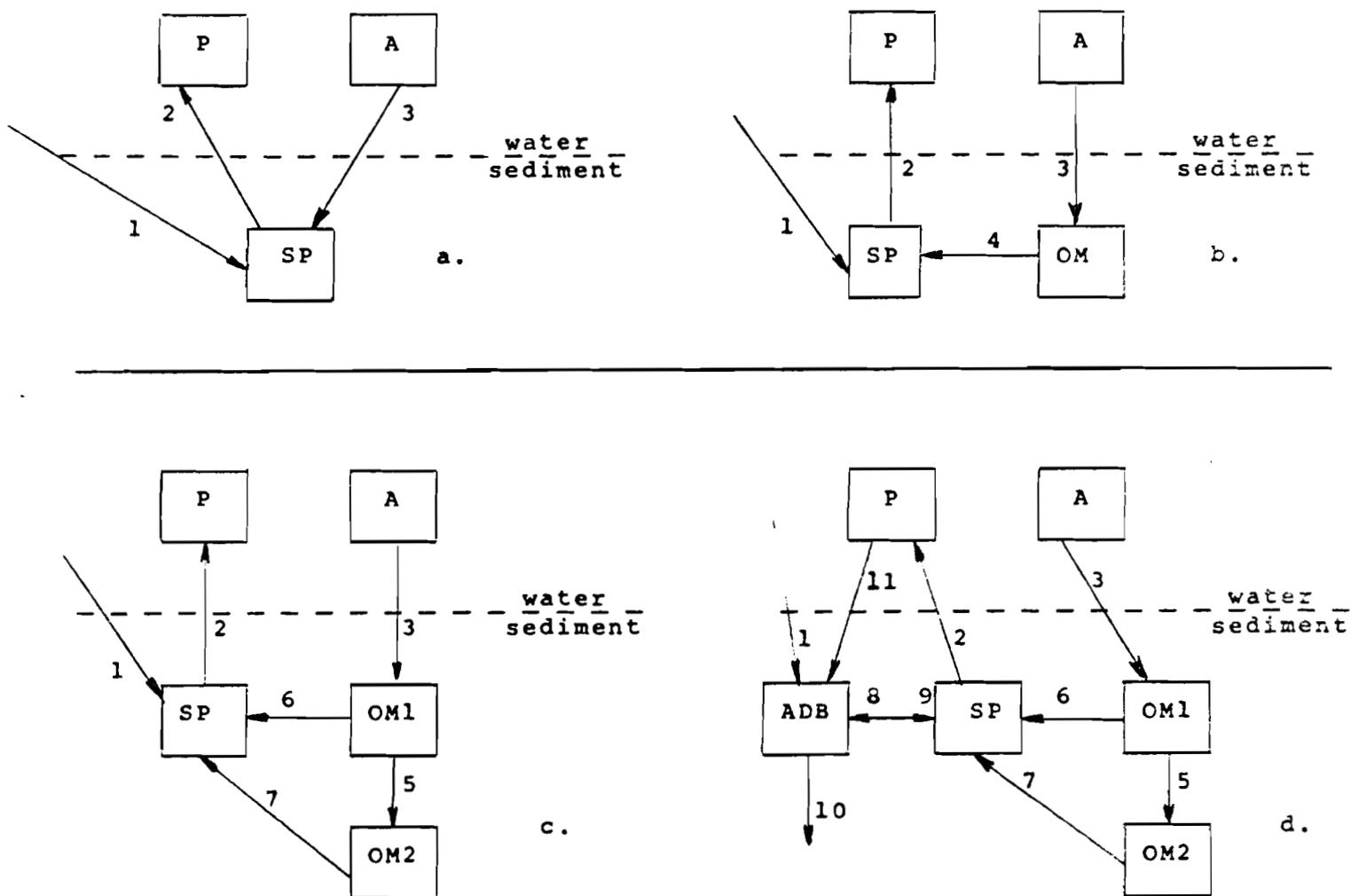
Figure 15.   Models of Phosphorus Exchange in Sediment-Water
Interface for Lake Balaton Ecosystem after
Wittman et al.(1980)

(2) Diffusion (or stirring up) (STIR):

$$STIR = SP \cdot (1 - e^{(-P_1 \cdot WIND)})$$ (82)

where P_1 is the parameter for wind dependency of stirring up;

WIND is wind speed average of eight measurements per day.

(3) Algae settling (ASET):

$$\text{ASET} = \frac{0.5 \cdot (\text{MORT}) \cdot (\text{DEPTH})}{d} \tag{83}$$

where MORT is rate of algae mortality which is equal to $(0.1 \cdot A)$.

(4) Decomposition of organic matter (DEC):

$$\text{DEC} = P_2 \cdot \text{OM} \tag{84}$$

where P_2 is the decomposition rate.

(5) Transformation of organic matter from aerobic to anaerobic (DEC^*):

$$\text{DEC}^* = P_2 \cdot \text{OM1} \tag{85}$$

(6) Rate of aerobic decomposition of organic matter to sediment phosphorus (DEC1):

$$\text{DEC1} = P_5 \cdot P_2 \cdot \text{OM1} \tag{86}$$

where P_5 is the aerobically decomposable part of organic matter.

(7) Rate of anaerobic decomposition of organic matter to sediment phosphorus (DEC2):

$$\text{DEC2} = P_3 \cdot \text{OM2} \tag{87}$$

where P_3 is OM2 decomposition rate.

(8) Adsorption of sediment phosphorus (ADS):

$$\text{ADS} = P_6 \cdot \text{SP} \tag{88}$$

where P_6 is the adsorption rate.

(9) Desorption of adsorbed sediment phosphorus (DES):

$$\text{Des} = P_7 \cdot \text{ADB} \tag{89}$$

where P_7 is the desorption rate.

(10) <u>Mineralization of sediment phosphorus (MIN)</u>:

$$MIN = P_8 \cdot ADB \tag{90}$$

where P_8 is the mineralization rate.

(11) <u>Phosphorus precipitation (PREC)</u>:

$$PREC = 0.03 \cdot PROD \tag{91}$$

where PROD is algae uptake and is equal to

$$PROD = \frac{0.03 \cdot T \cdot A \cdot P}{0.01 + P} \tag{92}$$

In equation (92) T is water temperature in ^oC.

5.28 The Mejer et al. (1980) Approach

The authors proposed the model in the form of the partial differential equations representing the phosphorus and oxygen dynamics in the lake sediments. The following processes were considered in the given model: anaerobic and aerobic decomposition, diffusion, adsorption and chemosorption, sedimentation and resuspension.

The model equations are:

$$\frac{\partial P_e}{\partial t} = -K(\tau) \cdot g(T,OX) \cdot P_e - \frac{dZ}{dt} \cdot \frac{\partial P_e}{\partial z} \tag{93}$$

$$\frac{\partial P_{ne}}{\partial t} = -\frac{dZ}{dt} \cdot \frac{\partial P_{ne}}{\partial z} \begin{cases} \text{if } P_i > P_{i,th} \text{ at any time or depth,} \\ r \cdot (P_i - P_{i,s}) \text{ is added to } P_{ne} \end{cases} \tag{94}$$

$$\frac{\partial P_i}{\partial t} = -\frac{dZ}{dt} \cdot \frac{\partial P_i}{\partial z} + \frac{\frac{\partial}{\partial z}[D_p(T,DM) \cdot \frac{\partial P_i}{\partial z}] + r \cdot K \cdot g \cdot P_e - r \cdot \frac{\partial P_i}{\partial OX} \cdot \frac{\partial OX}{\partial t}}{1 + r \cdot (P_a' + \frac{\partial P_c}{\partial P_i})} \tag{95}$$

if $P_i > P_{i,th}$ at any time or depth, P_i is set equal to $P_{i,s}$.

$$\frac{\partial OX}{\partial t} = \frac{\partial}{\partial z} D_o(T,DM) \cdot \frac{\partial OX}{\partial z} - \frac{dZ}{dt} \cdot OX - \begin{cases} 118 \cdot r \cdot K(\tau) \cdot g \cdot P_e & \text{when } OX > OX_{th} \\ 0 & \text{when } OX \leq OX_{th} \end{cases}$$

(96)

$$\frac{\partial}{\partial t} = g(T,OX) - \frac{dZ}{dt} \cdot \frac{\partial}{\partial z}$$

(97)

$$\frac{dZ}{dt} = \frac{S - R}{10 \cdot DM_o \cdot P_{sed}} - \int_o^{z_{max}} \frac{K(\tau) \cdot g(T,OX) \cdot P_e}{P_{tot}} dZ$$

(98)

where OX and OX_o are interstitial and bottom water oxygen concen-

trations (mgO_2/ℓ) respectively and

OX = OX(t,z) where t is time coordinate (24 hours) and z

is depth coordinate (m) changing from zero to z_{max};

OX_{th} is threshold oxygen concentration above which condi-

tions are considered to be aerobic (mg O_2/ℓ);

DM is dry matter (g DM/100 mℓ) and

DM = DM(t,z); while DM_0 = DM(t,0)   ,

pH is function of t and z and pH=pH(t,z) and it is calculated

as

$$pH = pH(t,0) + \frac{18 \cdot \xi \cdot pH_b}{1 + 18 \cdot \xi}$$

(99)

where $\xi = z/z_{max}$ and pH_b is pH at $z=z_{max}$;

T is temperature in ^{o}C and T = T(t);

g is empirical coefficient showing the influence of T

and OX on "Biological age" of sediment, $\tau = \tau(t,z)$,

relative to chronological age and

$$g = g(t,OX) = \begin{cases} (OX/OX_{th}) \cdot \theta^{(T-T_{ref})} & \text{when } OX > OX_{th} \\ \theta^{(T-T_{ref})} & \text{when } OX \leq OX_{th} \end{cases}$$

(100)

where θ is temperature coefficient;

P_e is exchangeable phosphorus in the sediment-water interface,

mg P/kg DM and $P_e = P_e(t,z)$;

P_{ne} is non-exchangeable phosphorus in the sediment-water interface,

mg P/kg DM and $P_{ne} = P_{ne}(t,z)$;

f is ratio P_e/P_{ne};

P_i is interstitial phosphorus, mg P/ℓ and $P_i = P_i(t,z)$;

$P_{i,s}$ is solubility of phosphate, mg P/ℓ and $P_{i,s} = P_{i,s}(pH)$;

$P_{i,th}$ is threshold of P_i above which phosphate precipitates

at an amount of $P_i - P_{i,s}$ and $P_{i,th} = P_{i,th}(pH)$;

P_a is adsorbed phosphorus in mg P/kg DM and it is in equilibrium

with interstitial phosphorus

$$P_a = P_a(P_i) = k \cdot P_i^{\alpha} \qquad (101)$$

where k and α are Freundlich adsorption constants;

P_{cn} is native chemosorbed phosphorus, mg P/kg DM;

P_c is chemosorbed phosphorus, mg P/kg DM and

$$P_c = P_c(P_i, OX) = \max \left\{ 0, P_c^{max} \cdot \gamma \cdot \frac{P_i}{K_P + P_i} - P_{cn} \right\} \qquad (102)$$

where γ is switch describing reduced chemosorption at anoxic

sediment and

$$\gamma = \frac{1}{1 + e^{-4(OX-1.5)}} \qquad (103)$$

K_p is half saturation constant, mg P/ℓ and $K_p = K_p(pH)$;

P_c^{max} is maximum chemosorption capacity in mg P/kg DM and

$$P_c^{max} = P_c^{max}(pH);$$

r is relative dry matter content, kg DM/ℓ and

$$r = \frac{DM}{100 - DM} \tag{104}$$

1/(1+r) is relative water volume, 1/kg DM available for diffusion;

P_{tot} is total phosphorus mg P/kg DM and

$$P_{tot} = P_e + P_{ne} + P_a + P_c + P_{cn} + P_i/r \quad , \tag{105}$$

D_p is diffusion coefficient for phosphorus in interstitial water, m^2/day and

$$D_P = D_P(T,DM) = \begin{cases} D_P^{max} \cdot (1 + \phi \cdot T) \cdot (\beta/(1+r)) & \text{at } z > 0 \\ D_P^{max} \cdot (1 + \phi \cdot T) & \text{at } z = 0 \end{cases} \tag{106}$$

where β is diffusion resistance coefficient;

ϕ is temperature coefficient;

D_O is diffusion coefficient for oxygen in interstitial water, m^2/day and

$$D_O = D_O(T,DM) = \begin{cases} D_O^{max} \cdot (1 + \phi\, T) \cdot (\beta/(1+r)) & \text{at } z > 0 \\ D_O^{max} \cdot (1 + \phi\, T) & \text{at } z = 0 \end{cases} \tag{107}$$

$K(\tau)$ and k are rate constants of decay for the total distribution of P_e-fractions and one single fraction respectively (both day^{-1}) and

$$K(\tau) = \frac{\displaystyle\int_0^\infty k \cdot p_O(k) \cdot e^{-k \cdot \tau} \cdot dk}{\displaystyle\int_0^\infty p_O(k) \cdot e^{-k \cdot \tau} \cdot dk} \tag{108}$$

where $p_O(k)$ is distribution (density function) of rate constants (k) for various P_e-fractions in new sedimented matter;

Z is displacement of water/sediment interface relative to value at t = 0 (m) and Z = Z(t).

Boundary conditions at $Z = 0$ for this model is

$$P_e(t,0) = \frac{f}{1 + f} \cdot P_{sed}$$

$$P_{ne}(t,0) = \frac{1}{1 + f} \cdot P_{sed}$$

$$P_i(t,0) = P_s \tag{109}$$

$$OX(t,0) = OX_o$$

$$(t,0) = 0$$

This model was applied for the analysis of the data on the phosphorus changes in Lake Esrøm (Denmark) sediments. Model output showed a reasonable agreement with observations except at the top of the sediment layer in the April-May period. The authors give two possible reasons. The first one is that some of the essential mechanisms of phosphorus transformations are not included in the given model and the second is due to insufficient measurements in the period mentioned.

5.29 Jacobsen's (1980) Approach

The theoretical model suggested by Jacobsen (1980) is based on consideration of the mineral and chemical properties of the sediments and the sorption processes in the sediment-water interface. Sorption is defined as the difference between chemosorption, adsorption and desorption. It was suggested that the process of chemosorption is a chemical reaction fixing the soluble (or adsorbed) compounds by particles and it is important that this reaction is not reversible by lowering the soluble and adsorbed compound concentrations. On the other hand, adsorption is considered a physical fixation of the soluble compounds by particles

and the amount of adsorbed (or desorbed) matter is constantly equilibrated by the concentration of matter in a soluble form.

The scheme of the reactions considered by the model may be presented as follows:

$$P_s + AC \underset{k_d}{\overset{k_a}{\rightleftarrows}} AP \overset{k_c}{\longrightarrow} CP + AS \qquad (110)$$
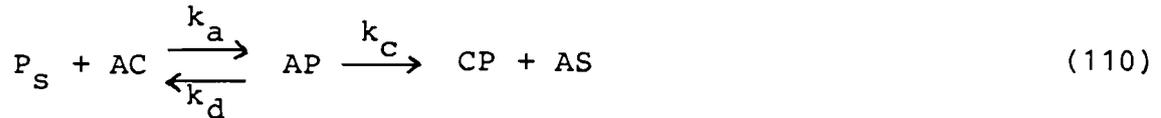
where P_s, AD and CP are soluble, adsorbed and chemosorbed phosphate

concentrations respectively;

AC is adsorption capacity;

k_a, k_d and k_c are reaction rate constants.

The kinetics equations of the given model are written as:

$$\frac{dP_s}{dt} = k_d \cdot AP - k_a \cdot P_s \cdot AC + S \qquad (111)$$

$$\frac{dAP}{dt} = k_a \cdot P_s \cdot AC - k_d \cdot AP - \frac{dCP}{dt} \qquad (112)$$

$$\frac{dCP}{dt} = \max \{0, k_c [CC(AP) - CP]\} \qquad (113)$$

where S is external phosphorus flux;

CC is maximum chemosorption capacity described as

$$CC = \alpha \cdot CC_{Ca} + \beta \cdot CC_{Fe3+} =$$

$$= \alpha \cdot \left(\frac{2.51 \cdot AP}{AP + 4.71}\right) + \beta \cdot \left(\frac{(11-pH) \cdot 9 \cdot AP}{AP + \varphi(pH)}\right) \qquad (114)$$

α is concentration of $CaCO_3$ in dry sediments;

β is concentration of $Fe(OOH)$ in dry sediment.

In the equation (114) $\varphi(pH)$ is the model function regulating the rate of exchange processes by pH and it is described by

$$\varphi(pH) = \begin{cases} 0.25 & \text{when } pH \leq 8.5 \\ (10.5 \ pH - 89) & \text{when } pH \geq 8.5 \end{cases} \qquad (115)$$

The Freundlich formula is used in this model to describe the adsorption isotherm:

$$AP = k_f \cdot (P_s)^p \qquad (116)$$

where k_f and p are Freundlich coefficients.

It was assumed that the model parameters such as CC, kf and p are defined by conditions in sediments and their values depend on the environmental characteristics (E_h, pH and temperature) and mineralogical properties of sediments. This theoretical model is under experimental study at present.

5.30 Leonov's (1981) Approach

Phosphorus exchange in the sediment-water interface was considered in the phosphorus transformation model named BALSECT (BALATON SECTOR MODEL) used for the analysis of phosphorus cycling and phytoplankton growth in the Lake Balaton ecosystem. Previously, the phosphorus exchange processes in the sediment-water interface were considered in the simplest way (Leonov, 1980). An improved version of this model takes into account the sedimentation and resuspension of non-living particulate phosphorus (P_D) and the release of the dissolved inorganic phosphorus (DIP) from the sediment. These processes are modeled

on the basis of the approach suggested by Somlyódy (1980) who studied the wind influence on the exchange processes in the sediment-water interface in the central part of Lake Balaton, the Szemes Basin with a mean depth of about 4.3 m.

Because BALSECT considers the phosphorus dynamics in different parts of Lake Balaton, namely in Keszthely Bay, Sliliget, Szemes and Siofok Basins, corrections for the varied depths were introduced in the model equations for each basin.

The equation for the dynamics of P_D is written as

$$\frac{dP_D}{dt} = \pm R - K_{sed} \cdot \left(\frac{4.3}{d}\right) \cdot P_D + P_{Dres} \cdot \left(\frac{4.3}{d}\right)^2 \cdot W^v \qquad (117)$$

where R is the rate of P_D transformations that take into account the effects of biochemical and hydrodynamical processes and external loading (mg P/ℓ-day);

K_{sed} is rate constant of P_D sedimentation (day^{-1});

d is averaged depth of the basin considered (m);

W is wind speed in m/sec;

v is empirical coefficient;

P_{Dres} is time-averaged flux of particulate phosphorus from the sediment (mg P/ℓ-day).

The equation for dynamics of DIP in BALSECT is written as

$$\frac{dDIP}{dt} = \pm R' + DIP_{rel} \cdot \exp(K \cdot T) \cdot W \qquad (118)$$

where R' is rate of DIP transformation as a result of biochemical and hydrodynamical processes and external loading (mg P/ℓ-day);

K is rate constant of phosphorus transformation in sediment (day^{-1});

T is water temperature in °C;

DIP_{rel} is rate of internal loading or phosphorus release

from sediment (mg P/ℓ-day) and it is equal to

$$DIP_{rel} = DIP_{sed} \cdot (\frac{4.3}{d}) \cdot \frac{A}{V} \qquad (119)$$

where A and V are surface area (m^2) and volume (m^3)

of the basin considered;

DIP_{sed} is time-averaged flux of mineral phosphorus

from sediment (mg P/ℓ-day).

The values of parameters such as d, A, V, P_{Dres} and DIP_{sed} are specific for each basin of Lake Balaton. The values of temperature, T, and wind speed, W, are considered to be similar for all basins and they are taken during the model run from a special file with a real set of measurements as input data. Temperature is the daily mean value for each day within the year while wind data includes eight measurements for speed and direction per day, for the whole year.

5.31 Kozerski's (1981) Approach

The author proposed a model of the nutrient exchange between the water and sediments, for shallow, eutrophic lakes. The interactions of phosphorus compounds in the sediment-water layer modeled is schematically shown in Figure 16. The original version of the model (Kozerski, 1977) takes into account:

- the release of dissolved phosphorus from the sediment to water by diffusion;

- the resuspension and sedimentation of the detritus and the particulate phosphorus adsorbed by the suspended solids;

- the resuspension of algae;
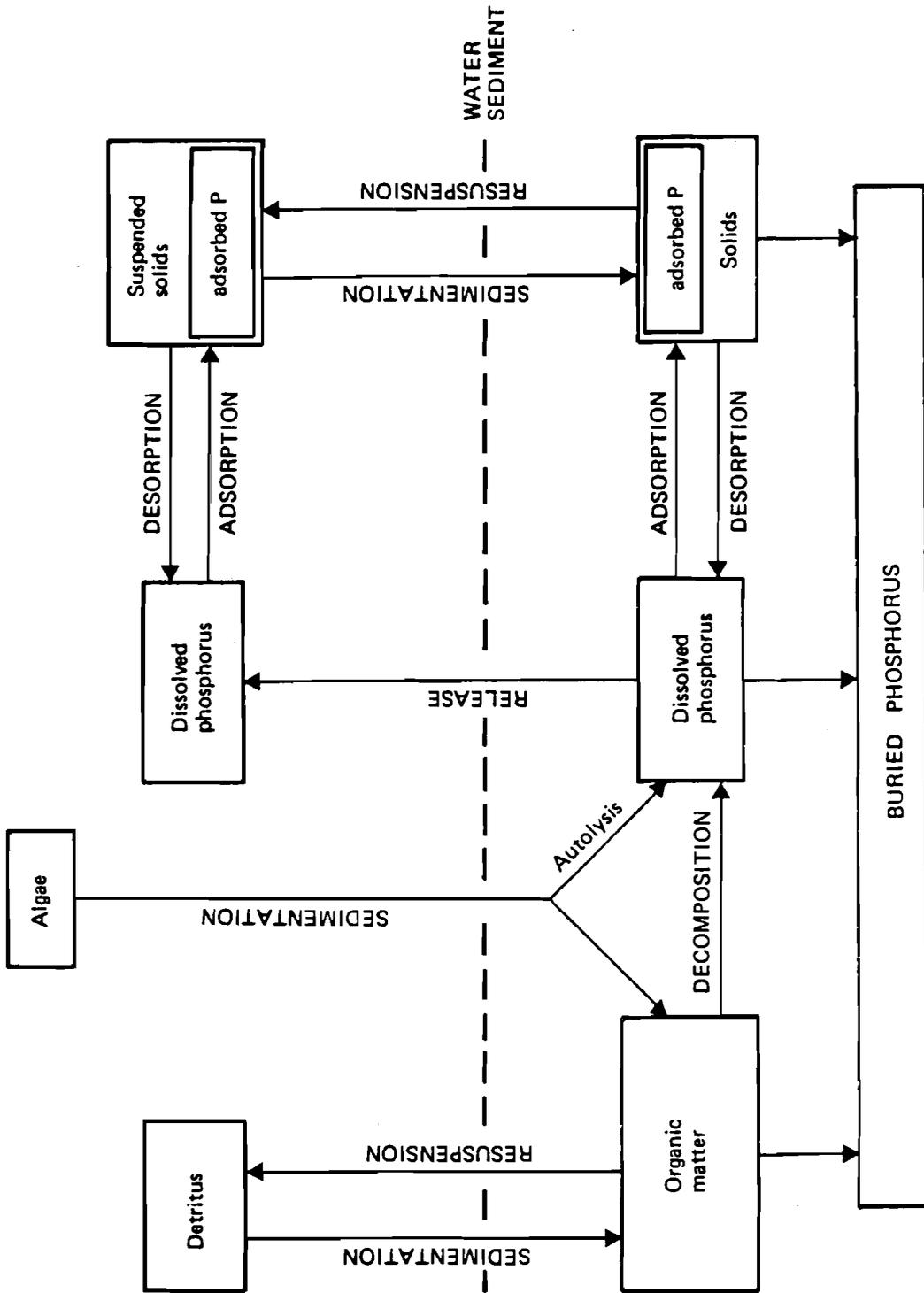
Figure 16. Interactions of Phosphorus Compounds in the Sediment-Water Interface after Kozerski (1981)

- the adsorption and desorption of phosphate by the
  sediment particles and especially the iron compounds;

- the decomposition of organic matter, including the
  liberation of nutrients and oxygen demand in proportion
  to the intensity of the decomposition process.

The diffusion exchange of the dissolved phosphorus through
the sediment-water interface is written as

$$ZPS = Z \ (P_i - P_s) \tag{120}$$

where ZPS is the rate of the phosphorus exchange by diffusion;

Z is the exchange velocity (m/d) derived from the eddy
diffusion.

A similar mathematical term is assumed for the description
of the resuspension of the particulate organic matter (but with
a much smaller rate coefficient). The adsorption of the dissolved
phosphorus on the sediment particles is based on the Langmuir
isotherm and is given by

$$ADS = K_{ADS} \cdot P_i \cdot (ISS \cdot AS - PAS) \tag{121}$$

where K_{ADS} is the rate coefficient;

ISS is the maximum adsorption capacity (which is higher
in oxic than in anoxic conditions);

PAS is the concentration of adsorbed phosphorus;

AS is the concentration of adsorbates.

The desorption of the dissolved phosphorus written as a
first-order kinetic equation is:

$$DES = K_{DES} \cdot PAS \tag{122}$$

where K_{DES} is the rate coefficient; its value differs for oxic and
anoxic conditions.

The transfer from oxic to anoxic conditions is controlled by the oxygen balance in the sediment. The oxygen conditions in the sediment is considered to be oxic if the oxygen supply to the sediment is greater than the oxygen demand for the decomposition of organic matter. This is written as

$$OXW \cdot Z > DEM \cdot (\text{specific } O_2 \text{ demand}) \qquad (123)$$

where OXW is the oxygen concentration in water (pelagial);

DEM is the intensity of the decomposition of organic

matter.

A detailed description of the model is given elsewhere (Kozerski, 1977). The last version of this model (Kozerski, 1981) is being studied now and it is assumed this model will be used to reflect the basic features of the phosphorus budget of Lake Balaton.

5.32 Brief Comparison of the Models Considered

The purposes of the models considered in this report are more or less connected to the problem of phosphorus cycling in water bodies and the influence of sediment as a potential nutrient source. The models described differ considerably in their underlying concepts. It is mainly defined by significant differences in the role attributed to the individual processes regulating the phosphorus exchange in the sediment-water interface.

The general information on the models described, summarized arbitrarily, is given in Table 3. It indicates that four theoretical principles are used in constructing the phosphorus exchange models. These are: (i) balance relations; (ii) empirical dependencies; (iii) simple chemical kinetics and (iv) combined interactions to reproduce the mechanisms of phosphorus

Table 3. General Information for Models Described

NN	Authors	Model basis	Main objectives			Type of equations			
			scientific understanding	fore-casting	empi-rical	reg-res-sion	ba-lan-ce	dif-feren-tial	partial differen-tial
1	Olsen(1958,1964)	Simple chemical kinetics		x	x				
2	Porcella et al(1971)	Balance relations		x			x		
3	Li et al(1972)	Simple chemical kinetics		x				x	
4	Lorenzen(1973)	Simple chemical kinetics		x				x	
5	Wildung and Schmidt(1973)	Empirical dependencies		x		x			
6	Dahl-Madsen,Nielsen(1974)	Simple chemical kinetics		x				x	
7	Berner(1975)	Simple chemical kinetics		x				x	
8	Gaume and Duke(1975)	Simple chemical kinetics		x				x	
9	Kamp-Nielsen(1974,1975b)	Empirical dependencies		x	x				
10	Jørgensen et al(1975)	Combined interactions		x	x			x	
11	Kamp-Nielsen(1976)	Combined interactions		x	x			x	
12	Jørgensen(1976)	Combined interactions	x	x	x			x	
13	Fillos and Biswas(1976)	Balance relations		x			x		
14	DiGiano and Snow(1976)	Simple chemical kinetics		x				x	
15	Lam and Jacuet(1976)	Empirical dependencies		x	x				
16	Thibodenaus,Cheng(1976)	Empirical dependencies		x	x				
17	Lung et al(1976)	Simple chemical kinetics		x				x	
18	Spear,Hornberger(1978)	Combined interactions		x	x			x	
19	Poon(1977)	Simple chemical kinetics		x				x	
20	Dahl-Madsen(1978)	Simple chemical kinetics		x				x	
21	Nyholm(1978)	Simple chemical kinetics		x				x	
22	Theis and McCabe(1978)	Simple chemical kinetics		x	x				
23	Kremer and Nixon(1978)	Empirical dependencies		x	x				
24	Ulen(1978 b)	Simple chemical kinetics		x	x				
25	Imbøden and Gahter(1978)	Empirical dependencies	x	x			x		
26	Kamp-Nielsen(1978)	Combined interactions		x	x			x	
27	Wittmann et al(1980)	Simple chemical kinetics	x	x	x			x	
28	Mejer et al(1980)	Combined interactions		x	x				x
29	Jacobsen(1980)	Combined interactions		x	x			x	
30	Leonov(1981)	Combined interactions		x	x			x	
31	Kozerski (1981)	Simple chemical kinetics	x	x	x			x	

transformations in the sediment-water interface. Models with balance relations may only give very rough approximations in the description of the effects of sediment in phosphorus dynamics, while other models intended for evaluating phosphorus cycling in water as result of complex physical-chemical interactions, including contribution of sediment. For example, the models constructed on the basis of empirical dependencies consider:

(i) correlation between total phosphorus in solution, with temperature, organic phosphorus and total solid contents in sediment, and temperature-organic phosphorus interaction (Wildung and Schmidt, 1973);

(ii) regenerated amount of phosphorus as result of wave oscillatory and sediment mean grain size (Lam and Jaquet, 1976);

(iii) sediment phosphorus release defined by:

(a) diffusion (Kamp-Nielsen, 1974);

(b) desorption, diffusion and biological degradation in anaerobic and aerobic conditions (Kamp-Nielsen, 1975b);

(c) thermal structure within water body and turbulent diffusion (Thibodenaus and Cheng, 1976);

(d) primary production (Imboden and Gachter, 1978) and phosphorus content in sediment, water column depth and temperature (Kremer and Nixon, 1978);

(iv) interaction of plankton organisms, soluble phosphorus and sediment (Spear and Hornberger, 1978);

(v) relationship of phosphorus diffusion with sediment phosphorus and wind speed, as well as phosphorus precipitation as a function of primary production (Wittman et al. 1980).

The models constructed on the principles of simple chemical
kinetics include consideration of the following important proces-
ses:

    (i)   phosphorus adsorption and desorption (Olsen, 1958; 1964);

   (ii)   equilibrium between phosphorus fractions in sediments
           (Li et al. 1972);

  (iii)   interactions between sedimentation and resuspension
           (Lorenzen, 1973; Lorenzen et al. 1976);

   (iv)   phosphorus exchange as a temperature dependent process
           (Gaume and Duke, 1975; Dahl-Madsen, 1978; Nyholm, 1978)
           and without temperature correction (Dahl-Madsen and
           Nielsen, 1974);

    (v)   diffusion (Berner, 1975; Spear and Hornberger, 1978;
           Theis and McCabe, 1978; Ulen, 1978b);

   (vi)   diffusion and sedimentation (DiGiano and Snow, 1977);

  (vii)   diffusion, sedimentation and phosphorus transformation
           in sediment (Lung et al. 1976);

 (viii)   diffusion and phosphorus transformation in sediment
           (Poon, 1977);

   (ix)   diffusion, algae sedimentation, decomposition of organic
           matter, adsorption of sedimentary phosphorus and
           mineralization of sediment phosphorus (Wittman et al.
           1980);

    (x)   phosphorus sediment release by diffusion, resuspension
           and sedimentation of phosphorus compounds, adsorption
           and desorption, decomposition of sediment organic
           material (Kozerski, 1981).

The models constructed on the basis of combined interactions between empirical dependencies and chemical kinetics simulate the course of the following processes:

(i) accumulation and mineralization of exchangeable phosphorus in sediment, resuspension of total sedimentary phosphorus, desorption-adsorption interactions as well as diffusion (Kamp-Nielsen, 1977);

(ii) temperature dependent phosphorus transformation in sediment and phosphorus diffusion (Jørgensen et al. 1975) and also phosphorus sedimentation (Jørgensen, 1976);

(iii) biochemical mineralization of particulate phosphorus, sorption equilibrium between dissolved and adsorbed phosphate, phosphorus sedimentation, diffusion of phosphorus and oxygen as well as oxygen consumption in phosphorus mineralization in sediment (Kamp-Nielsen, 1978);

(iv) anaerobic and aerobic decomposition of sediment phosphorus, diffusion, adsorption and chemosorption, sedimentation and resuspension, oxygen and pH dynamics (Mejer et al. 1980);

(v) phosphorus sorption as the difference between chemosorption, adsorption and desorption as a function of environmental characteristics (E_h, pH and temperature) (Jacobsen, 1980);

(vi) interaction between sedimentation and resuspension of nonliving particulate phosphorus and release of mineral phosphorus from the sediment as functions of phosphorus content in sediments, water column depth, wind speed and temperature (Leonov, 1981).

It should be noted that only a few of the models have been developed with the aim of arriving at a better understanding of the complex processes in the phenomenon of phosphorus exchange across the sediment-water interface. Table 3 also gives an indication of the type of equations used in the models described. It can be seen that empirical and differential equations are more often used than other equations. Most of the models include the rate coefficients with the order of the time scale equal to a day, and it allows one to simulate the phosphorus dynamics and phosphorus exchange in large periods of time, such as months and years. The information on the values of rate coefficients and other model parameters used in the simulation of phosphorus transformations and phosphorus release from sediment is given in Table 4. The symbols used in Table 4 are similar to those in the model equations reviewed in this report and are used by the authors in formulating their models.

5.33 Other Models Relevant to the Problem of
      Nutrient Transport in the Sediment Water Layer

In the literature there are a number of models not directly connected with the phosphorus exchange in the sediment-water interface, but indirectly relevant to the problem of the nutrient transport and release from the sediment. Lerman (1977) formulated general theoretical approaches to modeling the migration processes and physical-chemical reactions within the sediment-water layer and his modeling principles for migration of anionic species and reactions of chemical ingredients in deep sea sediments may be used after slight modification for studying shallower sediments in fresh water bodies.

Table 4. Review of Rate Coefficients used in the Modeling
the Phosphorus Release from Sediments

Authors	Number of equations in given report	Parameters	Symbol	Dimensions	Values
Kramer et al(1972)	7	Freundlich coefficients for oxidised sediments	K V	- -	2.6 0.26
		Coefficients for exchange term for oxidized sediments	K_b V_b	- -	2.2 -0.05
		Freundlich coefficients for reduced sediments	K V	- -	1.8 0.26
		Coefficients for exchange term for reduced sediments	K_b V_b	- -	2.4 -0.05
Stumm and Leckie (1971)	-	Diffusion coefficient	D	cm^2/sec	$1 \cdot 10^{-6}$
Porcella et al(1971)	-	Constant rate of P release from sediment	K_1	day^{-1}	0.005
Welch et al(1973)	-	Constant sedimentation rate	S	g/m^2-year	2.7
		Constant release rate	R	- " -	2.2
Lorenzen(1973)	17-18	Specific rate of nutrient transfer to sediment	K_1	m/year	40.0
		Specific rate of nutrient transfer from sediment	K_2	- " -	0.0085
Imboden(1974)	-	Phosphorus release rate from sediments	S	mgP/m^2-day	0.27-500
Kamp-Nielsen(1974)	-	Diffusion coefficients	D	cm^2/sec	$0.6 \cdot 10^{-6}$
Jørgensen et al(1975)	26-27	Decomposition rate of exchangeable-P to interstitial-P	k	day^{-1}	$2 \cdot 10^{-4}$
		Temperature coefficient	θ	-	1.02
Lorenzen et al(1976)	17-18a	Total exchangeable-P in sediments	C_s	g/m^3	240.0
		Specific rate of phosphorus transfer to sediment	K_1	m/year	36.0
		Specific rate of phosphorus transfer from sediment	K_2	- " -	0.0012
		Fraction of total-P input to sediment available for exchange	K_3	- " -	0.6
Jørgensen(1976)	38-40	Phosphorus content in phytoplankton	PP	-	1/144
		Settling fate	SA	day^{-1}	0.04
		Biodegradation rate of detritus	K4	- " -	0.1
		Biodegradation rate of organic-P in sediment	K5	- " -	0.0018
		Temperature coefficient	K6	-	1.02
		Dry matter of upper layer in sediemnt	DMU	kg/kg	0.925
		Upper unstabilized layer of sediment	LUL	mm	100.0
		Ratio of total-P to exchangeable-P in sediment	f	-	29/12
Schindler et al(1976)	-	Diffusion coefficient	D	cm^2/sec	$2 \cdot 10^{-5}$
DiGiano and Snow (1976)	42-44	Phosphorus release rate	K_1	mgP/l-day	0.091
		Phosphorus sedimentation rate	K_2	day^{-1}	0.176
Lam and Jaquet(1976)	45	Proportionality constant	k_r	-	$6.4 \cdot 10^{-4}$
		Sediment density	ρ_s	g/cm^3	2.6
		Velocity	u_a	cm/sec	1.0

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Table 4. (contd..)

Authors	Number of equations in given report	Parameters	Symbol	Dimensions	Values
Lung et al(1976); Lung and Canale (1976)	48-52	Degradation rate of particulate-P to dissolved-P in hypolimnion	μ_2	day^{-1}	0.108
		Degradation rate of particulate-P to dissolved-P in sediment	μ_3	day^{-1}	$1.4 \cdot 10^{-4}$
		Diffusion coefficient in interstitial water	D	cm^2/sec	$2 \cdot 10^{-6}$
		Settling velocity in hypolimnion	V_{s2}	m/day	0.3-0.5
		Eddy diffusion coefficient	k^{s2}	cm^2/sec	0.4
Freedman and Canale(1977)	-	Diffusion coefficient	D	cm^2/sec	1 - 1.5
		Porosity	$\emptyset$	-	0.8-0.?5
Poon(1977)	58	Flushing rate	$D^{\bullet}$	1/day	0.025-0.1
		Rate of P-concentration change	K	day^{-1}	0.04-0.11
Dahl-Madsen(1978)	59	Rate constant of sediment mineralization	KMSP	day^{-1}	1.5-1.9
		Temperature coefficient	Θ	-	1.14
Nyhoul(1978)	60	Rate constant of P-release from sediment	$K_{r(20°)}$	day^{-1}	1.0-1.7
		Temperature coefficient	Θ	-	1.14
Spear and Hornberger (1978)	48	Porosity	$\emptyset$	-	0.2-0.4
		Diffusion coefficient	D	cm^2/sec	$(1-2) \cdot 10^{-5}$
		Characteristic length for diffusion process	L	cm	10.0
Imboden and Gachter (1978)	-	Diffusion coefficient	K	cm^2/sec	0.03-0.25
Kamp-Nielsen(1978)	66-80	Aerobic mineralization constant in sediment layers	KAE	$1/mgO_2$-day	0.0002-0.14
		Anaerobic mineralization constant in sediment layers	KAN	- " - " -	0.0001-0.05
		Anaerobic equilibrium constant for sorption	KAPA	1/kg dry matter	45.0
		Diffusion constant for P	KDIF	1/day	0.0012
		Diffusion constant for O_2	KDOX	- " -	0.00016
		Half saturation constant	KPS	mgP/l	0.104
		Threshold oxygen level	LOX	mgO_2/l	0.67
		Native sorbed P	NAP	mgP/kg dry matter	20.0
		Maximum sorbed P in sediment at aerobic condition	PAMXAE	- " - " - " -	44.65
		Maximum sorbed P in sediment at anaerobic condition	PAMXAN	- " - " - " -	19.0
		Non-exchangeable P	PNE	- " - " - " -	1300.0
		Temperature coefficient	Θ	-	1.09
		Diffusion resistance coefficient	t	-	0.3
Wittman et al(1980)	81-92	Sediment thickness	d	cm	10.0
		Parameter for wind dependency of stirring	P_1	day^{-1}	0.001-0.004
		Rate of organic matter decay in aerobic conditions	P_2	- " -	0.08-0.2
		Rate of anaerobic decay of organic matter	P_3	- " -	0.08-0.2
		Threshold level of average wind velocity	P_4	m/sec	2-2.5
		Aerobically decomposable part of organic matter	P_5	-	0.4-0.6
		Adsorption rate of sediment P:	P_6	day^{-1}	
		in aerobic conditions			0.05
		in anaerobic conditions			0-0.01
		Desorption rate of adsorbed sediment phosphorus:	P_7	- " -	
		in aerobic conditions			0-0.01
		in anaerobic conditions			0.05
		Mineralization rate of sediment P	P_8	- " -	0.05

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Table 4. (contd..)

Authors	Number of equations in given report	Parameters	Symbol	Dimensions	Values
Mejer et al.(1980)	93-109	Diffusion coefficient for O_2 in interstitial water	D_o^{max}	m^2/day	$3 \cdot 10^{-4}$
		Diffusion coefficient for P in interstitial water	D_p^{max}	- " -	$4 \cdot 10^{-4}$
		Ratio exchangeable-P to non-exchangeable-P in sediment	f	-	1.717
		Decomposition rate constant	k	day^{-1}	0.68
		Threshold oxygen level above which conditions are aerobic	OX_{th}	mgO_2/l	1.0
		pH on maximum depth of sediment	pH_b	-	6.8
		Maximum depth of sediment	z_{max}	m	0.1
		Temperature coefficient	Θ	$-$	1.091
		Temperature coefficient	ϕ	$°C^{-1}$	0.04
		Freundlich coefficient	α	-	0.79
		Freundlich coefficient	k	-	1000.0
		Diffusion resistance due to dry matter	β	-	0.3
		Native chemosorbed P	P_{cn}	mgP/kg dry matter	100.0
Leonov(1981)	117-119	Rate constant of non-living particulate-P sedimentation	X_{sed}	day^{-1}	0.25
		Time-averaged flux of particulate-P from sediments	P_{Dres}	mgP/l-day	$7 \cdot 10^{-4}$
		Empirical coefficient showing wind effect on resuspension of non-living particulate-P	v	-	1.0
		Rate constant of P transformation in sediment	x	day^{-1}	0.125
		Averaged depth for:	depth	m	
		Basin I			2.28
		Basin II			2.87
		Basin III			3.22
		Basin IV			3.68
		Time-averaged flux of DIP from sediment for:	DIP_{rel}	mgP/l-day	
		Basin I			$1.45 \cdot 10^{-5}$
		Basin II			$5.2 \cdot 10^{-6}$
		Basin III			$4.2 \cdot 10^{-6}$
		Basin IV			$3.3 \cdot 10^{-6}$

Many papers describe the models of physical and chemical processes in the sediment-water layer. Moore and Silver (1972) considered theoretical models of nutrient transport due to sediment-water interactions with specific emphasis on the nutrient diffusion for an infinitely deep lake, for a lake of finite depth and for a well stirred lake of finite depth, using in all of these cases the hypothesis on the infinitely deep sediment layer. The diffusion model of nutrient transport for longitudinal mixing in the porous media is given by Cassel et al. (1974). DiGiano (1971) suggested several models of nutrient transport owing to deposit-water reactions with emphasis on (i) pore diffusion through interstitial water of deposit; (ii) interfacial transport in the sediment-water interface; (iii) diffusion with simultaneous adsorption and (iv) nutrient release via diffusion. Tzur (1971) proposed a model to describe the physical processes such as diffusion and advection in accumulating sediments.

Modeling principles of the adsorption-desorption phenomenon are considered in the papers describing the movement of chemicals through adsorbing porous media (Hashimoto et al. 1964; Lindstrom et al. 1967, 1971; Oddson et al. 1970). Models of adsorption equilibrium between the solution and adsorbed phases have been proposed by Lapidus and Amundsen (1952). Hashimoto et al. (1964) considered a longitudinal mixing process as well as equilibrium and linear adsorption for a one-dimensional flow. Lindstrom et al. (1967) and Davidson and Chang (1972) described the movement of organic chemicals through porous media, using the hypothesis on instantaneous adsorption with linear as well as single-valued relations between adsorption and desorption. The mathematical models of the movement of an adsorbed chemical through a porous medium for steady-state conditions in the soil-water

Some of the mathematical models describing the transport of cohesive sediments in water bodies are used for the quantitative determination of the sediment transport as well as the fate of sediments and associated pollutants and their effects on the water quality (Sakhan et al. 1972; Lick et al. 1976; Sheng and Lick, 1979; Fukuda and Lick, 1980). Simons and Sentürk (1977) considered the basic ideas and fundings upon which knowledge of sedimentation is based including transport concepts, formulas of bed load, models of suspended solid load and methods of measurements and estimation of the sediment discharge of streams. Partheniades (1972) summarized the results of recent laboratory research and reviewed the literature on erosion and deposition of cohesive sediments. Models of sediment suspension due to diffusion and oscillatory water waves were considered by Willis (1972) and Das (1972). Herczynski and Pienkowska (1980) reviewed the classical approaches in modeling the process of sediment suspension.

A large number of reports appeared, dealing with the modeling of particulate transport. Hahn et al. (1978) suggested a model for particles transport and sedimentation which considered (i) the mixing process; (ii) the aggregation process determined by chemical and hydrodynamic parameters; (iii) the aggregation controlled sedimentation process and (iv) erosion. Somlyódy (1978) attempted to conceptually incorporate in the hydrodynamical model all the important processes in a river such as turbulent diffusion, convection, deposition, reentrainment and combined interactions responsible for the transport of micropollutants, dissolved as well as solid forms. The models presented by

Nihoul and Adam (1975), Ariathurai and Krone (1976), and Smith and O'Conner (1977) consider the convection and dispersion of particulates in a two-dimensional flow.

CONCLUSIONS

Sediments should not be ignored as a nutrient sources owing to the high level of nutrients, in particular, phosphorus in the sediments and its importance in the nutrient cycling within water bodies. The role of sediments in water quality problems, including eutrophication, must therefore be considered and realistic models of phosphorus transformation in the sediment-water interface and phosphorus exchange need to be developed. This report summarizes the information available on studies of the phosphorus system in the sediment-water interface.

Estimates of the sediment phosphorus release rates are based on laboratory experiments as well as on simple balance calculations. Therefore these rates may be considered only as approximations of the characteristics of phosphorus exchange reactions in nature. The effectiveness of phosphorus release from the sediment is defined by the combined effect of environmental factors determining the development of physical, chemical and biological processes. To the present time, the theoretical consideration of the role of these processes are complicated, owing to their interactions and simultaneous accomplishment. On the basis of available information, an attempt was made to show the role of some of these processes in the phosphorus release from the sediments, namely mixing and diffusion, as well as factors of environment such as temperature, levels of oxygen and organic matter, oxidative state of sediment, redox

conditions and bacterial activity. These processes and factors
are considered to be rather important for the mathematical for-
mulation of the model equations intended for use in estimating
impacts of the sediment on the nutrient cycling within water
bodies. The present level of knowledge on the dynamics of these
processes is far from complete because of the difficulties in
studying them. However, theoretically the mechanisms of phos-
phorus transformations in the sediment-water layer and the
phosphorus exchange across the sediment-water interface seem
to be imaginatively and extensively studies. This fact is
reflected in the numerous mathematical models describing the
phosphorus exchange in the sediment-water interface as a result
of the combined effect of the processes mentioned.

A review of the available information shows that existing
approaches to simulate the phosphorus release depends on the
availability of the data on the sediment-water interactions
and physical-chemical characteristics of the sediment-water
interface as far as they are relevant for phosphorus transforma-
tion in the water and sediment. A sufficiently detailed descrip-
tion of the models is given in this report which provides infor-
mation on the type of equations and on the degree of sophistica-
tion in the reproduction of important processes responsible for
phosphorus transformation as well as phosphorus exchange. The
review of models shows that only a limited number of models are
formulated such as to enable a better understanding of the
physical, chemical and biological processes regulating the
phosphorus exchange in the sediment-water interface. Most of
the models concentrate on the evaluation of sediment impact on
phosphorus cycling in a comparatively small time period. In

only a limited number of cases there was a testing of the models developed by careful experimental studies of the kinetics of phosphorus transformations in the sediment-water layer, to establish an active mechanism of phosphorus exchange and to determine the fluxes of phosphorus across the sediment-water interface.

Efforts in modeling the phosphorus cycling and release from the sediments vary widely in their complexity. The models described in this report may be arbitrarily subdivided into groups on the basis of similarity in the principles of their formulation. Four groups of models were identified, based on (i) balance relations; (ii) empirical dependencies; (iii) simple chemical kinetics and (iv) combined interactions between empirical dependencies and chemical kinetics in reproducing the mechanisms of phosphorus transformations and phosphorus exchange reactions in the sediment-water interface. The development of these models was based also on the theoretical knowledge, on physical and chemical processes and on experimental studies of sediment phosphorus release. The models described differ considerably in their concepts owing to significant differences attributed to the role of individual processes in regulating the phosphorus exchange across the sediment-water interface.

The balance and empirical equations used in some mathematical models are established for different conditions and the usage of these equations should be restricted to conditions for which they are applicable. Furthermore, very few direct measurements or experimental studies to identify the model coefficients have been made and therefore a meaningful comparison of measured and calculated phosphorus concentrations in the sediment-water layer is difficult.

The mechanisms of active phosphorus release from the sediments is so complex that it is extremely unlikely that a full understanding will ever be accomplished. The phosphorus release from the sediment results from several simultaneous processes of a physical, chemical and biological nature. Since these processes have quite different characteristics, they are usually studied separately. This fact explains why not all important processes responsible for phosphorus exchange are taken into account in mathematical models and why the regularities in the phosphorus exchange and state variable dynamics is often considered, without any relation to each other.

Among the processes modeled, diffusion is considered to be most important and it is included in a number of the models reviewed. The well known mechanisms of phosphorus exchange defined by mixing and phosphorus adsorption are also taken into account by many models. The other important mechanisms of phosphorus exchange defined by bacterial activity is not often taken into consideration in the models. As a rule, bacterial activity is described in the simplest way by first order kinetics and restricted efforts have been made to quantify relationships between biological processes within the sediment-water interface. More studies are needed to identify and to find acceptable mathematical descriptions of biological processes and to determine the influence of microorganisms on the conversion and movement of sedimentary matter.

Among the environmental factors temperature is more often taken into consideration in the models as the regulator of the phosphorus exchange rate or the individual reactions in the

phosphorus transformations in the sediment-water interface.
The influence of other factors on the phosphorus exchange,
such as oxygen, pH, E_h, organic matter content and wind speed,
is not yet widely considered in the models, because a larger number
of input data on sediment characteristics and environmental condi-
tions are rarely available together.

In using the mathematical models as well as model parameters
for a special problem, the extreme case should be taken to select
equations and rate coefficients that have been developed under
conditions similar to the problem given. The major objective
of the present phase, in modeling phosphorus transformation in
the sediment-water interface is to develop a simulation model
to integrate the known theoretical knowledge on sediment-water
interactions and to take into account the environmental influence
on the regulation of phosphorus exchange through the sediment-
water interface.

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