PHOSPHORUS INACTIVATION IN SEDIMENTS OF SHALLOW LAKES

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S A M E N V A T T I N G

Fosfaat wordt algemeen beschouwd de belangrijkste oorzaak te zijn van de eutrofiëring van plassen en meren. In Nederland worden grote inspanningen verricht om de fosfaatbelasting op meren en plassen te verminderen, teneinde de eutrofiëring te stoppen en zelfs om te keren. Het Rijn Aktie Plan en aanvullende regionale maatregelen zijn bedoeld om deze vermindering van de belasting tot stand te brengen. Een hoge interne fosfaatbelasting door de bodem kan dan de verbetering van de waterkwaliteit vertragen. Dit probleem kan door baggeren worden opgelost, zij het tegen hoge kosten. De toevoeging van fosfaatbindende stoffen aan het sediment kan een effectief en veel goedkoper alternatief zijn, maar sommige van deze stoffen kunnen schadelijk zijn voor het milieu. IJzer is een veelbelovende, niet giftige, fosfaatbindende stof. Zij is al verantwoordelijk voor het merendeel van de fosfaatbinding in veel meren. Een mogelijk nadeel van de toepassing van ijzer is dat ijzerfosfaat complexen er van worden verdacht bij lage redoxpotentialen weer fosfaat af te geven. In laboratoriumexperimenten bleek een dosis van 100 g $Fe^{3+}m^{-2}$ echter ook onder anoxische condities de fosfaatnalevering aanzienlijk te verminderen. Daarom kan de toevoeging van dit middel aan sedimenten een goed alternatief zijn voor baggeren. Het is ongeveer tienmaal goedkoper. De lange termijn effecten van de methode moeten echter nog in **in situ** experimenten worden onderzocht.

S U M M A R Y

Phosphorus is generally considered to be the primary factor controlling eutrophication in lake ecosystems. Large efforts have currently been made in The Netherlands, to decrease the phosphorus loading of lakes in order to stop or reverse the process of eutrophication. The Rhine Action Programme and additional regional measures will decrease the phosphorus loading on most Dutch lakes. A high internal phosphorus loading from the sediments can delay the improvement of the water quality. This problem can be solved by dredging, but at high costs. Addition of phosphate-binding agents to the sediments can be an effective and much cheaper alternative, but some of these agents may introduce hazardous chemicals into the ecosystem. Iron is a

promising nontoxic phosphate-binding agent, which is already responsible for the phosphate-binding in many lakes. A possible drawback of iron application is that ironphosphate complexes are suspected to release phosphate at low redox conditions. In laboratory experiments, however, a dose of 100 g $Fe^{3+}m^{-2}$ appeared to decrease phosphorus release rates under oxic, but also under anoxic conditions. Therefore, the addition of this agent to sediments can be a good alternative for dredging, and about ten times cheaper. The long term effects of this method have to be tested in **in situ** experiments.

KEY WORDS : Eutrophication, Phosphorus, Lake treatment, Internal loading, Phosphorus inactivation.

VOORWOORD

Deze nota is gebaseerd op het onderzoek dat de heer W.A.D.D. Wijesooriya heeft uitgevoerd in het kader van zijn M. Sc. studie aan het International Institute for Hydraulic and Environmental Engineering in Delft bij DBW/RIZA in Lelystad. Deze tekst is ook uitgegeven als M. Sc. Thesis Report EE 16 van het IHE. Omdat de heer Wijesooriya afkomstig is uit Shri Lanka is dit rapport in het Engels geschreven. Dit zal, naar wij aannemen, geen beletsel zijn om kennis te nemen van de inhoud van deze nota.

C O N T E N T S

PART B.

1. INTRODUCTION.

One of the most obvious and world wide water quality problems is the eutrophication of lakes and reservoirs. Water bodies receiving excessive amounts of plant nutrients, organic matter, and silt suffer from an excessive growth of aquatic life such as algae and rooted plants. This could cause the decrease of the lake or reservoir volume. Aesthetic value of lakes and reservoirs of this nature deteriorate rapidly. They lose much of their beauty, their attractiveness for recreation, and their usefulness as a drinking water and industrial water supply (Derr 1972, Vollenweider 1981, Cooke,et.al. 1986). Eutrophication is basically considered as a natural process, often described as the natural aging of lakes. Peat bogs, coal and oil deposits are some of the results of this very slow process over centuries. However, this natural phenomena is getting very little interest within the present context. The process of cultural eutrophication, which is of most concern and which is being reported everywhere, has taken place within a very short time span.

Vollenweider (1981) cited some essential causes for this kind of sudden eutrophication which are interrelated and directly linked to worldwide demographic changes, namely:

1) rapid general increase in population with a strong tendency towards urbanization and resulting in rapid increase in urban waste discharged directly into the waterways, lakes and coastal areas.

2) rapid industrialization linked to population growth with the corresponding increase in industrial waste of all kinds, some of them containing the nutrients needed for the growth of algae and macrophytes,

3) intensification of agriculture and changes in production methods, through preferential development of monoculture, increased use of chemical fertilizers, concentration of live stock breeding, direct discharge of agricultural waste into the waterways,and overproduction of manure.

4) An additional factor to this since the end of World war II is the use of detergents containing polyphosphates,

"Preservation of clean water systems" is now a miracle, specially for the industrialized world. Almost all water bodies, in those regions are severely damaged by the influence of man. Even some newly built reservoirs suddenly experienced eutrophication from the decomposition of materials left in the flooded basin or from nutrient rich soils (Vollenweider 1981, Cooke et.al. 1986).

So the control of eutrophication and restoration of eutrophic water bodies has become one of the most important issues since many years, because the supply of clean, fresh surface water is limited and the demand for recreational, industrial, and domestic uses of water is increasing.

It is widely accepted that phosphorus (P) is the critical nutrient in determining the degree of lake eutrophication (Likens 1972, Hooper 1973, Wetzel 1983, Vollenweider 1981, Gächter et. al 1985). Therefore, programmes for lake restoration were usually directed at reducing phosphorus loading to water bodies. In most countries massive amounts of money are spent to introduce advanced waste water treatment plants including phosphorus removing facilities in order to reduce nutrients entering to water bodies. But the response to those measures were not promising for several years. It was reported that in certain instances no recovery has taken place during a period of ten years after that external loading was decreased. The most important reason for this is identified as the release of nutrients stored in the sediment of lake with overlying waters. This release is usually called as internal nutrient loading (Bjork 1972, Welch et. al. 1974, Ahlgren 1977, Digiano 1977,).

To overcome this problem, techniques to manipulate or alter the internal nutrient loading are needed. Various physical, chemical and biological methods have been proposed, tested, and applied in numerous lake restoration programmes:

- dredging to remove nutrient rich sediment,
- artificial circulation or aeration of stagnated water layers, to keep bottom waters oxygenated (Cooke et. al. 1986),
- chemical treatment of sediment or lake water in order to

suppress the liberation of phosphorus from the sediment, some used compounds are: sodium aluminate (Peterson et. al. 1974), ferric chloride (Ripl 1976, Klapper 1980), lanthanum chloride (Peterson et. al. 1974), zirconium tetrachloride (Peterson et. al. 1974, Sanville et. al. 1982), fly ash (Higgins et. al. 1976), gypsum (Higgins et. al. 1976), iron ore slag (Yamada et. al. 1987),

- biological oxidation of sediment with nitrate (Ripl 1976),
- chemical oxidation of sediment with peroxide (Cooke et. al. 1986).

The objective of this project is, firstly, to study those lake restoration methods that are aimed at reducing the internal nutrient loading and select a suitable technique to inactivate phosphorus-release for the sediments of the shallow lakes in The Netherlands. The second objective is to perform some laboratory release experiments to investigate the phosphorus-release rates and inactivation capacity of those selected techniques.

Since the reversal or the abatement of eutrophication is the ultimate goal of phosphorus-inactivation, the factors effecting eutrophication and measures to control eutrophication are also discussed briefly in this report.

2. EUTROPHICATION OF LAKES AND RESERVOIRS.

2.1 INTRODUCTION.

Likens (1972) defined eutrophication as nutrient or organic matter enrichment or both, resulting in high biological productivity and decreased volume within an ecosystem. Cooke et.al. (1986) modified this definition to include the input of silt. They defined eutrophication as the process of excessive addition of inorganic nutrients, organic matter, and/or silt to lakes and reservoirs, leading to increased biological production and decreased lake or reservoir volume.

Gradual increase of plant nutrients in the lake or reservoir is the ultimate result of all these processes and it leads to high primary productivity of the ecosystem. When the production of algae, rooted and floating plants or both is increased, it could lead to:

- taste and odor problems in drinking water,
- sudden fish kills due to oxygen depletion,
- decrease of recreational value of the water course
- sometimes killing of animals consuming water, due to the toxicity of some algae.

For these reasons, excessive algal and other blooms are considered to be a nuisance and their dominance in freshwater lakes is highly undesirable.

2.2 NUTRIENTS INVOLVED IN AQUATIC PLANT GROWTH AND GROWTH LIMITATIONS.

Biological growth requires favorable environmental conditions, including supply of chemicals needed to manufacture new cells. The nutrients needed in relatively large quantities by aquatic plants include carbon, hydrogen, oxygen, sulfur, potassium, calcium, magnesium, nitrogen and phosphorus. Several others nutrients must also be present, at least in trace amounts. Table.1 summarizes these micro nutrients.

PROCESS	TRACER ELEMENT REQUIRED
Photosynthesis	Manganese, iron, chloride, zinc and vanadium
Nitrogen Fixation	Iron, boron, molybdenum and cobalt
Other functions	Manganese, boron, cobalt, copper and silicate

Table. 1 Aquatic Plant Micronutrient Requirements (Source: Rust and Lee 1978)

Most often plant growth is limited by one of the nutrients which is not present in adequate amounts in the system. This phenomenon was identified as early as 1840 by Justus Liebig. He noted that a nutrient will be consumed or assimilated by an organism in proportion to the organism's need for that nutrient. The Liebig's "law of the Minimum" which is one of the oldest laws of plant nutrition is based on this observation. The Liebig's law states that "growth of a plant is dependent on the amounts of foodstuff which is available to it in minimum quantities relative to its needs for growth or reproduction" (Odum, 1971).

Among the macro- and micro- nutrient requirements mentioned above, nitrogen and phosphorus are generally considered to be the aquatic plant nutrients of major importance in the eutrophication process. However, various other elements or compounds have been suggested as affecting or limiting the eutrophication process, including iron, molybdenum, nitrate and sulphate, vitamins and other essential organic growth factors, carbon and silica. The principle of growth limitation has also been applied to factors other than nutrients, including light and temperature. However, most of these effects are temporal in nature and do not persist over the annual cycle.

Today, it is generally accepted that either phosphorus or nitrogen in a water body, rather than above mentioned other compounds, control or limit the eutrophication or can be made limiting the eutrophication. Not only the absolute amounts of phosphorus and nitrogen in a water body are important in the eutrophication process, but their relative quantity also is

considered to be a key factor in particular in determining which of these two elements will limit the overall process.

As cited in Golterman (1975), Vallentyne (1973) has indicated the special significance of nitrogen and phosphorus among the 15 to 20 elements commonly needed for the growth of aquatic plants by calculating the **demand : supply** ratios of these essential elements. According to this, aquatic plants have a certain demand for nutrients for their growth and reproduction, in proportion to the quantities of the nutrients in the cells. When one or more of these nutrients is present in short supply relative to the others, then the overall primary productivity of the aquatic plant population will be limited by the rates of supply of these nutrients. Thus, a demand : supply ratio can indicate the nutrient most likely to limit productivity. The higher the demand : supply ratio the more a particular nutrient will limit the growth. Demand : supply ratios based on a "world average" were calculated by determination of the chemical composition of an average aquatic plant community and dividing this composition by the mean chemical composition of the river waters of the world.These ratios are presented in table 2, they clearly illustrate the dominant role of phosphorus and nitrogen by their very high demand : supply ratio.

Element	Demand : Supply	
	Late Winter[a]	Mid Summer[b]
Phosphorus	80,000	up to 800,000
Nitrogen	30,000	up to 300,000
Carbon	5,000	up to 6,000
Iron, silicon	Variable, but very low	
All other elements	< 1,000	

[a] Prior to spring bloom, [b] At algal maximum growth period

Table. 2: Demand:supply ratios for the major aquatic plant nutrients

Summarizing, it is clear that nitrogen & phosphorus are the two elements most often found to be limiting aquatic plant growth.

2.3 EFFECT OF N : P ATOMIC RATIO ON ALGAL GROWTH.

The composition of algal cell can be represented crudely by a chemical formula, that summarizes elements contained in them. One of several that has been proposed is $C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1$. This formula is based on the simple stoichiometry of the photosynthesis/ respiration reaction as illustrated in the following equation.

$$106\ CO_2 + 16\ NO^-_3 + HPO^+_4 + 122\ H_2O + 18\ H^+ + \text{trace elements} + \text{Energy} \rightleftharpoons (C_{106}H_{263}O_{110}N_{16}P_1) + 138\ O_2$$

According to this formula the atomic ratio of N : P in a algal cell is 16 : 1 and it was proved by several workers that algae need a relatively fixed ratio of carbon to nitrogen to phosphorus of 106 : 16 : 1 (Redfield 1958, Vollenweider 1968).

Depending on the environmental conditions and variations in species, this ratio can vary considerably in a vast range. For example, Yell Rhee (1978) reported the optimal cellular N : P ratio of *Scenedesmus sp.* to be 30 and the growth is determined solely by N limitation below the N : P ratio of 30 and growth is limited by phosphorus above this value.

It is now generally accepted, that even in spite of some variations, the N : P atomic ratio in natural algal populations remains constant enough to be used in making reasonable predictions as to which of these two elements limit the algal growth in natural waters.

According to the formula given in the photosynthesis reaction, ($C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1$) algae will assimilate nitrogen and phosphorus from their aquatic environment in a stoichiometric atomic ratio of approximately 16N:1P until one of these two nutrients becomes depleted in the water body. At that time, the nutrient present in the water body in the lowest concentration, relative to the stoichiometric needs of the algae, will limit subsequent growth. If the N:P atomic ratio in the water falls

below 16, the algal biomass in the water body at that time would be controlled or limited by the quantity of nitrogen present in the water course. The amount of phosphorus present in the water body at that time would have no influence, in terms of limiting growth of algae, since it would be present in excess quantities. In contrast, if the N:P ratio is greater than 16, the growth is limited by phosphorus (Rhee, 1978, Vollenweider, 1982).

An important characteristic of unpolluted, natural water is that they are extremely diluted (Lamb, 1985) and also that the N : P ratio of natural water is about 23 : 1 (Odum, 1971). So the algal productivity of many fresh water lakes actually is limited by low concentrations of phosphorus in the water (Welch, 1975, Golterman, 1975, Vollenweider, 1968). When phosphorus is added to such a lake by land runoff, waste discharge or from other sources, extreme growth of algae could be observed. It can be illustrated by a simple calculation that 1kg of phosphorus has the potential of producing 76kg of algal biomass whereas 1kg of nitrogen has only potential to produce 12kg of algal biomass.

2.4 MAJOR SOURCES OF PHOSPHORUS ENTERING LAKES.

Rocks and other deposits which were formed in past geological ages form the main reservoir of phosphorus in nature. So the main natural origin of phosphorus in lakes or oceans are due to erosion, that is the chemical and mechanical weathering of rocks (Altschuler, 1973).The contribution of this natural supply, however is very low (Hakanson and Jansson, 1983). Excavating phosphate baring rocks (specially apatite baring deposits) for use as a fertilizer influences the natural cycle, and most of the phosphate rock mined is washed away to natural waters. Drainage water from agricultural areas may contain large amounts of phosphates due to the application of excessive amounts of manure and fertilizers. In many areas the present supply of phosphorus from farm lands is in order of about ten times higher than the natural supply (Hakanson and Jansson, 1983).

Another important source of phosphorus is human excrements and detergents. It is estimated that 2g of PO_4-P per person per day is excreted as urine and faeces. Another 2g of tri-phosphate phosphorus is emanating from detergents. Municipal sewage discharge to freshwater bodies and urban storm water runoffs increase the phosphorus concentration in fresh water. In addition to these sources, considerable amounts of phosphorus are emitted from food industries, smelters,and industries producing fertilizers. (Fig.1). Phosphorus loading to some lake areas in the Netherlands are given in table 3.

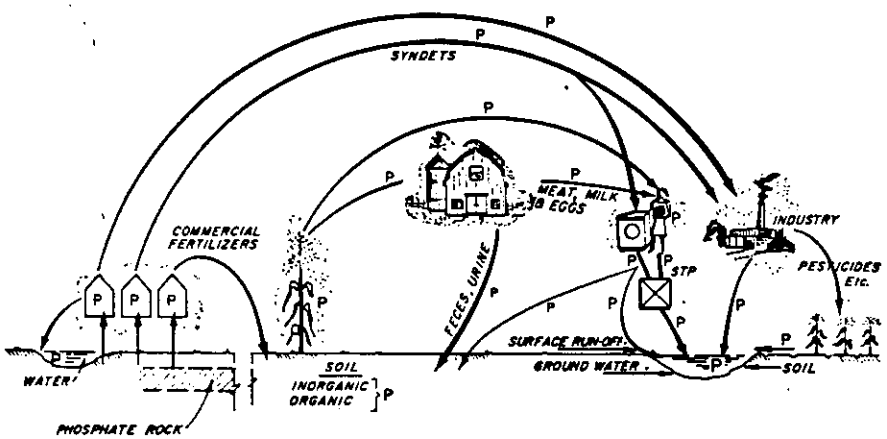


Fig 1. Phosphorus distribution in a complex urban economy. (source : Sawyer, 1973)

Table.3: Amounts (tons/year) and percentage contribution (with in brackets) of phosphate inputs of various sources, to some surface water bodies in the Netherlands.

Source	Noord-Hol	Uitw-sl	Rijnland	Friesland
Domastic/Industrial				
-treated waste water	1088(56.8)	340 (50)	688 (52.8)	380 (39.5)
-untreated waste water	200(10.4)	95 (14)	190 (14.6)	114 (11.8)
Agricultural runoff	246(12.7)	140 (21)	111 (8.5)	275 (28.5)
Sepage	312(16.3)	61 (9)	143 (11.0)	
Inlet water	44(2.3)	40 (5.9)	191 (14.6)	
Precipitation	27(1.4)	4 (0.6)	5 (0.4)	12 (1.2)
Total :	1917(100)	680 (100)	1304 (100)	964 (100)

2.5 FORMS OF PHOSPHORUS IN AQUATIC ECOSYSTEM.

The phosphates that enter lakes are inorganic or organic in nature, both in soluble or particulate form. Among those the major share of phosphorus found in lake water is in organic form and the inorganic phosphorus compounds often make up less than 10% of the total phosphorus of many aquatic systems (Hooper, 1973 and Wetzel, 1983).

Within the ecosystem, several forms of phosphorus may be identified, e.g. phosphorus in phytoplankton, phosphorus in zooplankton, phosphorus in fish, dissolved organic and dissolved inorganic phosphorus, and particulate inorganic phosphorus.

There are several classification methods involved in categorization of phosphorus in the ecosystem, viz., chemically based, biologically based or a combination of both. One classification method is strictly based on analytical chemistry. It is based upon the separation between soluble and insoluble components by filtration and between reactive and non-reactive forms. The insoluble phosphorus is commonly referred to as particulate phosphorus, **PP**, (or sometimes as suspended or sestonic P). The soluble phosphorus, **SP**, (also referred to as total dissolved phosphorus, **TDP**,) can itself be divided into a fraction which is biologically available, the soluble reactive phosphorus, **SRP**, (also referred to as soluble inorganic phosphorus, mostly ortho-Phosphate, **SIP**) and soluble unreactive phosphorus, **SUP**. The sum of the **PP** and the **SP** is termed total phosphorus, **TP** (Hakanson and Jansson, 1983).

2.6 FATE OF PHOSPHORUS ENTERING LAKES.

Inorganic orthophosphate in lake water is consumed by algae and other aquatic plants for their growth requirements and removed from the water phase. But following the death, it can be released to the water phase directly as a result of the mineralization or sink to the bottom and be released to the water phase subsequently as the result of mineralization.

Dissolved organic phosphates entering lakes can also be converted into inorganic orthophosphate through mineralization and contribute to the algal growth.

Dissolved inorganic phosphates can also precipitate with some cations such as Al, Fe, and Ca found in lake water, if the concentrations are sufficiently high and depending on pH and redox conditions. The most important mechanism of phosphorus-removing from natural waters is the sorption of Phosphate to metal hydroxy gels. The formed phosphorus-containing precipitates or sorbet material subsequently sink to the bottom of the lake (Appendix 4).

2.7 FORMS OF PHOSPHORUS IN LAKE SEDIMENTS.

A major portion of the phosphorus that enters the lake system is sinking to the bottom in various forms viz.,

1. dead phytoplankton and dead zooplankton phosphorus (detritus) **(organic P)**,
2. inorganic phosphorus present as orthophosphate ions sorbed on the surface of phosphorus-retaining compounds **(nonoccluded P)**
3. inorganic phosphorus present as orthophosphate ions within the matrices of phosphorus-retaining compounds **(occluded P)**,
4. orthophosphate phosphorus present in discrete phosphate minerals such as apatite [Ca_{10} $(PO_4)_6$ X_2, where X = OH, F, $1/2CO_2$] and vivianite [$Fe_3(PO_4)_2.8H_2O$]. **(discrete P)**, (Williams et. al. 1971) and in phosphorus-containing precipitates, formed in the lake.

The chemical nature of the phosphorus in sediment is one of the most important characteristics to be studied in the context of phosphorus release from sediments. However the present knowledge of chemical fractionation schemes, which are based on chemical extraction procedures, only account for a limited number of phosphorus fractions of the sediment. For example, the fractionation scheme developed by Williams et. al. (1976), which is one of the most relevant fractionation schemes, is valid only to yield non-apatite inorganic phosphorus (NAI-P), apatite

phosphorus (A-P), and organic phosphorus (O-P). The NAI-P compartment consists basically of Fe-and Al-bound phosphorus (see appendix 1A).

Hosomi et. al. (1982) used a scheme to fractionate inorganic phosphorus in sediments based on the procedure proposed by Chang and Jackson (1957). This procedure defined three fractions of inorganic phosphorus in sediment (see appendix 1B) as
- Aluminum-bound phosphorus (AL-P, extraction by NH_4F)
- iron-bound phosphorus (Fe-P, extraction by NaOH) and
- calcium-bound phosphorus (Ca-P) , extraction by H_2SO_4).

Hieltjes and Lijklema (1980) characterized the fractions of phosphorus in sediments by the extraction media, used to dissolve them,

NH_4Cl- extractable P (Approximately loosely bound P)
NaOH - extractable P (Approximately Fe+Al bound P)
HCl - extractable P (Approximately Ca bound P)

Both total phosphorus content and the distribution of various phosphorus fractions in the sediment differ from one lake sediment to another. Fig.3 is an example of this.

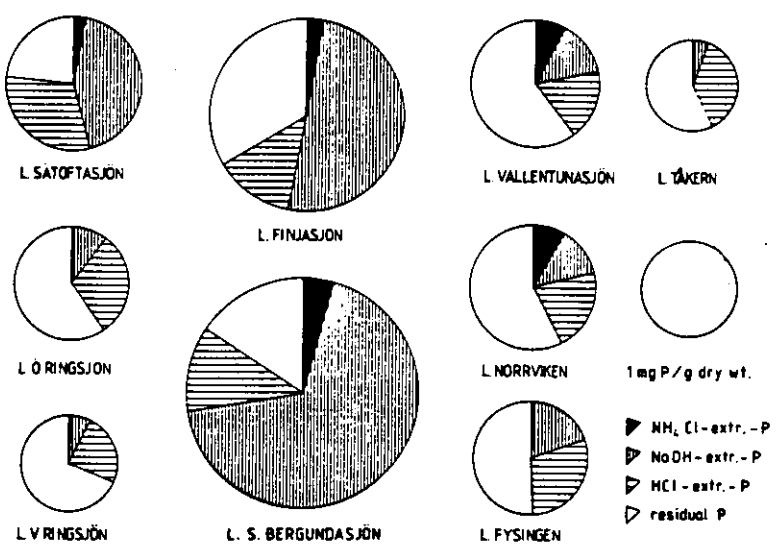


Fig 3. Total concentration and fractional composition of phosphorus in the sediments of nine Swedish lakes. The total concentrations are proportional to the size of the circles (Boström 1984).

Similar variations can be found in different locations in one lake (fig 4).

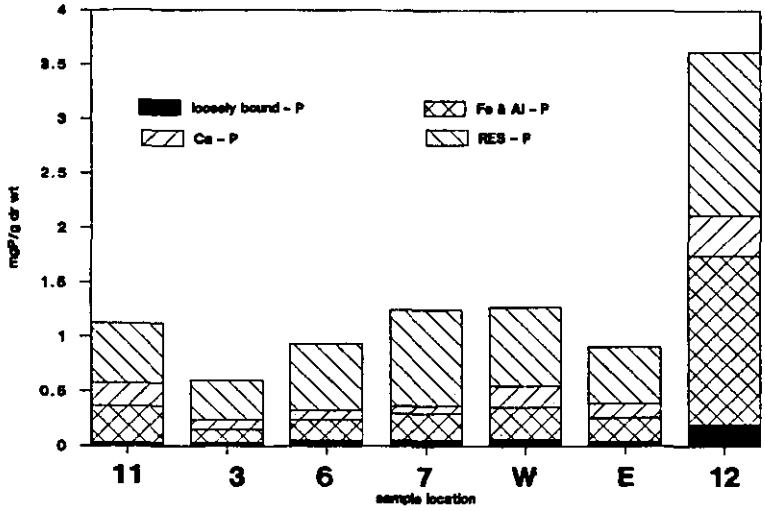


Fig. 4 : Variation of different phosphorus fractions and total phosphorus content of sediments collected from different locations in Loosdrecht lakes, the Netherlands. The hight of each column is equal to the total phosphorus content of the location (redrawn from Boers et. al., 1984)

2.8 FATE OF PHOSPHORUS IN LAKE SEDIMENT

As there is no gaseous component in the biogeochemical cycle, phosphorus is considered as a conservative substance. The sediment is considered to be a sink for phosphorus entering to lakes.

As cited in Hakanson & Jansson (1983), in the years around 1940, various investigators established release of phosphorus from sediments under certain conditions. The redox conditions at the surface of the sediment were identified as the most important condition for phosphorus release to the overlying water. The only explanation given for phosphorus release from sediments was the reduction of iron(III) to iron(II) whereby phosphorus bound to iron(III) in salts or sorbed to iron complexes was returned to the overlying water. But in recent years, there has been an increasing awareness that phosphorus is released from sediments also under apparently well oxygenated conditions (Ryding & Fosberg 1977, Stevens & Gibson 1977, Ryding 1985).

The release of phosphorus from sediments to well aerated water has been observed in a number of shallow lakes which have received sewage water for a long period. Highly reduced loadings by diversion or by treatment seldom gave the expected results since decrease in external input , at least partly, was compensated by a net flux from the sediment (see also sec. 3.3.2). (Larsen et. al. 1976, Ahlgren, 1977, Neame, 1977, Bengtsson, 1978, EPA, 1980, Welch et.al. 1980, Boers et. al. 1984, Sondergaard et. al. 1987, Forsberg, 1987,).

It is emphasized that in all oligotrophic lakes and also in most eutrophic waters, the net flux of phosphorus on a yearly basis is towards the sediments. However, under certain conditions, particularly in nutrient rich lakes, the release from the sediments may exceed the inputs by sedimentation. This phenomenon, which occurs predominantly in summer, is called internal phosphorus loading.

2.9 CONDITIONS GOVERNING PHOSPHORUS RELEASE FROM SEDIMENTS.

The liberation of phosphorus from sediment occurs mostly through the comparatively small pool of phosphorus dissolved in the sediment pore water. The size of this pool is in turn regulated by the equilibria with particulate phosphorus present in the sediment (Fig. 5).

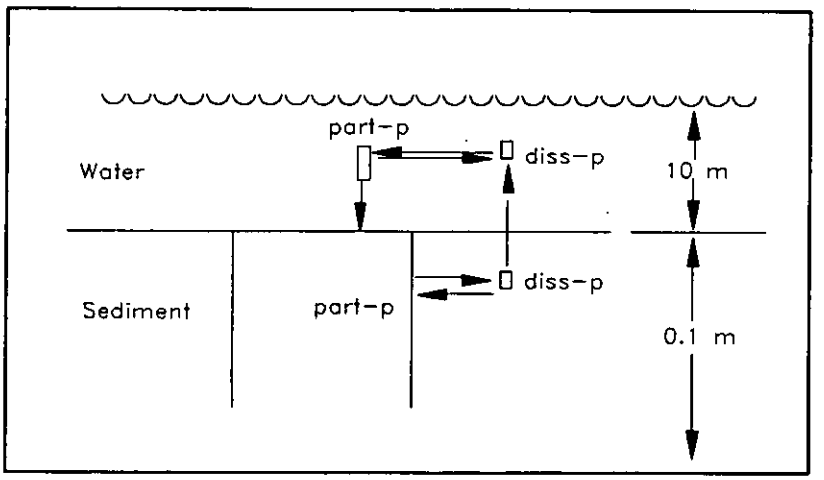


Fig. 5: Schematic illustration of the distribution of particulate and dissolved phosphorus in a lake-sediment system. A hypothetical example assuming a mean lake depth of 10m and active sediment layer of 0.1m, that the concentration of 50ugL^{-1} in the lake water and 2mg g ds^{-1} in the sediments, and a water content of the sediment of 90%. (source : Hakanson and Jansson, 1983)

Consequently, before a substantial release can occur, two fundamentally different processes must function more or less simultaneously. Phosphorus must be mobilized from particulate to dissolved form by the action of physical, chemical, and biological reactions and dissolved phosphorus must be transported to the lake mainly through physical processes (Fig. 6).

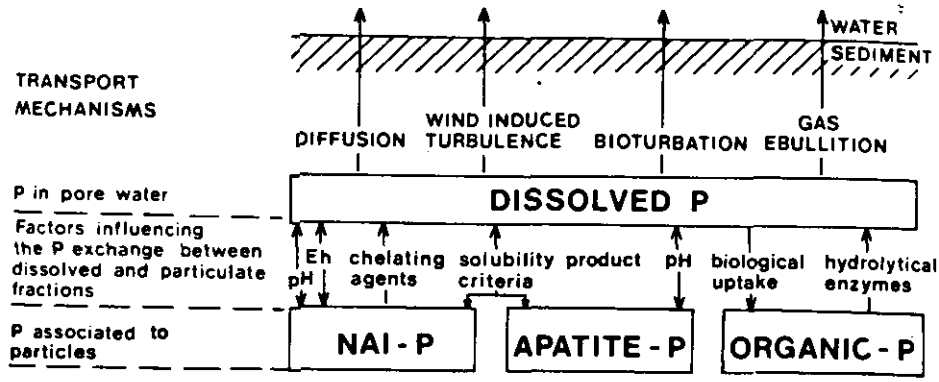


Fig. 6. Illustration of the dominating processes regulating the release of phosphorus from lake sediments (source, Hakanson and Jansson, 1983)

Table.4 summarizes the major mobilization and transport mechanisms which are or can be relevant with respect to phosphorus release from the sediment to the lake water. Some important mobilization mechanisms are discussed in detail below.

Table. 4: Summary of the causal relationships determining the release of phosphorus from lake sediments (source: Hakanson & Jansson, 1983).

Environmental parameters	Effects on phosphorus mobilization
Redox potential	Iron-bound phosphorus is released at potentials below 200 mV when iron (III) reduced to iron (II).
pH	An increase in pH decreases the phosphorus binding capacity of iron and aluminum compounds, primarily due to ligand -exchange reactions where hydroxide ions replace phosphate. Calcite and apatite formation at higher pH-values increase the phosphorus- binding capacity of calcium
Temperature	An increase in temperature gives primarily indirect effects due to increased bacterial activity, which increases oxygen consumption and decreases the redox potential. The production of phosphate-mobilizing enzymes and chelating agents might increase accordingly.
Equilibrium criteria	Affects adsorption-desorption and dissociations of precipitates.
Chelating agents	Replace phosphate from slats with calcium, iron and aluminum. Chelating agents can be produced by bacteria and algae or occur as a pollutant.
Processes	**Effects on phosphorus transport**
Diffusion	Phosphorus transported upwards to compensate the concentration gradient between the sediment and the lake water. Important when the sediments are superimposed by stagnant water.
Turbulence	Linked to mechanical transport, resuspension and bottom dynamics. Enhances diffusion transport. Possibly the most efficient process of transport in shallow lakes.
Bioturbation	Creates physical mixing and enhances transport in aerobic sediments.
Gas convection	Mainly methane, which creates physical mixing and enhances transport. Important in highly reduced, organic sediments.

2.10 SOME IMPORTANT FACTORS FOR THE MOBILIZATION OF PHOSPHORUS IN LAKE SEDIMENTS.

2.10.1 Adsorption and Desorption capacity of sediment.

Exchange of phosphorus between the sediment and pore water can be controlled by adsorption and desorption reactions. Sediments of different lakes differ significantly in adsorption and desorption capacity. Sorption capacities are highly related to fractional distribution of various forms of phosphorus in the sediment (Mortimer 1971, Williams et.al. 1971, Syers et. al. 1973). According to Boström and Pettersson (1982) lake sediments can be separated into three categories, based on the adsorption and desorption capacities (Boström and Pettersson, 1982).

Category	Characters	Lake types.
1st.	Low adsorption and high desorption capacity of phosphorus	Shallow lakes that received or are receiving agricultural runoffs.
2nd.	High adsorption and low desorption capacity of phosphorus.	Normally deep lakes that received waste water.
3rd.	Negligible net sorption of phosphorus	Shallow lakes that received or are receiving sewage effluent water.

The input history of a lake is directly connected with the phosphorus release properties of the sediment. The more phosphorus, that is supplied to sediments, the lower the sediment's capacity to store and retain the phosphorus. With an excessive loading, such as in lakes polluted by sewage water, the sediments will eventually become saturated. Subsequent release of phosphorus from those sediments are experienced, in spite of good oxygenation of the water column. (Ex. Lake Vallentunasjon, cited in Boström & Pettersson 1982).

Not all the lakes of this nature show a similar pattern of internal loading. This is due to the fact that the binding capacity of sediments of different lakes differs as a result of

the chemical nature of the sediment and of incoming material and water. So the fractional distribution of particulate phosphorus in sediments is also an important factor for the determination of internal loading.

2.10.2 Fractional distribution of particulate phosphorus.

As mentioned before, the release of phosphorus from sediments is mainly taking place through the dissolution of particulate phosphorus in sediment pore water. The solubility of particulate phosphates in the sediment under prevailing conditions of pH, redox potential and ionic strength is controlled by the chemical composition of the phosphate present in the sediment and their interactions with other minerals or amorphous material (Hieltjes & Lijklema, 1980).

Sediments from sewage - loaded lakes contain considerably more loosely adsorbed phosphorus (nonoccluded phosphorus) than unpolluted lake sediments (Williams et. al., 1971). The nonoccluded inorganic phosphorus fraction is more closely in contact with the surrounding aqueous phase than other categories of inorganic phosphorus. It may be anticipated that the nonoccluded fraction responds much more readily to changes in environmental conditions than occluded or discrete phosphorus.

Phosphorus release is redox sensitive and strongly favored by a high content of aluminum and iron - bound phosphorus. Some sediments release primarily organic and loosely adsorbed phosphorus, and in such cases less phosphorus is released and redox and pH conditions have less effect (Boström, 1984).

2.10.3 Redox conditions.

The early findings on phosphorus exchange between sediment and lake water are based on the interactions between iron and phosphorus during aerobic and anaerobic conditions.

In oxidized situations, phosphorus is sorbet to iron(III) hydroxide gels. Such aggregates may be formed in the oxidized

surface sediments or precipitated from overlying waters. When the sediment becomes reduced, iron(III) is reduced to iron(II), whereby both iron and sorbed phosphate are returned to solution. Subsequently dissolved phosphate is transported back to the water column from the sediment pore water or the sediment surface.

There is no doubt that these early findings are still valid and the redox depending process are well explained one of the most important reasons for phosphorus release from lake sediments. This is one of the most common processes taking place in productive stratifying lakes during stagnation periods (summer & winter), when oxygen is depleted in the bottom water.

At neutral pH conditions, the reduction of iron(III) takes place at redox potentials around 200 mV. This corresponds to an O_2 concentration of approximately 0.1 mgL^{-1}. The process of reduction of iron(III) to iron(II) could be hindered by high concentrations of nitrate or manganese which are reduced before iron (Foy 1986).

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = +0.77\ V$$

$$Mn^{4+} + e^- \rightleftharpoons Mn^{2+} \qquad E^0 = +1.65\ V$$

$$2NO^-_3 + 12H^+ + 10e^- \rightleftharpoons N_{2(g)} + H_2O \qquad E^0 = +1.24\ V$$

(Snoeyink and Jankins, 1980)

In general, iron reduction is considered to be a chemical process where iron is reduced by e.g.,organic compounds or S^{2-}. However, iron can also be reduced by bacteria, which utilize iron(III) as electron acceptor during anaerobic respiration (Fig.7) (Sörensen 1982).

2.10.4 pH.

pH mediated phosphorus mobilization is a rather common andquantitatively important phenomenon. Phosphorus bound to Al or Fe or sorbed to Al or Fe hydroxy gels are firmly bound at neutral pH values, but dissolve in acid or alkaline waters.

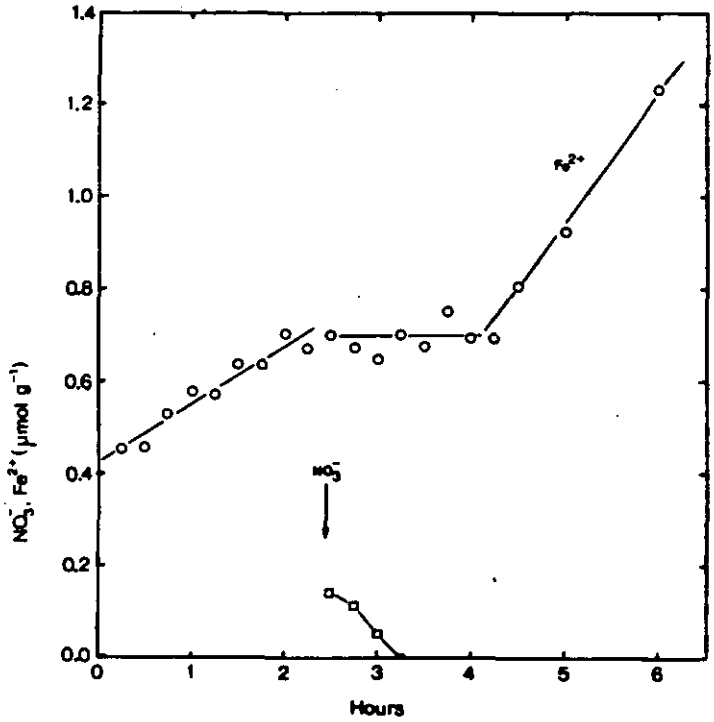


Fig.7: Effect of NO^-_3 on reduction of Fe^{3+}. Arrow indicates addition of 0.2 mM $NaNO_3$. Symbols O, Fe^{2+}, ·, NO3-.After depletion of NO3- facultative bacteria start to utilize Fe^{3+} as an electron acceptor (Source: Sörensen 1982, modified).

Ca bound phosphorus (usually apatite) has a smaller solubility at high pH values (fig 8). Hence the phosphorus mobilization governed by pH does not generally follow the same pattern from lake to lake but will depend on sediment and water composition.

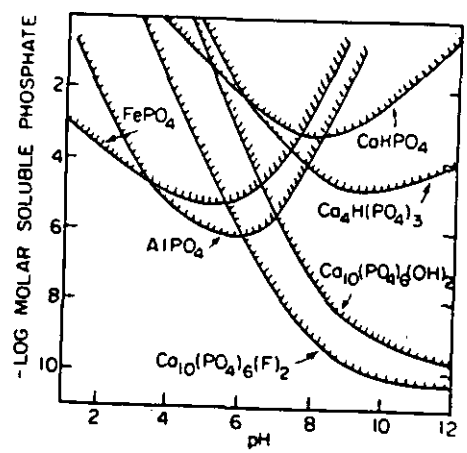


Fig.8: Solubility of the metal phosphates (Source: Stumm and Morgan, 1981).

Anderson (1975) reported increase of phosphorus release rate with increasing pH above 8 for a Danish lake, Kvind so. (Fig.9). Rippey (1977) also showed increase in phosphorus release rates from lake sediments, when on iron(III) or Al(III) hydroxide gel adsorbed phosphorus is subjected to a pH increase in the alkaline regime (Fig.10).

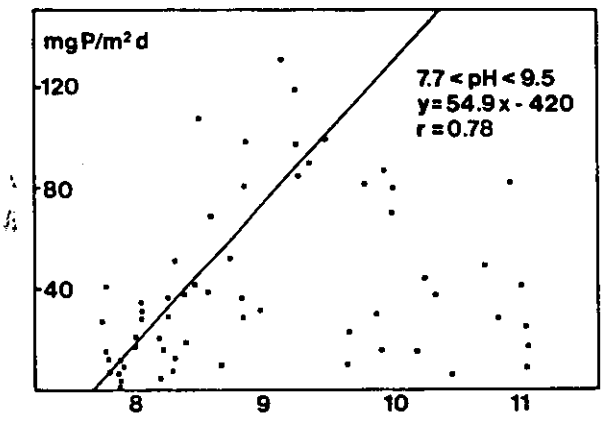


Fig.9: Rate of orthophosphate release from undisturbed Kvind so sediments. (source: Anderson, 1975)

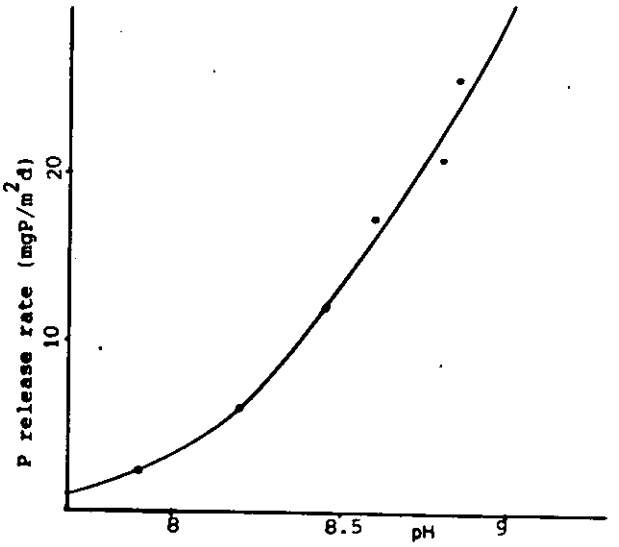


Fig.10: Variation of phosphorus release with pH at 20°C. (source: Rippey, 1977) Lough Lake, N. Ireland.

This type of pH-regulated phosphorus mobilization from sediments is important in shallow productive lakes. In these lakes, in summer the pH in the lake water is often increased by two or three units due to the photosynthetic activity of planktonic algae, besides, the whole water mass in these lakes is in more or less continuous contact with the sediment surface. Fig.11 shows the commonly observed increase in pH during summer and the relationship with phosphorus mobilization.

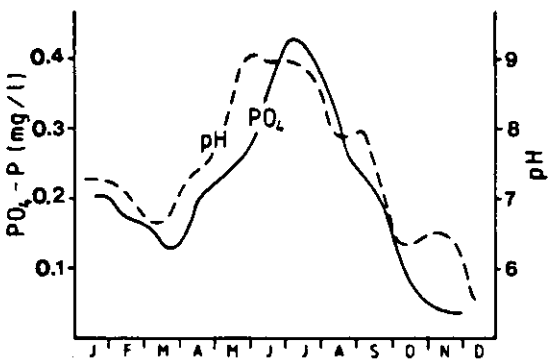


Fig.11: Seasonal variation of pH and phosphorus concentrations in Lake Glaningen, Sweden (source: Hakanson and Jansson, 1983)

In contrast, Kamp-Nielsen (1975) reported a decrease in phosphorus release with increase of pH above about 8 for another Danish lake, Fure so (Fig.12). (Lake Fure so is an eutrophic lake with a surface of $9km^{-2}$ and max. depth of 36m. Sediment type is identified as calcarious and contains about 50 $\%CaCO_3$).

The decrease of the phosphorus release rate in this lake is explained by the formation of hydroxy apatite ($Ca_{10}(PO_4)_6(OH)_2$), upon settling of CaCO3 particles, formed as a result of increased pH, or co-precipitation of PO^{3-}_4 with $CaCO_3$. So the pH increase in calcium rich waters may have the effect that phosphate is removed from the water column and fixed in the sediment.

2.10.5 MICROBIOLOGICAL ACTIVITY.

Mineralization of degradable organic matter present in the sediment enhance the dissolution of organic phosphorus.In mineralization process, organic phosphate esters are hydrolyzed by enzymes called phosphatase which are often located on the bacterial cell surfaces or occurring as free dissolved enzymes. Hydrolysis rates are often optimal at slightly alkaline-conditions. (Hakanson and Jansson, 1983).

Boström et.al.(1985) showed that internal phosphorus-loading in lake Vallentunasjön (a sewage polluted Swedish lake, Z= 2.7 m.), was associated with a high microbial activity in the surface sediments, and with a substantial loss of organic-phosphorus from the surface sediment.

The process of microbiological degradation could be stimulated, for a certain extent, by increasing the temperature. Kelderman and Van de Repe (1982) found that the temperature is an important controlling factor for phosphorus-release patterns in sediment cores from lake Grevelingen.

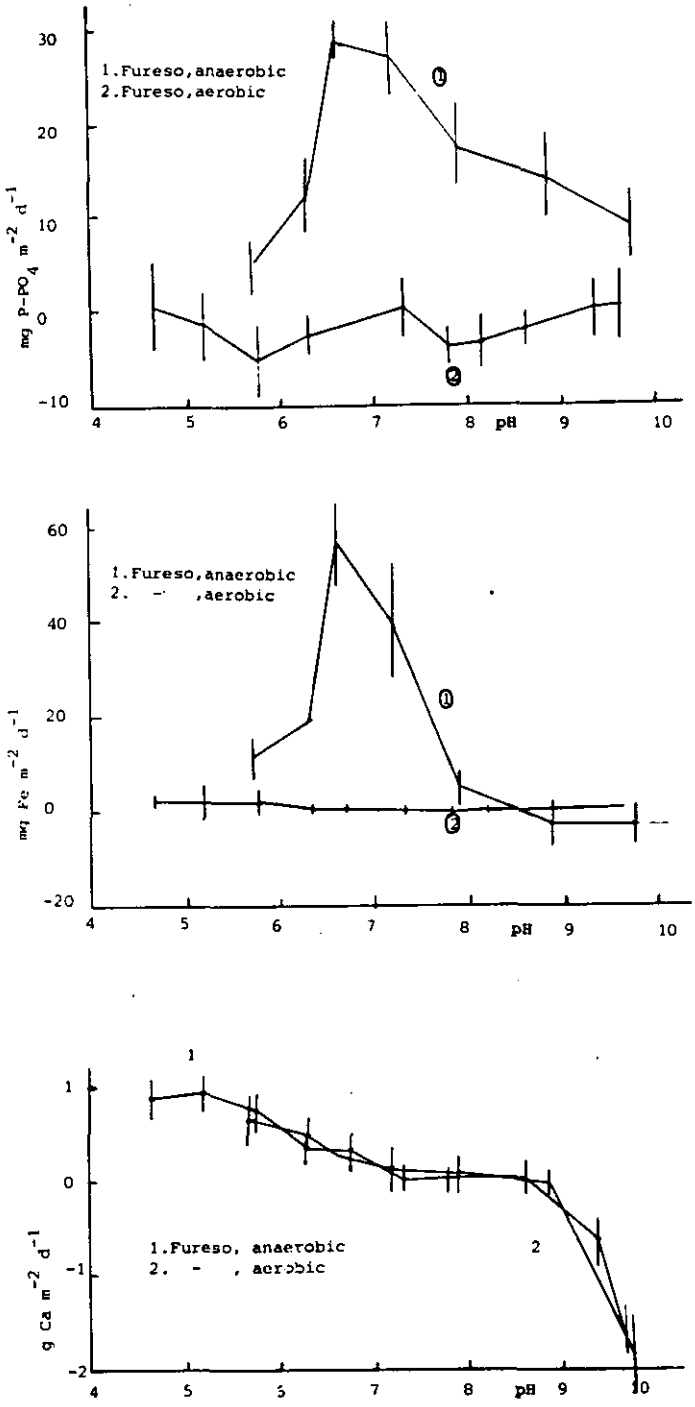


Fig.12: The influence of pH on the release of phosphate, iron and calcium from sediments of lake Fure so in Denmark. Below pH 7, calcium was dissolved from the sediment and above pH 9 it is precipitated. The effect on an aerobic exchange of iron and phosphate follows the same course, and the release had a pronounced maxima at pH 7 (Source: Kamp-Nielsen (1974): modified).

3. LAKE AND RESERVOIR RESTORATION

3.1 INTRODUCTION.

Control of eutrophication is one of the most important tasks of water authorities in most countries of the world. In lake restoration programmes, the major attention is given to decreasing the input of phosphorus from point sources, such as municipal waste waters and industrial effluent. Millions of dollars have already been spent to construct advanced waste water treatment plants including facilities to reduce the phosphorus content in the effluent. However the success of these measures was disappointing and there is no evidence of a case in which a once deteriorated lake has completely been recovered as a result of such measures alone.(Gächter and Imboden, 1985).

One of the two major reasons for this is identified as the significant contribution of non point sources to the phosphorus loading to lakes. Agricultural runoff and urban stormwater are often rich in phosphorus. These sources are not easily controlled.

The second major reason is the phosphorus release from sediments by re-dissolution. So the additional attempt of lake restoration programmes are aimed at control or reduce the phosphorus-sources and/or of the phosphorus release from bottom sediments. The following simple mathematical model shows the main factors in eutrophication control clearly.

3.2 A SIMPLE MODEL FOR LAKE RESTORATION.

The phosphorus balance in a lake is determined by the phosphorus input (M_{in}), the phosphorus export through the outlet (M_{out}), and sedimentation (M_s):

$$V\, dP/dt = M_{in} - M_{out} - M_s \qquad \text{.....(1)}$$

where V = volume of total lake (m^3)

P = mean total phosphorus concentration in lake (mg m^{-3})

t = time (years)

P_{in} is the average of all inlet concentrations $P_{in,i}$ (rivers, sewage pipes, ect.) weighted by the corresponding flow rates Q_i:

$P_{in} = \Sigma P_{in.i} Q_i / \Sigma Q_i = M_{in} / \Sigma Q_i$

Then, $M_{in} = P_{in} \cdot Q$

Q = water input or output ($m^3 yr^{-1}$)

P_{in} = mean total phosphorus supply from external sources (mg m^{-3})

It is possible to write the output terms (M_{out}, M_s) as the product of the total phosphorus content in the lake (VP) and some rate constants given below, and transform Eq. 1 into:

$$dP/dt = Q P_{in} / V - Q P_0 / V - \sigma_p P$$
$$= (Q/V) P_{in} - \{(Q/V)(P_0/P) + \sigma_p\} P$$
$$= \rho P_{in} - (\beta\rho + \sigma_p)P \quad \ldots\ldots\ldots(2)$$

$\rho = Q/V$, Water renewal rate (or flushing rate). (yr^{-1})

σ_p = Net sedimentation rate. (yr^{-1})

$\beta = P_0/P$, Vertical form factor (--)

P_0 = Mean total P concentration in surface outflow (mg m^{-3})

The steady state solution of Eq 2 could be written as:

$$P_\infty = P_{in} \frac{\rho}{\beta\rho + \sigma_p} \quad \ldots\ldots\ldots(3)$$

One goal of lake restoration is to decrease phosphorus concentration. Equation 3 serves to demonstrate the three different possibilities to achieve this goal:

1. Reduction of external phosphorus loading (i.e. P_{in}) by sewage treatment or diversion, or (in some cases) flushing the lake with water contain low phosphorus, and by decrease of phosphorus runoff from agricultural areas and at phosphorus load in urban stormwater runoff.
2. Increase of phosphorus export through the outlet (i.e. increasing β). This is achieved by diversion of hypolimnitic water which, during stagnation, has higher phosphorus concentrations than the surface water. However. this is not applicable to shallow lakes.
3. Increase of phosphorus retention (i.e. increase of σ) by increasing sedimentation or decreasing phosphorus re-dissolution at the sediments.

3.3 CONTROL OF EXTERNAL PHOSPHORUS LOADS.

Point discharges of sewage or industrial effluent, and non point sources such as surface runoffs from agricultural and urban areas are considered as external loads to lakes or reservoirs. The first and obvious step in a eutrophication control programme is removal or treatment of direct inputs of waste water, storm water or both that contain high contractions of nitrogen and phosphorus. Those point sources can be controlled by implementing waste water treatment plants or by diverting those streams to other receiving water bodies.

3.3.1 DIVERSION OF INFLOW WATER.

This technique prevents nutrient rich waters from entering a lake by diverting them. This seems to be simply transferring the problem to somewhere else. But in many cases careful diversion may not cause large problems, especially when the diverted water is used for agricultural irrigation or diverted to a receiving water body, where nutrient supply does not limit growth of planktonic algae. For example, if light is limiting in the receiving water, such that nutrients are not fully utilized, then added extra nutrients will not cause increased algal abundance. The impact of waste water diversion in 16 lakes in Europe and the USA is summarized in table 5.

In shallow lakes, improvements were generally found to be limited. This suggests that after the removal of a large inflow of nutrients, concentrations in the water column are maintained primarily by release from the sediments (Henderson-sellers and Markland,1987).

3.3.2 WASTEWATER TREATMENT.

By studying experiences all over the world, it can be noted that millions or, in some instances, billions of dollars have been spent in building waste water treatment plants to reduce discharges into surface water bodies. However, most of these wastewater treatment plants did not accommodate for the

Lake	Mean depth (m)	Result of diversion
d'Annecy (France)	41.5	Improved following diversion
Fairmont (5 lakes: Minnesota)	2-3	slight improvement with diversion but dredging provided remarkable improvement
Jordan (Michigan)	16(max)	Secondary effluent removed in 1971
Lansing (Michigan)	3	Remains eutrophic, dredging necessary
Lyngby So (Denmark)	2.8(max)	Good recovery,but increased macrophytes
Madisin lakes (Wisconsin)	9-25	Only slight improvement
Norrviken (Sweden)	5.4	Slight improvement, but P concentration still remains high
Rotsee (Switzerland)	0.2	Diversion in 1933, but no improvement
Sammamish Washington)	17.7	No change in winter P, Slight reduction in blue-green algae
Schiersee (Germany)	40(max)	Partial diversion in 1964, reduced oxygen depletion by 1967
Snake (Wisconsin)	7(max)	No improvement
Stone (Michigan)	20(max)	Improved only after addition of fly ash
Tegernsee (Germany)	70 (max)	Improved oxygen conditions, *Oscillatoria* still present, reduced numbers
Trummen (Sweden)	1.1	No recovery until after dredging
Washington (Washington)	32	Excellent recovery
Zurich (Switzerland)	50	Still eutrophic

Table 5. Representative lakes in which sewage has been diverted (Henderson-Sellers and Markland, 1987).

elimination of phosphorus in the treatment process. At present, in the industrialized countries, emphasis is given to improve these existing treatment plants.

The following examples illustrate the cost and the success of the efforts taken to improve lake water quality by implementing advanced waste water treatment plants. In Switzerland, over one billion dollars per year is spent for

water pollution control measures. A major portion of that amount is aimed to decrease the input of phosphorus into the surface water. Studies of AmbÜhl (cited in Gächter and Imboden, 1985) demonstrated that the efforts taken to decrease the phosphorus concentration were only successful in few cases and these have also not completely recovered from eutrophication. (Fig. 13).

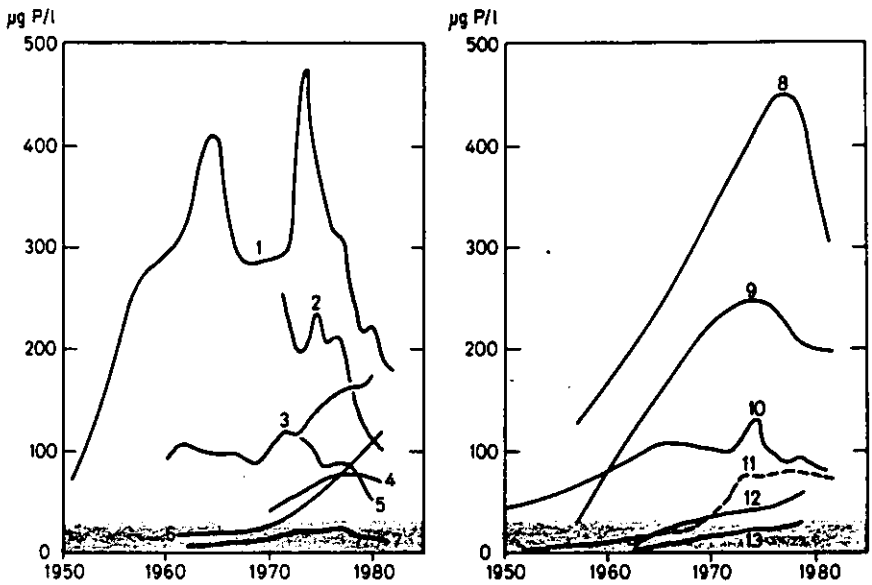


Fig 13. The evaluation of average concentration of soluble reactive phosphorus at spring overturn in various lakes. 1, Greifensee; 2, Pfäffikersee; 3, Zugersee; 4, Lac Lèman; 5, Bielersee; 6, Sempachersee; 7, Walensee; 8, Baldeggersee; 9, Hallwilersee; 10, Zürichsee; 11, Bodensee; 12, Lac de Neuchâtel; 13, Vierwaldstättersee. Shaded area indicates the water quality goal (Source: Gächter and Imboden 1985).

Another example is given in Larsen et.al. (1979), it concerns the effects of wastewater phosphorus removed from Shagawa lake, Minnesota. In early 1973, a tertiary treatment plant came into operation, which reduced the phosphorus supply to the lake with about 80%. In their study period, Larsen et.al. observed that significant reductions in total and soluble reactive phosphate (SRP) concentrations have occurred in the lake. By 1976, the average total phosphorus and SRP had declined from about 51 and 21 μgL^{-1} to about 30 and 4.5 μgL^{-1}, respectively, giving 40 & 80% reduction. During 1975 and 1976, chlorophyll a had decreased to less than 50% of the pretreatment level during May-June, but during July-August little change had occurred. They used the following mathematical model (see section

3.2), to predict changes of phosphorus levels in the lake, assuming a well mixed system.

$$dP/dt = (Q/V).P_{in} - (Q/V).P - \sigma_p P \quad ....(1)$$

The steady state solution of equation (1),(assuming J, S, & Q are constants) is :

$$P = P_{in} (1-Rp)^{-1} \quad ....(2)$$

Where Rp is the TP retention coefficient (= fraction of inflowing TP which is lost to the lake bottom).

The tertiary wastewater treatment plant reduced the inflow of phosphorus into the lake and significant reduction in the TP and SRP concentrations in Shagawa lake were observed in the years after influent phosphorus reduced. But total phosphorus concentration has not declined to levels projected from equation (2) using actual inflow water quality.

The main reason for this difference was identified as phosphorus feed back from sediment. To incorporate this feed back the TP dynamic equation was modified as follows:

$$dP/dt = (Q/V).P_{in} - (Q/V).P - \sigma_p P + J_{int}/V \quad ...(3)$$

Where J_{int} is an estimate of the rate of internal TP supply. J_{int}, σ_p, and the time interval over which TP was supplied internally were estimated from the pretreatment 1971-1972 data base. σ_p, was assumed to have two constant values. A winter rate, σ_p^w, applied to the periods when the lake was ice-covered, and a summer rate, σ_p^s, applied to the ice-free periods.

J_{int} was assumed to have the following form:

$$J_{int} = \begin{cases} C_1, & t_1 \le t \le t_2 \text{ (spring pulse)} \\ C_2, & t_3 \le t \le t_4 \text{ (summer pulse)} \\ 0, & \text{all other times of the year,} \end{cases}$$

Computer simulated parameter estimates for equation (3) are given below.

Ice-covered season	Ice-free season
σ_p^w = 0.035 week^{-1}	σ_p^s = 0.072 week^{-1}
C_1^p = 280 kg week^{-1}	C_2^p = 500 kg week^{-1}
= 4.4 mg P m^{-2} d^{-1}	= 7.9 mg P m^{-2} d^{-1}
t_1 = week 12	t_3 = week 25
t_2 = week 14	t_4 = week 34

The observed data and simulated values for TP in lake water for 1973-76 period were agreed best (Fig 14).

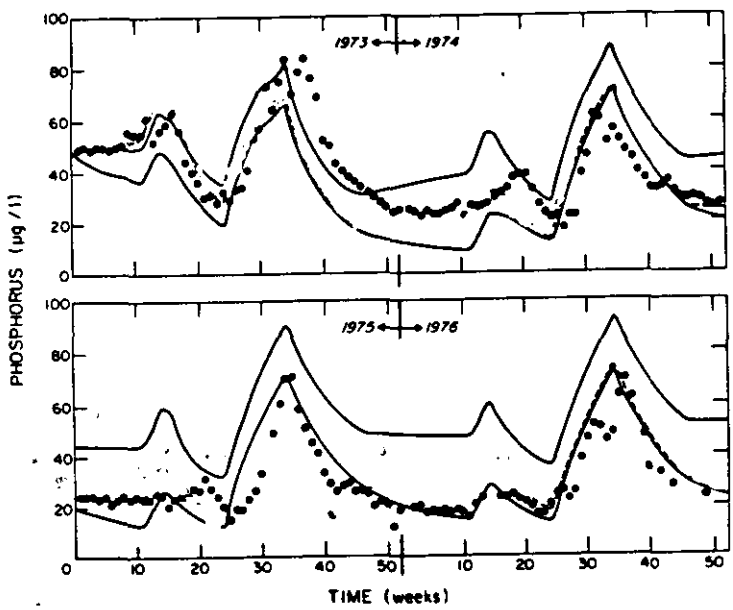


Fig.14. Comparison of output from equation 3 with total phosphorus (volume weighted average) data for the years subsequent to treatment. Upper solid line is projection as if treatment had not been instituted; lower solid line is projection incorporating external loading reduction.

The main conclusion of this study was, that even when external TP supplies to lakes have been reduced to a significant extent, corresponding decreases in lake TP levels, and hence decrease in lake productivity might not occur within an acceptable time scale. This means that additional measures are needed to achieve acceptable TP levels in lake water within a reasonable time span.

For this reason, various inlake restoration methods have been developed in recent years to control nuisance algae,

macrophytes and rooted plants. Bio-manipulation, mechanical removal of macrophytes, the application of herbicides, diversion of hypolimnetic water, hypolimnetic aeration, chemical precipitation of phosphate, sealing of the sediment surface, and removal of sediment by dredging are such internal lake restoration measures. Some of those techniques such as diversion of hypolimnetic water or hypolimnetic aeration are not applicable for shallow lakes, and hence not discussed in this report.

3.4 BIOMANIPULATION.

Controlling nuisance of algae and marcophytes by using biological measures is a developing lake improvement technique. The basic idea behind this is reducing algal biomass by increasing grazing capacity and/or reducing the turbation of the sediment by removing bottom feeding animals. The use of this technique is not yet wide spread, because the knowledge concerning this technique and its effects on aquatic ecosystems is limited and so it is still in an experimental phase. As it is possible to use the technique without adding chemicals to the ecosystem and there is no sediment removal, it may seem to have less environmental impacts than other in-lake measures. However, introducing foreign fish species to the ecosystem could cause severe biological damages such as the decline of native fish species or ultimate nuisance of the introduced species etc (Cooke et. al 1986).

3.5 DREDGING.

Sediment removal by dredging is a widely applied lake restoration technique. It is the only appropriate technique, when the purpose of the lake improvement is to deepen the lake. With subject to some limitations this technique can be applied for nutrient control of the removal of toxic substances, or for the removal of rooted macrophytes.

A major portion of phosphorus entering a lake, is deposited in the sediment and subsequently released to the lake water, yielding growth of algae or other nuisance plants, even though

incoming phosphorus is controlled by e.g. introducing advanced waste water treatment plants. In such a situation removal of nutrient rich sediment might be expected to reduce the rate of internal nutrient recycling, thus improving overall water quality.

Accumulation and subsequent release of toxic substances or heavy metals is another problem, which directly affects the aquatic life. Most of these micro-pollutants accumulate in the sediment. Uptake of these pollutants could cause accumulation in aquatic plants and animals to harmful levels. One of the most famous examples is the mercury pollution of Minimata bay in Japan. Dredging is the best measure to get rid of those type of pollutants, at least as far as the aquatic environment in concerned.

Dredging of sediment can remove nutrients toxic substances from lakes and hence improve the lake environment, but dredging itself gives various environmental damages. Sometimes, dredging is said to be transferring the problem from one place to another place or sometimes increase the problem. If the disposal site is not properly designed, or not properly maintained, nutrients, heavy metals, and other toxic substances could leach into the ground water or wash off to another surface water source. The pollutants may end up in places they never would reach by natural processes. Apart from those hazards involved in disposal, there are various inlake problems linked with dredging operation. Most of them are associated with the re-suspension of sediment during dredging. Liberation of nutrients, and/or toxic substances, fish gill blocking due to the increase of turbidity, destruction of the benthic fish food web and water level lowering in case large amounts of sediment are removed from a shallow lake, are some of these inlake problems. Noise, dust and truck traffic also pose additional nuisance problems (Cooke et. al. 1986).

Most of the dredging projects carried out so far, demonstrated improvements in lake water quality. Compared to the long term benefits, some problems arising during dredging could be neglected. Dredging projects having only marginal success are

due to inaccurate pre-dredging problem assessment and inadequate amounts of sediment removed (Peterson 1981, Salomons et.al. 1987).

Table 6 : PER-HECTARE COST FOR ALUM TREATMENT

Lake Treated	Mean depth (m)	Surface area (ha)	Chemical and dose (g Al/m^3)	Treatment cost ($/ha)
Horseshoe Lake	4.0	8.9	2.6	101
Lake San Marcos	2.3	18.2	6.0	126
Welland Canal	9.0	74.0	2.5	204
Mirror Lake	7.8	5.1	6.6	400
Shadow Lake	5.3	17.1	5.7	400
Cline's Pond	2.4	0.4	10.0	420
West Twin Lake	4.4	34.0	26.0	425
Dollar Lake	3.9	2.2	20.9	504
			Average:	322.5

Table 7.a : PER-HECTARE COST FOR DREDGING

Lake Dredged	Mean depth (m)	Surface area (ha)	Sediment removed (m^3)	% of basin dredged	Treatment cost ($/ha)
Half Moon Lake	1.7	53.4	25000	30	2137
Lilly Lake	1.4	35.6	680000	100	4586
Commonwealth Lake	0.9	2.6	19000	100	5769
Steinmetz(*)	1.5	1.2	2000	75	7233
Carnegie Lake	3.0	110.0	765000	75	12054
Lenox Lake	0.9	13.4	76000	100	13328
Nutting Lake	1.3	31.6	275000	56	18858
Sunshine Lake	0.5	0.4	5100	100	26832
Krause Springs	0.34	0.3	4900	100	31754
Collins Park Lake	0.7	24.3	52000	15	39178
			Average:		16173

Table 7.b :

Lake Geeplas	2	30	150000	100	17000
Lake Binnen Schelde	2	180	150000	20	2800

Cost of dredging operations are a matter of concern. In general it is agreed that dredging is more expensive than other nutrient inactivation techniques if only cost are concerned. But it is very difficult to compare even different dredging projects, due to the large number of variables involved, such as type of equipment used, project size, volume of material dredge, availability of disposal sites, the density of the material being

removed, the distance to the disposal site and the ultimate use of the dredged material, etc. Now it is obvious that comparison of dredging, with other sediment inactivation techniques such as chemical treatment is much more complicated due to some other variables also involved. Additionally, in most of the cases cost of dredging is given in cost per amount of material removed, while in sediment inactivation techniques the cost is given per hectare treated.

Peterson (1981) compared cost of dredging and chemical treatment processes for some lake restoration projects. The following tables (table 6 & 7.a) suggests that the average cost for dredging is about 50 times higher than the cost for chemical treatment. Table 7.b shows cost involved in two dredging projects carried out in the netherlands.

4. NUTRIENT PRECIPITATION AND INACTIVATION.

4.1 INTRODUCTION.

Nuisance caused by algal blooms can be reduced if the concentration of an essential nutrient in the lake is lowered to growth-limiting level. It is widely accepted that phosphorus is the critical nutrient in determining the degree of lake eutrophication and thus the controlling factor for the algae blooms. So almost all lake improvement programmes based on nutrient control are directed to the reduction of external phosphorus inputs from domestic and industrial sources. As remarked earlier those efforts were not completely successful to control the nuisance of algal blooms because of the fact that sediment phosphorus release contributes to a significant extent to the phosphorus budget in the lake. To overcome this problem, various inlake chemical treatment methods have been developed in the recent years. These methods include:

- phosphorus precipitation from the lake water
- inactivation of phosphorus in the sediment to retard further release of phosphorus to the overlying water
- chemical oxidation of sediment
- biological oxidation of sediment.

4.2 PRECIPITATION AND INACTIVATION OF PHOSPHORUS.

The purpose of this effort is to lower the lake's phosphorus content by removing phosphorus from the water column by precipitation and retarding subsequent release of phosphorus from lake sediment by inactivation. Most techniques for removal of phosphorus are based on precipitation of orthophosphate by metal ions. Aluminum, iron or calcium salts and salts of rare earth elements such as zirconium, lanthanum, and titanium, have been for this purpose. Among these salts lanthanum rare earth mixtures and Zirconium salts showed the most efficient phosphate precipitation and inactivation capacity; and aluminum came on the third place (Peterson et.al 1974). However, a major drawback of the use of lanthanum and zirconium salts for phosphorus inactivation in lakes are the potential toxic effects and the high costs. Therefore, the use of those salts is not addressed in detail in this report.

Fly ash and iron ore slag were also used in some lakes for P precipitation and inactivation (Higgins et. al. 1976). These materials could not be recommended for application to lakes due to high concentrations of heavy metals, and specially fly ash causes clogging of fish gill and is a further threat to aquatic life (Cooke et. al. 1986).

Artificial circulation or aeration is mostly restricted to stratified deep lakes and is not an applicable method for shallow lakes.

At present the most widely used phosphorus inactivation agent is Aluminum in the form of aluminum sulphate or sodium aluminate or a mixture of both (Cooke et. al. 1986).

4.2.1 PHOSPHORUS INACTIVATION USING ALUMINUM SALTS

The first attempt to use aluminum as a lake restoration agent is reported in 1968 in Lake Longsjon in Sweden. This deep lake was treated with Boliden Pellets (Primarily Aluminum Sulphate) and showed remarkable improvement with reduction in algal blooms during the following summer. Unfortunately, the

effect was not longlasting. This was probably due to the additional sewage inflow to the lake and a second treatment was necessary in 1970 (cited in Peterson et. al. 1974 and Foy, 1985)

A number of deep lakes in Europe and in North America were also treated with aluminum salts and showed remarkable improvements in lake water quality. A few examples are given below:

- Horseshoe lake in Wisconsin, was treated with aluminum in 1970 and subsequently showed low phosphorus contents in the lake water and reduced blue green algal biomass. The treatment was still efficient after 10 years and no indications of toxicity to benthic invertebrates or other aquatic organisms were observed (Cooke and Kennedy, 1981, Garrison & Knauer, 1984, Cooke et. al. 1986).
- Snake lake in Wisconsin is an another example of aluminum treatment. The lake was treated in 1972 with a mixture of aluminum sulphate and sodium aluminate. The treatment was effective in lowering phosphorus concentration and increasing water transparency and the treatment was also effective for about 10 years. In 1982, the water quality deteriorated. This was probably due to severe loads of nutrients from storm water runoff (Garrison and Knauer, 1984).

Medical lake, Washington (treated in 1977, EPA 1980(a)), Annabessacook lake, Maine (treated in 1978, Dominie II 1980), Dollar lake, Ohio (treated in 1974), are some of other North American deep lakes which were treated with aluminum and showed positive results for several years.

Attempts to reduce phosphorus release from sediments by the addition of aluminum salts have been least effective in shallow lakes, lacking a well-defined hypoliminion, and often little improvement in phosphorus status was observed within 1 year of treatment. Some examples are given below.

- Pickrel lake Wisconsin (Z = 2.4, treated in 1973, Knauer & Garrison 1980)
- Long lake, Washington (Z = 2.0, treated in 1982),

- Clines Pond, Origon (Z = 2.4, treated in 1971 Sanville et. al. 1976, and Dominie II 1980),

showed improvements following aluminum treatment, but the effect was not long lasting. Especially in Pickeral lake, the water quality deteriorated year following the treatment. Analysis of aluminum in sediment cores showed that the formed aluminum flock had been redistributed to the lake's center following a series of holomictic occurrences, which left areas of the sediment free to release phosphorus to the overlying water (Cooke et. al. 1986). Positive results of the treatment in Long Lake, however, lasted for a few years (Jacoby et. al. 1983).

4.2.1.1 MECHANISMS GOVERNING PHOSPHORUS PRECIPITATION AND INACTIVATION BY Al.

When aluminum salts such as aluminum sulphate or sodium aluminate are added to water, hydrolysed aluminum species like polymerized aluminum hydroxide, aluminate, or $Al(H_2O)_6^{3+}$ are formed, depending on the pH of the solution. At pH between 6-8 insoluble and settleble, polymerized, aluminum hydroxide forms. In alkaline solution (ie. pH above 8) the aluminate ion and pH below 6 the $Al(H_2O)_6^{3+}$ ion predominates.

Aluminum ions found in water are generally coordinated with six water molecules and the solutions are normally acidic due to the hydrolysis equilibrium.

$$Al(H_2O_6)^{3+} + H_2O \rightleftharpoons Al(H_2O)_5OH^{2+} + H_3O^+$$

Further hydrolysis of this divalent ion leads to the univalent ion and, finally, to colloidal aluminum hydroxide.

$$Al(H_2O)_5(OH)^{2+} + H_2O \rightleftharpoons Al(H_2O)_4(OH)^+_2 + H_3O^+$$

$$Al(H_2O)_4(OH)^+_2 + H_2O \rightleftharpoons Al(H_2O)_3(OH)_3 + H_3O^+$$

In basic solutions, aluminum hydroxides exhibits its amphoteric nature by further hydrolysis to form the aluminate ion.

$$Al(H_2O)_3(OH)3 + H_2O \rightleftharpoons Al(H_2O)_2(OH)^-_4 + H_3O^+$$

Figure.15 shows the relation between pH and solubility of monomeric aluminum species at 25^0C.

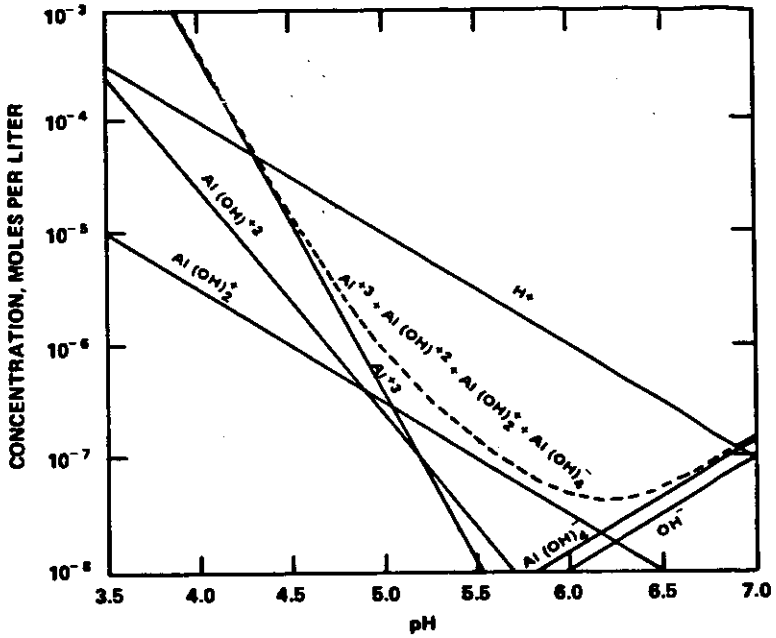


Fig.15: Solubilities of monomeric aluminum species at 25^0C as a function of pH (Source: Burrows 1977).

The most important species for phosphorus removal from water is $Al(OH)_3$. When $Al(OH)_3$ is formed by the addition of aluminum salts to water, pH is decreased and also total alkalinity falls. If the initial alkalinity is low or an excessive lode of aluminum salt is added to a lake pH will fall below 6.0 and the toxic Al^{3+} is formed. At the same time the amount of $Al(OH)_3$ flock is decreased. This flock should be available to remove phosphorus from water, or prevent phosphorus release from lake sediment. Therefore, the pH and the alkalinity are the most important factors in determinating the dose to be applied.

Aluminum phosphate ($AlPO_4$) precipitation, adsorption of phosphorus on the surface of $Al(OH)_3$ polymer or floc or entrapment and sedimentation of phosphorus containing particles in the $Al(OH)_3$ floc are the main phosphorus removal mechanisms from lake water involved in aluminum application. $AlPO_4$ does not form readily, however, in the phosphorus concentrations and pH found in normal lake water. The reaction is enhanced at a high Al:P ratio. In the pH range of 6-8, both inorganic dissolved phosphorus and particulate phosphorus are effectively removed by sorption to the $Al(OH)_3$ floc (Burrows 1977, Snoeyinks and Jenkins 1980, Stumm and Morgan 1981, Cooke et. al. 1986).

4.2.1.2 MAJOR DRAWBACKS OF Al APPLICATION.

The main part of the information available on the efficiency of aluminum treatment of lakes, concerns physical and chemical parameters, and only few papers deal with the effects on phyto- and zoo-plankton (Zarini et. al. 1983). However, the toxicity of aluminum on freshwater plants and animals has been well documented (Bengtsson 1978, Baker and Schofield 1982, Dave 1985, Friberg et. al. 1986, Skogheim and Rosseland 1986, Playle 1987 to cite but a few).

The level of aluminum toxicity to freshwater fish depends on chemical factors such as pH, calcium concentration, concentrations of ligands and chelators and degree of chemical stability and biological factors such as species and life stage.

Both low pH levels and elevated inorganic aluminum concentrations are found to be toxic to aquatic animals. This toxicity occurs at pH level of 5.0, which otherwise may not be acutely toxic to fish (Playle 1987). Cook et. al. (1986) confirmed from the data published on this subject, that a dissolved aluminum concentration below 50 µg Al/L will have no harmful effect on (*Daphnia magna*), rainbow trout (*Salmo gairdneri*), or chironomid larvae (*Tanytarsus dissimilis*). Kennedy and Cooke (1982) prepared a scheme to estimate the aluminum dose (mg Al/L), in water of varying initial alkalinity and pH. It is based upon the fact that at pH > 6 the dissolved aluminum concentration remains below 50 µg Al/L.

Human toxicity.

Aluminum has long been considered as a virtually non-toxic and non-absorbable from the gastrointestinal track. Because of this, neither the international nor the European standards for drinking water list aluminum among those substances for which limits are specified (WHO 1970, 1971). More recent studies have shown that ingested aluminum compounds are absorbed to a certain extent (Friberg et. al. 1986). As a result of aluminum

accumulation in the body, specially in the brain, severe health effects on the central nervus system (CNS) may occur. Aluminum concentrations of 50 µg/L in drinking water is considered to be safe (NRC, 1982).

Efficiency in shallow lakes.

All shallow lakes treated with aluminum salts got surface application of aluminum salts. Phosphorus removal from lake water occurs by coagulation/entrapment of phosphorus containing particles, precipitation of $AlPO_4$ or by sorption of phosphorus on the surface of aluminum hydroxide polymers. The alum flocks sink to the sediments and is eventually mixed into the sediment by bioturbation. The long term effectiveness of aluminum treatment will depend on the ability of the deposited aluminum hydroxide to retain phosphorus at the sediment/water interface and thus reduce the internal recycling of phosphorus (Kennedy and Cooke 1982). The major drawback reported for the failure of aluminum treatment in shallow lakes is the dispersion and redistribution of lake water.

4.2.2 PHOSPHORUS INACTIVATION USING IRON SALTS.

Iron salts have been used for long time in water treatment plants as a flocculent and in advanced waste water treatment plants as a phosphate removing agent. But the use of iron as a phosphate removing agent in lake restoration projects is not given much interest due to the suspension of release of phosphate and iron(II) in low redox conditions.

Singer (1972) cited two lakes in Michigan, where ferrous ion has been used for the removal of phosphate, lake Odessa and lake Grayling. Ripl (1976) reported a Swedish lake, treated with $FeCl_3$ followed by addition of CaCO3 and Ca(NO3), and obtained interesting results in controlling eutrophication.

4.2.2.1 AQUEOUS CHEMISTRY OF IRON(III).

One of the most prominent features of ferric iron in aqueous solutions is it's tendency to hydrolysis and/or formation of complexes. Due to this in the natural aqueous environment simple species such as Fe^{3+} do not exist, and iron mostly occurs as hydrated aquocomplex ions such as $Fe(H_2O)_6^{3+}$. The addition of an Fe(III) salt to water leads to the formation of soluble monomeric, dimeric or polymeric hydroxoiron complexes, in addition to the free aquoferric ion. The formation of hydroxoferrics complexes from the hydrolysis of the $Fe(H_2O)_6^{3+}$ ion takes place, according to the following equilibrium reactions:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$
$$[Fe(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H_3O^+$$
$$[Fe(H_2O)_4(OH)_2]^+ + H_2O \rightleftharpoons [Fe(H_2O)_3(OH)_3] + H_3O^+$$
$$[Fe(H_2O)_3(OH)_3] + H_2O \rightleftharpoons [Fe(H_2O)_2(OH)_4]^- + H_3O^+$$

(Cotton and Wilkinson 1976, Snoeyink and Jenkins 1983)

It can be seen, from those equilibrium reactions that the concentrations of the hydroxocomplexes depend on the pH of the solution. Cotton and Wilkinson (1976) stated that the pH of a solution containing mainly Fe(III) in the form of hexaquo ion (i.e. 99% $Fe(H_2O)_6^{3+}$) must be around zero due to the reason of hydrolysis equilibrium reactions.

Snoeyink and Jenkins (1983) noted that the hydroxo complexes, or hydrolysis products, of Fe(III) ion have a dramatic effect on the solubility of iron. The equilibrium of ferric ions in pure water is governed in its initial stages by the following equilibrium constants:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad \log K = -2.165$$
$$Fe(H_2O)_6^{3+} + 2H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + 2H_3O^+ \quad \log K = -6.74$$
$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3(OH)^- \quad \log K_{so} = -38$$
$$Fe(H_2O)_6^{3+} + 4H_2O \rightleftharpoons [Fe(H_2O)_2(OH)_4]^- + 4H_3O^+ \quad \log K = -23$$
$$2Fe(H_2O)_6^{3+} + 2H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+} + 2H_3O^+ \quad \log K = -2.85$$

The effect of these hydroxo complexes on solubility is most conveniently illustrated by a pC-pH diagram (Fig.16).

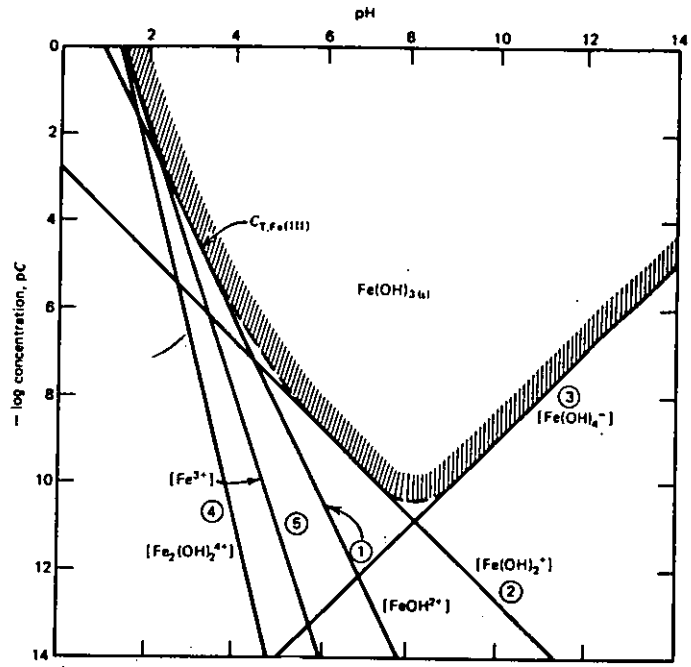
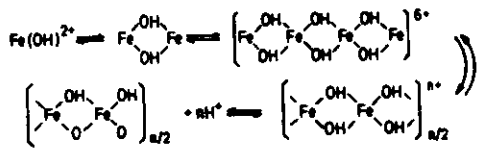


Fig. 16. Equilibrium concentrations of hydroxo iron(III) complexex in a solution in contact with freshly precipitated $Fe(OH)_{3(s)}$ at 25^0C. (source: Snoeyink and Jenkins)

The pC-pH diagram can be used for the rapid evaluation of both total concentration of all species present as well as to provide a graphic representation the concentrations of individual species at various pH values (Snoeyink and Jenkins 1983). Fig 16 shows that, in the pH range from 4.5 to 8 (which cover all natural waters), the predominant species is $[Fe(H_2O)_4(OH)_2]+$. The dimer $[Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+}$ does not predominate at any pH value in this range but is a significant species below pH 2.5. Moreover, at pH typically encountered in natural waters, $Fe(H_2O)_6^{3+}$ is only a minor component of the ferric iron species.

The possibilities of formation of large hydroxoferric complexes were studied by Dousma and de Bruyn (cited in Hong-Xiao and Stumm 1987) and Hong-Xiao and Stumm, 1987. Fig 17 (a) and (b) gives two reaction schemes suggested for the hydrolysis precipitation process of iron(III) solutions ending with large polymers.



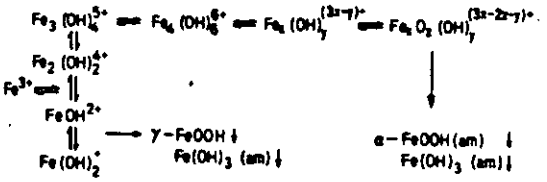
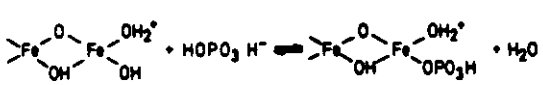


Fig.17(a). The seheme of hydrolysis precipitation process proposed by Dousma and de Bruyn (cited in Hong-Xiao and Stumm, 1987), (b). A comprehensive scheme of hydrolysis polymerization precipitation process proposed by Hong-Xiao and Stumm, 1987, and chemical species (in 0.3 M $FeCl_3$, solution).

4.4.2.2 MECHANISMS OF P REMOVAL.

Interactions between iron and phosphate in lake water and sediment are in a complex way governed by redox potential and pH. As shown in the previous chapter a major portion of aqueous solutions of ferric iron, is in monomeric or polymeric hydroxy complex form. The existence of these species is governed by the pH of the solution and the solubility of individual species.

In aerobic lake waters, the major mechanism of phosphorus removal could be the adsorption of phosphate to iron(III)-hydroxo complexes as shown by Lijklema (1980) or hydroxo ligand exchange reactions between phosphate and the iron(III)-hydroxo polymers.



Apart from these complex reactions, direct precipitation of $FePO_4$ is also possible, according to the following reaction:

$$Fe^{3+} + PO^{3-}_4 \rightleftharpoons FePO_4 \ (s)$$

In an anaerobic condition Fe(III) can be reduced to Fe(II) and then, precipitated and/or sorbet PO4 is expected to be released to the water column (Lijklema, 1980; Hakanson et. al., 1973). Thomas, 1965 (as cited in Singer, 1972) observed a small release of phosphate during anaerobic digestion of activated sludge from waste water treatment plant of Mannedorf, Switzerland and other treatment facilities in Switzerland.

Einsele (as cited in Singer, 1972) showed that the amount of available orthophosphate in aquatic eco-systems depends on the extent of ferrous iron oxidation and, consequently, on the concentration of oxygen and the ratio of $Fe(OH)_3$ to $FePO_4$. Fig.18 depicts the limnological cycle of iron showing its interactions with phosphate.

Oxygenated conditions

$$Fe^{+2} + O_2 \longrightarrow Fe^{+3} \xrightarrow{+ PO_4^{-3}} Fe\,PO_4(s) \downarrow Fe(OH)_3(s)$$

Redox conditions

$$Fe\,PO_4(s) \longrightarrow Fe^{+2} + PO_4^{-3} \xrightarrow{?} Fe_3(PO_4)_2(s)$$
$$SO_4^{-2} \longrightarrow S^{-2} \longrightarrow Fe\,S(s)$$

Fig.18: Interactions of aqueous iron and orthophosphate in limnological systems.

In well oxygenated conditions ferrous iron is oxidized to ferric iron which subsequently reacts with phosphate to form ferric phosphate or hydroxyferric phosphate complexes. During periods in which the whole sediment is anaerobic (stagnation or high biomass production periods), ferric phosphate and hydroxyferric phosphate complexes are reduced to ferrous iron and phosphate, and both are released to water column. Then, depending on the concentration of sulphate and the extent of sulphate reduction, the ferrous iron may react to form the relatively insoluble ferrous sulphide (log K_{SO} = -18.4). On the other hand, formation of ferrous phosphates could also be

expected in those conditions as the solubility of ferrous phosphate is also low (log K_{so} = -29.9). Williams et. al. (1971), and Singer (1972), cited the occurrence of vivianite ($Fe_3(PO_4)_2.8H_2O$) in reducing environments and the X-ray analysis of phosphate precipitates in sediments of ferrous ion treated Odessa lake and Grayling lake in Michigan, and showing those to be vivianite (Green et. al., 1967 as cited in Singer, 1972). Emerson (1976) and Emerson (1978) indicated the presence of vivianite in the solid phase of interstitial waters from sediment cores taken from Greifensee, Switzerland.

4.3 SEDIMENT OXIDATION.

A lake restoration technique involving the oxidation of the top 15 to 20 cm of anaerobic lake sediment with the aid of nitrate has been developed by Ripl (1976). The objective was to reduce the internal phosphorus loading in lakes with anaerobic sediment and high interstitial water phosphorus concentrations, in which iron controls phosphorus exchange between the sediment and the overlying water. By oxidizing the organic matter through increased denitrification, increased binding of interstitial water phosphorus with ferric hydroxide complexes should be induced, resulting in lower phosphorus release rates (Ripl 1976, Ripl & Lindmark 1978, Foy 1986).

To reduce the labile organic matter content in sediment through the action of denitrifying bacteria and thereby restore an oxidized state, a solution of $Ca(NO_3)_2$ (141 gN m^{-2}) was injected into the sediment of Lake Lillesjön in Sweden. Prior to this addition, ferric chloride (146 gFe m^{-2}) was added to remove hydrogen sulfide and to form ferric hydroxide, which binds interstitial phosphorus. Addition of ferric chloride decrease the pH. In order to raise the pH, to an optimal level and encourage microbial denitrification, lime (180 gCa m^2) was added next,. This treatment showed successful results to in reducing the interstitial phosphorus content by 70-85%, compared to per treatment levels. Laboratory experiments with sediments from White Lough, N.Ireland, evidenced, that a dosage of 61 gN m^{-2} suppressed the phosphorus release completely. Foy (1986) showed

that the ferric chloride and calcium hydroxide addition was not necessary in White Lough sediments , reasoning the naturally occurring iron in lake sediment was adequate.

Sörensen (1982) and Tirèn & Pettersson (1985) showed a release of phosphorus after NO_3^- is depleted in some sediments treated with nitrate. Sörensen (1982) suggested that iron can be reduced also by bacteria, which utilize iron(III) as electron acceptor during anaerobic respiration (Fig.7). Tirén and Pettersson (1985) further showed that addition of NO_3^- to sediments of some lakes could directly increase the phosphorus release. This is due to an oxygen depleted sediment leads to a stimulation of the mineralization process if a major part of the nutrient is dissimiltorily reduced. Tsicritsis and Mourkides (1988) showed that addition of NO_3^- cannot inhibit the release of phosphorus in shallow lakes when the lack of thermal stratification layer and the result of mixing of the water results distribution of NO_3^-through the water column.

PART B

5. PHOSPHATE RELEASE EXPERIMENTS.

5.1 INTRODUCTION

One of the aims of this work is to perform some laboratory experiments to study the inactivation efficiency of iron salts in both oxic and anoxic conditions and to determine the optimal dose. To achieve this goal, a series of release experiments were carried out using continuous flow reactors, giving different doses of ferric chloride. Oxic and anoxic conditions were simulated along with each dosages.

The second objective was to compare different chemicals. This was done in batch experiments using sediment samples mixed with some inactivation agents reported in literature (eg. Al, NO_3^-). Sediment samples treated with $FeCl_3$ doses, equivalent to the continuous flow experiments were also included to this batch experiment setup. The aim of this approach was to compare the relevant inactivation efficiency of iron with aluminum, both in aerobic and anaerobic conditions and to study the effect of biological oxidation of sediment on P release.

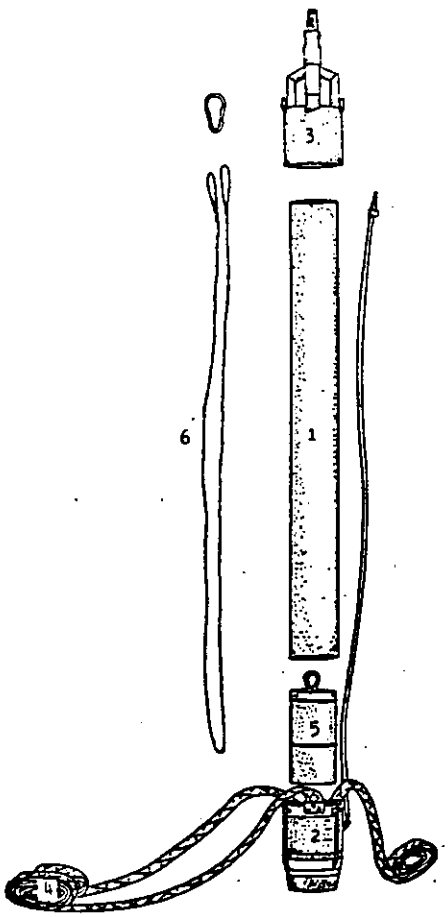
5.2 MATERIALS AND METHODS.

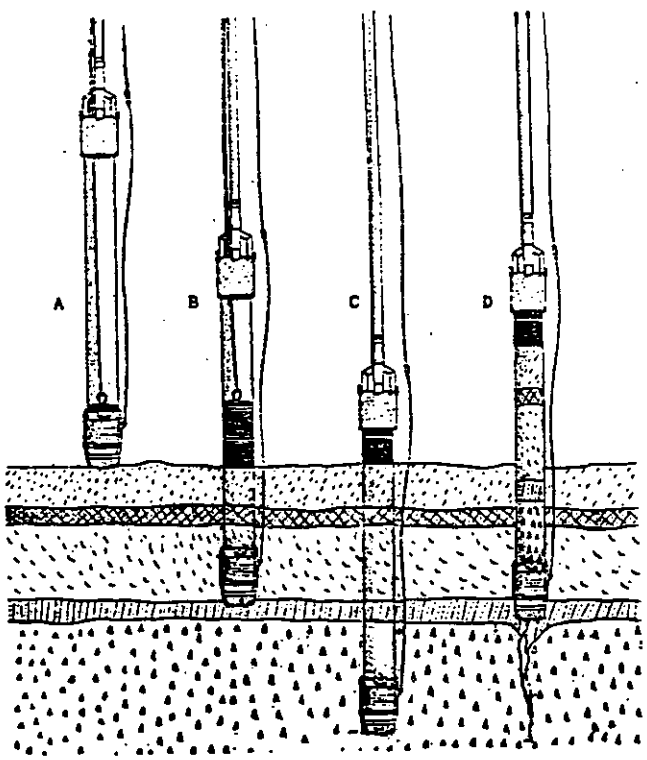
SEDIMENT SAMPLE

Undisturbed sediment samples were collected from one station in the lake area in the polders Wormer, Jisp and Neck, for all experiments using a Beekers sampler (Fig.19). Sediment cores were transported to the laboratory and stored at 4^0C until experiments were started.

Table 8. Chemical characters of lake water

Constituent		Concentration (mg/L)
Calcium	(Ca)	59
Magnesium	(Mg)	11.1
Sodium	(Na)	75
Potassium	(K)	7.1
Sulphate	(SO_4)	72
Chloride	(Cl^-)	129
Bicarbonate	(HCO3)	132





BEEKERS SAMPLER.

1. Sampling tube.
2. Cutter head.
3. Sampler head.
4. Fixing tie.
5. Plunger.
6. Plunger cable.

REAGENTS USED

Table 9.

Solution	Strength	Preparation
1 Ferric Chloride	10gFe^{3+}/L	48.4g Ferric Chloride hexahydrate in 1L demineralized water
2 Calcium nitrate	8gNO^{3-}-N/L	16.87g Calcium Nitrate tetrahydrate in 1L demineralized water
3 Aluminum sulphate	1gAl^{3+}/L	3.08g Aluminum sulphate octadecahydrate in 1L demineralized water
4 Sodium aluminate	0.5gAl^{3+}/L	10% NaOH soln. was added to a 100ml of aluminum sulphate solution in a 200mL volumetric flask until all precipitate was dissolves and then make up to the mark with demineralized water
5 Sodium Hydroxide	~10%	10g NaOH in 1L demineralized water

Table.10 Recipe for preparing 1.0L Synthetic Water
(Amounts were calculated using the BASIC computer programme given in appendix 2)

Compound	Amount (mg)
Calcium Chloride	162.3
Magnesium Sulphate	113.5
Potassium Chloride	13.5
Sodium Sulphate	93.3
Sodium Bicarbonate	182.6
Sodium Chloride	29.3

5.3 CONTINUOUS FLOW EXPERIMENTS.

RELEASE REACTOR

Schematic diagram of continuous flow reactor is given in Fig.20. Sediments were treated according to the scheme given in table 11.

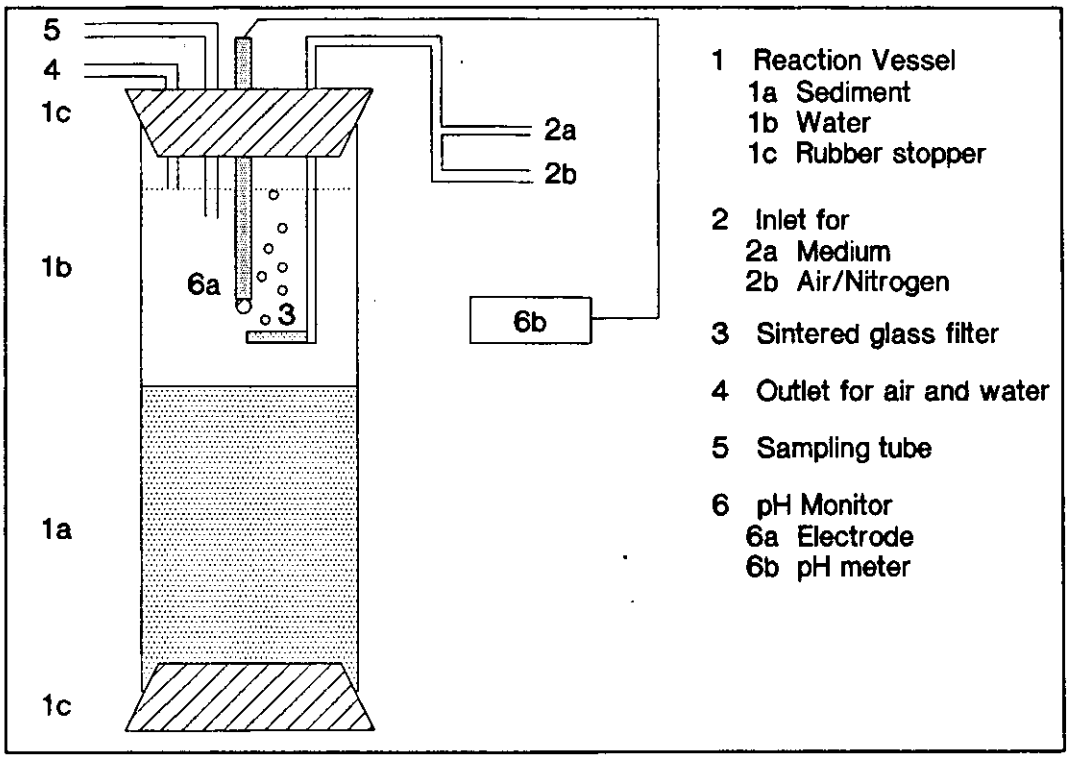


Fig. 20 : Schematic Diagram of Continuous Flow Reactor

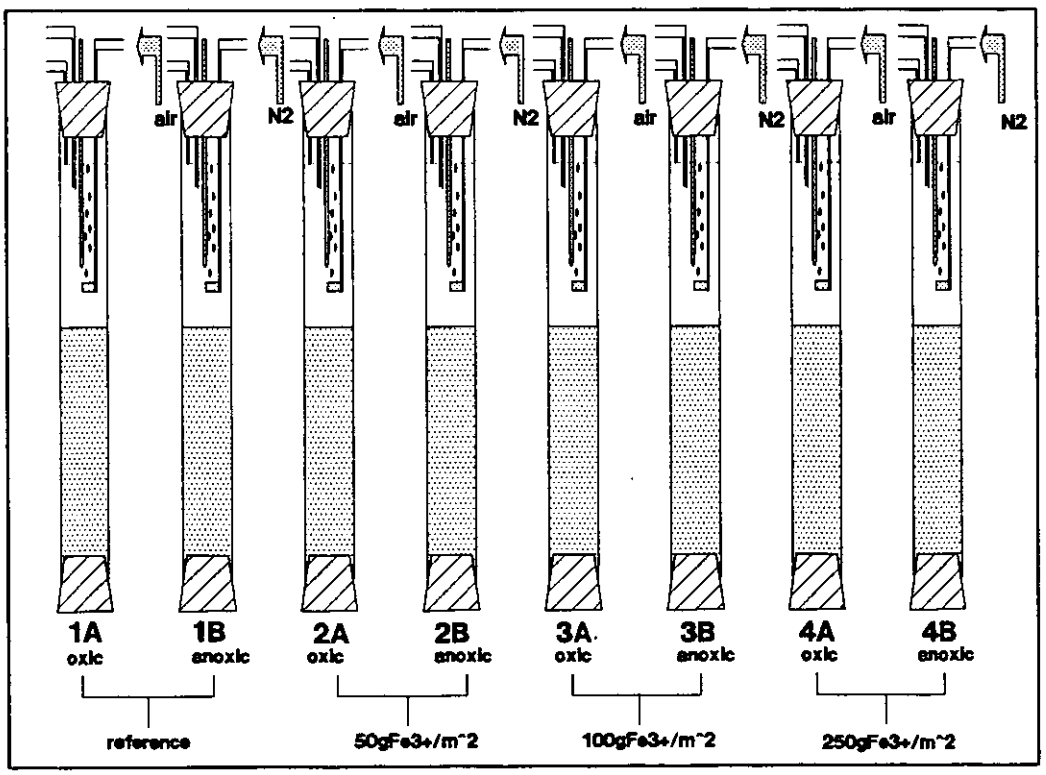


Fig. 20(b) : Chemical Treatment Scheme
(Continuous Flow Reactors)

Table.11 Sediment treatment scheme

Sediment core	Chemical treatment	Redox condition	Amount $FeCl_3$ soln. added (10gFe3+/L)
1A	none	oxic	-
1B	none	anoxic	-
2A	$50gFe^{3+}/m^2$	oxic	25ml
2B	$50gFe^{3+}/m^2$	anoxic	25ml
3A	$100gFe^{3+}/m^2$	oxic	50ml
3B	$100gFe^{3+}/m^2$	anoxic	50ml
4A	$250gFe^{3+}/m^2$	oxic	125ml
4B	$250gFe^{3+}/m^2$	anoxic	125ml

The upper 20cm of sediment cores No. 1A & 1B were combined in a large glass beaker and stirred to obtain a homogeneous and identical sample for oxic and anoxic release experiments. After mixing, the pH of the mixture was measured. Mixture was then returned back to the initial columns in two equal portions and allowed to settle.

In the same way sediment for cores No. (2A,2B), (3A,3B) and (4A,4B) two sediment samples were combined separately in large glass beakers and stirred with 25ml, 50ml, and 125ml of $FeCl_3$ solution ($10gFe^{+3}/L$) respectively. After measuring the pH, the mixtures were returned back to initial columns and allowed to settle.

After two days, the eight sediment cores were installed in continuous flow reactors (Fig.2(b)). Artificial lake water (Table.10) with ion composition similar to that of lake water (Table.8) was used to continuously replace the overlying water using Gilson Minipulse 2 peristaltic pump. The residence time of water was 1.5 days and was checked regularly. The purpose of this flushing is to prevent build-up of high phosphorus concentration in the overlying water, which may decrease the

release rates. In the lakes, such a build-up is prevented by consumption of the released phosphorus by the phytoplankton (Boers 1986).

The water of release reactors 1A, 2A, 3A and 4A was aerated by bubbling with air at a rate of $0.8 Lh^{-1}$. Nitrogen gas (Technical grade) was bubbled through the water of reactors 1B, 2B, 3B and 4B in order to simulate anaerobic conditions in the overlying water.

The overlying water was sampled 5 times a week and filtered immediately over a 0.45μm filter and analyzed for soluble reactive phosphate. the pH and the dissolved oxygen content (D.O) of the overlying water and the pH of the sediment were measured regularly.

Phosphorus release rates of continuous flow reactors were calculated using following mass balance equation.

$$F = [\{(P_{n+1} - P_n) / (t_{n+1} - t_n)\} + \{(P_{n+1} + P_n) / 2R\}\ h$$

where F = Phosphorus flux across sediment-water interface (mg P m^{-2} d^{-1}).

P_{n+1}, P_n = SRP concentration of the overlying water at time t_{n+1} and t_n (mg P m^{-3}).

t_n, t_{n+1} = Successive SRP determination days (d)

R = Water residence time (d)

h = Height of the water column of release reactors(m)

Dry weight, organic matter, total phosphorus, total iron and organic and inorganic carbon content of raw sediment were also determined.

5.4 BATCH EXPERIMENTS.

The upper 20cm fragment of two sediment cores were mixed in a erlenmeyer flask and used as a bulk sediment for all batch experiments. $50cm^3$ portions were transferred to 250mL erlenmeyer flasks and treated according to the scheme given in table 12.

Table.12. Experimental conditions and scheme of sediment treatment for batch experiment.

Sediment		Treatment g/m^2	Redox status	Amount reagent added
1	A1	none	oxic	-
2	B1	none	anoxic	-
3	A2	50 Fe^{+3}	oxic	1.25mL $FeCl_3$ soln
4	B2	50 Fe^{+3}	anoxic	1.25mL $FeCl_3$ soln
5	A3	100 Fe^{+3}	oxic	2.50mL $FeCl_3$ soln
6	B3	100 Fe^{+3}	anoxic	2.50mL $FeCl_3$ soln
7	A4	250 Fe^{+3}	oxic	6.25mL $FeCl_3$ soln
8	B4	250 Fe^{+3}	anoxic	6.25mL $FeCl_3$ soln
9	A5	50 Fe^{+3} +140(NO3-N)	oxic	1.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
10	B5	50 Fe^{+3} +140 (NO3-N)	anoxic	1.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
11	A6	100 Fe^{+3}+140 (NO3-N)	oxic	2.50mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
12	B6	100 Fe^{+3}+140 (NO3-N)	anoxic	2.50mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
13	A7	250 Fe^{+3}+140 (NO3-N)	oxic	6.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
14	B7	250 Fe^{+3}+140 (NO3-N)	anoxic	6.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
15	A8	50 Al^{3+}	oxic	6.25ml $Al_2(SO_4)_3$
16	B8	50 Al^{3+}	anoxic	6.25ml $Al_2(SO_4)_3$
17	A9	100 Al^{3+}	oxic	12.5ml $Al_2(SO_4)_3$
18	B9	100 Al^{3+}	anoxic	12.5ml $Al_2(SO_4)_3$
19	A10	none	oxic	-
20	B10	none	anoxic	-
21	A11	25 Al^{3+}	oxic	6.25ml $Al_2(SO_4)_3$
22	B11	50 Al^{3+}	anoxic	12.5ml $Al_2(SO_4)_3$
23	A12	125 Al^{3+}	oxic	31.25ml $Al_2(SO_4)_3$
24	B12	25 Al^{3+}	anoxic	3.125ml $Al_2(SO_4)_3$ +6.25ml $NaAl(OH)_4$
25	A13	50 Al^{3+}	anoxic	6.25ml $Al_2(SO_4)_3$ +12.5ml $NaAl(OH)_4$
26	B13	125 Al^{3+}	oxic	15.625ml $Al_2(SO_4)_3$ +31.25ml $NaAl(OH)_4$

25, 50, and 125 g Al^{3+}/m^2 treatment is equal to 50, 100, and 250 g Fe^{3+}/m^2 treatment.

Samples were shaken, after addition of appropriate amounts of inactivant and then made up to the mark of 200mL with synthetic lake water (Table.3) . pH of the mixture was measured.

Sample No: B1-B26 were incubated in an anaerobic chamber of room temperature (20^0C). This chamber was purged with technical grade nitrogen gas. The oxygen concentration inside the chamber was less than $0.1mgL^{-1}$. Samples No: A1-A26 were incubated at room temperature. After one week of incubation, 50mL of overlying water was taken away by means of a pipet and filtered immediately on 0.45 μm Milipore filter and analyzed for SRP. On the same day 140g $(NO3-N)m^{-2}$ (i.e. 4.38mL of 8g NO3-N/L solution) was added to flasks No. A5, B5, A6, B6, A7, AND B7 in order to study the effect of biological oxidation of sediment on P release in anaerobic conditions. After another week of incubation the overlying water was sampled and analyzed for SRP.

Table 13.

Analytical Techniques and Equipment

	Parameter	Instrument	Technique	Detection limit	Interferences	Reference
1.	SRP of water	Technicon AA2 Auto Analyzer	Automated Ascobic acid reduction method	1ug/L	* No influence up to 50mg/L iron * Salts concentration up to 20%(w/v) cause an error lessthan 1%	Standarded methods APHA-AWWA-WPCF 1981
2.	Total iron of sediment	Varian Spectra 400 (Atomic Absorption Spectro photometer)	i. Freeze dried sample destructed with HCL/HNO3 ii. AAS-Flame	0.014 mg/L	Alkali metals	Anderson, 1976
3.	Inorganic carbon content of the sediment	NA 1500 Carlo Frba	i.Freeze dried sample ii.Ignition with Tin iii.Gas Chromatographic analysis of CO2 (Column : Porpack)	0.08%		

6. RESULTS AND DISCUSSION.

6.1. GENERAL.

Some chemical and physical parameters of the sediment are given in tables (14).

Table (14).
Chemical and physical parameters of sediment

Parameter	
total iron	13.5 g/Kg
dry wt.	6.4%
LOI	70.3%
pH	7.3
colour	black
sediment type	peaty
organic carbon	35.1%
inorganic carbon	4.1%

6.2. CONTINUOUS RELEASE EXPERIMENTS.

6.2.1 pH.

Fig (21) and (22) illustrate variation of pH in the sediment and the water phase of continuous phosphorus release reactors.

pH of the sediment was reduced substantially, when it was mixed with acidic FeCl3 solution (pH of the bulk FeCl3 solution was 1.3). Two days after mixing pH of the lowest two dosages (col. 2A, 2B, 3A, and 3B) was improved very close to the original sediment pH (i.e. 7.3). The pH of the highest dosed columns (4A and 4B), however, remained at a low value(~ 5.5).

Recovery of pH of the sediment, after mixing with $FeCl_3$ or any other acidic solution is depending on the buffering capacity of the sediment. The buffering system in the sediment is the $CaCO_3/HCO_3^-$ system.

When $FeCl_3$ is added to water it undergoes various hydrolysis equilibrium reactions (section 4.4.2). The end result is:

$$FeCl_3 + 6H_2O \rightleftharpoons Fe(H_2O)_6(OH)_3 + 3Cl^- + 3H^+$$

Liberated H^+ ions can be neutralized by $CaCO_3$ in the sediment.

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$

This means that, apart from the initial pH of the sediment, the amount of $CaCO_3$ present in the sediment dictates the pH after mixing with acidic $FeCl_3$. As these proton transfer reactions are very fast (half lives less than milli seconds, Stumm and Morgen, 1981), one can expect the equilibrium to be reached within a short period. The pH data of the sediments of release reactors show an equilibrium time of a few days. This may be due to the availability of $CaCO_3$ and the exchange of the CO_2 produced with the atmosphere.

6.2.2 RELEASE RATES.

Phosphorus release rates of continuous flow reactors,which were calculated using the mass balance equation described in section 5.3 are given in appendix 3.

Fig 23 (a), (b),and (c) illustrate the variation of phosphorus release rates with time. Average (time weighted) phosphorus release rates of each reactor was calculated by dividing, the total amount of phosphorus released from the column by the duration of the experiment. The results are given in table 15.

Table 15. Average phosphorus release rates of continuous flow reactors

column No:	Condition	P release rate (mgP/m^2.d)	D.O (in water) mg/L
1A	Reference(oxic)	5.01	8.8
1B	Reference(anoxic)	9.33	0.6
2A	50mgFe/m^2(oxic)	1.12	8.7
2B	50mgFe/m^2(anoxic)	8.76	0.7
3A	100mgFe/m^2(oxic)	0.94	8.8
3B	100mgFe/m^2(anoxic)	1.67	0.6
4A	250mgFe/m^2(oxic)	0.60	9.0
4B	250mgFe/m^2(anoxic)	0.57	0.6

The anoxic phosphorus release from the reference column is about 2 times higher than that from the oxic reference column (Fig 24). There is no large difference in release rates of reference anoxic column (1B) and 50gFe/m^2 treated anoxic column (2B). However, 100gFe/m^2 and 250gFe/m^2 treatment suppressed the anaerobic phosphorus release by about 82% and 94%, relative to the reference anoxic phosphorus release.

All oxic columns showed lower phosphorus release rates compared to the corresponding anoxic columns except the two highest dosed columns. These columns (4A and 4B), showed no significant difference.

The phosphorus release reduction in iron treated oxic columns are about 78%, 81%, and 88%, compared to the oxic reference column.

6.3. BATCH EXPERIMENTS.

pH and SRP concentrations of batch experiments are given in table.16. The pH variation of FeCl3 treated flasks showed the same pattern as the continuous release experiments. Higher aluminum sulphate doses gave slightly lower pH values than corresponding FeCL3 doses. However, the 50%AlSO4 + 50%NaAL(OH)4 treatment did not make any adverse pH changes.

The O-PO_4 concentrations of the overlying water of flasks can be considered as equilibrium concentrations of the relevant experimental condition.

The high equilibrium concentrations found in non treated flasks indicate the presence of high amounts of releasable P in the sediment. The average equilibrium concentration of non treated anoxic flasks is about 5 times as high as those of the non treated oxic flasks. This indicates the possibility of redox mediated phosphorus release.

Table No 16

Results of batch experiments

Flask Number	Condition	Treatment	Initial pH	pH after one week	pH after two weeks	O-PO4 Concentration ug/L after one week		O-PO4 Concentration ug/L after two weeks
A1	oxic	none	7.39	7.65	7.65	248.00		304.00
A10	oxic	none	7.20	7.60	7.75	170.00		322.00
B1	anoxic	none	7.42	8.34	8.95	1,032.00		1,819.00
B10	anoxic	none	7.19	8.10	8.15	1,937.00		1,640.00
A2	oxic	50gFe3+/m^2 (as FeCl3)	6.50	7.39	7.55	13.00		22.00
A5	oxic	50gFe3+/m^2 (as FeCl3)	6.09	7.27	6.39	11.00	+140g NO3	21.00
B2	anoxic	50gFe3+/m^2 (as FeCl3)	6.53	8.16	8.62	144.00		356.00
B5	anoxic	50gFe3+/m^2 (as FeCl3)	6.38	8.22	7.94	241.00	+140g NO3	15.00
A3	oxic	100gFe3+/m^2(as FeCl3)	6.10	7.15	7.40	30.00		33.00
A6	oxic	100gFe3+/m^2(as FeCl3)	5.91	7.07	6.39	32.00	+140g NO3	10.00
B3	anoxic	100gFe3+/m^2(as FeCl3)	5.84	7.45	7.96	56.00		23.00
B6	anoxic	100gFe3+/m^2(as FeCl3)	5.97	7.89	7.67	47.00	+140g NO3	21.00
A4	oxic	250gFe3+/m^2(as FeCl3)	4.75	3.65	3.75	8.00		11.00
A7	oxic	250gFe3+/m^2(as FeCl3)	4.85	3.47	4.32	19.00	+140g NO3	19.00
B4	anoxic	250gFe3+/m^2(as FeCl3)	4.72	6.62	6.72	10.00		8.00
B7	anoxic	250gFe3+/m^2(as FeCl3)	4.91	6.86	6.60	17.00	+140g NO3	19.00
A11	oxic	25gAl3+/m^2 (as AlSO4)	6.50	7.50	7.90	30.00		110.00
B12	anoxic	25gAl3+/m^2 (as AlSO4 + NaAl(OH)4)	7.04	7.90	8.25	199.00		248.00
A8	oxic	50gAl3+/m^2 (as AlSO4)	5.56	6.73	6.73	9.00		19.00
A13	oxic	50gAl3+/m^2 (as AlSO4 + NaAl(OH)4)	6.98	7.80	8.01	9.00		33.00
B11	anoxic	50gAl3+/m^2 (as AlSO4)	5.78	7.20	7.86	36.00		56.00
B8	anoxic	50gAl3+/m^2 (as AlSO4)	5.54	7.41	7.55	13.00		16.00
A9	oxic	100gAl3+/m^2(as AlSO4)	4.31	4.56	4.35	9.00		12.00
B9	anoxic	100gAl3+/m^2(as AlSO4)	4.43	5.35	5.21	8.00		33.00
A12	oxic	125gAl3+/m^2(as AlSO4)	4.43	4.50	4.66	11.00		24.00
B13	anoxic	125gAl3+/m^2(as AlSO4 + NaAl(OH)4)	6.85	7.30	8.23	20.00		20.00

The results of the iron treated flasks are in well agrement with iron treated continuous flow experiments. All iron treated oxic flasks showed low P release in comparison to the non treated oxic flasks, and only the anoxic flasks treated with 50 gFe^{3+}/m^2 had a high P release compared to the other iron treated anoxic flasks. The addition of NO_3^- showed a significant reduction of equilibrium concentration in oxic the 50 gFe^{3+}/m^2 treated flask. There was no such a remarkable effect on NO_3^- addition to 100 and 250 gFe^{3+}/m^2 treated flasks.

One reason for this is that the P release of these flasks were already hindered by high doses of iron. This result is in well agreement with Foy (1986). Ripl (1976) proceeded the addition of nitrate by inputs of ferric chloride and lime in order to improve the phosphate binding capacity of the sediment. Foy (1986) showed that there it was not necessary to add iron to a lake sediment, before treatment with nitrate, if there is enough iron to cope with phosphate.

The reduction of P release under oxic conditions by iron treatment can be explained by the classical iron/phosphate model. The pH of the overlying water of the continuous release reactors and the batch experiment reactors is between 7 and 9. In this pH range the predominant, dissolved hydroxoiron complexes are the $Fe(OH)_2^+$ and $Fe(OH)_4^-$. Also iron(III) has it's solubility minimum in this pH range and the dominant species is ferric hydroxide. In such a situation P release from the sediment is hindered by the adsorption of phosphates on iron-hydroxide gels.

High P release under anaerobic reference column and iron treated (50 gFe^{3+}/m^2) anaerobic column are explained as follows. In reduced conditions iron(III) phosphate-hydroxy complexes in the sediment will be solubilized as iron(II) and phosphate. This mechanism results in a high P release in the reference anoxic column.

The formed iron(II) can react with phosphate for the formation of ferrous phosphate (vivianite, $Fe_3(PO_4)_2.8H_2O$). Several other compounds also exert a demand for ferrous iron,

examples being the carbonate and sulfide ions, oxygen and organic complexing agents (Singer 1972).

$Fe^{2+} + PO_4^{3-} \longrightarrow Fe_3(PO_4)_2(s)$, Vivianite $\log K_{so} = -29.9$
$Fe^{2+} + S^{2-} \longrightarrow FeS(s)$, $\log K_{so} = -18.1$
$Fe^{2+} + CO_3^{2-} \longrightarrow FeCO_3(s)$, Siderite $\log K_{so} = -10.7$
(Singer, 1982; Stumm and Morgan, 1981)

The solubility product of vivianite, FeS, and siderite shows that the precipitation of FeS and siderite takes place before vivianite, in a system containing Fe^{2+}, PO_4^{3-}, S^{2-} and CO_3^{2-}. The chemical reaction for sulphate reduction can be written as:

$$2CH_2O + SO_4^{2-} + 2H^+ \longrightarrow 2CO_2 + H_2S + 2H_2O$$

and the Fe(III) reduction as:

$$CH_2O + 4FeOOH + 8H^+ \longrightarrow CO_2 + 4Fe^{2+} + 7H_2O$$

The combination of these two reactions explain the overall reaction of Fe(III) reduction, sulphate reduction and burial of FeS:

$$9CH_2O + 4SO_4^{2-} + 4FeOOH + 8H^+ \longrightarrow 9CO_2 + 4FeS + 15H_2O$$

Inorganic sulphur may be barred in forms other than FeS. For example FeS can further react with H_2S to form FeS_2 (Pyrite). However, in fresh water sediments, because of low SO_4^{2-} concentrations, the FeS minerals are not converted to pyrite. Consequently, Fe^{2+} can barred in fresh water sediments as ferrous sulfide minerals, vivianite and/or siderite (Berner 1980).

This means that the inhibition of the P release in anoxic conditions, is depending on the amount of SO_4^{2-} present and the degree of sulphate reduction and the amount of sulfide generated due to the mineralization of organic matter.
In other words, the formation of ferrous phosphate ($Fe_3(PO_4)_2$) is possible only if the amount of Fe^{2+} present in the system exceed the stoichiometric need for the above reaction.

This explains the P release reduction in high iron dosed columns and flasks. The reason for high anoxic P release observed in the 50 gFe^{3+}/m^2 treatment, could be the inadequacy of Fe^{2+} present in the sediment to satisfy the competitors for PO_4^{2-}.

6.4 GENERAL REMARKS ON THE TREATMENT OF LAKE SEDIMENTS WITH IRON.

1. The results of release experiments shows that sediments treated with iron (100 gFe^{3+}/m^2 and above), efficiently reduce the P release, even in anoxic conditions. However, the sudden pH changes, which could be taken place as a result of mixing the sediment with acidic $FeCl_3$ solutions must be considered before applying $FeCl_3$ to lake sediments.

The substantial decrease in pH with higher doses of $FeCl_3$ could cause undesirable effects to the aquatic eco-system. To get more insights on this problem a series of laboratory experiments should be carried out to establish the relationship between the P inactivation efficiency, $FeCl_3$ dose, pH changes, and the $CaCO_3$ content, etc. in the sediment.

2. The major drawback for the failure of alum application of shallow lakes is the dispersion and redistribution of flocks due to mixing of lake water. This will also be true for the iron treatment, if the $FeCl_3$ is applied on the surface of the lake water. Mixing of the sediment with $FeCl_3$ solution is a good alternative to overcome this problem.

The proposed lake treatment based upon this research is carrying out by mixing the sediment with a solution of $FeCl_3$. The upper 20cm sediment layer of the lake Groot Vogelenzang is proposed to be treated with commercially available 40 $FeCl_3$ solution.

3. Attention must be paid to the amounts of heavy metals present in the ferric chloride solution before applying it to the lake eco-system. Chemical specifications of, two commercially available ferric chloride solutions and calculated maximum concentrations of heavy metals, which could be incorporated into the lake water, as a result of the addition of

$FeCl_3$ to the lake sediment are given in table 16. (Lake depth = 1.5m, Treatment = 100 gFe^{3+}/m^2). It is assumed that all the heavy metals which is present in the ferric solution could be released to the lake water.

Table 16.

Heavy metal	Dutch Norm (µg/L)		A	B	C
	dissolved	total			
SIDERA (dut)					
Cd	0.04	0.2	1	0.34	1.7
Cr	4	36	50	17.1	0.475
Cu	2	4.7	50	17.1	0.275
Ni	11	14	50	17.1	0.819
Hg	0.008	0.05	0.1	0.034	0.68
Zn	10	42	100	34.2	0.814
Pb	2	38	50	17.1	0.450
SIDRA (belg)					
As	19	24	1	0.34	0.014
Cd	0.04	0.2	0.5	0.17	0.85
Hg	0.008	0.05	0.01	0.0034	0.065
Pb	2	38	3	1.03	0.027
Cr	4	36	50	17.1	0.475
Ni	11	14	20	6.84	0.48

A = Chemical specification of $FeCl_3$ solution (mg/L).
B = Maximum concentration which could be incorporated to the lake water, as a result of $FeCl_3$ application (µg/L).
C = A/norm (total)

4. Treatment cost (100 gFe^{3+}/m^2)

Chemicals	dfl	2000	per ha.
Labor and equipment	dfl	±3000	per ha.
Total	dfl	±5000	per ha.

5. The retardation of P release in anaerobic environments is explained by the formation of ferrous phosphate ($Fe_3(PO_4)_2$), and, high P release from sediments treated with low doses of iron salts or untreated sediments is explained by the formation of FeS and the inadequacy of Fe^{2+} to precipitate all S^{2-} and PO_4^{3}.

To demonstrate this, two sets of release experiments can be carried out. A first set of sediments gets different doses of ferric chloride and the release experiments runs for about 3 weeks. After that period a known amount of SO^{2-}_4 is injected to the sediment and the release experiments are carried out for another few weeks.The second set of release experiments is carried out with the same amounts of iron salts.

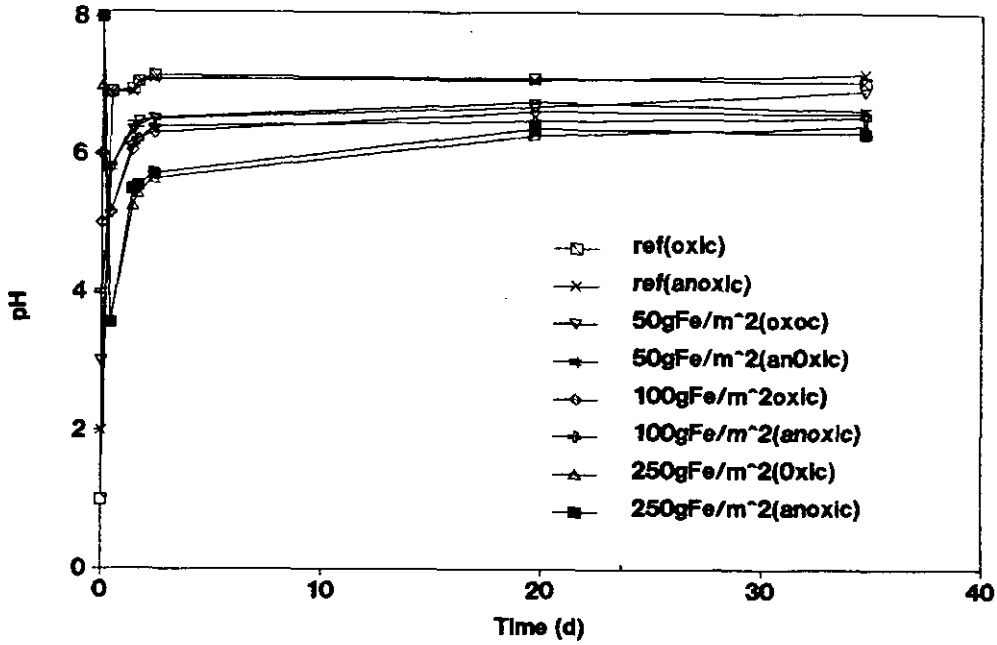


Fig. 21 (a): pH CHANGES IN THE SEDIMENT
(Continuous flow reactors)

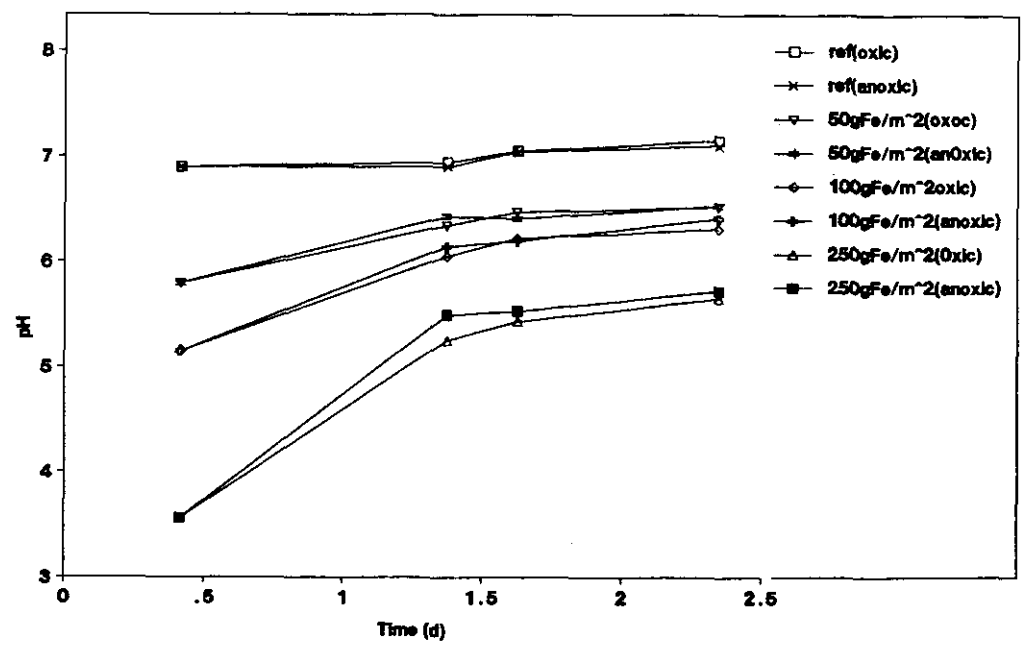


Fig. 21(b) : pH changes in the sediment
(First 3 days after mixing with $FeCl_3$ solution)

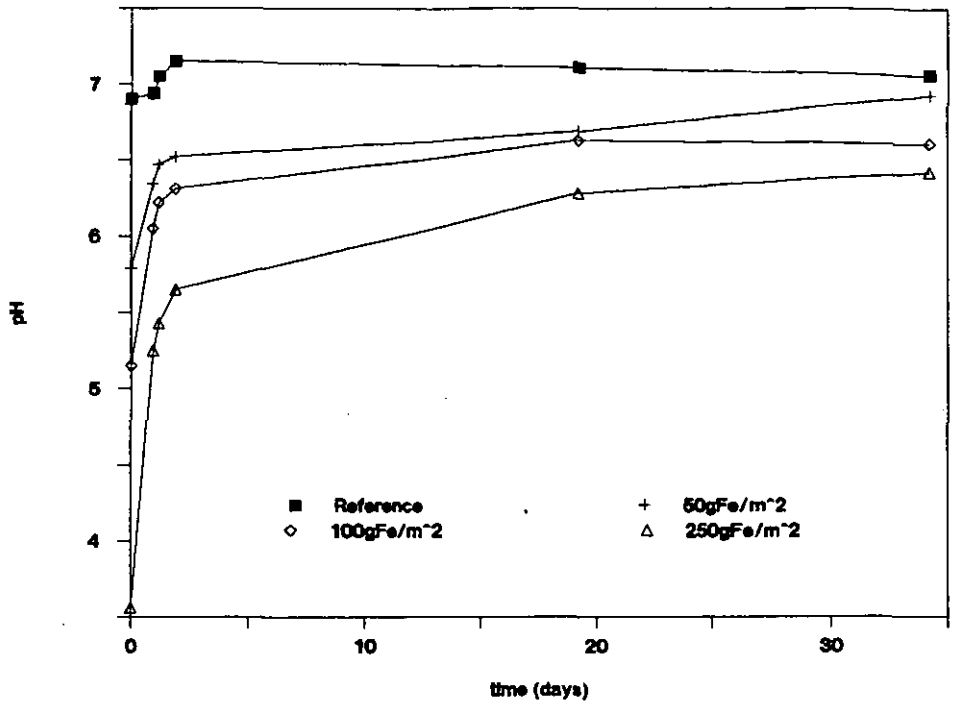


Fig. 21(c) : pH changes in the sediment Oxic columns

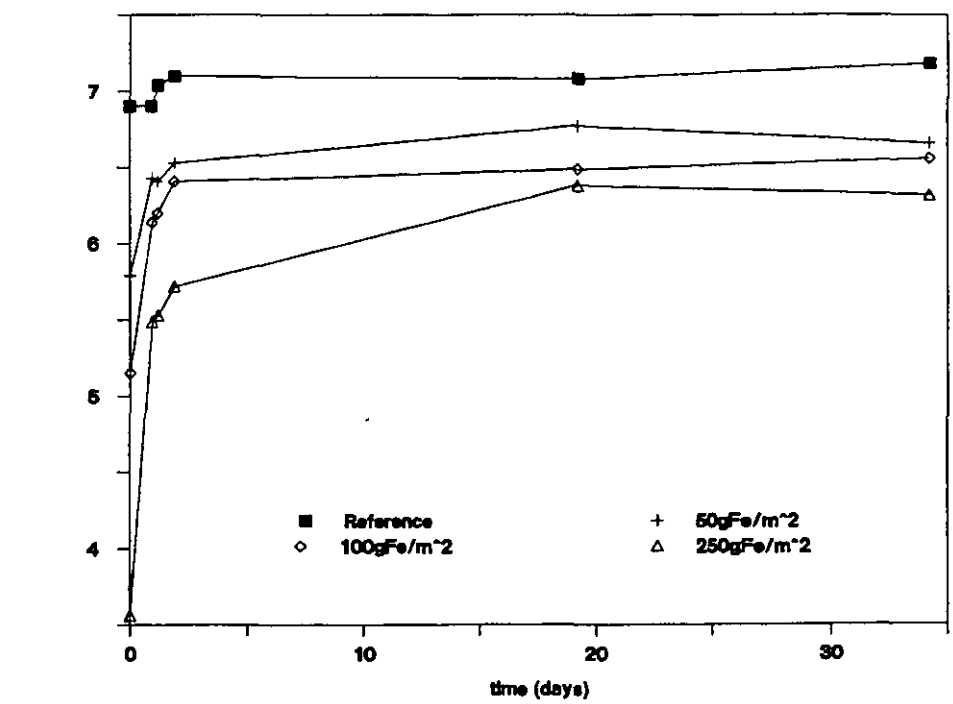


Fig. 21 (d) : pH changes in the sediment Anoxic columns

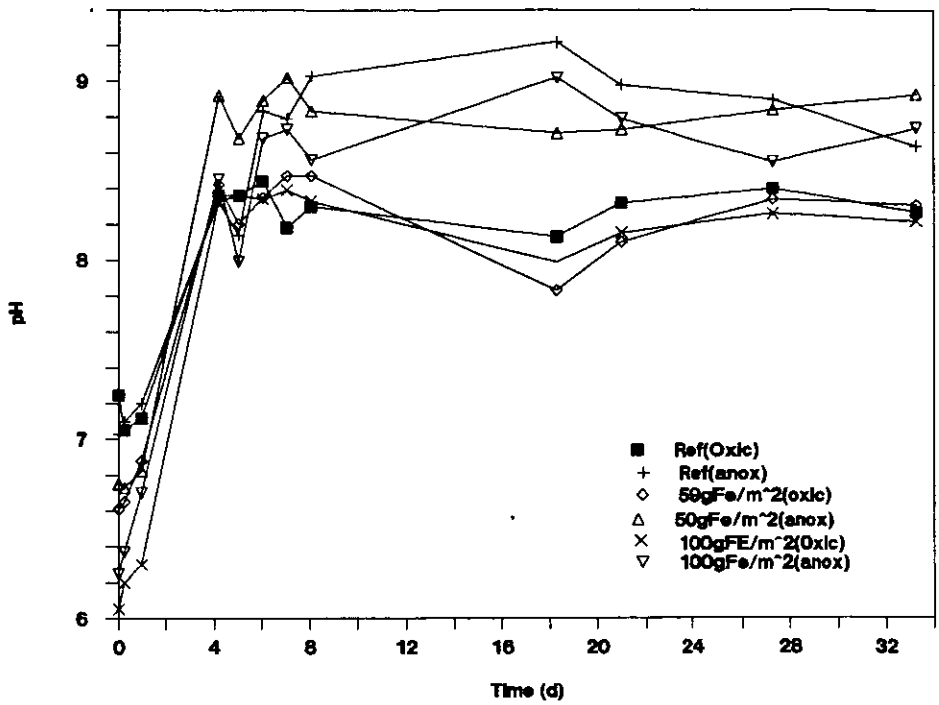


Fig. 22(a) : pH variations of release reactors
(Water phase, Column 1A, 1B, 2A, 2B, 3A, 3B)

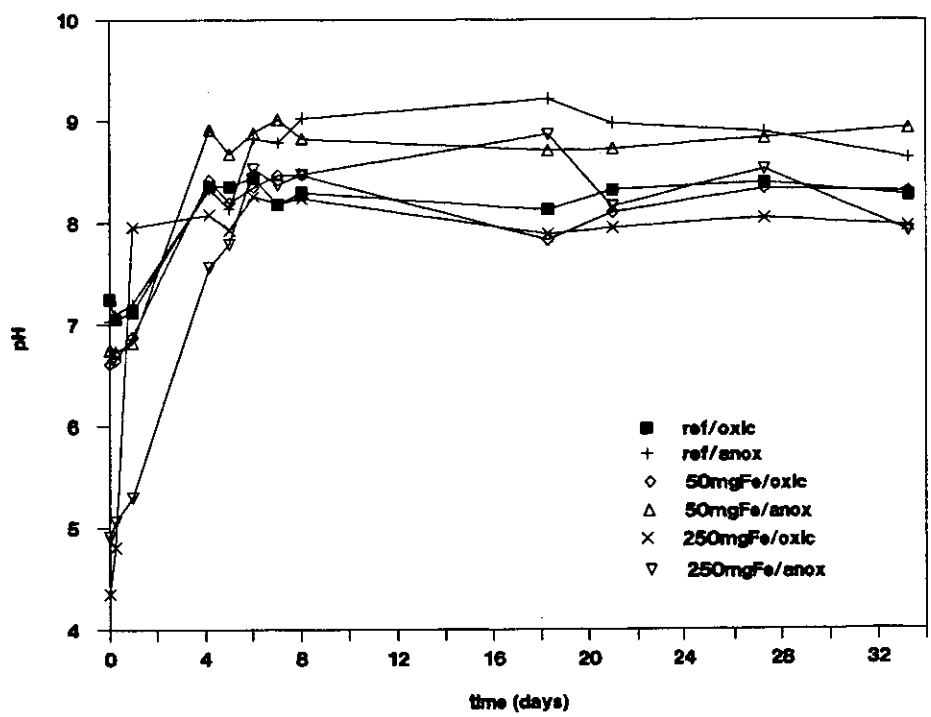


Fig. 22(b) : pH variations of release reactors
(Water phase Çolumn 1A, 1B, 2A, 2B, 4A, 4B)

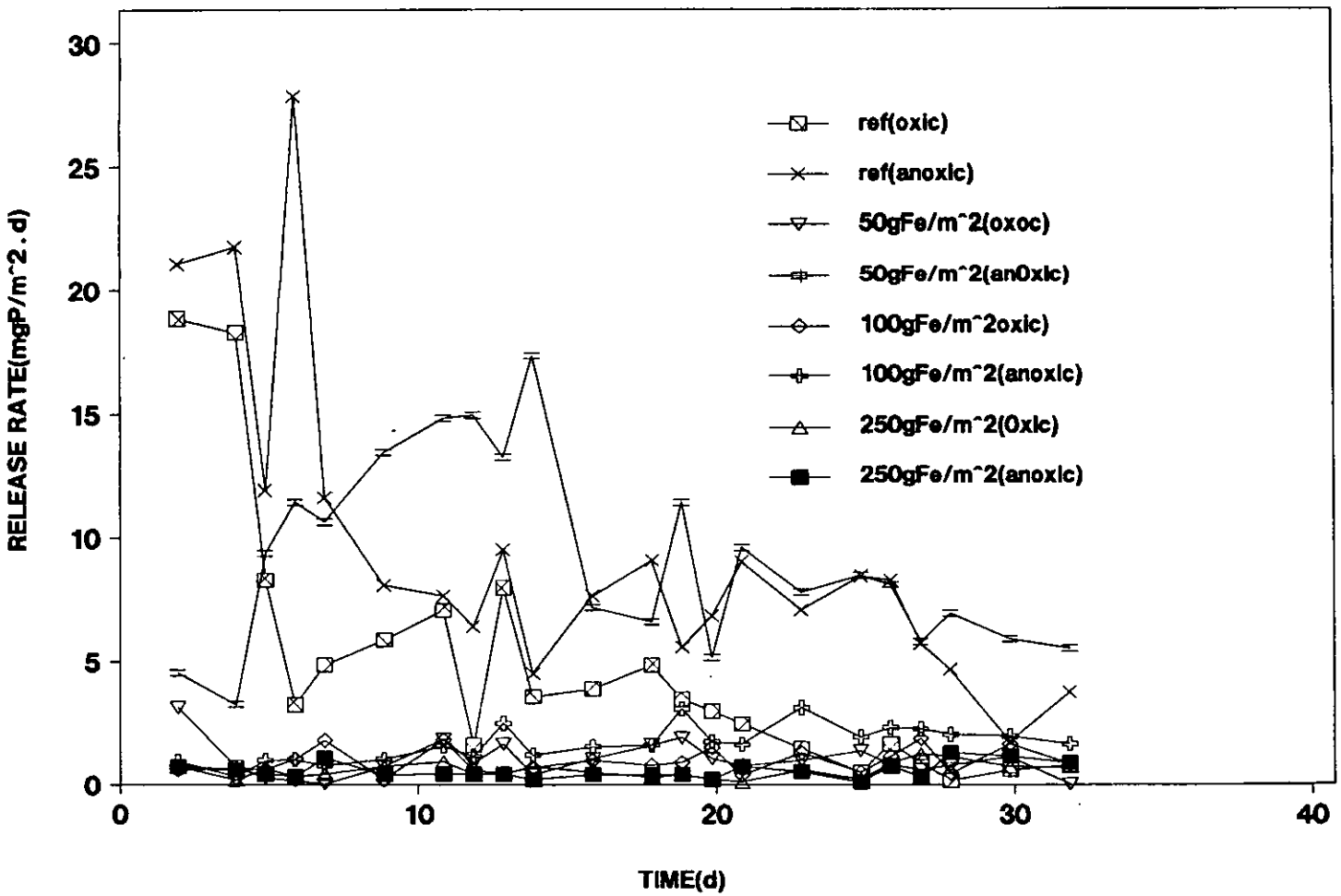


Fig. 23(a) : Variation of Phosphorus Release Rates With Time

(continus flow reactors)

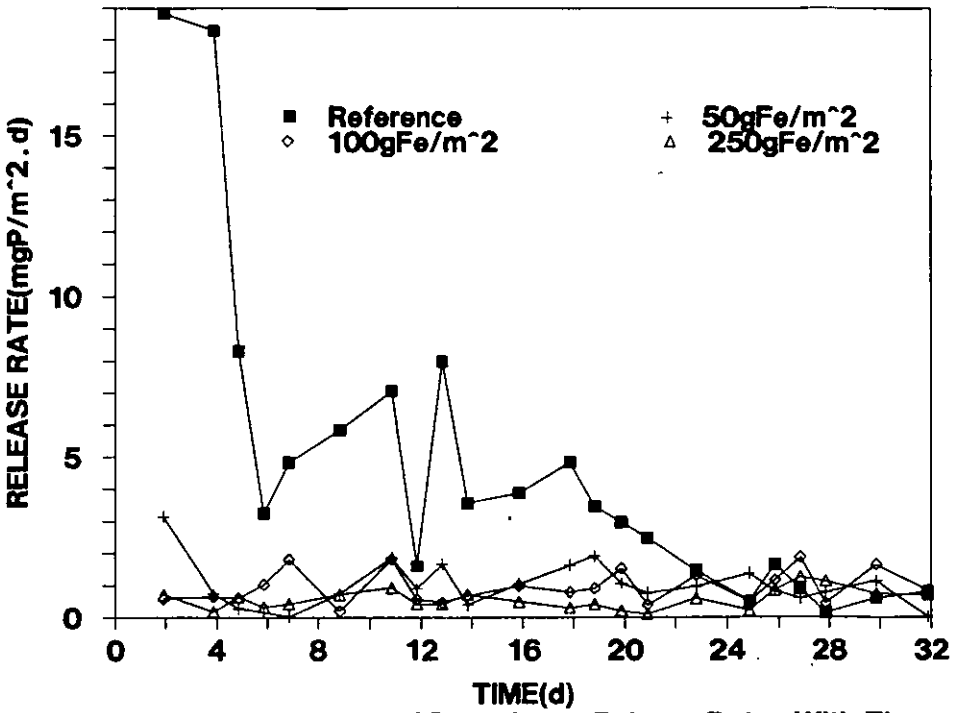


Fig. 23(b) : Variation of Phosphorus Release Rates With Time (continus flow reactors - oxic columns)

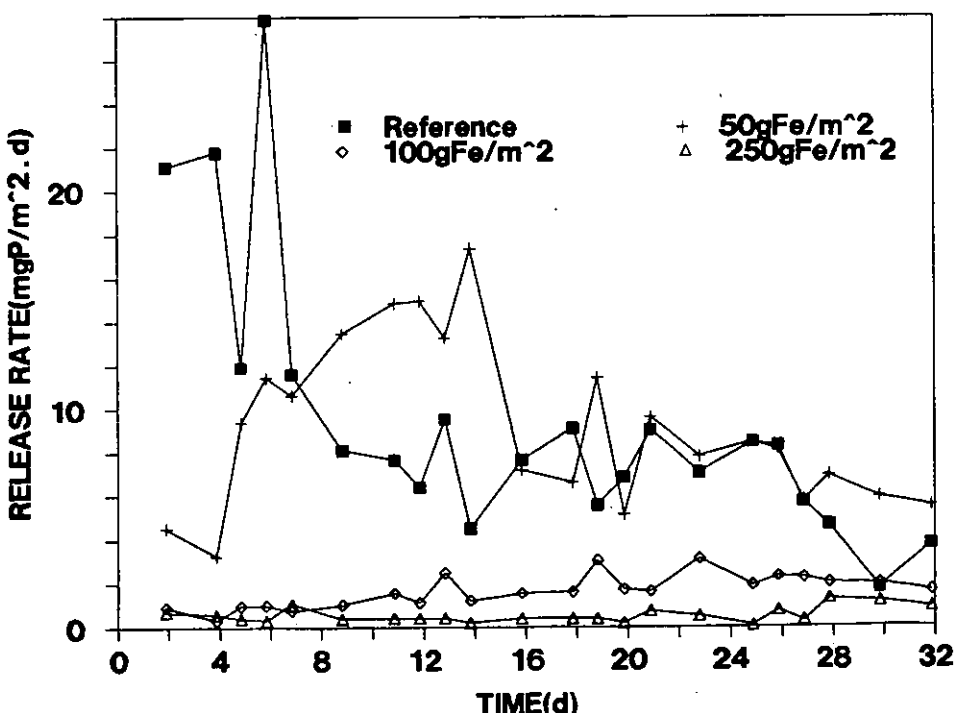
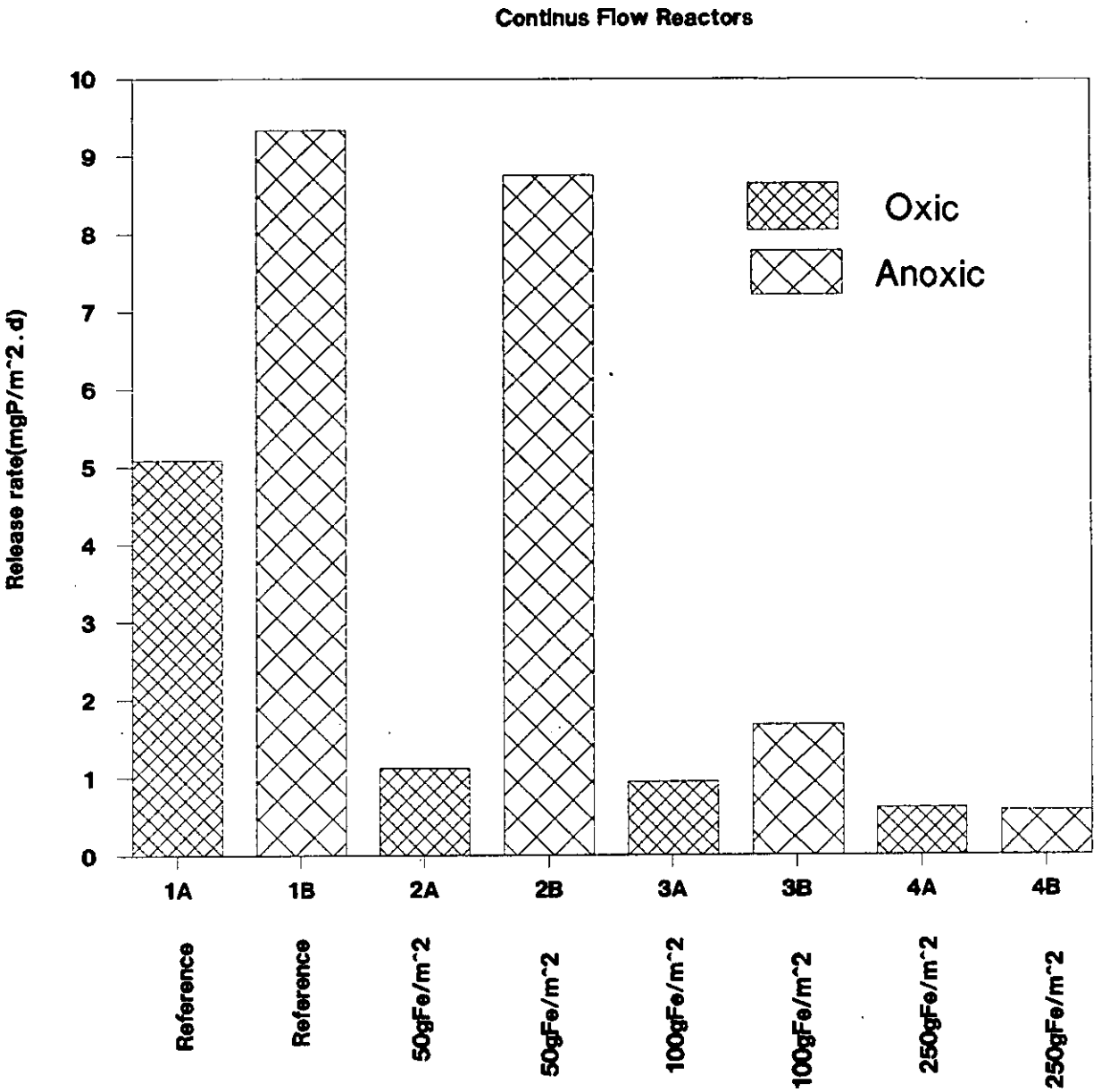


Fig. 23(c) : Variation of Phosphorus Release Rates With Time (continus flow reactors - anoxic columns)

Fig. 24 : **Average (time weighted) Phosphorus release rates**



7. CONCLUSIONS.

1. Aluminum salts can be used for the control of P release in deep lakes, subject to some restrictions. Most of the adverse effects do not exist if the pH of the treated lake water does not fall below 6. At this pH, harmful Al^{3+} species do not predominate and the dissolved Al concentration is less than 50 $\mu g/L$. That is the maximum acceptable Al concentration for drinking water. Aluminum salts should not be used for phosphorus inactivation in shallow lakes.

2. NO_3^- addition could cause some environmental damages due to the following reasons:

i). NO_3^- is a plant nutrient.

ii). NO_3^- addition could enhance the P release in sediments with high amounts of organically bound Phosphorus, by dissimilation.

iii). Iron bound phosphorus also can be released, when NO_3^- is depleted in the sediment. NO_3^- reducing bacteria can utilize iron(III) as an electron acceptor.

3. When comparing the three ferric chloride doses, on the basis of P inactivation efficiency and the initial pH change, the 100 gFe^{3+}/m^2 dose can be taken as a reasonable treatment for the sediment tested. This treatment suppressed the P release rate about 80%, both in oxic and anoxic conditions, compared to the corresponding non treated sediments. The pH reduction after mixing is only about 1.5 pH units from the initial sediment pH, and it also recovered within two days. There is no necessity to add NO_3^- to the sediment if a reasonable amount of iron is added to the sediment.

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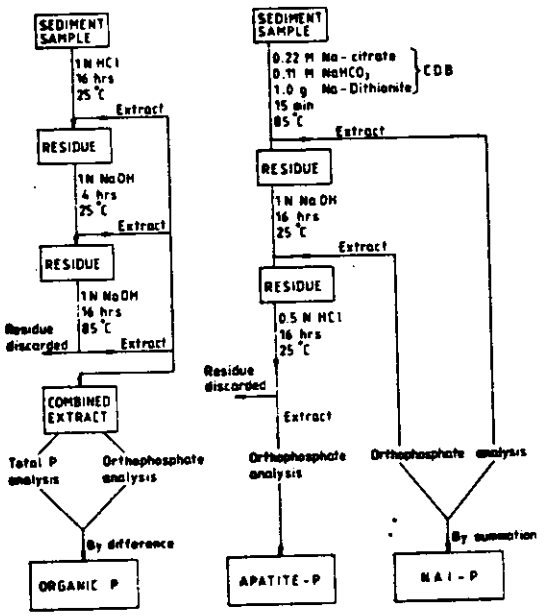
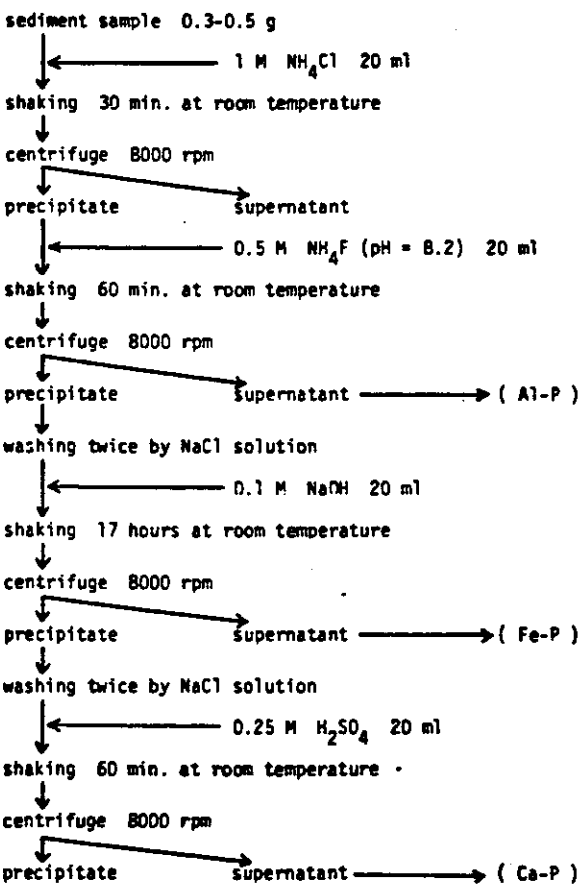
APPENDIX 1.



A. Outline of analytical procedure to determine apatite-P, NAI-P and organic-P. (source: Williams et. al. 1976, Modified)



B. Inorganic phosphorus fractionation in lake sediments (source: Hosomi, 1982)

APPENDIX 2.

Computer programme in BASIC for calculating the amounts of chemicals need for preparing artificial lake water.

```
10 REM RECIPE FOR PREPARING SYNTHETIC WATER
20 REM WRITTEN BY W.A.D.D.WIJESOORIYA
30 REM INPUT DATA
40 INPUT "Volume of synthetic water need, in L = ";N
50 PRINT:PRINT
60 LPRINT:LPRINT
70 INPUT "Give K concentration in lake water mg/L ";K
80 INPUT "Give Na concentration in lake water mg/L";NA
90 INPUT "Give Ca concentration in lake water mg/L";CA
100 INPUT "Give Mg concentration in lake water mg/L";MG
110 INPUT "Give Cl concentration in lake water mg/L";CL
120 INPUT "Give SO4concentration in lake water mg/L";SO4
130 INPUT "Give HCO3 mg/L,If unknown press ENTER ";HCO3
140 IF HCO3 = 0 THEN 150 ELSE 170
150 HCO3 = ((K/39.1)+(NA/23)+(CA*2/40)+(MG*2/24.3)-(CL/35.5)-(SO4*2/96))*61
160 IF HCO3 < 0 THEN GOTO 330 ELSE 170
170 REM CALCULATION
180 A = 110*CA/40
190 B = MG*248.48/24.3
200 C = K*74.56/39.1
210 E = HCO3*84/61
220 F = ((CL/35.5)-(A*2/110)-(C/74.56))*58.44
230 D = ((SO4/96)-(B/246.48))*322.19
240 G=A*N/1000
250 H=B*N/1000
260 I=C*N/1000
270 J=D*N/1000
280 L=E*N/1000
290 M=F*N/1000
300 REM OUTPUT PART
310 PRINT:PRINT:PRINT
320 LPRINT:PRINT
330 LPRINT "INPUT DATA"
340 LPRINT "-----------"
350 PRINT "INPUT DATA"
360 PRINT "----------"
370 LPRINT:PRINT
380 LPRINT "K+ Concentration      =";K;"mg/L"
390 PRINT "K+ Concentration      =";K;"mg/L"
400 LPRINT "Na+Concentration      =";NA;"mg/L"
410 PRINT "Na+Concentration      =";NA;"mg/L"
420 LPRINT"Ca++ Concentration     =";CA;"mg/L"
430 PRINT"Ca++ Concentration     =";CA;"mg/L"
440 LPRINT"Mg++ Concentration     =";MG;"mg/L"
450 PRINT"Mg++ Concentration     =";MG;"mg/L"
460 LPRINT"Cl-  Concentration     =";CL;"mg/L"
470 PRINT"Cl-  Concentration     =";CL;"mg/L"
480 LPRINT"SO4= Concentration     =";SO4;"mg/L"
490 PRINT"SO4= Concentration     =";SO4;"mg/L"
500 LPRINT"HCO3-Concentration     =";HCO3;"mg/L"
510 PRINT"HCO3-Concentration     =";HCO3;"mg/L"
520 IF HCO3 < 0 THEN GOTO 920 ELSE 530
530 IF A<0 OR B<0 OR C<0 OR D<0 OR E<0 OR F<0 THEN GOTO 920 ELSE 540
540 LPRINT:PRINT
```

```
550 PRINT "AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER"
560 PRINT "-----------------------------------------------"
570 LPRINT "AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER"
580 LPRINT "-----------------------------------------------"
590 LPRINT:PRINT:PRINT
600 PRINT "Amount Calcium Chloride  =";A      ;"mg"
610 LPRINT "Amount Calcium Chloride  =";A      ;"mg"
620 PRINT "Amount Magnesium sulphate=";B      ;"mg"
630 LPRINT "Amount Magnesium sulphate=";B      ;"mg"
640 PRINT "Amount Potasium Chloride =";C      ;"mg"
650 LPRINT "Amount Potasium Chloride =";C      ;"mg"
660 PRINT "Amount Sodium Sulphate   =";D      ;"mg"
670 LPRINT "Amount Sodium Sulphate   =";D      ;"mg"
680 PRINT "Amount Sodium bicarbonate=";E      ;"mg"
690 LPRINT "Amount Sodium bicarbonate=";E      ;"mg"
700 PRINT "Amount sodium chloride   =";F      ;"mg"
710 LPRINT "Amount sodium chloride   =";F      ;"mg"
720 PRINT:PRINT
730 LPRINT:PRINT:PRINT
740 PRINT "RECIPE FOR PREPARING";N;"L SYNTHETIC WATER"
750 PRINT "---------------------------------------"
760 LPRINT "RECIPE FOR PREPARING";N;"L SYNTHETIC WATER"
770 LPRINT "---------------------------------------"
780 LPRINT:PRINT:PRINT
790 PRINT "Amount Calcium Chloride  =";G      ;"g"
800 LPRINT "Amount Calcium Chloride  =";G      ;"g"
810 PRINT "Amount Magnesium sulphate=";H      ;"g"
820 LPRINT "Amount Magnesium sulphate=";H      ;"g"
830 PRINT "Amount Potasium Chloride =";I      ;"g"
840 LPRINT "Amount Potasium Chloride =";I      ;"g"
850 PRINT "Amount Sodium Sulphate   =";J      ;"g"
860 LPRINT "Amount Sodium Sulphate   =";J      ;"g"
870 PRINT "Amount Sodium bicarbonate=";L      ;"g"
880 LPRINT "Amount Sodium bicarbonate=";L      ;"g"
890 PRINT "Amount sodium chloride   =";M      ;"g"
900 LPRINT "Amount sodium chloride   =";M      ;"g"
910 GOTO 960
920 PRINT:PRINT
930 LPRINT:PRINT
940 PRINT "ERROR: PLEASE CHECK INPUT DATA"
950 LPRINT "ERROR: PLEASE CHECK INPUT DATA"
960 END
```

```
INPUT DATA
----------

K+ Concentration      = 7.1 mg/L
Na+Concentration      = 75 mg/L
Ca++ Concentration    = 59 mg/L
Mg++ Concentration    = 11.1 mg/L
Cl-  Concentration    = 129 mg/L
SO4= Concentration    = 72 mg/L
HCO3-Concentration    = 132.5062 mg/L
```

```
AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER
------------------------------------------------

Amount Calcium Chloride  = 162.25 mg
Amount Magnesium sulphate= 113.5032 mg
Amount Potasium Chloride = 13.53903 mg
Amount Sodium Sulphate   = 93.27509 mg
Amount Sodium bicarbonate= 182.4676 mg
Amount sodium chloride   = 29.34957 mg

RECIPE FOR PREPARING 50 L SYNTHETIC WATER
-----------------------------------------

Amount Calcium Chloride  = 8.1125 g
Amount Magnesium sulphate= 5.675161 g
Amount Potasium Chloride = .6769515 g
Amount Sodium Sulphate   = 4.663755 g
Amount Sodium bicarbonate= 9.123377 g
Amount sodium chloride   = 1.467479 g
```

APPENDIX 3.

Phosphate Release Experiment : Column 1A

Condition:	reference oxic	INPUT DATA Vol. sampl	75.00	(ml)	Calculations
		Hight colu	15.00	(cm)	average release rate: 5.10
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	220.000	0	0.46			
4	9.40	221.000	550	3.39	1.93	18.8438	55.2750
5	8.40	192.000	190	4.35	3.87	18.3016	72.8140
6	8.45	135.000	183	5.35	4.85	8.3059	81.1372
7	8.45	82.000	183	6.35	5.85	3.2472	84.3844
8	8.45	64.000	183	7.35	6.85	4.8336	89.2180
11	8.30	58.000	680	10.35	8.85	5.8529	106.7400
12	8.30	65.000	170	11.35	10.85	7.0770	113.8170
13	8.30	41.000	170	12.35	11.85	1.5940	115.4110
14	8.30	61.000	170	13.35	12.85	7.9980	123.4090
15	8.50	49.000	170	14.35	13.85	3.5603	126.9990
18	8.05	40.000	650	17.34	15.84	3.8759	138.5540
19	8.30	44.000	180	18.35	17.84	4.8336	143.4380
20	8.45	39.000	180	19.35	18.85	3.4614	146.9210
21	8.45	34.000	180	20.35	19.85	2.9730	149.8940
22	8.45	29.000	180	21.35	20.85	2.4630	152.3570
25	8.35	15.000	660	24.35	22.85	1.4580	156.7250
26	8.40	10.000	175	25.35	24.85	0.4990	157.2250
27	8.40	13.000	185	26.35	25.85	1.6460	158.8710
28	8.20	11.000	170	27.34	26.85	0.8834	159.7470
29	8.40	6.000	190	28.35	27.85	0.1498	159.8980
32	8.35	6.000	670	31.35	29.85	0.5964	161.6860
33	8.30	7.000	170	32.35	31.85	0.7886	162.4730

Phosphate Release Experiment : Column 1B

Condition:	reference anoxic	INPUT DATA Vol. sampl	75.00	(ml)	Calculations
		Hight colu	14.00	(cm)	average release rate: 9.44
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	220.000	0	0.46			
4	9.40	226.000	610	3.39	1.93	21.1166	61.9420
5	8.40	239.000	130	4.35	3.87	21.7930	82.8270
6	8.45	176.000	175	5.35	4.85	11.9052	94.7570
7	8.45	230.000	175	6.35	5.85	27.8600	122.6170
8	8.45	170.000	175	7.35	6.85	11.6000	134.2170
11	8.30	77.000	680	10.35	8.85	8.1092	158.4940
12	8.30	76.000	180	11.35	10.85	7.6630	166.1570
13	8.30	69.000	180	12.35	11.85	6.4150	172.5720
14	8.30	82.000	180	13.35	12.85	9.5210	182.0930
15	8.50	62.000	180	14.35	13.85	4.5064	186.6370
18	8.05	79.000	650	17.34	15.84	7.6562	209.4620
19	8.30	85.000	180	18.35	17.84	9.1091	218.6660
20	8.45	69.000	180	19.35	18.85	5.5791	224.2800
21	8.45	68.000	180	20.35	19.85	6.8470	231.1270
22	8.45	79.000	180	21.35	20.85	9.0370	240.1640
25	8.35	72.000	660	24.35	22.85	7.0822	261.3810
26	8.40	78.000	180	25.35	24.85	8.4723	269.8710
27	8.40	79.000	185	26.35	25.85	8.3040	278.1750
28	8.20	68.000	170	27.34	26.85	5.7106	283.8380
29	8.40	55.000	190	28.35	27.85	4.6602	288.5370
32	8.35	35.000	660	31.35	29.85	3.4791	298.9670
33	8.30	26.000	170	32.35	31.85	2.1114	301.0740

Posohate Release Experiment : Column 2A

Condition: Fe(50)/oxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	14.50	(cm)	average release rate (mgP/m^2.d)	1.10
	Area.colu	25.00	(cm^2)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	38.000	0	0.46			
4	9.40	38.000	530	3.39	1.93	3.1350	9.1960
5	8.40	25.000	130	4.35	3.87	0.7283	9.8940
6	8.45	15.000	140	5.35	4.85	0.2694	10.1640
7	8.45	9.000	140	6.35	5.85	0.1620	10.3260
8	8.45	5.000	140	7.35	6.85	0.0220	10.3480
11	8.30	7.000	720	10.35	8.85	0.7342	12.5460
12	8.30	13.000	170	11.35	10.85	1.8500	14.3960
13	8.30	11.000	170	12.35	11.85	0.8860	15.2820
14	8.30	14.000	170	13.35	12.85	1.6600	16.9420
15	8.50	9.000	170	14.35	13.85	0.3987	17.3440
18	8.05	11.000	630	17.34	15.84	1.0432	20.4540
19	8.30	14.000	165	18.35	17.84	1.6181	22.0890
20	8.45	17.000	165	19.35	18.85	1.9111	24.0120
21	8.45	14.000	165	20.35	19.85	1.0530	25.0650
22	8.45	11.000	165	21.35	20.85	0.7650	25.8300
25	8.35	10.000	650	24.35	22.85	0.9680	28.7300
26	8.40	12.000	170	25.35	24.85	1.3652	30.0980
27	8.40	10.000	175	26.35	25.85	0.8100	30.9080
28	8.20	8.000	170	27.34	26.85	0.5970	31.5000
29	8.40	8.000	170	28.35	27.85	0.7775	32.2840
32	8.35	9.000	630	31.35	29.85	0.8479	34.8260
33	8.30	6.000	170	32.35	31.85	0.3006	35.1260

Phosphate Release Experiment :Column 2B

Condition: Fe(50)/anoxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	14.00	(cm)	average release rate: (mgP/m^2.d)	8.76
	Area.colu	25.00	(cm^2)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	50.000	0	0.46			
4	9.40	50.000	590	3.39	1.93	4.5341	13.3000
5	8.40	49.000	90	4.35	3.87	3.2630	16.4270
6	8.45	74.000	165	5.35	4.85	9.3844	25.8310
7	8.45	97.000	165	6.35	5.85	11.4280	37.2590
8	8.45	104.000	165	7.35	6.85	10.6280	47.8870
11	8.30	138.000	660	10.35	8.85	13.4727	88.2210
12	8.30	145.000	170	11.35	10.85	14.8470	103.0680
13	8.30	149.000	170	12.35	11.85	14.9660	118.0340
14	8.30	142.000	170	13.35	12.85	13.2790	131.3130
15	8.50	161.000	170	14.35	13.85	17.3623	148.8200
18	8.05	74.000	640	17.34	15.84	7.1866	170.2450
19	8.30	71.000	170	18.35	17.84	6.6161	176.9300
20	8.45	95.000	170	19.35	18.85	11.4226	188.4240
21	8.45	73.000	170	20.35	19.85	5.1520	193.5760
22	8.45	86.000	170	21.35	20.85	9.6110	203.1870
25	8.35	83.000	630	24.35	22.85	7.8139	226.5960
26	8.40	85.000	170	25.35	24.85	8.4943	235.1080
27	8.40	83.000	175	26.35	25.85	8.1200	243.2280
28	8.20	72.000	160	27.34	26.85	5.7933	248.9730
29	8.40	72.000	168	28.35	27.85	6.9406	255.9714
32	8.35	60.000	660	31.35	29.85	5.9121	273.6954
33	8.30	58.000	170	32.35	31.85	5.5135	279.1974

Phosphate Release Experiment : Column 3A

Conditions		INPUT DATA			Calculations	
Fe(100)/oxic		Vol. sampl	75.00	(ml)		
		Hight colu	15.50	(cm)	average release rate:	0.94
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	7.000	0	0.46			
4	9.40	7.000	550	3.39	1.93	0.5966	1.7500
5	8.40	6.000	220	4.35	3.87	0.6386	2.3620
6	8.45	6.000	180	5.35	4.85	0.6107	2.9740
7	8.45	8.000	180	6.35	5.85	1.0240	3.9980
8	8.45	6.000	680	7.35	6.85	1.8040	5.8020
11	8.30	6.000	170	10.35	8.85	0.1964	6.3900
12	8.30	12.000	170	11.35	10.85	1.8120	8.2020
13	8.30	9.000	170	12.35	11.85	0.5640	8.7660
14	8.30	7.000	170	13.35	12.85	0.4740	9.2400
15	8.50	7.000	170	14.35	13.85	0.6803	9.9260
18	8.05	10.000	650	17.34	15.84	0.9828	12.8560
19	8.30	9.000	175	18.35	17.84	0.7868	13.6510
20	8.45	9.000	175	19.35	18.85	0.8944	14.5510
21	8.45	12.000	175	20.35	19.85	1.5150	16.0660
22	8.45	8.000	175	21.35	20.85	0.3800	16.4460
25	8.35	13.000	670	24.35	22.85	1.3031	20.3500
26	8.40	9.000	180	25.35	24.85	0.5010	20.8520
27	8.40	10.000	185	26.35	25.85	1.1430	21.9950
28	8.20	14.000	180	27.34	26.85	1.8595	23.8390
29	8.40	9.000	190	28.35	27.85	0.4403	24.2830
32	8.35	16.000	690	31.35	29.85	1.6378	29.1930
33	8.30	12.000	185	32.35	31.85	0.8377	30.0290

Phosphate Release Experiment : Column 3B

Conditions		INPUT DATA			Calculations	
Fe(100)/anoxic		Vol. sampl	75.00	(ml)		
		Hight colu	13.00	(cm)	average release rate:	1.67
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	10.200	0	0.46			
4	9.40	10.000	610	3.39	1.93	0.9346	2.7414
5	8.40	6.000	180	4.35	3.87	0.3089	3.0374
6	8.45	8.000	185	5.35	4.85	0.9859	4.0254
7	8.45	9.000	185	6.35	5.85	1.0140	5.0394
8	8.45	8.000	185	7.35	6.85	0.7540	5.7934
11	8.30	10.000	710	10.35	8.85	1.0308	8.8794
12	8.30	13.000	180	11.35	10.85	1.5630	10.4424
13	8.30	12.000	180	12.35	11.85	1.1450	11.5874
14	8.30	19.000	180	13.35	12.85	2.4910	14.0784
15	8.50	15.000	180	14.35	13.85	1.2040	15.2924
18	8.05	16.000	650	17.34	15.84	1.5514	19.9174
19	8.30	16.000	180	18.35	17.84	1.6152	21.5494
20	8.45	24.000	180	19.35	18.85	3.0609	24.6294
21	8.45	20.000	180	20.35	19.85	1.7240	26.3534
22	8.45	18.000	175	21.35	20.85	1.6400	27.9934
25	8.35	32.000	680	24.35	22.85	3.1277	37.3634
26	8.40	24.000	190	25.35	24.85	1.9240	39.2914
27	8.40	22.000	205	26.35	25.85	2.3160	41.6074
28	8.20	21.000	200	27.34	26.85	2.2538	43.8424
29	8.40	20.000	190	28.35	27.85	2.0261	45.8854
32	8.35	19.000	695	31.35	29.85	1.9600	51.7614
33	8.30	17.000	190	32.35	31.85	1.6514	53.4094

Phosphate Release Experiment : Column 4A

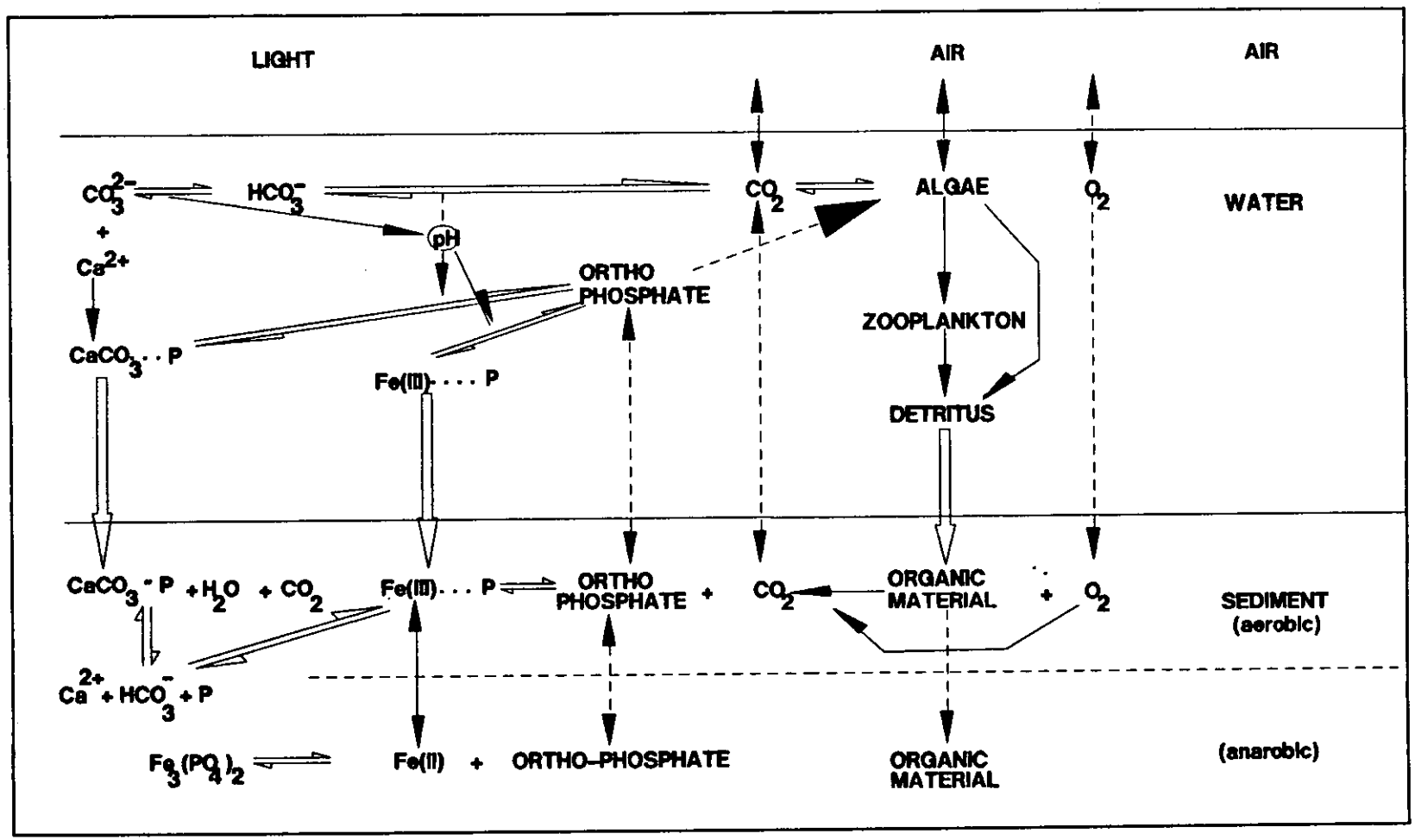
	INPUT DATA			Calculations		
Conditions Fe(250)/oxic	Vol. sampl	75.00	(ml)			
	Hight colu	15.00	(cm)	average release rate:		0.59
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	6.000	0	0.46			
4	9.40	6.000	790	3.39	1.93	0.7077	2.0760
5	8.40	4.000	160	4.35	3.87	0.1774	2.2460
6	8.45	5.000	190	5.35	4.85	0.6257	2.8730
7	8.45	4.000	190	6.35	5.85	0.3270	3.2000
8	8.45	4.000	190	7.35	6.85	0.4240	3.6240
11	8.30	7.000	690	10.35	8.85	0.7125	5.7570
12	8.30	8.000	185	11.35	10.85	0.9300	6.6870
13	8.30	6.000	185	12.35	11.85	0.4280	7.1150
14	8.30	5.000	185	13.35	12.85	0.4220	7.5370
15	8.50	6.000	185	14.35	13.85	0.7160	8.2590
18	8.05	5.000	670	17.34	15.84	0.4995	9.7480
19	8.30	4.000	180	18.35	17.84	0.3058	10.0570
20	8.45	4.000	180	19.35	18.85	0.4055	10.4650
21	8.45	3.000	175	20.35	19.85	0.2000	10.6650
22	8.45	2.000	175	21.35	20.85	0.1000	10.7650
25	8.35	6.000	670	24.35	22.85	0.5982	12.5570
26	8.40	4.000	180	25.35	24.85	0.2096	12.7670
27	8.40	6.000	200	26.35	25.85	0.8500	13.6170
28	8.20	9.000	190	27.34	26.85	1.2555	14.8620
29	8.40	10.000	185	28.35	27.85	1.1286	16.0000
32	8.35	7.000	698	31.35	29.85	0.7266	18.1782
33	8.30	7.000	175	32.35	31.85	0.7015	18.8782

Phosphate Release Experiment : Column 4B

	INPUT DATA			Calculations		
Condition:Fe(250)/anoxic	Vol. sampl	75.00	(ml)			
	Hight colu	16.50	(cm)	average release rate:		0.57
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	6.000	0	0.46			
4	9.40	6.000	790	3.39	1.93	0.7077	2.0760
5	8.40	6.000	160	4.35	3.87	0.5885	2.6400
6	8.45	5.000	190	5.35	4.85	0.4171	3.0580
7	8.45	4.000	190	6.35	5.85	0.3120	3.3700
8	8.45	7.000	190	7.35	6.85	1.0780	4.4480
11	8.30	4.000	690	10.35	8.85	0.3968	5.6360
12	8.30	4.000	185	11.35	10.85	0.4160	6.0520
13	8.30	4.000	185	12.35	11.85	0.4160	6.4680
14	8.30	4.000	185	13.35	12.85	0.4160	6.8840
15	8.50	3.000	185	14.35	13.85	0.1974	7.0830
18	8.05	4.000	670	17.34	15.84	0.4052	8.2910
19	8.30	4.000	180	18.35	17.84	0.4038	8.6990
20	8.45	4.000	180	19.35	18.85	0.4055	9.1070
21	8.45	3.000	180	20.35	19.85	0.1920	9.2990
22	8.45	5.000	180	21.35	20.85	0.7380	10.0370
25	8.35	5.000	695	24.35	22.85	0.5140	11.5770
26	8.40	3.000	180	25.35	24.85	0.0778	11.6550
27	8.40	5.000	190	26.35	25.85	0.7540	12.4090
28	8.20	4.000	180	27.34	26.85	0.2965	12.7030
29	8.40	8.000	190	28.35	27.85	1.2853	13.9990
32	8.35	11.000	698	31.35	29.85	1.1449	17.4314
33	8.30	10.000	175	32.35	31.85	0.8868	18.3164



APPENDIX 4 : Phosphorus cycling in lake eco-system.

G L O S S A R Y.

ADVANCED WASTE TREATMENT : Often abbreviated AWT and also referred to as tertiary treatment. Wastewater treatment usually directed at major plant nutrients, results in a high quality effluent.

AEROBIC : Environment in which oxygen is present. Also refers to processes occurring in presence of oxygen.

ALGAE : Simplest green plants having neither roots, stems, nor leaves; those in fresh water are usually microscopic in size.

ALGAE BLOOM OR ALGAL BLOOM : Very rapid growth of algae with formation of large concentrations which sometimes form floating mats or distinct coloration of the water.

ANAEROBIC: Environment in which oxygen is absent. Also refers to processes occurring in absence of oxygen.

AQUATIC PLANTS: Plants that grow in water. Some aquatic plants are rooted, some are free floating.

CULTURAL EUTROPHICATION: The acceleration by human activities of the natural aging processes in a lake.

D.O. Dissolved oxygen required for the maintenance of aerobic aquatic organisms. Low D.O. levels approach anaerobic conditions.

ECOLOGY: A branch of science concerned with the interrelationship of organisms to one another and to their environment.

EFFLUENT: Treated or untreated wastewater that flows from sewers, treatment plants, or industrial plants.

ENVIRONMENT: All the external conditions that surround living, such as soil, water, and air.

EPILIMNION: Upper warm circulating layer in a stratified lake.

DECOMPOSITION: Breakdown of materials into simpler forms by action of aerobic or anaerobic microorganisms.

DETRITUS: Minute particles of the decaying remains of dead plants and animals.

EROSION: Process by which soils are loosened and moved from one place to another.

EUTROPHIC: Waters with high rate of nutrient supply and resulting high levels of organic production.

EUTROPHICATION: The addition of inorganic nutrients organic matte and/or silt to a lake, leading to decreased volume and increased biological material. This can occur either as a natural stage in lake maturation or in an accelerated fashion due to human activities. (Cultural eutrophication).

FLUSHING RATE: Time it takes for the total volume of a lake to be replaced. Also known as retention time.

HYPOLIMNION: The deep, cold, lower level of a stratified lake.

LITTORAL ZONE: Shallow water interface area between the land of the drainage basin and the open waters of the lake.

LIMNOLOGY: the study of freshwater systems.

MACROPHYTE: Large, rooted aquatic plant.

MESOTROPHIC: Waters with a moderate supply of nutrients and moderate level of organic production.

NUTRIENT: A chemical element or compound which promotes the growth and development of organisms.

PHOTOSYNTHESIS: Synthesis of organic compounds with the aid of light by chlorophyll-containing cells.

PLANKTON: Microscopic free floating plants and animals.

POLLUTANT: A substance, medium, or agent that causes physical impurity. Official EPA definition is: dredged spoil, solid waste, incinerator residue, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials, heat, wrecked or discarded equipment, rock, sand, cellar dirt, and industrial, municipal, and agricultural waste discharged into water.

RESIDENCE TIME: Amount of time a substance will remain in a lake before being flushed or settled out.

SECCHI DISK: A white disk 20 centimeters (8 inches) in diameter used to measure transparency of water.

SEDIMENT: Particles of material transported to a lake or suspended in its water. Also refers to bottom material in lakes that result from its formation, the remains of organisms, erosion from land.

STRATIFICATION: Thermal layering of a lake in which the water column is divided by density into a cold lower region and a warm upper region with a relatively thin boundary area between.

THERMOCLINE: Region of rapid temperature transition in a stratified lake that separates the epilimnion.

TRIBUTARY: Stream or river that flows into a lake.

TURBIDITY: Condition of opacity or muddiness in water resulting from particles in suspension.

PHOSPHORUS INACTIVATION IN SEDIMENTS OF SHALLOW LAKES

DBW/RIZA nota 89.022

Rijkswaterstaat

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S A M E N V A T T I N G

Fosfaat wordt algemeen beschouwd de belangrijkste oorzaak te zijn van de eutrofiëring van plassen en meren. In Nederland worden grote inspanningen verricht om de fosfaatbelasting op meren en plassen te verminderen, teneinde de eutrofiëring te stoppen en zelfs om te keren. Het Rijn Aktie Plan en aanvullende regionale maatregelen zijn bedoeld om deze vermindering van de belasting tot stand te brengen. Een hoge interne fosfaatbelasting door de bodem kan dan de verbetering van de waterkwaliteit vertragen. Dit probleem kan door baggeren worden opgelost, zij het tegen hoge kosten. De toevoeging van fosfaatbindende stoffen aan het sediment kan een effectief en veel goedkoper alternatief zijn, maar sommige van deze stoffen kunnen schadelijk zijn voor het milieu. IJzer is een veelbelovende, niet giftige, fosfaatbindende stof. Zij is al verantwoordelijk voor het merendeel van de fosfaatbinding in veel meren. Een mogelijk nadeel van de toepassing van ijzer is dat ijzerfosfaat complexen er van worden verdacht bij lage redoxpotentialen weer fosfaat af te geven. In laboratoriumexperimenten bleek een dosis van 100 g $Fe^{3+}m^{-2}$ echter ook onder anoxische condities de fosfaatnalevering aanzienlijk te verminderen. Daarom kan de toevoeging van dit middel aan sedimenten een goed alternatief zijn voor baggeren. Het is ongeveer tienmaal goedkoper. De lange termijn effecten van de methode moeten echter nog in **in situ** experimenten worden onderzocht.

S U M M A R Y

Phosphorus is generally considered to be the primary factor controlling eutrophication in lake ecosystems. Large efforts have currently been made in The Netherlands, to decrease the phosphorus loading of lakes in order to stop or reverse the process of eutrophication. The Rhine Action Programme and additional regional measures will decrease the phosphorus loading on most Dutch lakes. A high internal phosphorus loading from the sediments can delay the improvement of the water quality. This problem can be solved by dredging, but at high costs. Addition of phosphate-binding agents to the sediments can be an effective and much cheaper alternative, but some of these agents may introduce hazardous chemicals into the ecosystem. Iron is a

promising nontoxic phosphate-binding agent, which is already responsible for the phosphate-binding in many lakes. A possible drawback of iron application is that ironphosphate complexes are suspected to release phosphate at low redox conditions. In laboratory experiments, however, a dose of 100 g $Fe^{3+}m^{-2}$ appeared to decrease phosphorus release rates under oxic, but also under anoxic conditions. Therefore, the addition of this agent to sediments can be a good alternative for dredging, and about ten times cheaper. The long term effects of this method have to be tested in **in situ** experiments.

KEY WORDS : Eutrophication, Phosphorus, Lake treatment, Internal loading, Phosphorus inactivation.

VOORWOORD

Deze nota is gebaseerd op het onderzoek dat de heer W.A.D.D. Wijesooriya heeft uitgevoerd in het kader van zijn M. Sc. studie aan het International Institute for Hydraulic and Environmental Engineering in Delft bij DBW/RIZA in Lelystad. Deze tekst is ook uitgegeven als M. Sc. Thesis Report EE 16 van het IHE. Omdat de heer Wijesooriya afkomstig is uit Shri Lanka is dit rapport in het Engels geschreven. Dit zal, naar wij aannemen, geen beletsel zijn om kennis te nemen van de inhoud van deze nota.

C O N T E N T S

PART B.

1. INTRODUCTION.

One of the most obvious and world wide water quality problems is the eutrophication of lakes and reservoirs. Water bodies receiving excessive amounts of plant nutrients, organic matter, and silt suffer from an excessive growth of aquatic life such as algae and rooted plants. This could cause the decrease of the lake or reservoir volume. Aesthetic value of lakes and reservoirs of this nature deteriorate rapidly. They lose much of their beauty, their attractiveness for recreation, and their usefulness as a drinking water and industrial water supply (Derr 1972, Vollenweider 1981, Cooke,et.al. 1986). Eutrophication is basically considered as a natural process, often described as the natural aging of lakes. Peat bogs, coal and oil deposits are some of the results of this very slow process over centuries. However, this natural phenomena is getting very little interest within the present context. The process of cultural eutrophication, which is of most concern and which is being reported everywhere, has taken place within a very short time span.

Vollenweider (1981) cited some essential causes for this kind of sudden eutrophication which are interrelated and directly linked to worldwide demographic changes, namely:

1) rapid general increase in population with a strong tendency towards urbanization and resulting in rapid increase in urban waste discharged directly into the waterways, lakes and coastal areas.

2) rapid industrialization linked to population growth with the corresponding increase in industrial waste of all kinds, some of them containing the nutrients needed for the growth of algae and macrophytes,

3) intensification of agriculture and changes in production methods, through preferential development of monoculture, increased use of chemical fertilizers, concentration of live stock breeding, direct discharge of agricultural waste into the waterways,and overproduction of manure.

4) An additional factor to this since the end of World war II is the use of detergents containing polyphosphates,

"Preservation of clean water systems" is now a miracle, specially for the industrialized world. Almost all water bodies, in those regions are severely damaged by the influence of man. Even some newly built reservoirs suddenly experienced eutrophication from the decomposition of materials left in the flooded basin or from nutrient rich soils (Vollenweider 1981, Cooke et.al. 1986).

So the control of eutrophication and restoration of eutrophic water bodies has become one of the most important issues since many years, because the supply of clean, fresh surface water is limited and the demand for recreational, industrial, and domestic uses of water is increasing.

It is widely accepted that phosphorus (P) is the critical nutrient in determining the degree of lake eutrophication (Likens 1972, Hooper 1973, Wetzel 1983, Vollenweider 1981, Gächter et. al 1985). Therefore, programmes for lake restoration were usually directed at reducing phosphorus loading to water bodies. In most countries massive amounts of money are spent to introduce advanced waste water treatment plants including phosphorus removing facilities in order to reduce nutrients entering to water bodies. But the response to those measures were not promising for several years. It was reported that in certain instances no recovery has taken place during a period of ten years after that external loading was decreased. The most important reason for this is identified as the release of nutrients stored in the sediment of lake with overlying waters. This release is usually called as internal nutrient loading (Bjork 1972, Welch et. al. 1974, Ahlgren 1977, Digiano 1977,).

To overcome this problem, techniques to manipulate or alter the internal nutrient loading are needed. Various physical, chemical and biological methods have been proposed, tested, and applied in numerous lake restoration programmes:
- dredging to remove nutrient rich sediment,
- artificial circulation or aeration of stagnated water layers, to keep bottom waters oxygenated (Cooke et. al. 1986),
- chemical treatment of sediment or lake water in order to

suppress the liberation of phosphorus from the sediment, some used compounds are: sodium aluminate (Peterson et. al. 1974), ferric chloride (Ripl 1976, Klapper 1980), lanthanum chloride (Peterson et. al. 1974), zirconium tetrachloride (Peterson et. al. 1974, Sanville et. al. 1982), fly ash (Higgins et. al. 1976), gypsum (Higgins et. al. 1976), iron ore slag (Yamada et. al. 1987),
- biological oxidation of sediment with nitrate (Ripl 1976),
- chemical oxidation of sediment with peroxide (Cooke et. al. 1986).

The objective of this project is, firstly, to study those lake restoration methods that are aimed at reducing the internal nutrient loading and select a suitable technique to inactivate phosphorus-release for the sediments of the shallow lakes in The Netherlands. The second objective is to perform some laboratory release experiments to investigate the phosphorus-release rates and inactivation capacity of those selected techniques.

Since the reversal or the abatement of eutrophication is the ultimate goal of phosphorus-inactivation, the factors effecting eutrophication and measures to control eutrophication are also discussed briefly in this report.

2. EUTROPHICATION OF LAKES AND RESERVOIRS.

2.1 INTRODUCTION.

Likens (1972) defined eutrophication as nutrient or organic matter enrichment or both, resulting in high biological productivity and decreased volume within an ecosystem. Cooke et.al. (1986) modified this definition to include the input of silt. They defined eutrophication as the process of excessive addition of inorganic nutrients, organic matter, and/or silt to lakes and reservoirs, leading to increased biological production and decreased lake or reservoir volume.

Gradual increase of plant nutrients in the lake or reservoir is the ultimate result of all these processes and it leads to high primary productivity of the ecosystem. When the production of algae, rooted and floating plants or both is increased, it could lead to:

- taste and odor problems in drinking water,
- sudden fish kills due to oxygen depletion,
- decrease of recreational value of the water course
- sometimes killing of animals consuming water, due to the toxicity of some algae.

For these reasons, excessive algal and other blooms are considered to be a nuisance and their dominance in freshwater lakes is highly undesirable.

2.2 NUTRIENTS INVOLVED IN AQUATIC PLANT GROWTH AND GROWTH LIMITATIONS.

Biological growth requires favorable environmental conditions, including supply of chemicals needed to manufacture new cells. The nutrients needed in relatively large quantities by aquatic plants include carbon, hydrogen, oxygen, sulfur, potassium, calcium, magnesium, nitrogen and phosphorus. Several others nutrients must also be present, at least in trace amounts. Table.1 summarizes these micro nutrients.

PROCESS	TRACER ELEMENT REQUIRED
Photosynthesis	Manganese, iron, chloride, zinc and vanadium
Nitrogen Fixation	Iron, boron, molybdenum and cobalt
Other functions	Manganese, boron, cobalt, copper and silicate

Table. 1 Aquatic Plant Micronutrient Requirements (Source: Rust and Lee 1978)

Most often plant growth is limited by one of the nutrients which is not present in adequate amounts in the system. This phenomenon was identified as early as 1840 by Justus Liebig. He noted that a nutrient will be consumed or assimilated by an organism in proportion to the organism's need for that nutrient. The Liebig's "law of the Minimum" which is one of the oldest laws of plant nutrition is based on this observation. The Liebig's law states that "growth of a plant is dependent on the amounts of foodstuff which is available to it in minimum quantities relative to its needs for growth or reproduction" (Odum, 1971).

Among the macro- and micro- nutrient requirements mentioned above, nitrogen and phosphorus are generally considered to be the aquatic plant nutrients of major importance in the eutrophication process. However, various other elements or compounds have been suggested as affecting or limiting the eutrophication process, including iron, molybdenum, nitrate and sulphate, vitamins and other essential organic growth factors, carbon and silica. The principle of growth limitation has also been applied to factors other than nutrients, including light and temperature. However, most of these effects are temporal in nature and do not persist over the annual cycle.

Today, it is generally accepted that either phosphorus or nitrogen in a water body, rather than above mentioned other compounds, control or limit the eutrophication or can be made limiting the eutrophication. Not only the absolute amounts of phosphorus and nitrogen in a water body are important in the eutrophication process, but their relative quantity also is

considered to be a key factor in particular in determining which of these two elements will limit the overall process.

As cited in Golterman (1975), Vallentyne (1973) has indicated the special significance of nitrogen and phosphorus among the 15 to 20 elements commonly needed for the growth of aquatic plants by calculating the **demand : supply** ratios of these essential elements. According to this, aquatic plants have a certain demand for nutrients for their growth and reproduction, in proportion to the quantities of the nutrients in the cells. When one or more of these nutrients is present in short supply relative to the others, then the overall primary productivity of the aquatic plant population will be limited by the rates of supply of these nutrients. Thus, a demand : supply ratio can indicate the nutrient most likely to limit productivity. The higher the demand : supply ratio the more a particular nutrient will limit the growth. Demand : supply ratios based on a "world average" were calculated by determination of the chemical composition of an average aquatic plant community and dividing this composition by the mean chemical composition of the river waters of the world.These ratios are presented in table 2, they clearly illustrate the dominant role of phosphorus and nitrogen by their very high demand : supply ratio.

Element	Demand : Supply	
	Late Winter[a]	Mid Summer[b]
Phosphorus	80,000	up to 800,000
Nitrogen	30,000	up to 300,000
Carbon	5,000	up to 6,000
Iron, silicon	Variable, but very low	
All other elements	< 1,000	

[a] Prior to spring bloom, [b] At algal maximum growth period

Table. 2: Demand:supply ratios for the major aquatic plant nutrients

Summarizing, it is clear that nitrogen & phosphorus are the two elements most often found to be limiting aquatic plant growth.

2.3 EFFECT OF N : P ATOMIC RATIO ON ALGAL GROWTH.

The composition of algal cell can be represented crudely by a chemical formula, that summarizes elements contained in them. One of several that has been proposed is $C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1$. This formula is based on the simple stoichiometry of the photosynthesis/ respiration reaction as illustrated in the following equation.

$$106\ CO_2 + 16\ NO^-_3 + HPO^+_4 + 122\ H_2O + 18\ H^+ + \text{trace elements} + \text{Energy} \rightleftharpoons (C_{106}H_{263}O_{110}N_{16}P_1) + 138\ O_2$$

According to this formula the atomic ratio of N : P in a algal cell is 16 : 1 and it was proved by several workers that algae need a relatively fixed ratio of carbon to nitrogen to phosphorus of 106 : 16 : 1 (Redfield 1958, Vollenweider 1968).

Depending on the environmental conditions and variations in species, this ratio can vary considerably in a vast range. For example, Yell Rhee (1978) reported the optimal cellular N : P ratio of *Scenedesmus sp.* to be 30 and the growth is determined solely by N limitation below the N : P ratio of 30 and growth is limited by phosphorus above this value.

It is now generally accepted, that even in spite of some variations, the N : P atomic ratio in natural algal populations remains constant enough to be used in making reasonable predictions as to which of these two elements limit the algal growth in natural waters.

According to the formula given in the photosynthesis reaction, ($C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1$) algae will assimilate nitrogen and phosphorus from their aquatic environment in a stoichiometric atomic ratio of approximately 16N:1P until one of these two nutrients becomes depleted in the water body. At that time, the nutrient present in the water body in the lowest concentration, relative to the stoichiometric needs of the algae, will limit subsequent growth. If the N:P atomic ratio in the water falls

below 16, the algal biomass in the water body at that time would be controlled or limited by the quantity of nitrogen present in the water course. The amount of phosphorus present in the water body at that time would have no influence, in terms of limiting growth of algae, since it would be present in excess quantities. In contrast, if the N:P ratio is greater than 16, the growth is limited by phosphorus (Rhee, 1978, Vollenweider, 1982).

An important characteristic of unpolluted, natural water is that they are extremely diluted (Lamb, 1985) and also that the N : P ratio of natural water is about 23 : 1 (Odum, 1971). So the algal productivity of many fresh water lakes actually is limited by low concentrations of phosphorus in the water (Welch, 1975, Golterman, 1975, Vollenweider, 1968). When phosphorus is added to such a lake by land runoff, waste discharge or from other sources, extreme growth of algae could be observed. It can be illustrated by a simple calculation that 1kg of phosphorus has the potential of producing 76kg of algal biomass whereas 1kg of nitrogen has only potential to produce 12kg of algal biomass.

2.4 MAJOR SOURCES OF PHOSPHORUS ENTERING LAKES.

Rocks and other deposits which were formed in past geological ages form the main reservoir of phosphorus in nature. So the main natural origin of phosphorus in lakes or oceans are due to erosion, that is the chemical and mechanical weathering of rocks (Altschuler, 1973).The contribution of this natural supply, however is very low (Hakanson and Jansson, 1983). Excavating phosphate baring rocks (specially apatite baring deposits) for use as a fertilizer influences the natural cycle, and most of the phosphate rock mined is washed away to natural waters. Drainage water from agricultural areas may contain large amounts of phosphates due to the application of excessive amounts of manure and fertilizers. In many areas the present supply of phosphorus from farm lands is in order of about ten times higher than the natural supply (Hakanson and Jansson, 1983).

Another important source of phosphorus is human excrements and detergents. It is estimated that 2g of PO_4-P per person per day is excreted as urine and faeces. Another 2g of tri-phosphate phosphorus is emanating from detergents. Municipal sewage discharge to freshwater bodies and urban storm water runoffs increase the phosphorus concentration in fresh water. In addition to these sources, considerable amounts of phosphorus are emitted from food industries, smelters,and industries producing fertilizers. (Fig.1). Phosphorus loading to some lake areas in the Netherlands are given in table 3.

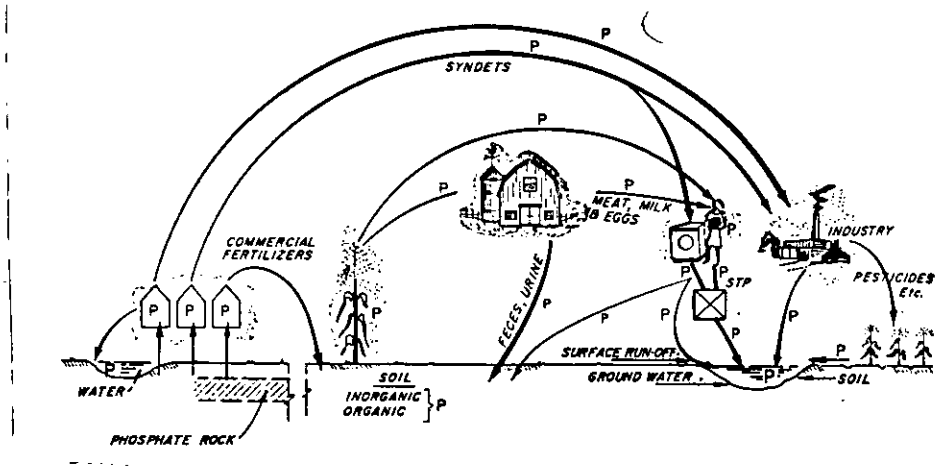


Fig 1. Phosphorus distribution in a complex urban economy. (source : Sawyer, 1973)

Table.3: Amounts (tons/year) and percentage contribution (with in brackets) of phosphate inputs of various sources, to some surface water bodies in the Netherlands.

Source	Noord-Hol	Uitw-sl	Rijnland	Friesland
Domastic/Industrial				
-treated waste water	1088(56.8)	340 (50)	688 (52.8)	380 (39.5)
-untreated waste water	200(10.4)	95 (14)	190 (14.6)	114 (11.8)
Agricultural runoff	246(12.7)	140 (21)	111 (8.5)	275 (28.5)
Sepage	312(16.3)	61 (9)	143 (11.0)	
Inlet water	44(2.3)	40 (5.9)	191 (14.6)	
Precipitation	27(1.4)	4 (0.6)	5 (0.4)	12 (1.2)
Total :	1917(100)	680 (100)	1304 (100)	964 (100)

2.5 FORMS OF PHOSPHORUS IN AQUATIC ECOSYSTEM.

The phosphates that enter lakes are inorganic or organic in nature, both in soluble or particulate form. Among those the major share of phosphorus found in lake water is in organic form and the inorganic phosphorus compounds often make up less than 10% of the total phosphorus of many aquatic systems (Hooper, 1973 and Wetzel, 1983).

Within the ecosystem, several forms of phosphorus may be identified, e.g. phosphorus in phytoplankton, phosphorus in zooplankton, phosphorus in fish, dissolved organic and dissolved inorganic phosphorus, and particulate inorganic phosphorus.

There are several classification methods involved in categorization of phosphorus in the ecosystem, viz., chemically based, biologically based or a combination of both. One classification method is strictly based on analytical chemistry. It is based upon the separation between soluble and insoluble components by filtration and between reactive and non-reactive forms. The insoluble phosphorus is commonly referred to as particulate phosphorus, **PP**, (or sometimes as suspended or sestonic P). The soluble phosphorus, **SP**, (also referred to as total dissolved phosphorus, **TDP**,) can itself be divided into a fraction which is biologically available, the soluble reactive phosphorus, **SRP**, (also referred to as soluble inorganic phosphorus, mostly ortho-Phosphate, **SIP**) and soluble unreactive phosphorus, **SUP**. The sum of the **PP** and the **SP** is termed total phosphorus, **TP** (Hakanson and Jansson, 1983).

2.6 FATE OF PHOSPHORUS ENTERING LAKES.

Inorganic orthophosphate in lake water is consumed by algae and other aquatic plants for their growth requirements and removed from the water phase. But following the death, it can be released to the water phase directly as a result of the mineralization or sink to the bottom and be released to the water phase subsequently as the result of mineralization.

Dissolved organic phosphates entering lakes can also be converted into inorganic orthophosphate through mineralization and contribute to the algal growth.

Dissolved inorganic phosphates can also precipitate with some cations such as Al, Fe, and Ca found in lake water, if the concentrations are sufficiently high and depending on pH and redox conditions. The most important mechanism of phosphorus-removing from natural waters is the sorption of Phosphate to metal hydroxy gels. The formed phosphorus-containing precipitates or sorbet material subsequently sink to the bottom of the lake (Appendix 4).

2.7 FORMS OF PHOSPHORUS IN LAKE SEDIMENTS.

A major portion of the phosphorus that enters the lake system is sinking to the bottom in various forms viz.,

1. dead phytoplankton and dead zooplankton phosphorus (detritus) **(organic P)**,
2. inorganic phosphorus present as orthophosphate ions sorbed on the surface of phosphorus-retaining compounds **(nonoccluded P)**
3. inorganic phosphorus present as orthophosphate ions within the matrices of phosphorus-retaining compounds **(occluded P)**,
4. orthophosphate phosphorus present in discrete phosphate minerals such as apatite [Ca_{10} $(PO_4)_6$ X_2, where X = OH, F, $1/2CO_2$] and vivianite [$Fe_3(PO_4)_2.8H_2O$]. **(discrete P)**, (Williams et. al. 1971) and in phosphorus-containing precipitates, formed in the lake.

The chemical nature of the phosphorus in sediment is one of the most important characteristics to be studied in the context of phosphorus release from sediments. However the present knowledge of chemical fractionation schemes, which are based on chemical extraction procedures, only account for a limited number of phosphorus fractions of the sediment. For example, the fractionation scheme developed by Williams et. al. (1976), which is one of the most relevant fractionation schemes, is valid only to yield non-apatite inorganic phosphorus (NAI-P), apatite

phosphorus (A-P), and organic phosphorus (O-P). The NAI-P compartment consists basically of Fe-and Al-bound phosphorus (see appendix 1A).

Hosomi et. al. (1982) used a scheme to fractionate inorganic phosphorus in sediments based on the procedure proposed by Chang and Jackson (1957). This procedure defined three fractions of inorganic phosphorus in sediment (see appendix 1B) as

- Aluminum-bound phosphorus (AL-P, extraction by NH_4F)
- iron-bound phosphorus (Fe-P, extraction by NaOH) and
- calcium-bound phosphorus (Ca-P) , extraction by H_2SO_4).

Hieltjes and Lijklema (1980) characterized the fractions of phosphorus in sediments by the extraction media, used to dissolve them,

NH_4Cl- extractable P (Approximately loosely bound P)
NaOH - extractable P (Approximately Fe+Al bound P)
HCl - extractable P (Approximately Ca bound P)

Both total phosphorus content and the distribution of various phosphorus fractions in the sediment differ from one lake sediment to another. Fig.3 is an example of this.

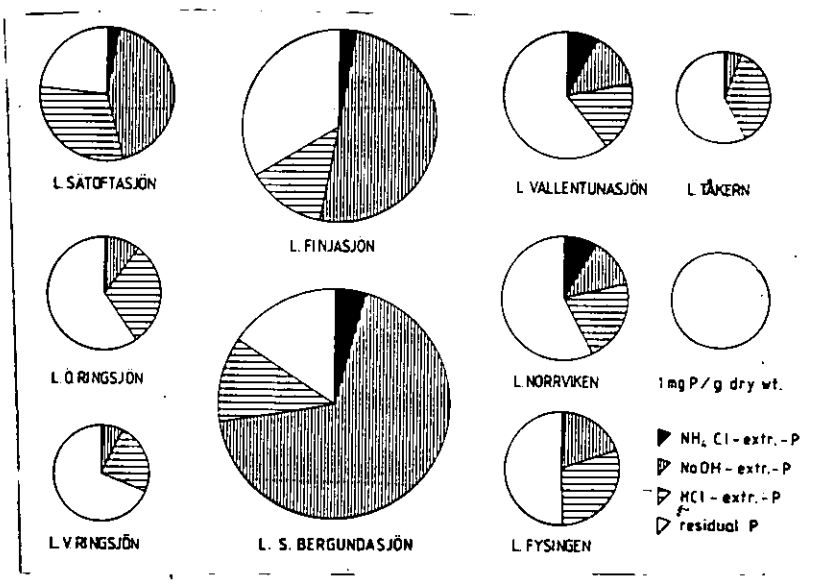


Fig 3. Total concentration and fractional composition of phosphorus in the sediments of nine Swedish lakes. The total concentrations are proportional to the size of the circles (Boström 1984).

Similar variations can be found in different locations in one lake (fig 4).

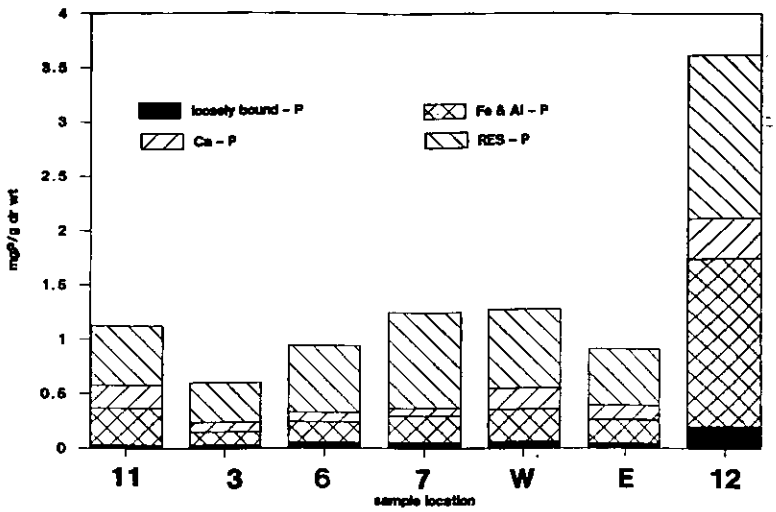


Fig. 4 : Variation of different phosphorus fractions and total phosphorus content of sediments collected from different locations in Loosdrecht lakes, the Netherlands. The hight of each column is equal to the total phosphorus content of the location (redrawn from Boers et. al., 1984)

2.8 FATE OF PHOSPHORUS IN LAKE SEDIMENT

As there is no gaseous component in the biogeochemical cycle, phosphorus is considered as a conservative substance. The sediment is considered to be a sink for phosphorus entering to lakes.

As cited in Hakanson & Jansson (1983), in the years around 1940, various investigators established release of phosphorus from sediments under certain conditions. The redox conditions at the surface of the sediment were identified as the most important condition for phosphorus release to the overlying water. The only explanation given for phosphorus release from sediments was the reduction of iron(III) to iron(II) whereby phosphorus bound to iron(III) in salts or sorbed to iron complexes was returned to the overlying water. But in recent years, there has been an increasing awareness that phosphorus is released from sediments also under apparently well oxygenated conditions (Ryding & Fosberg 1977, Stevens & Gibson 1977, Ryding 1985).

The release of phosphorus from sediments to well aerated water has been observed in a number of shallow lakes which have received sewage water for a long period. Highly reduced loadings by diversion or by treatment seldom gave the expected results since decrease in external input , at least partly, was compensated by a net flux from the sediment (see also sec. 3.3.2). (Larsen et. al. 1976, Ahlgren, 1977, Neame, 1977, Bengtsson, 1978, EPA, 1980, Welch et.al. 1980, Boers et. al. 1984, Sondergaard et. al. 1987, Forsberg, 1987,).

It is emphasized that in all oligotrophic lakes and also in most eutrophic waters, the net flux of phosphorus on a yearly basis is towards the sediments. However, under certain conditions, particularly in nutrient rich lakes, the release from the sediments may exceed the inputs by sedimentation. This phenomenon, which occurs predominantly in summer, is called internal phosphorus loading.

2.9 CONDITIONS GOVERNING PHOSPHORUS RELEASE FROM SEDIMENTS.

The liberation of phosphorus from sediment occurs mostly through the comparatively small pool of phosphorus dissolved in the sediment pore water. The size of this pool is in turn regulated by the equilibria with particulate phosphorus present in the sediment (Fig. 5).

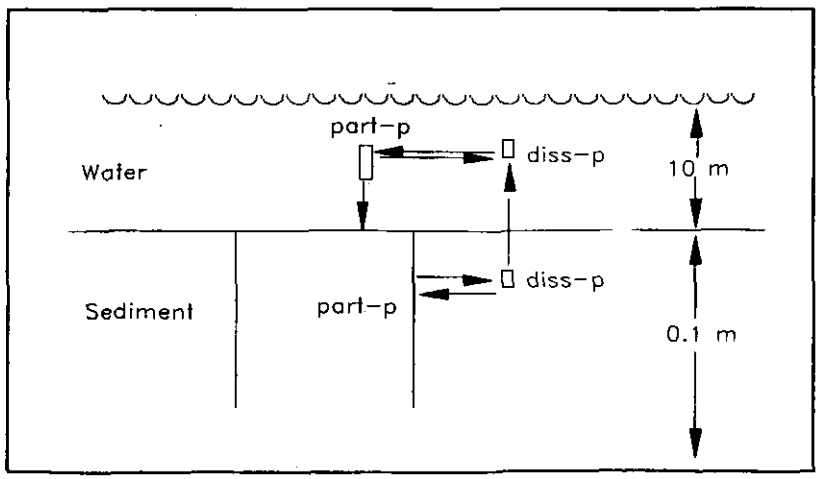


Fig. 5: Schematic illustration of the distribution of particulate and dissolved phosphorus in a lake-sediment system. A hypothetical example assuming a mean lake depth of 10m and active sediment layer of 0.1m, that the concentration of 50ugL^{-1} in the lake water and 2mg g ds^{-1} in the sediments, and a water content of the sediment of 90%. (source : Hakanson and Jansson, 1983)

Consequently, before a substantial release can occur, two fundamentally different processes must function more or less simultaneously. Phosphorus must be mobilized from particulate to dissolved form by the action of physical, chemical, and biological reactions and dissolved phosphorus must be transported to the lake mainly through physical processes (Fig. 6).

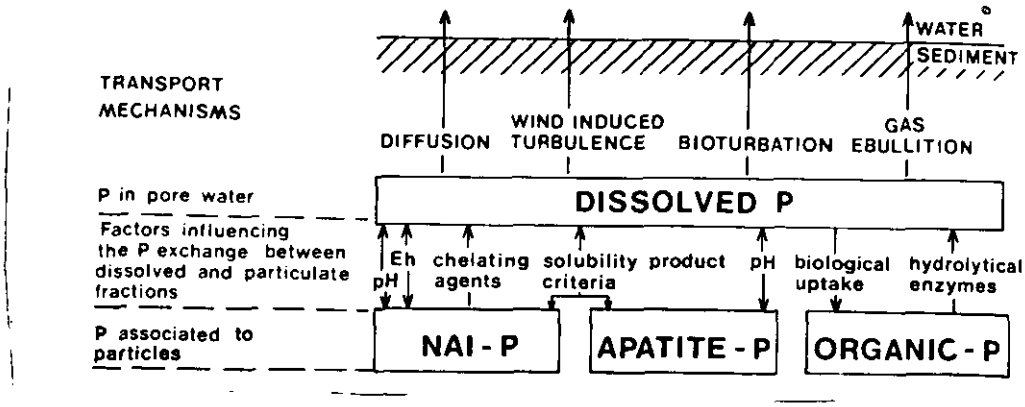


Fig. 6. Illustration of the dominating processes regulating the release of phosphorus from lake sediments (source, Hakanson and Jansson, 1983)

Table.4 summarizes the major mobilization and transport mechanisms which are or can be relevant with respect to phosphorus release from the sediment to the lake water. Some important mobilization mechanisms are discussed in detail below.

Table. 4: Summary of the causal relationships determining the release of phosphorus from lake sediments (source: Hakanson & Jansson, 1983).

Environmental parameters	Effects on phosphorus mobilization
Redox potential	Iron-bound phosphorus is released at potentials below 200 mV when iron (III) reduced to iron (II).
pH	An increase in pH decreases the phosphorus binding capacity of iron and aluminum compounds, primarily due to ligand -exchange reactions where hydroxide ions replace phosphate. Calcite and apatite formation at higher pH-values increase the phosphorus- binding capacity of calcium
Temperature	An increase in temperature gives primarily indirect effects due to increased bacterial activity, which increases oxygen consumption and decreases the redox potential. The production of phosphate-mobilizing enzymes and chelating agents might increase accordingly.
Equilibrium criteria	Affects adsorption-desorption and dissociations of precipitates.
Chelating agents	Replace phosphate from slats with calcium, iron and aluminum. Chelating agents can be produced by bacteria and algae or occur as a pollutant.
Processes	**Effects on phosphorus transport**
Diffusion	Phosphorus transported upwards to compensate the concentration gradient between the sediment and the lake water. Important when the sediments are superimposed by stagnant water.
Turbulence	Linked to mechanical transport, resuspension and bottom dynamics. Enhances diffusion transport. Possibly the most efficient process of transport in shallow lakes.
Bioturbation	Creates physical mixing and enhances transport in aerobic sediments.
Gas convection	Mainly methane, which creates physical mixing and enhances transport. Important in highly reduced, organic sediments.

2.10 SOME IMPORTANT FACTORS FOR THE MOBILIZATION OF PHOSPHORUS IN LAKE SEDIMENTS.

2.10.1 Adsorption and Desorption capacity of sediment.

Exchange of phosphorus between the sediment and pore water can be controlled by adsorption and desorption reactions. Sediments of different lakes differ significantly in adsorption and desorption capacity. Sorption capacities are highly related to fractional distribution of various forms of phosphorus in the sediment (Mortimer 1971, Williams et.al. 1971, Syers et. al. 1973). According to Boström and Pettersson (1982) lake sediments can be separated into three categories, based on the adsorption and desorption capacities (Boström and Pettersson, 1982).

Category	Characters	Lake types.
1st.	Low adsorption and high desorption capacity of phosphorus	Shallow lakes that received or are receiving agricultural runoffs.
2nd.	High adsorption and low desorption capacity of phosphorus.	Normally deep lakes that received waste water.
3rd.	Negligible net sorption of phosphorus	Shallow lakes that received or are receiving sewage effluent water.

The input history of a lake is directly connected with the phosphorus release properties of the sediment. The more phosphorus, that is supplied to sediments, the lower the sediment's capacity to store and retain the phosphorus. With an excessive loading, such as in lakes polluted by sewage water, the sediments will eventually become saturated. Subsequent release of phosphorus from those sediments are experienced, in spite of good oxygenation of the water column. (Ex. Lake Vallentunasjon, cited in Boström & Pettersson 1982).

Not all the lakes of this nature show a similar pattern of internal loading. This is due to the fact that the binding capacity of sediments of different lakes differs as a result of

the chemical nature of the sediment and of incoming material and water. So the fractional distribution of particulate phosphorus in sediments is also an important factor for the determination of internal loading.

2.10.2 Fractional distribution of particulate phosphorus.

As mentioned before, the release of phosphorus from sediments is mainly taking place through the dissolution of particulate phosphorus in sediment pore water. The solubility of particulate phosphates in the sediment under prevailing conditions of pH, redox potential and ionic strength is controlled by the chemical composition of the phosphate present in the sediment and their interactions with other minerals or amorphous material (Hieltjes & Lijklema, 1980).

Sediments from sewage - loaded lakes contain considerably more loosely adsorbed phosphorus (nonoccluded phosphorus) than unpolluted lake sediments (Williams et. al., 1971). The nonoccluded inorganic phosphorus fraction is more closely in contact with the surrounding aqueous phase than other categories of inorganic phosphorus. It may be anticipated that the nonoccluded fraction responds much more readily to changes in environmental conditions than occluded or discrete phosphorus.

Phosphorus release is redox sensitive and strongly favored by a high content of aluminum and iron - bound phosphorus. Some sediments release primarily organic and loosely adsorbed phosphorus, and in such cases less phosphorus is released and redox and pH conditions have less effect (Boström, 1984).

2.10.3 Redox conditions.

The early findings on phosphorus exchange between sediment and lake water are based on the interactions between iron and phosphorus during aerobic and anaerobic conditions.

In oxidized situations, phosphorus is sorbet to iron(III) hydroxide gels. Such aggregates may be formed in the oxidized

surface sediments or precipitated from overlying waters. When the sediment becomes reduced, iron(III) is reduced to iron(II), whereby both iron and sorbed phosphate are returned to solution. Subsequently dissolved phosphate is transported back to the water column from the sediment pore water or the sediment surface.

There is no doubt that these early findings are still valid and the redox depending process are well explained one of the most important reasons for phosphorus release from lake sediments. This is one of the most common processes taking place in productive stratifying lakes during stagnation periods (summer & winter), when oxygen is depleted in the bottom water.

At neutral pH conditions, the reduction of iron(III) takes place at redox potentials around 200 mV. This corresponds to an O_2 concentration of approximately 0.1 mgL^{-1}. The process of reduction of iron(III) to iron(II) could be hindered by high concentrations of nitrate or manganese which are reduced before iron (Foy 1986).

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = +0.77\ V$$

$$Mn^{4+} + e^- \rightleftharpoons Mn^{2+} \qquad E^0 = +1.65\ V$$

$$2NO^-_3 + 12H^+ + 10e^- \rightleftharpoons N_{2(g)} + H_2O \qquad E^0 = +1.24\ V$$

(Snoeyink and Jankins, 1980)

In general, iron reduction is considered to be a chemical process where iron is reduced by e.g.,organic compounds or S^{2-}. However, iron can also be reduced by bacteria, which utilize iron(III) as electron acceptor during anaerobic respiration (Fig.7) (Sörensen 1982).

2.10.4 pH.

pH mediated phosphorus mobilization is a rather common andquantitatively important phenomenon. Phosphorus bound to Al or Fe or sorbed to Al or Fe hydroxy gels are firmly bound at neutral pH values, but dissolve in acid or alkaline waters.

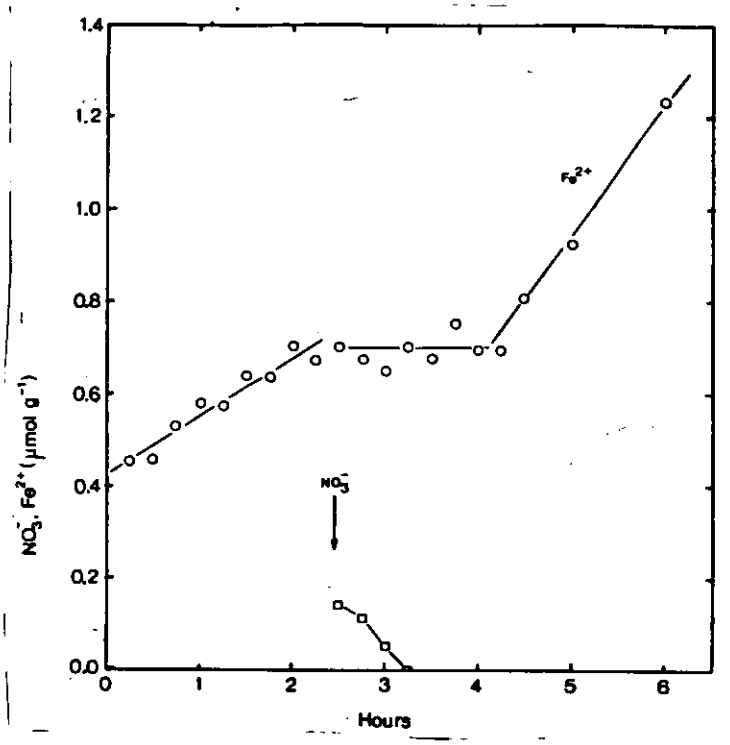


Fig.7: Effect of NO^-_3 on reduction of Fe^{3+}. Arrow indicates addition of 0.2 mM $NaNO_3$. Symbols O, Fe^{2+}, ·, NO3-.After depletion of NO3- facultative bacteria start to utilize Fe^{3+} as an electron acceptor (Source: Sörensen 1982, modified).

Ca bound phosphorus (usually apatite) has a smaller solubility at high pH values (fig 8). Hence the phosphorus mobilization governed by pH does not generally follow the same pattern from lake to lake but will depend on sediment and water composition.

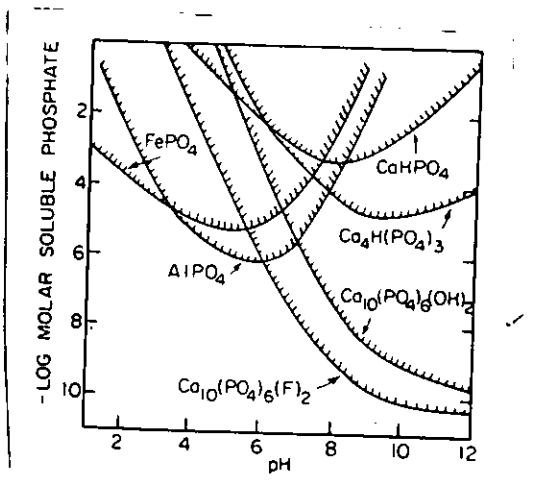


Fig.8: Solubility of the metal phosphates (Source: Stumm and Morgan, 1981).

Anderson (1975) reported increase of phosphorus release rate with increasing pH above 8 for a Danish lake, Kvind so. (Fig.9). Rippey (1977) also showed increase in phosphorus release rates from lake sediments, when on iron(III) or Al(III) hydroxide gel adsorbed phosphorus is subjected to a pH increase in the alkaline regime (Fig.10).

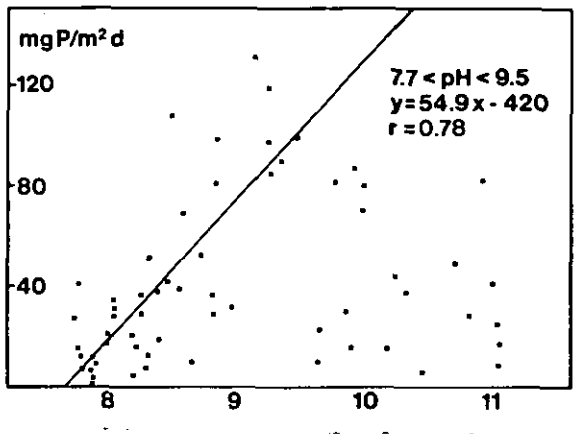


Fig.9: Rate of orthophosphate release from undisturbed Kvind so sediments. (source: Anderson, 1975)

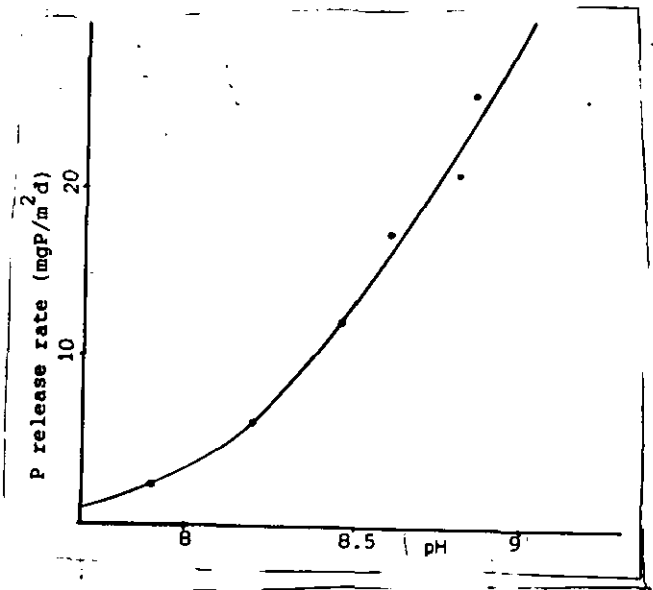
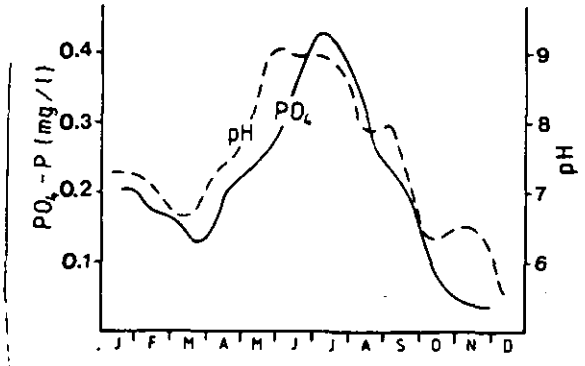


Fig.10: Variation of phosphorus release with pH at 20°C. (source: Rippey, 1977) Lough Lake, N. Ireland.

This type of pH-regulated phosphorus mobilization from sediments is important in shallow productive lakes. In these lakes, in summer the pH in the lake water is often increased by two or three units due to the photosynthetic activity of planktonic algae, besides, the whole water mass in these lakes is in more or less continuous contact with the sediment surface. Fig.11 shows the commonly observed increase in pH during summer and the relationship with phosphorus mobilization.

Fig.11: Seasonal variation of pH and phosphorus concentrations in Lake Glaningen, Sweden (source: Hakanson and Jansson, 1983)



In contrast, Kamp-Nielsen (1975) reported a decrease in phosphorus release with increase of pH above about 8 for another Danish lake, Fure so (Fig.12). (Lake Fure so is an eutrophic lake with a surface of $9km^{-2}$ and max. depth of 36m. Sediment type is identified as calcarious and contains about 50 $\%CaCO_3$).

The decrease of the phosphorus release rate in this lake is explained by the formation of hydroxy apatite ($Ca_{10}(PO_4)_6(OH)_2$), upon settling of CaCO3 particles, formed as a result of increased pH, or co-precipitation of PO^{3-}_4 with $CaCO_3$. So the pH increase in calcium rich waters may have the effect that phosphate is removed from the water column and fixed in the sediment.

2.10.5 MICROBIOLOGICAL ACTIVITY.

Mineralization of degradable organic matter present in the sediment enhance the dissolution of organic phosphorus.In mineralization process, organic phosphate esters are hydrolyzed by enzymes called phosphatase which are often located on the bacterial cell surfaces or occurring as free dissolved enzymes. Hydrolysis rates are often optimal at slightly alkaline-conditions. (Hakanson and Jansson, 1983).

Boström et.al.(1985) showed that internal phosphorus-loading in lake Vallentunasjön (a sewage polluted Swedish lake, Z= 2.7 m.), was associated with a high microbial activity in the surface sediments, and with a substantial loss of organic-phosphorus from the surface sediment.

The process of microbiological degradation could be stimulated, for a certain extent, by increasing the temperature. Kelderman and Van de Repe (1982) found that the temperature is an important controlling factor for phosphorus-release patterns in sediment cores from lake Grevelingen.

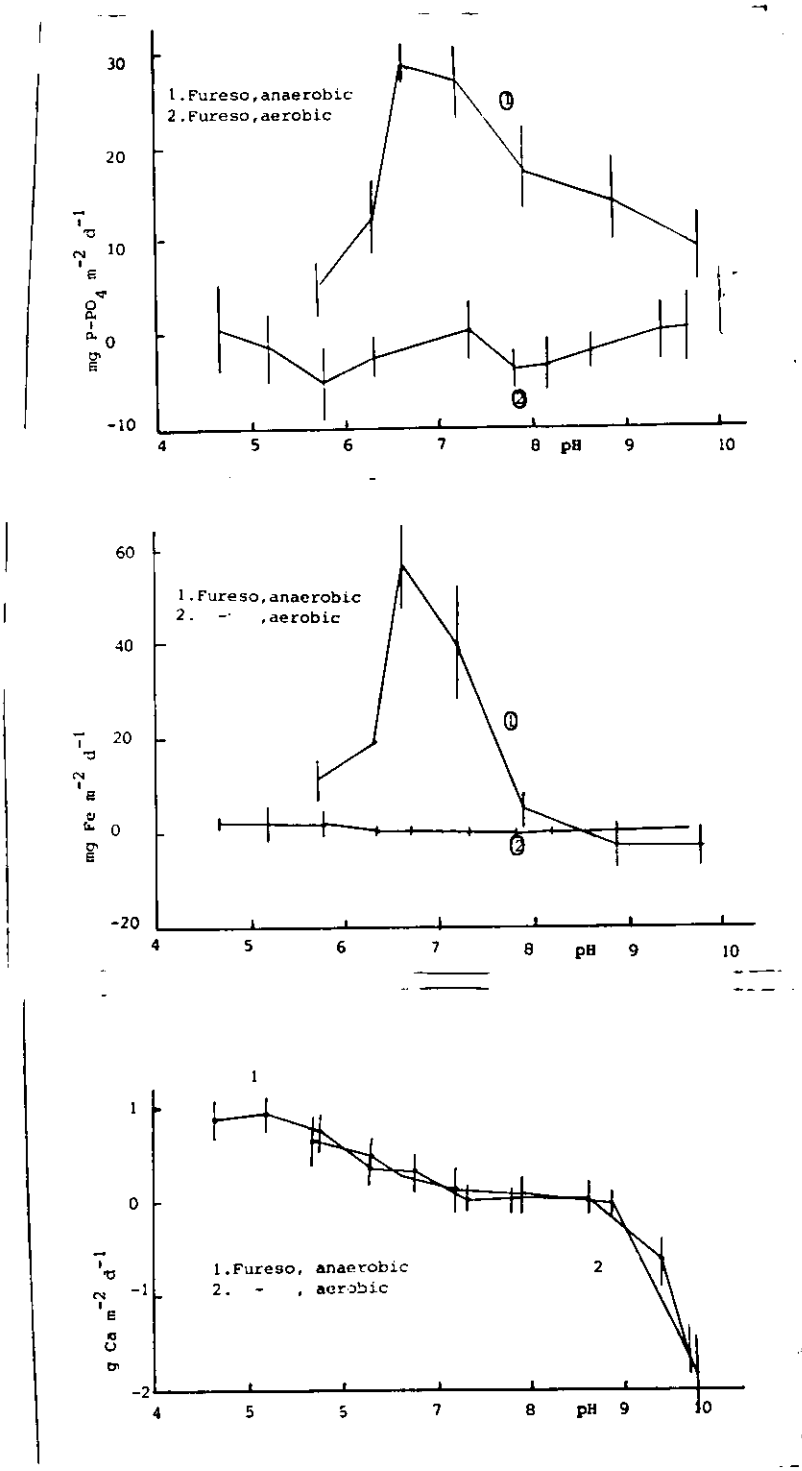


Fig.12: The influence of pH on the release of phosphate, iron and calcium from sediments of lake Fure so in Denmark. Below pH 7, calcium was dissolved from the sediment and above pH 9 it is precipitated. The effect on an aerobic exchange of iron and phosphate follows the same course, and the release had a pronounced maxima at pH 7 (Source: Kamp-Nielsen (1974): modified).

3. LAKE AND RESERVOIR RESTORATION

3.1 INTRODUCTION.

Control of eutrophication is one of the most important tasks of water authorities in most countries of the world. In lake restoration programmes, the major attention is given to decreasing the input of phosphorus from point sources, such as municipal waste waters and industrial effluent. Millions of dollars have already been spent to construct advanced waste water treatment plants including facilities to reduce the phosphorus content in the effluent. However the success of these measures was disappointing and there is no evidence of a case in which a once deteriorated lake has completely been recovered as a result of such measures alone.(Gächter and Imboden, 1985).

One of the two major reasons for this is identified as the significant contribution of non point sources to the phosphorus loading to lakes. Agricultural runoff and urban stormwater are often rich in phosphorus. These sources are not easily controlled.

The second major reason is the phosphorus release from sediments by re-dissolution. So the additional attempt of lake restoration programmes are aimed at control or reduce the phosphorus-sources and/or of the phosphorus release from bottom sediments. The following simple mathematical model shows the main factors in eutrophication control clearly.

3.2 A SIMPLE MODEL FOR LAKE RESTORATION.

The phosphorus balance in a lake is determined by the phosphorus input (M_{in}), the phosphorus export through the outlet (M_{out}), and sedimentation (M_s):

$$V\, dP/dt = M_{in} - M_{out} - M_s \qquad \ldots\ldots\ldots\ldots (1)$$

where V = volume of total lake (m^3)

P = mean total phosphorus concentration in lake (mg m^{-3})

t = time (years)

P_{in} is the average of all inlet concentrations $P_{in,i}$ (rivers, sewage pipes, ect.) weighted by the corresponding flow rates Q_i:

$P_{in} = \Sigma\ P_{in.i}\ Q_i\ /\ \Sigma\ Q_i\ = M_{in}\ /\ \Sigma\ Q_i$

Then, $M_{in} = P_{in} \cdot Q$

Q = water input or output ($m^3\ yr^{-1}$)

P_{in} = mean total phosphorus supply from external sources (mg m^{-3})

It is possible to write the output terms (M_{out}, M_s) as the product of the total phosphorus content in the lake (VP) and some rate constants given below, and transform Eq. 1 into:

$$dP/dt = Q\ P_{in}\ /\ V - Q\ P_0\ /\ V - \sigma_p\ P$$
$$= (Q/V)\ P_{in} - \{(Q/V)(P_0/P) + \sigma_p\}\ P$$
$$= \rho P_{in} - (\beta\rho + \sigma_p)P \qquad \ldots\ldots\ldots(2)$$

ρ = Q/V, Water renewal rate (or flushing rate). (yr^{-1})

σ_p = Net sedimentation rate. (yr^{-1})

$\beta = P_0/P$, Vertical form factor (--)

P_0 = Mean total P concentration in surface outflow (mg m^{-3})

The steady state solution of Eq 2 could be written as:

$$P_\infty = P_{in}\ \frac{\rho}{\beta\rho + \sigma_p} \qquad \ldots\ldots\ldots(3)$$

One goal of lake restoration is to decrease phosphorus concentration. Equation 3 serves to demonstrate the three different possibilities to achieve this goal:

1. Reduction of external phosphorus loading (i.e. P_{in}) by sewage treatment or diversion, or (in some cases) flushing the lake with water contain low phosphorus, and by decrease of phosphorus runoff from agricultural areas and at phosphorus load in urban stormwater runoff.
2. Increase of phosphorus export through the outlet (i.e. increasing β). This is achieved by diversion of hypolimnitic water which, during stagnation, has higher phosphorus concentrations than the surface water. However. this is not applicable to shallow lakes.
3. Increase of phosphorus retention (i.e. increase of σ) by increasing sedimentation or decreasing phosphorus re-dissolution at the sediments.

3.3 CONTROL OF EXTERNAL PHOSPHORUS LOADS.

Point discharges of sewage or industrial effluent, and non point sources such as surface runoffs from agricultural and urban areas are considered as external loads to lakes or reservoirs. The first and obvious step in a eutrophication control programme is removal or treatment of direct inputs of waste water, storm water or both that contain high contractions of nitrogen and phosphorus. Those point sources can be controlled by implementing waste water treatment plants or by diverting those streams to other receiving water bodies.

3.3.1 DIVERSION OF INFLOW WATER.

This technique prevents nutrient rich waters from entering a lake by diverting them. This seems to be simply transferring the problem to somewhere else. But in many cases careful diversion may not cause large problems, especially when the diverted water is used for agricultural irrigation or diverted to a receiving water body, where nutrient supply does not limit growth of planktonic algae. For example, if light is limiting in the receiving water, such that nutrients are not fully utilized, then added extra nutrients will not cause increased algal abundance. The impact of waste water diversion in 16 lakes in Europe and the USA is summarized in table 5.

In shallow lakes, improvements were generally found to be limited. This suggests that after the removal of a large inflow of nutrients, concentrations in the water column are maintained primarily by release from the sediments (Henderson-sellers and Markland,1987).

3.3.2 WASTEWATER TREATMENT.

By studying experiences all over the world, it can be noted that millions or, in some instances, billions of dollars have been spent in building waste water treatment plants to reduce discharges into surface water bodies. However, most of these wastewater treatment plants did not accommodate for the

Lake	Mean depth (m)	Result of diversion
d'Annecy (France)	41.5	Improved following diversion
Fairmont (5 lakes: Minnesota)	2-3	slight improvement with diversion but dredging provided remarkable improvement
Jordan (Michigan)	16(max)	Secondary effluent removed in 1971
Lansing (Michigan)	3	Remains eutrophic, dredging necessary
Lyngby So (Denmark)	2.8(max)	Good recovery,but increased macrophytes
Madisin lakes (Wisconsin)	9-25	Only slight improvement
Norrviken (Sweden)	5.4	Slight improvement, but P concentration still remains high
Rotsee (Switzerland)	0.2	Diversion in 1933, but no improvement
Sammamish Washington)	17.7	No change in winter P, Slight reduction in blue-green algae
Schiersee (Germany)	40(max)	Partial diversion in 1964, reduced oxygen depletion by 1967
Snake (Wisconsin)	7(max)	No improvement
Stone (Michigan)	20(max)	Improved only after addition of fly ash
Tegernsee (Germany)	70 (max)	Improved oxygen conditions, *Oscillatoria* still present, reduced numbers
Trummen (Sweden)	1.1	No recovery until after dredging
Washington (Washington)	32	Excellent recovery
Zurich (Switzerland)	50	Still eutrophic

Table 5. Representative lakes in which sewage has been diverted (Henderson-Sellers and Markland, 1987).

elimination of phosphorus in the treatment process. At present, in the industrialized countries, emphasis is given to improve these existing treatment plants.

The following examples illustrate the cost and the success of the efforts taken to improve lake water quality by implementing advanced waste water treatment plants. In Switzerland, over one billion dollars per year is spent for

water pollution control measures. A major portion of that amount is aimed to decrease the input of phosphorus into the surface water. Studies of AmbÜhl (cited in Gächter and Imboden, 1985) demonstrated that the efforts taken to decrease the phosphorus concentration were only successful in few cases and these have also not completely recovered from eutrophication. (Fig. 13).

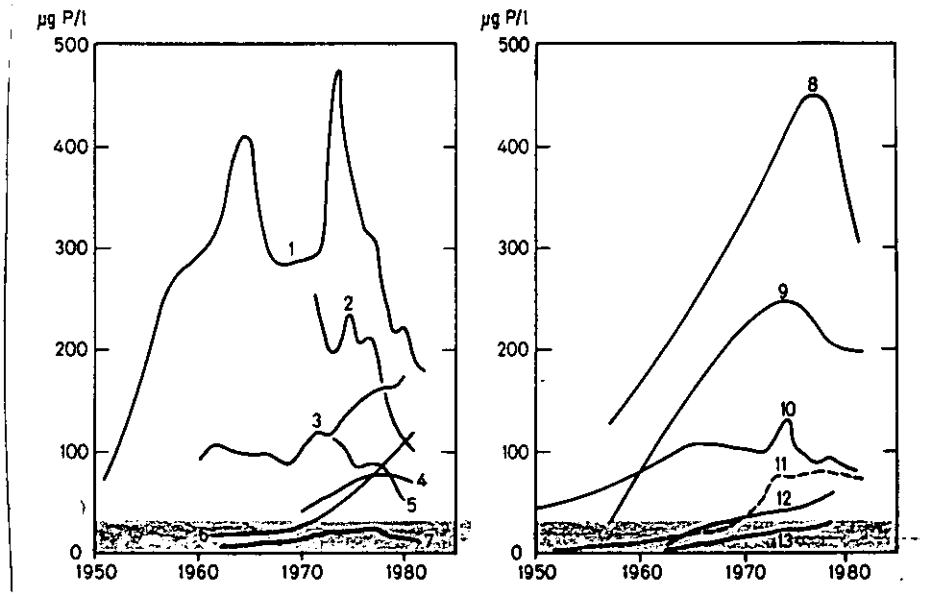


Fig 13. The evaluation of average concentration of soluble reactive phosphorus at spring overturn in various lakes. 1, Greifensee; 2, Pfäffikersee; 3, Zugersee; 4, Lac Lèman; 5, Bielersee; 6, Sempachersee; 7, Walensee; 8, Baldeggersee; 9, Hallwilersee; 10, Zürichsee; 11, Bodensee; 12, Lac de Neuchâtel; 13, Vierwaldstättersee. Shaded area indicates the water quality goal (Source: Gächter and Imboden 1985).

Another example is given in Larsen et.al. (1979), it concerns the effects of wastewater phosphorus removed from Shagawa lake, Minnesota. In early 1973, a tertiary treatment plant came into operation, which reduced the phosphorus supply to the lake with about 80%. In their study period, Larsen et.al. observed that significant reductions in total and soluble reactive phosphate (SRP) concentrations have occurred in the lake. By 1976, the average total phosphorus and SRP had declined from about 51 and 21 μgL^{-1} to about 30 and 4.5 μgL^{-1}, respectively, giving 40 & 80% reduction. During 1975 and 1976, chlorophyll a had decreased to less than 50% of the pretreatment level during May-June, but during July-August little change had occurred. They used the following mathematical model (see section

3.2), to predict changes of phosphorus levels in the lake, assuming a well mixed system.

$$dP/dt = (Q/V).P_{in} - (Q/V).P - \sigma_p P \quad ....(1)$$

The steady state solution of equation (1),(assuming J, S, & Q are constants) is :

$$P = P_{in} (1-Rp)^{-1} \quad ....(2)$$

Where Rp is the TP retention coefficient (= fraction of inflowing TP which is lost to the lake bottom).

The tertiary wastewater treatment plant reduced the inflow of phosphorus into the lake and significant reduction in the TP and SRP concentrations in Shagawa lake were observed in the years after influent phosphorus reduced. But total phosphorus concentration has not declined to levels projected from equation (2) using actual inflow water quality.

The main reason for this difference was identified as phosphorus feed back from sediment. To incorporate this feed back the TP dynamic equation was modified as follows:

$$dP/dt = (Q/V).P_{in} - (Q/V).P - \sigma_p P + J_{int}/V \quad ...(3)$$

Where J_{int} is an estimate of the rate of internal TP supply. J_{int}, σ_p, and the time interval over which TP was supplied internally were estimated from the pretreatment 1971-1972 data base. σ_p, was assumed to have two constant values. A winter rate, σ_p^w, applied to the periods when the lake was ice-covered, and a summer rate, σ_p^s, applied to the ice-free periods.

J_{int} was assumed to have the following form:

$$J_{int} = \begin{cases} C_1, & t_1 \le t \le t_2 \text{ (spring pulse)} \\ C_2, & t_3 \le t \le t_4 \text{ (summer pulse)} \\ 0, & \text{all other times of the year,} \end{cases}$$

Computer simulated parameter estimates for equation (3) are given below.

Ice-covered season	Ice-free season
σ_p^w = 0.035 week^{-1}	σ_p^s = 0.072 week^{-1}
C_1^p = 280 kg week^{-1}	C_2^p = 500 kg week^{-1}
= 4.4 mg P m^{-2} d^{-1}	= 7.9 mg P m^{-2} d^{-1}
t_1 = week 12	t_3 = week 25
t_2 = week 14	t_4 = week 34

The observed data and simulated values for TP in lake water for 1973-76 period were agreed best (Fig 14).

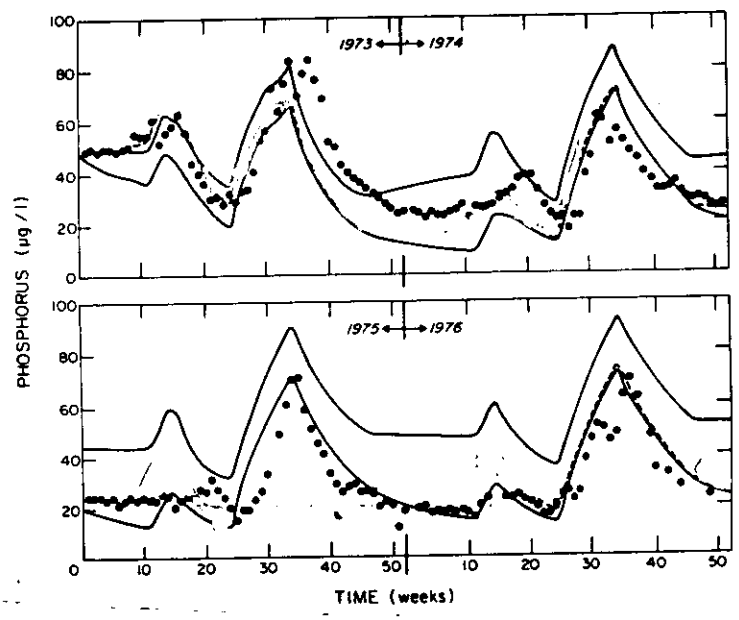


Fig.14. Comparison of output from equation 3 with total phosphorus (volume weighted average) data for the years subsequent to treatment. Upper solid line is projection as if treatment had not been instituted; lower solid line is projection incorporating external loading reduction.

The main conclusion of this study was, that even when external TP supplies to lakes have been reduced to a significant extent, corresponding decreases in lake TP levels, and hence decrease in lake productivity might not occur within an acceptable time scale. This means that additional measures are needed to achieve acceptable TP levels in lake water within a reasonable time span.

For this reason, various inlake restoration methods have been developed in recent years to control nuisance algae,

macrophytes and rooted plants. Bio-manipulation, mechanical removal of macrophytes, the application of herbicides, diversion of hypolimnetic water, hypolimnetic aeration, chemical precipitation of phosphate, sealing of the sediment surface, and removal of sediment by dredging are such internal lake restoration measures. Some of those techniques such as diversion of hypolimnetic water or hypolimnetic aeration are not applicable for shallow lakes, and hence not discussed in this report.

3.4 BIOMANIPULATION.

Controlling nuisance of algae and marcophytes by using biological measures is a developing lake improvement technique. The basic idea behind this is reducing algal biomass by increasing grazing capacity and/or reducing the turbation of the sediment by removing bottom feeding animals. The use of this technique is not yet wide spread, because the knowledge concerning this technique and its effects on aquatic ecosystems is limited and so it is still in an experimental phase. As it is possible to use the technique without adding chemicals to the ecosystem and there is no sediment removal, it may seem to have less environmental impacts than other in-lake measures. However, introducing foreign fish species to the ecosystem could cause severe biological damages such as the decline of native fish species or ultimate nuisance of the introduced species etc (Cooke et. al 1986).

3.5 DREDGING.

Sediment removal by dredging is a widely applied lake restoration technique. It is the only appropriate technique, when the purpose of the lake improvement is to deepen the lake. With subject to some limitations this technique can be applied for nutrient control of the removal of toxic substances, or for the removal of rooted macrophytes.

A major portion of phosphorus entering a lake, is deposited in the sediment and subsequently released to the lake water, yielding growth of algae or other nuisance plants, even though

incoming phosphorus is controlled by e.g. introducing advanced waste water treatment plants. In such a situation removal of nutrient rich sediment might be expected to reduce the rate of internal nutrient recycling, thus improving overall water quality.

Accumulation and subsequent release of toxic substances or heavy metals is another problem, which directly affects the aquatic life. Most of these micro-pollutants accumulate in the sediment. Uptake of these pollutants could cause accumulation in aquatic plants and animals to harmful levels. One of the most famous examples is the mercury pollution of Minimata bay in Japan. Dredging is the best measure to get rid of those type of pollutants, at least as far as the aquatic environment in concerned.

Dredging of sediment can remove nutrients toxic substances from lakes and hence improve the lake environment, but dredging itself gives various environmental damages. Sometimes, dredging is said to be transferring the problem from one place to another place or sometimes increase the problem. If the disposal site is not properly designed, or not properly maintained, nutrients, heavy metals, and other toxic substances could leach into the ground water or wash off to another surface water source. The pollutants may end up in places they never would reach by natural processes. Apart from those hazards involved in disposal, there are various inlake problems linked with dredging operation. Most of them are associated with the re-suspension of sediment during dredging. Liberation of nutrients, and/or toxic substances, fish gill blocking due to the increase of turbidity, destruction of the benthic fish food web and water level lowering in case large amounts of sediment are removed from a shallow lake, are some of these inlake problems. Noise, dust and truck traffic also pose additional nuisance problems (Cooke et. al. 1986).

Most of the dredging projects carried out so far, demonstrated improvements in lake water quality. Compared to the long term benefits, some problems arising during dredging could be neglected. Dredging projects having only marginal success are

due to inaccurate pre-dredging problem assessment and inadequate amounts of sediment removed (Peterson 1981, Salomons et.al. 1987).

Table 6 : PER-HECTARE COST FOR ALUM TREATMENT

Lake Treated	Mean depth (m)	Surface area (ha)	Chemical and dose (g Al/m^3)	Treatment cost ($/ha)
Horseshoe Lake	4.0	8.9	2.6	101
Lake San Marcos	2.3	18.2	6.0	126
Welland Canal	9.0	74.0	2.5	204
Mirror Lake	7.8	5.1	6.6	400
Shadow Lake	5.3	17.1	5.7	400
Cline's Pond	2.4	0.4	10.0	420
West Twin Lake	4.4	34.0	26.0	425
Dollar Lake	3.9	2.2	20.9	504
			Average:	322.5

Table 7.a : PER-HECTARE COST FOR DREDGING

Lake Dredged	Mean depth (m)	Surface area (ha)	Sediment removed (m^3)	% of basin dredged	Treatment cost ($/ha)
Half Moon Lake	1.7	53.4	25000	30	2137
Lilly Lake	1.4	35.6	680000	100	4586
Commonwealth Lake	0.9	2.6	19000	100	5769
Steinmetz(*)	1.5	1.2	2000	75	7233
Carnegie Lake	3.0	110.0	765000	75	12054
Lenox Lake	0.9	13.4	76000	100	13328
Nutting Lake	1.3	31.6	275000	56	18858
Sunshine Lake	0.5	0.4	5100	100	26832
Krause Springs	0.34	0.3	4900	100	31754
Collins Park Lake	0.7	24.3	52000	15	39178
			Average:		16173

Table 7.b :

Lake Geeplas	2	30	150000	100	17000
Lake Binnen Schelde	2	180	150000	20	2800

Cost of dredging operations are a matter of concern. In general it is agreed that dredging is more expensive than other nutrient inactivation techniques if only cost are concerned. But it is very difficult to compare even different dredging projects, due to the large number of variables involved, such as type of equipment used, project size, volume of material dredge, availability of disposal sites, the density of the material being

removed, the distance to the disposal site and the ultimate use of the dredged material, etc. Now it is obvious that comparison of dredging, with other sediment inactivation techniques such as chemical treatment is much more complicated due to some other variables also involved. Additionally, in most of the cases cost of dredging is given in cost per amount of material removed, while in sediment inactivation techniques the cost is given per hectare treated.

Peterson (1981) compared cost of dredging and chemical treatment processes for some lake restoration projects. The following tables (table 6 & 7.a) suggests that the average cost for dredging is about 50 times higher than the cost for chemical treatment. Table 7.b shows cost involved in two dredging projects carried out in the netherlands.

4. NUTRIENT PRECIPITATION AND INACTIVATION.

4.1 INTRODUCTION.

Nuisance caused by algal blooms can be reduced if the concentration of an essential nutrient in the lake is lowered to growth-limiting level. It is widely accepted that phosphorus is the critical nutrient in determining the degree of lake eutrophication and thus the controlling factor for the algae blooms. So almost all lake improvement programmes based on nutrient control are directed to the reduction of external phosphorus inputs from domestic and industrial sources. As remarked earlier those efforts were not completely successful to control the nuisance of algal blooms because of the fact that sediment phosphorus release contributes to a significant extent to the phosphorus budget in the lake. To overcome this problem, various inlake chemical treatment methods have been developed in the recent years. These methods include:

- phosphorus precipitation from the lake water
- inactivation of phosphorus in the sediment to retard further release of phosphorus to the overlying water
- chemical oxidation of sediment
- biological oxidation of sediment.

4.2 PRECIPITATION AND INACTIVATION OF PHOSPHORUS.

The purpose of this effort is to lower the lake's phosphorus content by removing phosphorus from the water column by precipitation and retarding subsequent release of phosphorus from lake sediment by inactivation. Most techniques for removal of phosphorus are based on precipitation of orthophosphate by metal ions. Aluminum, iron or calcium salts and salts of rare earth elements such as zirconium, lanthanum, and titanium, have been for this purpose. Among these salts lanthanum rare earth mixtures and Zirconium salts showed the most efficient phosphate precipitation and inactivation capacity; and aluminum came on the third place (Peterson et.al 1974). However, a major drawback of the use of lanthanum and zirconium salts for phosphorus inactivation in lakes are the potential toxic effects and the high costs. Therefore, the use of those salts is not addressed in detail in this report.

Fly ash and iron ore slag were also used in some lakes for P precipitation and inactivation (Higgins et. al. 1976). These materials could not be recommended for application to lakes due to high concentrations of heavy metals, and specially fly ash causes clogging of fish gill and is a further threat to aquatic life (Cooke et. al. 1986).

Artificial circulation or aeration is mostly restricted to stratified deep lakes and is not an applicable method for shallow lakes.

At present the most widely used phosphorus inactivation agent is Aluminum in the form of aluminum sulphate or sodium aluminate or a mixture of both (Cooke et. al. 1986).

4.2.1 PHOSPHORUS INACTIVATION USING ALUMINUM SALTS

The first attempt to use aluminum as a lake restoration agent is reported in 1968 in Lake Longsjon in Sweden. This deep lake was treated with Boliden Pellets (Primarily Aluminum Sulphate) and showed remarkable improvement with reduction in algal blooms during the following summer. Unfortunately, the

effect was not longlasting. This was probably due to the additional sewage inflow to the lake and a second treatment was necessary in 1970 (cited in Peterson et. al. 1974 and Foy, 1985)

A number of deep lakes in Europe and in North America were also treated with aluminum salts and showed remarkable improvements in lake water quality. A few examples are given below:

- Horseshoe lake in Wisconsin, was treated with aluminum in 1970 and subsequently showed low phosphorus contents in the lake water and reduced blue green algal biomass. The treatment was still efficient after 10 years and no indications of toxicity to benthic invertebrates or other aquatic organisms were observed (Cooke and Kennedy, 1981, Garrison & Knauer, 1984, Cooke et. al. 1986).
- Snake lake in Wisconsin is an another example of aluminum treatment. The lake was treated in 1972 with a mixture of aluminum sulphate and sodium aluminate. The treatment was effective in lowering phosphorus concentration and increasing water transparency and the treatment was also effective for about 10 years. In 1982, the water quality deteriorated. This was probably due to severe loads of nutrients from storm water runoff (Garrison and Knauer, 1984).

Medical lake, Washington (treated in 1977, EPA 1980(a)), Annabessacook lake, Maine (treated in 1978, Dominie II 1980), Dollar lake, Ohio (treated in 1974), are some of other North American deep lakes which were treated with aluminum and showed positive results for several years.

Attempts to reduce phosphorus release from sediments by the addition of aluminum salts have been least effective in shallow lakes, lacking a well-defined hypoliminion, and often little improvement in phosphorus status was observed within 1 year of treatment. Some examples are given below.

- Pickrel lake Wisconsin ($Z = 2.4$, treated in 1973, Knauer & Garrison 1980)
- Long lake, Washington ($Z = 2.0$, treated in 1982),

- Clines Pond, Origon (Z = 2.4, treated in 1971 Sanville et. al. 1976, and Dominie II 1980),
showed improvements following aluminum treatment, but the effect was not long lasting. Especially in Pickeral lake, the water quality deteriorated year following the treatment. Analysis of aluminum in sediment cores showed that the formed aluminum flock had been redistributed to the lake's center following a series of holomictic occurrences, which left areas of the sediment free to release phosphorus to the overlying water (Cooke et. al. 1986). Positive results of the treatment in Long Lake, however, lasted for a few years (Jacoby et. al. 1983).

4.2.1.1 MECHANISMS GOVERNING PHOSPHORUS PRECIPITATION AND INACTIVATION BY Al.

When aluminum salts such as aluminum sulphate or sodium aluminate are added to water, hydrolysed aluminum species like polymerized aluminum hydroxide, aluminate, or $Al(H_2O)_6^{3+}$ are formed, depending on the pH of the solution. At pH between 6-8 insoluble and settleble, polymerized, aluminum hydroxide forms. In alkaline solution (ie. pH above 8) the aluminate ion and pH below 6 the $Al(H_2O)_6^{3+}$ ion predominates.

Aluminum ions found in water are generally coordinated with six water molecules and the solutions are normally acidic due to the hydrolysis equilibrium.

$$Al(H_2O_6)^{3+} + H_2O \rightleftharpoons Al(H_2O)_5OH^{2+} + H_3O^+$$

Further hydrolysis of this divalent ion leads to the univalent ion and, finally, to colloidal aluminum hydroxide.

$$Al(H_2O)_5(OH)^{2+} + H_2O \rightleftharpoons Al(H_2O)_4(OH)^+_2 + H_3O^+$$

$$Al(H_2O)_4(OH)^+_2 + H_2O \rightleftharpoons Al(H_2O)_3(OH)_3 + H_3O^+$$

In basic solutions, aluminum hydroxides exhibits its amphoteric nature by further hydrolysis to form the aluminate ion.

$$Al(H_2O)_3(OH)3 + H_2O \rightleftharpoons Al(H_2O)_2(OH)^-_4 + H_3O^+$$

Figure.15 shows the relation between pH and solubility of monomeric aluminum species at 25°C.

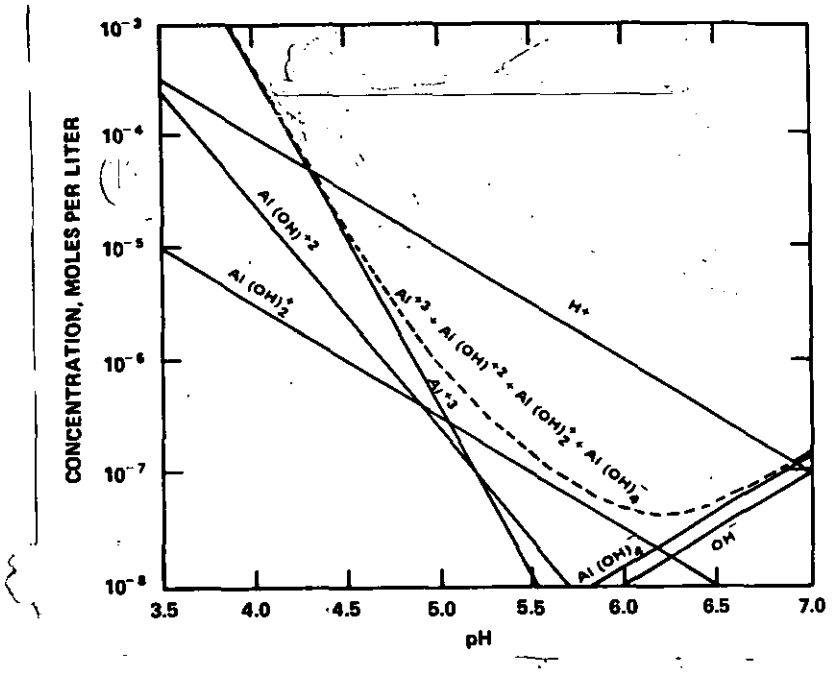


Fig.15: Solubilities of monomeric aluminum species at 25^0C as a function of pH (Source: Burrows 1977).

The most important species for phosphorus removal from water is $Al(OH)_3$. When $Al(OH)_3$ is formed by the addition of aluminum salts to water, pH is decreased and also total alkalinity falls. If the initial alkalinity is low or an excessive lode of aluminum salt is added to a lake pH will fall below 6.0 and the toxic Al^{3+} is formed. At the same time the amount of $Al(OH)_3$ flock is decreased. This flock should be available to remove phosphorus from water, or prevent phosphorus release from lake sediment. Therefore, the pH and the alkalinity are the most important factors in determinating the dose to be applied.

Aluminum phosphate ($AlPO_4$) precipitation, adsorption of phosphorus on the surface of $Al(OH)_3$ polymer or floc or entrapment and sedimentation of phosphorus containing particles in the $Al(OH)_3$ floc are the main phosphorus removal mechanisms from lake water involved in aluminum application. $AlPO_4$ does not form readily, however, in the phosphorus concentrations and pH found in normal lake water. The reaction is enhanced at a high Al:P ratio. In the pH range of 6-8, both inorganic dissolved phosphorus and particulate phosphorus are effectively removed by sorption to the $Al(OH)_3$ floc (Burrows 1977, Snoeyinks and Jenkins 1980, Stumm and Morgan 1981, Cooke et. al. 1986).

4.2.1.2 MAJOR DRAWBACKS OF Al APPLICATION.

The main part of the information available on the efficiency of aluminum treatment of lakes, concerns physical and chemical parameters, and only few papers deal with the effects on phyto- and zoo-plankton (Zarini et. al. 1983). However, the toxicity of aluminum on freshwater plants and animals has been well documented (Bengtsson 1978, Baker and Schofield 1982, Dave 1985, Friberg et. al. 1986, Skogheim and Rosseland 1986, Playle 1987 to cite but a few).

The level of aluminum toxicity to freshwater fish depends on chemical factors such as pH, calcium concentration, concentrations of ligands and chelators and degree of chemical stability and biological factors such as species and life stage.

Both low pH levels and elevated inorganic aluminum concentrations are found to be toxic to aquatic animals. This toxicity occurs at pH level of 5.0, which otherwise may not be acutely toxic to fish (Playle 1987). Cook et. al. (1986) confirmed from the data published on this subject, that a dissolved aluminum concentration below 50 µg Al/L will have no harmful effect on (*Daphnia magna*), rainbow trout (*Salmo gairdneri*), or chironomid larvae (*Tanytarsus dissimilis*). Kennedy and Cooke (1982) prepared a scheme to estimate the aluminum dose (mg Al/L), in water of varying initial alkalinity and pH. It is based upon the fact that at pH > 6 the dissolved aluminum concentration remains below 50 µg Al/L.

Human toxicity.

Aluminum has long been considered as a virtually non-toxic and non-absorbable from the gastrointestinal track. Because of this, neither the international nor the European standards for drinking water list aluminum among those substances for which limits are specified (WHO 1970, 1971). More recent studies have shown that ingested aluminum compounds are absorbed to a certain extent (Friberg et. al. 1986). As a result of aluminum

accumulation in the body, specially in the brain, severe health effects on the central nervus system (CNS) may occur. Aluminum concentrations of 50 μg/L in drinking water is considered to be safe (NRC, 1982).

Efficiency in shallow lakes.

All shallow lakes treated with aluminum salts got surface application of aluminum salts. Phosphorus removal from lake water occurs by coagulation/entrapment of phosphorus containing particles, precipitation of $AlPO_4$ or by sorption of phosphorus on the surface of aluminum hydroxide polymers. The alum flocks sink to the sediments and is eventually mixed into the sediment by bioturbation. The long term effectiveness of aluminum treatment will depend on the ability of the deposited aluminum hydroxide to retain phosphorus at the sediment/water interface and thus reduce the internal recycling of phosphorus (Kennedy and Cooke 1982). The major drawback reported for the failure of aluminum treatment in shallow lakes is the dispersion and redistribution of lake water.

4.2.2 PHOSPHORUS INACTIVATION USING IRON SALTS.

Iron salts have been used for long time in water treatment plants as a flocculent and in advanced waste water treatment plants as a phosphate removing agent. But the use of iron as a phosphate removing agent in lake restoration projects is not given much interest due to the suspension of release of phosphate and iron(II) in low redox conditions.

Singer (1972) cited two lakes in Michigan, where ferrous ion has been used for the removal of phosphate, lake Odessa and lake Grayling. Ripl (1976) reported a Swedish lake, treated with $FeCl_3$ followed by addition of CaCO3 and Ca(NO3), and obtained interesting results in controlling eutrophication.

4.2.2.1 AQUEOUS CHEMISTRY OF IRON(III).

One of the most prominent features of ferric iron in aqueous solutions is it's tendency to hydrolysis and/or formation of complexes. Due to this in the natural aqueous environment simple species such as Fe^{3+} do not exist, and iron mostly occurs as hydrated aquocomplex ions such as $Fe(H_2O)_6^{3+}$. The addition of an Fe(III) salt to water leads to the formation of soluble monomeric, dimeric or polymeric hydroxoiron complexes, in addition to the free aquoferric ion. The formation of hydroxoferrics complexes from the hydrolysis of the $Fe(H_2O)_6^{3+}$ ion takes place, according to the following equilibrium reactions:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$
$$[Fe(H_2O)_5(OH)]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + H_3O^+$$
$$[Fe(H_2O)_4(OH)_2]^+ + H_2O \rightleftharpoons [Fe(H_2O)_3(OH)_3] + H_3O^+$$
$$[Fe(H_2O)_3(OH)_3] + H_2O \rightleftharpoons [Fe(H_2O)_2(OH)_4]^- + H_3O^+$$

(Cotton and Wilkinson 1976, Snoeyink and Jenkins 1983)

It can be seen, from those equilibrium reactions that the concentrations of the hydroxocomplexes depend on the pH of the solution. Cotton and Wilkinson (1976) stated that the pH of a solution containing mainly Fe(III) in the form of hexaquo ion (i.e. 99% $Fe(H_2O)_6^{3+}$) must be around zero due to the reason of hydrolysis equilibrium reactions.

Snoeyink and Jenkins (1983) noted that the hydroxo complexes, or hydrolysis products, of Fe(III) ion have a dramatic effect on the solubility of iron. The equilibrium of ferric ions in pure water is governed in its initial stages by the following equilibrium constants:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad \log K = -2.165$$
$$Fe(H_2O)_6^{3+} + 2H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2]^+ + 2H_3O^+ \quad \log K = -6.74$$
$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3(OH)^- \quad \log K_{so} = -38$$
$$Fe(H_2O)_6^{3+} + 4H_2O \rightleftharpoons [Fe(H_2O)_2(OH)_4]^- + 4H_3O^+ \quad \log K = -23$$
$$2Fe(H_2O)_6^{3+} + 2H_2O \rightleftharpoons [Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+} + 2H_3O^+ \quad \log K = -2.85$$

The effect of these hydroxo complexes on solubility is most conveniently illustrated by a pC-pH diagram (Fig.16).

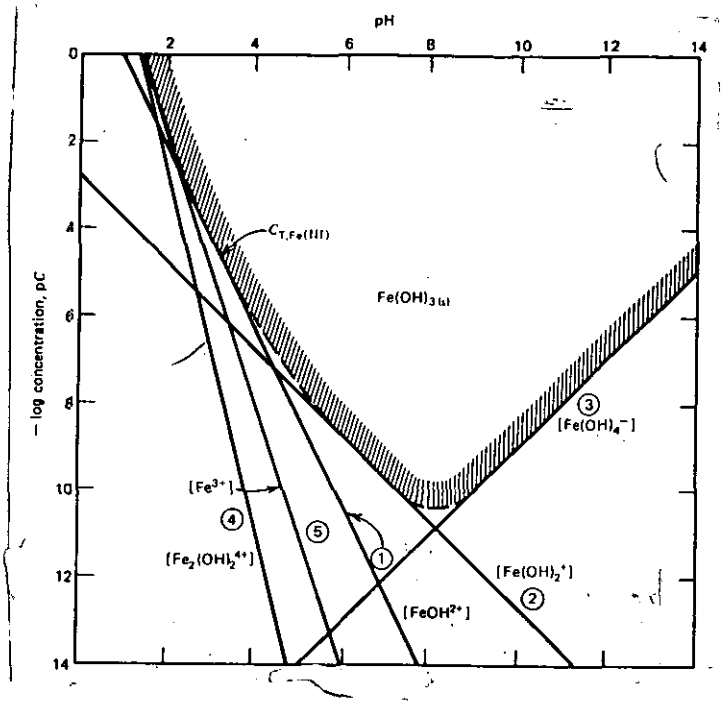
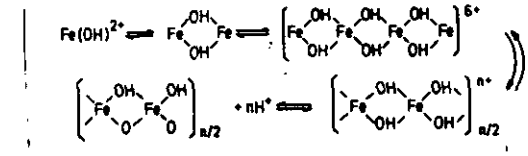


Fig. 16. Equilibrium concentrations of hydroxo iron(III) complexex in a solution in contact with freshly precipitated $Fe(OH)_{3(s)}$ at 25^0C. (source: Snoeyink and Jenkins)

The pC-pH diagram can be used for the rapid evaluation of both total concentration of all species present as well as to provide a graphic representation the concentrations of individual species at various pH values (Snoeyink and Jenkins 1983). Fig 16 shows that, in the pH range from 4.5 to 8 (which cover all natural waters), the predominant species is $[Fe(H_2O)_4(OH)_2]+$. The dimer $[Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+}$ does not predominate at any pH value in this range but is a significant species below pH 2.5. Moreover, at pH typically encountered in natural waters, $Fe(H_2O)_6^{3+}$ is only a minor component of the ferric iron species.

The possibilities of formation of large hydroxoferric complexes were studied by Dousma and de Bruyn (cited in Hong-Xiao and Stumm 1987) and Hong-Xiao and Stumm, 1987. Fig 17 (a) and (b) gives two reaction schemes suggested for the hydrolysis precipitation process of iron(III) solutions ending with large polymers.



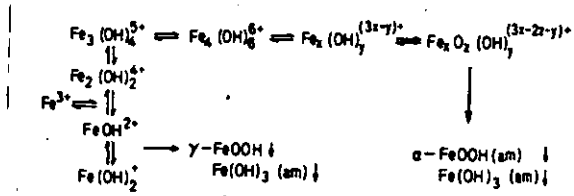
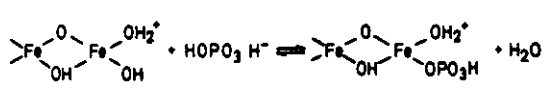


Fig.17(a). The seheme of hydrolysis precipitation process proposed by Dousma and de Bruyn (cited in Hong-Xiao and Stumm, 1987), (b). A comprehensive scheme of hydrolysis polymerization precipitation process proposed by Hong-Xiao and Stumm, 1987, and chemical species (in 0.3 M $FeCl_3$, solution).

4.4.2.2 MECHANISMS OF P REMOVAL.

Interactions between iron and phosphate in lake water and sediment are in a complex way governed by redox potential and pH. As shown in the previous chapter a major portion of aqueous solutions of ferric iron, is in monomeric or polymeric hydroxy complex form. The existence of these species is governed by the pH of the solution and the solubility of individual species.

In aerobic lake waters, the major mechanism of phosphorus removal could be the adsorption of phosphate to iron(III)-hydroxo complexes as shown by Lijklema (1980) or hydroxo ligand exchange reactions between phosphate and the iron(III)-hydroxo polymers.



Apart from these complex reactions, direct precipitation of $FePO_4$ is also possible, according to the following reaction:

$$Fe^{3+} + PO^{3-}_4 \rightleftharpoons FePO_4 \ (s)$$

In an anaerobic condition Fe(III) can be reduced to Fe(II) and then, precipitated and/or sorbet PO4 is expected to be released to the water column (Lijklema, 1980; Hakanson et. al., 1973). Thomas, 1965 (as cited in Singer, 1972) observed a small release of phosphate during anaerobic digestion of activated sludge from waste water treatment plant of Mannedorf, Switzerland and other treatment facilities in Switzerland.

Einsele (as cited in Singer, 1972) showed that the amount of available orthophosphate in aquatic eco-systems depends on the extent of ferrous iron oxidation and, consequently, on the concentration of oxygen and the ratio of $Fe(OH)_3$ to $FePO_4$. Fig.18 depicts the limnological cycle of iron showing its interactions with phosphate.

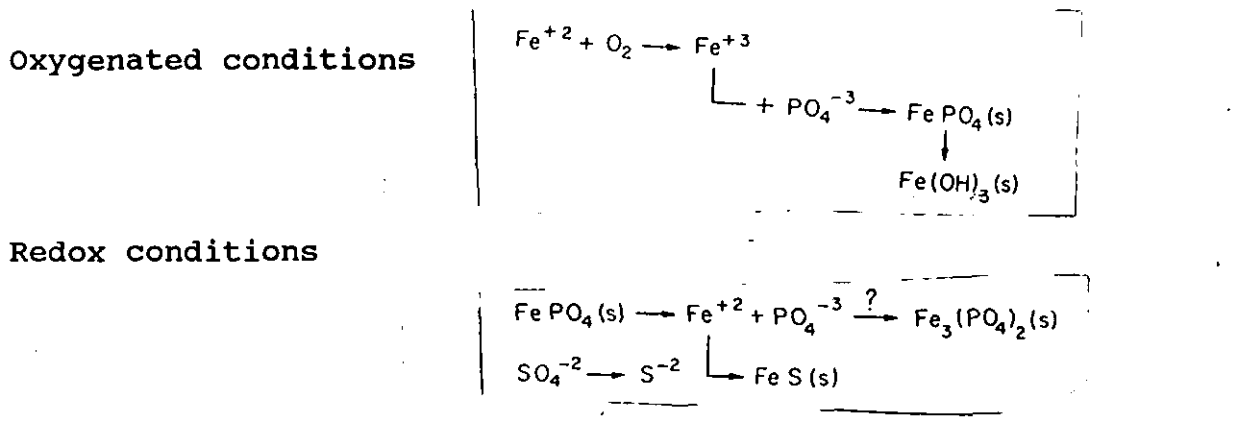


Fig.18: Interactions of aqueous iron and orthophosphate in limnological systems.

In well oxygenated conditions ferrous iron is oxidized to ferric iron which subsequently reacts with phosphate to form ferric phosphate or hydroxyferric phosphate complexes. During periods in which the whole sediment is anaerobic (stagnation or high biomass production periods), ferric phosphate and hydroxyferric phosphate complexes are reduced to ferrous iron and phosphate, and both are released to water column. Then, depending on the concentration of sulphate and the extent of sulphate reduction, the ferrous iron may react to form the relatively insoluble ferrous sulphide (log K_{SO} = -18.4). On the other hand, formation of ferrous phosphates could also be

expected in those conditions as the solubility of ferrous phosphate is also low (log K_{so} = -29.9). Williams et. al. (1971), and Singer (1972), cited the occurrence of vivianite ($Fe_3(PO_4)_2.8H_2O$) in reducing environments and the X-ray analysis of phosphate precipitates in sediments of ferrous ion treated Odessa lake and Grayling lake in Michigan, and showing those to be vivianite (Green et. al., 1967 as cited in Singer, 1972). Emerson (1976) and Emerson (1978) indicated the presence of vivianite in the solid phase of interstitial waters from sediment cores taken from Greifensee, Switzerland.

4.3 SEDIMENT OXIDATION.

A lake restoration technique involving the oxidation of the top 15 to 20 cm of anaerobic lake sediment with the aid of nitrate has been developed by Ripl (1976). The objective was to reduce the internal phosphorus loading in lakes with anaerobic sediment and high interstitial water phosphorus concentrations, in which iron controls phosphorus exchange between the sediment and the overlying water. By oxidizing the organic matter through increased denitrification, increased binding of interstitial water phosphorus with ferric hydroxide complexes should be induced, resulting in lower phosphorus release rates (Ripl 1976, Ripl & Lindmark 1978, Foy 1986).

To reduce the labile organic matter content in sediment through the action of denitrifying bacteria and thereby restore an oxidized state, a solution of $Ca(NO_3)_2$ (141 gN m^{-2}) was injected into the sediment of Lake Lillesjön in Sweden. Prior to this addition, ferric chloride (146 gFe m^{-2}) was added to remove hydrogen sulfide and to form ferric hydroxide, which binds interstitial phosphorus. Addition of ferric chloride decrease the pH. In order to raise the pH, to an optimal level and encourage microbial denitrification, lime (180 gCa m^2) was added next,. This treatment showed successful results to in reducing the interstitial phosphorus content by 70-85%, compared to per treatment levels. Laboratory experiments with sediments from White Lough, N.Ireland, evidenced, that a dosage of 61 gN m^{-2} suppressed the phosphorus release completely. Foy (1986) showed

that the ferric chloride and calcium hydroxide addition was not necessary in White Lough sediments , reasoning the naturally occurring iron in lake sediment was adequate.

Sörensen (1982) and Tirèn & Pettersson (1985) showed a release of phosphorus after NO_3^- is depleted in some sediments treated with nitrate. Sörensen (1982) suggested that iron can be reduced also by bacteria, which utilize iron(III) as electron acceptor during anaerobic respiration (Fig.7). Tirén and Pettersson (1985) further showed that addition of NO_3^- to sediments of some lakes could directly increase the phosphorus release. This is due to an oxygen depleted sediment leads to a stimulation of the mineralization process if a major part of the nutrient is dissimiltorily reduced. Tsicritsis and Mourkides (1988) showed that addition of NO_3^- cannot inhibit the release of phosphorus in shallow lakes when the lack of thermal stratification layer and the result of mixing of the water results distribution of NO_3^-through the water column.

PART B

5. PHOSPHATE RELEASE EXPERIMENTS.

5.1 INTRODUCTION

One of the aims of this work is to perform some laboratory experiments to study the inactivation efficiency of iron salts in both oxic and anoxic conditions and to determine the optimal dose. To achieve this goal, a series of release experiments were carried out using continuous flow reactors, giving different doses of ferric chloride. Oxic and anoxic conditions were simulated along with each dosages.

The second objective was to compare different chemicals. This was done in batch experiments using sediment samples mixed with some inactivation agents reported in literature (eg. Al, NO_3^-). Sediment samples treated with $FeCl_3$ doses, equivalent to the continuous flow experiments were also included to this batch experiment setup. The aim of this approach was to compare the relevant inactivation efficiency of iron with aluminum, both in aerobic and anaerobic conditions and to study the effect of biological oxidation of sediment on P release.

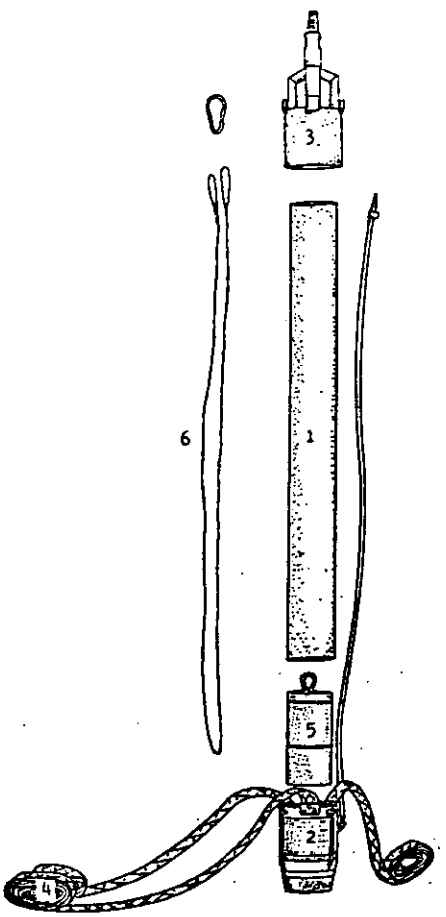
5.2 MATERIALS AND METHODS.

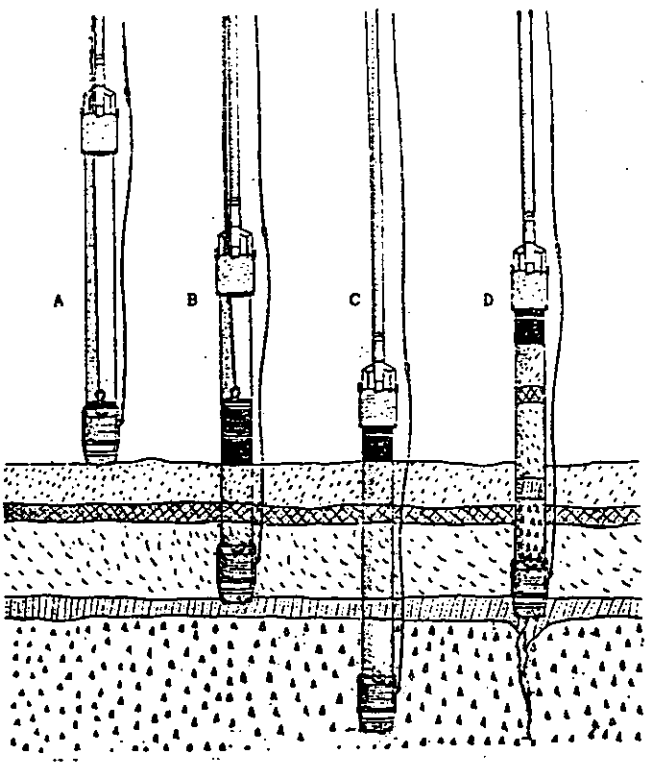
SEDIMENT SAMPLE

Undisturbed sediment samples were collected from one station in the lake area in the polders Wormer, Jisp and Neck, for all experiments using a Beekers sampler (Fig.19). Sediment cores were transported to the laboratory and stored at 4^0C until experiments were started.

Table 8. Chemical characters of lake water

Constituent		Concentration (mg/L)
Calcium	(Ca)	59
Magnesium	(Mg)	11.1
Sodium	(Na)	75
Potassium	(K)	7.1
Sulphate	(SO_4)	72
Chloride	(Cl^-)	129
Bicarbonate	(HCO3)	132





BEEKERS SAMPLER.

1. Sampling tube.
2. Cutter head.
3. Sampler head.
4. Fixing tie.
5. Plunger.
6. Plunger cable.

REAGENTS USED

Table 9.

Solution	Strength	Preparation
1 Ferric Chloride	10gFe^{3+}/L	48.4g Ferric Chloride hexahydrate in 1L demineralized water
2 Calcium nitrate	8gNO^{3-}-N/L	16.87g Calcium Nitrate tetrahydrate in 1L demineralized water
3 Aluminum sulphate	1gAl^{3+}/L	3.08g Aluminum sulphate octadecahydrate in 1L demineralized water
4 Sodium aluminate	0.5gAl^{3+}/L	10% NaOH soln. was added to a 100ml of aluminum sulphate solution in a 200mL volumetric flask until all precipitate was dissolves and then make up to the mark with demineralized water
5 Sodium Hydroxide	~10%	10g NaOH in 1L demineralized water

Table.10 Recipe for preparing 1.0L Synthetic Water
(Amounts were calculated using the BASIC computer programme given in appendix 2)

Compound	Amount (mg)
Calcium Chloride	162.3
Magnesium Sulphate	113.5
Potassium Chloride	13.5
Sodium Sulphate	93.3
Sodium Bicarbonate	182.6
Sodium Chloride	29.3

5.3 CONTINUOUS FLOW EXPERIMENTS.

RELEASE REACTOR

Schematic diagram of continuous flow reactor is given in Fig.20. Sediments were treated according to the scheme given in table 11.

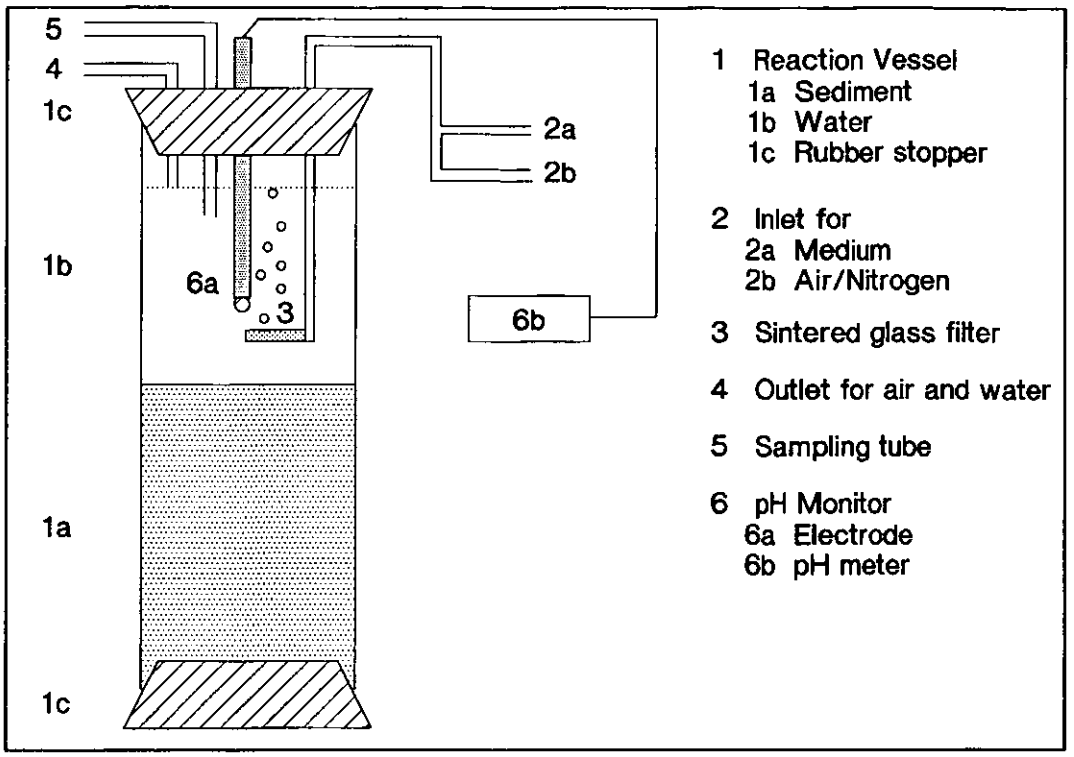


Fig. 20 : Schematic Diagram of Continuous Flow Reactor

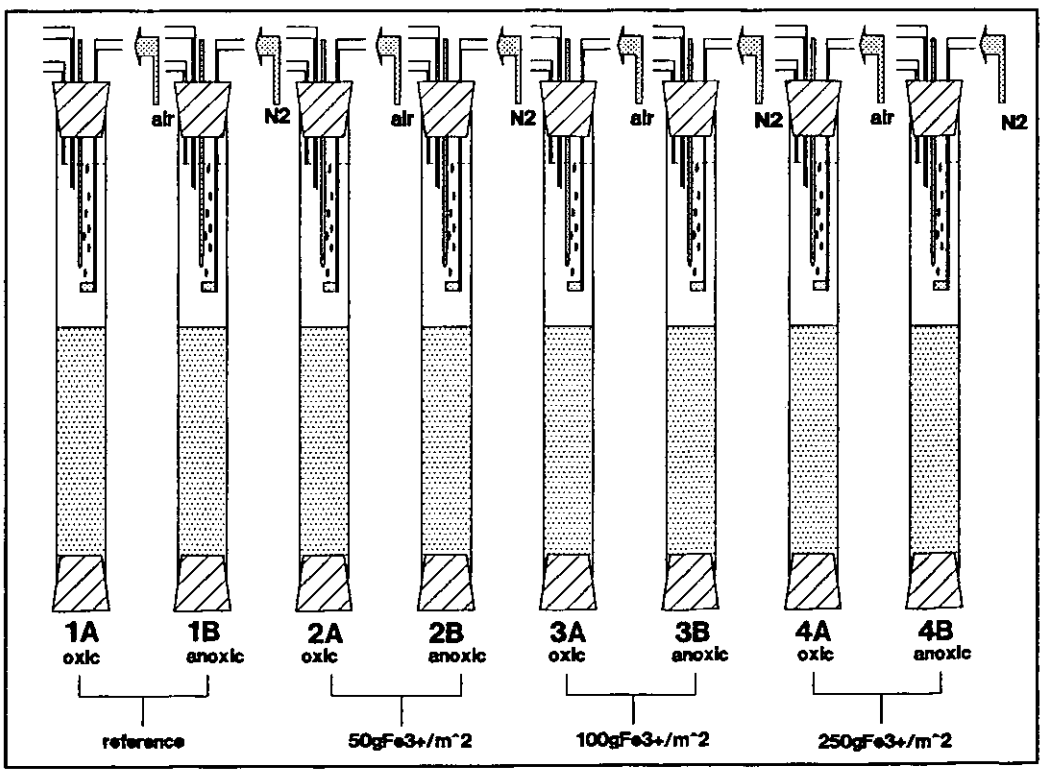


Fig. 20(b) : Chemical Treatment Scheme
(Continuous Flow Reactors)

Table.11 Sediment treatment scheme

Sediment core	Chemical treatment	Redox condition	Amount $FeCl_3$ soln. added (10gFe3+/L)
1A	none	oxic	-
1B	none	anoxic	-
2A	$50gFe^{3+}/m^2$	oxic	25ml
2B	$50gFe^{3+}/m^2$	anoxic	25ml
3A	$100gFe^{3+}/m^2$	oxic	50ml
3B	$100gFe^{3+}/m^2$	anoxic	50ml
4A	$250gFe^{3+}/m^2$	oxic	125ml
4B	$250gFe^{3+}/m^2$	anoxic	125ml

The upper 20cm of sediment cores No. 1A & 1B were combined in a large glass beaker and stirred to obtain a homogeneous and identical sample for oxic and anoxic release experiments. After mixing, the pH of the mixture was measured. Mixture was then returned back to the initial columns in two equal portions and allowed to settle.

In the same way sediment for cores No. (2A,2B), (3A,3B) and (4A,4B) two sediment samples were combined separately in large glass beakers and stirred with 25ml, 50ml, and 125ml of $FeCl_3$ solution ($10gFe^{+3}/L$) respectively. After measuring the pH, the mixtures were returned back to initial columns and allowed to settle.

After two days, the eight sediment cores were installed in continuous flow reactors (Fig.2(b)). Artificial lake water (Table.10) with ion composition similar to that of lake water (Table.8) was used to continuously replace the overlying water using Gilson Minipulse 2 peristaltic pump. The residence time of water was 1.5 days and was checked regularly. The purpose of this flushing is to prevent build-up of high phosphorus concentration in the overlying water, which may decrease the

release rates. In the lakes, such a build-up is prevented by consumption of the released phosphorus by the phytoplankton (Boers 1986).

The water of release reactors 1A, 2A, 3A and 4A was aerated by bubbling with air at a rate of $0.8 L h^{-1}$. Nitrogen gas (Technical grade) was bubbled through the water of reactors 1B, 2B, 3B and 4B in order to simulate anaerobic conditions in the overlying water.

The overlying water was sampled 5 times a week and filtered immediately over a 0.45μm filter and analyzed for soluble reactive phosphate. the pH and the dissolved oxygen content (D.O) of the overlying water and the pH of the sediment were measured regularly.

Phosphorus release rates of continuous flow reactors were calculated using following mass balance equation.

$$F = [\{(P_{n+1} - P_n) / (t_{n+1} - t_n)\} + \{(P_{n+1} + P_n) / 2R \} h$$

where F = Phosphorus flux across sediment-water interface (mg P/m^{-2} d^{-1}).

P_{n+1}, P_n = SRP concentration of the overlying water at time t_{n+1} and t_n (mg $P\ m^{-3}$).

t_n, t_{n+1} = Successive SRP determination days (d)

R = Water residence time (d)

h = Height of the water column of release reactors(m)

Dry weight, organic matter, total phosphorus, total iron and organic and inorganic carbon content of raw sediment were also determined.

5.4 BATCH EXPERIMENTS.

The upper 20cm fragment of two sediment cores were mixed in a erlenmeyer flask and used as a bulk sediment for all batch experiments. $50cm^3$ portions were transferred to 250mL erlenmeyer flasks and treated according to the scheme given in table 12.

Table.12. Experimental conditions and scheme of sediment treatment for batch experiment.

Sediment		Treatment g/m^2	Redox status	Amount reagent added
1	A1	none	oxic	-
2	B1	none	anoxic	-
3	A2	50 Fe^{+3}	oxic	1.25mL $FeCl_3$ soln
4	B2	50 Fe^{+3}	anoxic	1.25mL $FeCl_3$ soln
5	A3	100 Fe^{+3}	oxic	2.50mL $FeCl_3$ soln
6	B3	100 Fe^{+3}	anoxic	2.50mL $FeCl_3$ soln
7	A4	250 Fe^{+3}	oxic	6.25mL $FeCl_3$ soln
8	B4	250 Fe^{+3}	anoxic	6.25mL $FeCl_3$ soln
9	A5	50 Fe^{+3} +140(NO3-N)	oxic	1.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
10	B5	50 Fe^{+3} +140 (NO3-N)	anoxic	1.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
11	A6	100 Fe^{+3}+140 (NO3-N)	oxic	2.50mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
12	B6	100 Fe^{+3}+140 (NO3-N)	anoxic	2.50mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
13	A7	250 Fe^{+3}+140 (NO3-N)	oxic	6.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
14	B7	250 Fe^{+3}+140 (NO3-N)	anoxic	6.25mL $FeCl_3$ +4.38mL $Ca(NO_3)_2$
15	A8	50 Al^{3+}	oxic	6.25ml $Al_2(SO_4)_3$
16	B8	50 Al^{3+}	anoxic	6.25ml $Al_2(SO_4)_3$
17	A9	100 Al^{3+}	oxic	12.5ml $Al_2(SO_4)_3$
18	B9	100 Al^{3+}	anoxic	12.5ml $Al_2(SO_4)_3$
19	A10	none	oxic	-
20	B10	none	anoxic	-
21	A11	25 Al^{3+}	oxic	6.25ml $Al_2(SO_4)_3$
22	B11	50 Al^{3+}	anoxic	12.5ml $Al_2(SO_4)_3$
23	A12	125 Al^{3+}	oxic	31.25ml $Al_2(SO_4)_3$
24	B12	25 Al^{3+}	anoxic	3.125ml $Al_2(SO_4)_3$ +6.25ml $NaAl(OH)_4$
25	A13	50 Al^{3+}	anoxic	6.25ml $Al_2(SO_4)_3$ +12.5ml $NaAl(OH)_4$
26	B13	125 Al^{3+}	oxic	15.625ml $Al_2(SO_4)_3$ +31.25ml $NaAl(OH)_4$

25, 50, and 125 g Al^{3+}/m^2 treatment is equal to 50, 100, and 250 g Fe^{3+}/m^2 treatment.

Samples were shaken, after addition of appropriate amounts of inactivant and then made up to the mark of 200mL with synthetic lake water (Table.3) . pH of the mixture was measured.

Sample No: B1-B26 were incubated in an anaerobic chamber of room temperature (20^0C). This chamber was purged with technical grade nitrogen gas. The oxygen concentration inside the chamber was less than $0.1mgL^{-1}$. Samples No: A1-A26 were incubated at room temperature. After one week of incubation, 50mL of overlying water was taken away by means of a pipet and filtered immediately on 0.45 μm Milipore filter and analyzed for SRP. On the same day 140g $(NO3-N)m^{-2}$ (i.e. 4.38mL of 8g NO3-N/L solution) was added to flasks No. A5, B5, A6, B6, A7, AND B7 in order to study the effect of biological oxidation of sediment on P release in anaerobic conditions. After another week of incubation the overlying water was sampled and analyzed for SRP.

Table 13.

Analytical Techniques and Equipment

	Parameter	Instrument	Technique	Detection limit	Interferences	Reference
1.	SRP of water	Technicon AA2 Auto Analyzer	Automated Ascobic acid reduction method	1ug/L	* No influence up to 50mg/L iron * Salts concentration up to 20%(w/v) cause an error lessthan 1%	Standarded methods APHA-AWWA-WPCF 1981
2.	Total iron of sediment	Varian Spectra 400 (Atomic Absorption Spectro photometer)	i. Freeze dried sample destructed with HCL/HNO3 ii. AAS-Flame	0.014 mg/L	Alkali metals	Anderson, 1976
3.	Inorganic carbon content of the sediment	NA 1500 Carlo Frba	i.Freeze dried sample ii.Ignition with Tin iii.Gas Chromatographic analysis of CO2 (Column : Porpack)	0.08%		

6. RESULTS AND DISCUSSION.

6.1. GENERAL.

Some chemical and physical parameters of the sediment are given in tables (14).

Table (14).
Chemical and physical parameters of sediment

Parameter	
total iron	13.5 g/Kg
dry wt.	6.4%
LOI	70.3%
pH	7.3
colour	black
sediment type	peaty
organic carbon	35.1%
inorganic carbon	4.1%

6.2. CONTINUOUS RELEASE EXPERIMENTS.

6.2.1 pH.

Fig (21) and (22) illustrate variation of pH in the sediment and the water phase of continuous phosphorus release reactors.

pH of the sediment was reduced substantially, when it was mixed with acidic FeCl3 solution (pH of the bulk FeCl3 solution was 1.3). Two days after mixing pH of the lowest two dosages (col. 2A, 2B, 3A, and 3B) was improved very close to the original sediment pH (i.e. 7.3). The pH of the highest dosed columns (4A and 4B), however, remained at a low value(~ 5.5).

Recovery of pH of the sediment, after mixing with $FeCl_3$ or any other acidic solution is depending on the buffering capacity of the sediment. The buffering system in the sediment is the $CaCO_3/HCO_3^-$ system.

When $FeCl_3$ is added to water it undergoes various hydrolysis equilibrium reactions (section 4.4.2). The end result is:

$$FeCl_3 + 6H_2O \rightleftharpoons Fe(H_2O)_6(OH)_3 + 3Cl^- + 3H^+$$

Liberated H^+ ions can be neutralized by $CaCO_3$ in the sediment.

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$

This means that, apart from the initial pH of the sediment, the amount of $CaCO_3$ present in the sediment dictates the pH after mixing with acidic $FeCl_3$. As these proton transfer reactions are very fast (half lives less than milli seconds, Stumm and Morgen, 1981), one can expect the equilibrium to be reached within a short period. The pH data of the sediments of release reactors show an equilibrium time of a few days. This may be due to the availability of $CaCO_3$ and the exchange of the CO_2 produced with the atmosphere.

6.2.2 RELEASE RATES.

Phosphorus release rates of continuous flow reactors,which were calculated using the mass balance equation described in section 5.3 are given in appendix 3.

Fig 23 (a), (b),and (c) illustrate the variation of phosphorus release rates with time. Average (time weighted) phosphorus release rates of each reactor was calculated by dividing, the total amount of phosphorus released from the column by the duration of the experiment. The results are given in table 15.

Table 15. Average phosphorus release rates of continuous flow reactors

column No:	Condition	P release rate (mgP/m^2.d)	D.O (in water) mg/L
1A	Reference(oxic)	5.01	8.8
1B	Reference(anoxic)	9.33	0.6
2A	50mgFe/m^2(oxic)	1.12	8.7
2B	50mgFe/m^2(anoxic)	8.76	0.7
3A	100mgFe/m^2(oxic)	0.94	8.8
3B	100mgFe/m^2(anoxic)	1.67	0.6
4A	250mgFe/m^2(oxic)	0.60	9.0
4B	250mgFe/m^2(anoxic)	0.57	0.6

The anoxic phosphorus release from the reference column is about 2 times higher than that from the oxic reference column (Fig 24). There is no large difference in release rates of reference anoxic column (1B) and 50gFe/m^2 treated anoxic column (2B). However, 100gFe/m^2 and 250gFe/m^2 treatment suppressed the anaerobic phosphorus release by about 82% and 94%, relative to the reference anoxic phosphorus release.

All oxic columns showed lower phosphorus release rates compared to the corresponding anoxic columns except the two highest dosed columns. These columns (4A and 4B), showed no significant difference.

The phosphorus release reduction in iron treated oxic columns are about 78%, 81%, and 88%, compared to the oxic reference column.

6.3. BATCH EXPERIMENTS.

pH and SRP concentrations of batch experiments are given in table.16. The pH variation of FeCl3 treated flasks showed the same pattern as the continuous release experiments. Higher aluminum sulphate doses gave slightly lower pH values than corresponding FeCL3 doses. However, the 50%AlSO4 + 50%NaAL(OH)4 treatment did not make any adverse pH changes.

The O-PO_4 concentrations of the overlying water of flasks can be considered as equilibrium concentrations of the relevant experimental condition.

The high equilibrium concentrations found in non treated flasks indicate the presence of high amounts of releasable P in the sediment. The average equilibrium concentration of non treated anoxic flasks is about 5 times as high as those of the non treated oxic flasks. This indicates the possibility of redox mediated phosphorus release.

Table No 16

Results of batch experiments

Flask Number	Condition	Treatment	Initial pH	pH after one week	pH after two weeks	O-PO4 Concentration ug/L after one week	O-PO4 Concentration ug/L after two weeks
A1	oxic	none	7.39	7.65	7.65	248.00	304.00
A10	oxic	none	7.20	7.60	7.75	170.00	322.00
B1	anoxic	none	7.42	8.34	8.95	1,032.00	1,819.00
B10	anoxic	none	7.19	8.10	8.15	1,937.00	1,640.00
A2	oxic	50gFe3+/m^2 (as FeCl3)	6.50	7.39	7.55	13.00	22.00
A5	oxic	50gFe3+/m^2 (as FeCl3)	6.09	7.27	6.39	11.00 +140g NO3	21.00
B2	anoxic	50gFe3+/m^2 (as FeCl3)	6.53	8.16	8.62	144.00	356.00
B5	anoxic	50gFe3+/m^2 (as FeCl3)	6.38	8.22	7.94	241.00 +140g NO3	15.00
A3	oxic	100gFe3+/m^2(as FeCl3)	6.10	7.15	7.40	30.00	33.00
A6	oxic	100gFe3+/m^2(as FeCl3)	5.91	7.07	6.39	32.00 +140g NO3	10.00
B3	anoxic	100gFe3+/m^2(as FeCl3)	5.84	7.45	7.96	56.00	23.00
B6	anoxic	100gFe3+/m^2(as FeCl3)	5.97	7.89	7.67	47.00 +140g NO3	21.00
A4	oxic	250gFe3+/m^2(as FeCl3)	4.75	3.65	3.75	8.00	11.00
A7	oxic	250gFe3+/m^2(as FeCl3)	4.85	3.47	4.32	19.00 +140g NO3	19.00
B4	anoxic	250gFe3+/m^2(as FeCl3)	4.72	6.62	6.72	10.00	8.00
B7	anoxic	250gFe3+/m^2(as FeCl3)	4.91	6.86	6.60	17.00 +140g NO3	19.00
A11	oxic	25gAl3+/m^2 (as AlSO4)	6.50	7.50	7.90	30.00	110.00
B12	anoxic	25gAl3+/m^2 (as AlSO4 + NaAl(OH)4)	7.04	7.90	8.25	199.00	248.00
A8	oxic	50gAl3+/m^2 (as AlSO4)	5.56	6.73	6.73	9.00	19.00
A13	oxic	50gAl3+/m^2 (as AlSO4 + NaAl(OH)4)	6.98	7.80	8.01	9.00	33.00
B11	anoxic	50gAl3+/m^2 (as AlSO4)	5.78	7.20	7.86	36.00	56.00
B8	anoxic	50gAl3+/m^2 (as AlSO4)	5.54	7.41	7.55	13.00	16.00
A9	oxic	100gAl3+/m^2(as AlSO4)	4.31	4.56	4.35	9.00	12.00
B9	anoxic	100gAl3+/m^2(as AlSO4)	4.43	5.35	5.21	8.00	33.00
A12	oxic	125gAl3+/m^2(as AlSO4)	4.43	4.50	4.66	11.00	24.00
B13	anoxic	125gAl3+/m^2(as AlSO4 + NaAl(OH)4)	6.85	7.30	8.23	20.00	20.00

The results of the iron treated flasks are in well agrement with iron treated continuous flow experiments. All iron treated oxic flasks showed low P release in comparison to the non treated oxic flasks, and only the anoxic flasks treated with 50 gFe^{3+}/m^2 had a high P release compared to the other iron treated anoxic flasks. The addition of NO_3^- showed a significant reduction of equilibrium concentration in oxic the 50 gFe^{3+}/m^2 treated flask. There was no such a remarkable effect on NO_3^- addition to 100 and 250 gFe^{3+}/m^2 treated flasks.

One reason for this is that the P release of these flasks were already hindered by high doses of iron. This result is in well agreement with Foy (1986). Ripl (1976) proceeded the addition of nitrate by inputs of ferric chloride and lime in order to improve the phosphate binding capacity of the sediment. Foy (1986) showed that there it was not necessary to add iron to a lake sediment, before treatment with nitrate, if there is enough iron to cope with phosphate.

The reduction of P release under oxic conditions by iron treatment can be explained by the classical iron/phosphate model. The pH of the overlying water of the continuous release reactors and the batch experiment reactors is between 7 and 9. In this pH range the predominant, dissolved hydroxoiron complexes are the $Fe(OH)_2^+$ and $Fe(OH)_4^-$. Also iron(III) has it's solubility minimum in this pH range and the dominant species is ferric hydroxide. In such a situation P release from the sediment is hindered by the adsorption of phosphates on iron-hydroxide gels.

High P release under anaerobic reference column and iron treated (50 gFe^{3+}/m^2) anaerobic column are explained as follows. In reduced conditions iron(III) phosphate-hydroxy complexes in the sediment will be solubilized as iron(II) and phosphate. This mechanism results in a high P release in the reference anoxic column.

The formed iron(II) can react with phosphate for the formation of ferrous phosphate (vivianite, $Fe_3(PO_4)_2.8H_2O$). Several other compounds also exert a demand for ferrous iron,

examples being the carbonate and sulfide ions, oxygen and organic complexing agents (Singer 1972).

$Fe^{2+} + PO_4^{3-} \longrightarrow Fe_3(PO_4)_2(s)$, Vivianite $\log K_{so} = -29.9$
$Fe^{2+} + S^{2-} \longrightarrow FeS(s)$, $\log K_{so} = -18.1$
$Fe^{2+} + CO_3^{2-} \longrightarrow FeCO_3(s)$, Siderite $\log K_{so} = -10.7$
(Singer, 1982; Stumm and Morgan, 1981)

The solubility product of vivianite, FeS, and siderite shows that the precipitation of FeS and siderite takes place before vivianite, in a system containing Fe^{2+}, PO_4^{3-}, S^{2-} and CO_3^{2-}. The chemical reaction for sulphate reduction can be written as:

$$2CH_2O + SO_4^{2-} + 2H^+ \longrightarrow 2CO_2 + H_2S + 2H_2O$$

and the Fe(III) reduction as:

$$CH_2O + 4FeOOH + 8H^+ \longrightarrow CO_2 + 4Fe^{2+} + 7H_2O$$

The combination of these two reactions explain the overall reaction of Fe(III) reduction, sulphate reduction and burial of FeS:

$$9CH_2O + 4SO_4^{2-} + 4FeOOH + 8H^+ \longrightarrow 9CO_2 + 4FeS + 15H_2O$$

Inorganic sulphur may be barred in forms other than FeS. For example FeS can further react with H_2S to form FeS_2 (Pyrite). However, in fresh water sediments, because of low SO_4^{2-} concentrations, the FeS minerals are not converted to pyrite. Consequently, Fe^{2+} can barred in fresh water sediments as ferrous sulfide minerals, vivianite and/or siderite (Berner 1980).

This means that the inhibition of the P release in anoxic conditions, is depending on the amount of SO_4^{2-} present and the degree of sulphate reduction and the amount of sulfide generated due to the mineralization of organic matter.
In other words, the formation of ferrous phosphate ($Fe_3(PO_4)_2$) is possible only if the amount of Fe^{2+} present in the system exceed the stoichiometric need for the above reaction.

This explains the P release reduction in high iron dosed columns and flasks. The reason for high anoxic P release observed in the 50 gFe^{3+}/m^2 treatment, could be the inadequacy of Fe^{2+} present in the sediment to satisfy the competitors for PO_4^{2-}.

6.4 GENERAL REMARKS ON THE TREATMENT OF LAKE SEDIMENTS WITH IRON.

1. The results of release experiments shows that sediments treated with iron (100 gFe^{3+}/m^2 and above), efficiently reduce the P release, even in anoxic conditions. However, the sudden pH changes, which could be taken place as a result of mixing the sediment with acidic $FeCl_3$ solutions must be considered before applying $FeCl_3$ to lake sediments.

The substantial decrease in pH with higher doses of $FeCl_3$ could cause undesirable effects to the aquatic eco-system. To get more insights on this problem a series of laboratory experiments should be carried out to establish the relationship between the P inactivation efficiency, $FeCl_3$ dose, pH changes, and the $CaCO_3$ content, etc. in the sediment.

2. The major drawback for the failure of alum application of shallow lakes is the dispersion and redistribution of flocks due to mixing of lake water. This will also be true for the iron treatment, if the $FeCl_3$ is applied on the surface of the lake water. Mixing of the sediment with $FeCl_3$ solution is a good alternative to overcome this problem.

The proposed lake treatment based upon this research is carrying out by mixing the sediment with a solution of $FeCl_3$. The upper 20cm sediment layer of the lake Groot Vogelenzang is proposed to be treated with commercially available 40 $FeCl_3$ solution.

3. Attention must be paid to the amounts of heavy metals present in the ferric chloride solution before applying it to the lake eco-system. Chemical specifications of, two commercially available ferric chloride solutions and calculated maximum concentrations of heavy metals, which could be incorporated into the lake water, as a result of the addition of

$FeCl_3$ to the lake sediment are given in table 16. (Lake depth = 1.5m, Treatment = 100 gFe^{3+}/m^2). It is assumed that all the heavy metals which is present in the ferric solution could be released to the lake water.

Table 16.

Heavy metal	Dutch Norm (µg/L)		A	B	C
	dissolved	total			
SIDERA (dut)					
Cd	0.04	0.2	1	0.34	1.7
Cr	4	36	50	17.1	0.475
Cu	2	4.7	50	17.1	0.275
Ni	11	14	50	17.1	0.819
Hg	0.008	0.05	0.1	0.034	0.68
Zn	10	42	100	34.2	0.814
Pb	2	38	50	17.1	0.450
SIDRA (belg)					
As	19	24	1	0.34	0.014
Cd	0.04	0.2	0.5	0.17	0.85
Hg	0.008	0.05	0.01	0.0034	0.065
Pb	2	38	3	1.03	0.027
Cr	4	36	50	17.1	0.475
Ni	11	14	20	6.84	0.48

A = Chemical specification of $FeCl_3$ solution (mg/L).
B = Maximum concentration which could be incorporated to the lake water, as a result of $FeCl_3$ application (µg/L).
C = A/norm (total)

4. Treatment cost (100 gFe^{3+}/m^2)

Chemicals	dfl	2000	per ha.
Labor and equipment	dfl	±3000	per ha.
Total	dfl	±5000	per ha.

5. The retardation of P release in anaerobic environments is explained by the formation of ferrous phosphate ($Fe_3(PO_4)_2$), and, high P release from sediments treated with low doses of iron salts or untreated sediments is explained by the formation of FeS and the inadequacy of Fe^{2+} to precipitate all S^{2-} and PO_4^{3}.

To demonstrate this, two sets of release experiments can be carried out. A first set of sediments gets different doses of ferric chloride and the release experiments runs for about 3 weeks. After that period a known amount of SO^{2-}_4 is injected to the sediment and the release experiments are carried out for another few weeks.The second set of release experiments is carried out with the same amounts of iron salts.

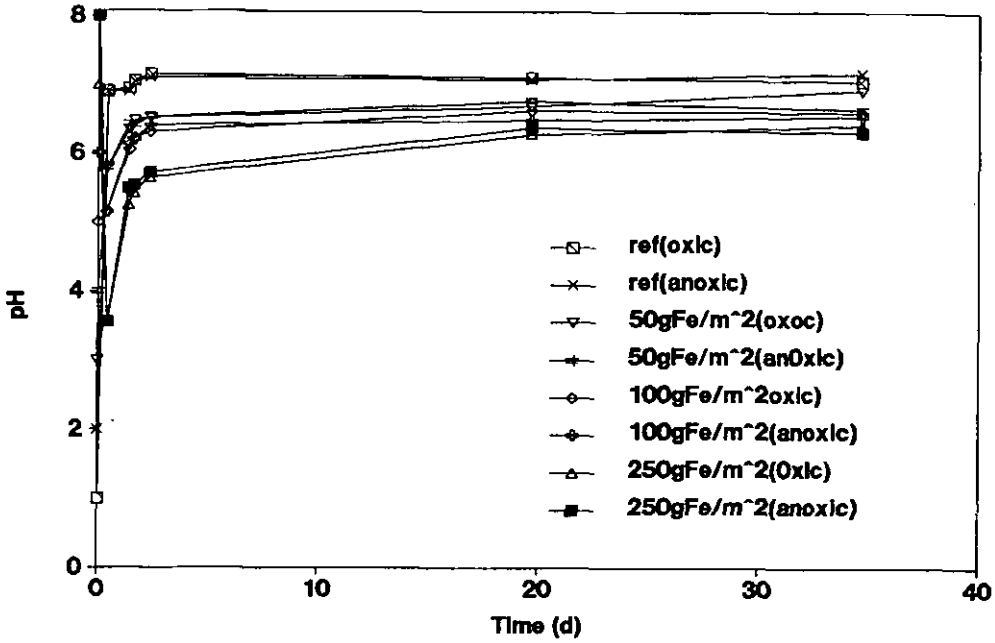


Fig. 21 (a): pH CHANGES IN THE SEDIMENT
(Continuous flow reactors)

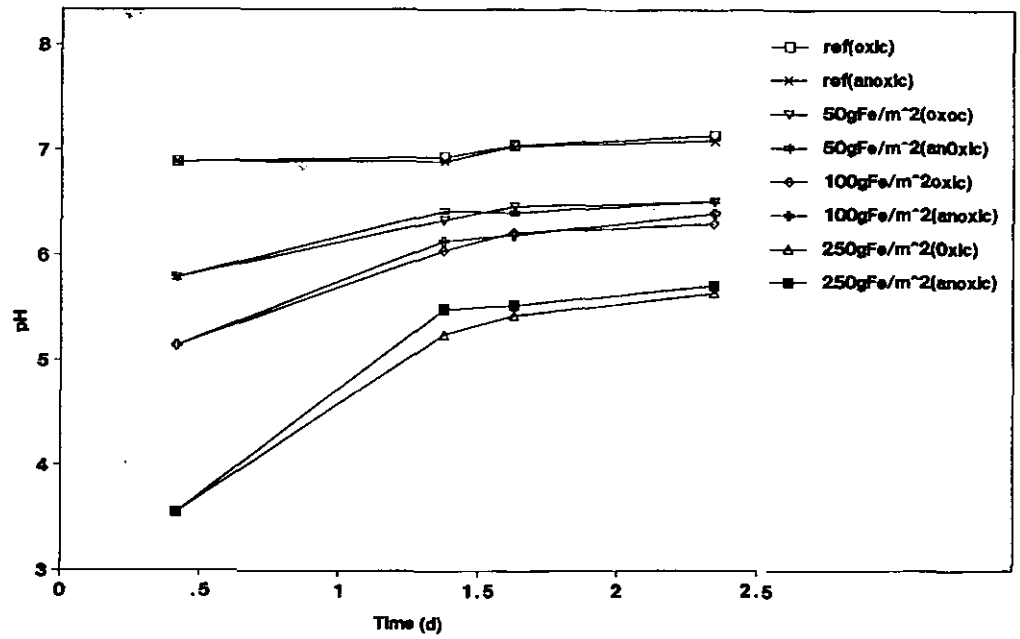


Fig. 21(b): pH changes in the sediment
(First 3 days after mixing with $FeCl_3$ solution)

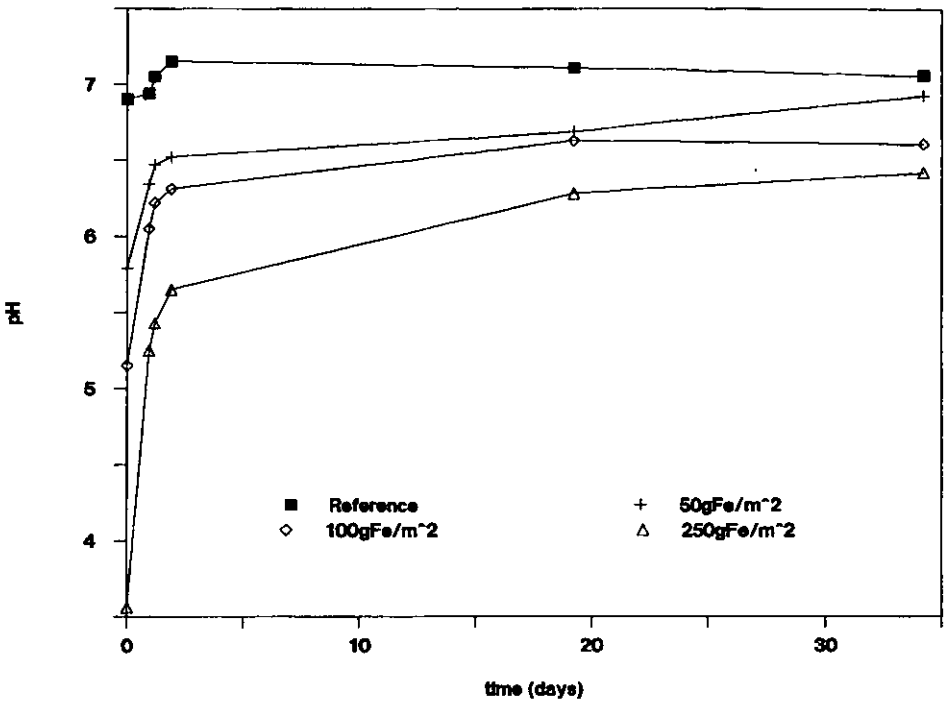


Fig. 21(c): pH changes in the sediment Oxic columns

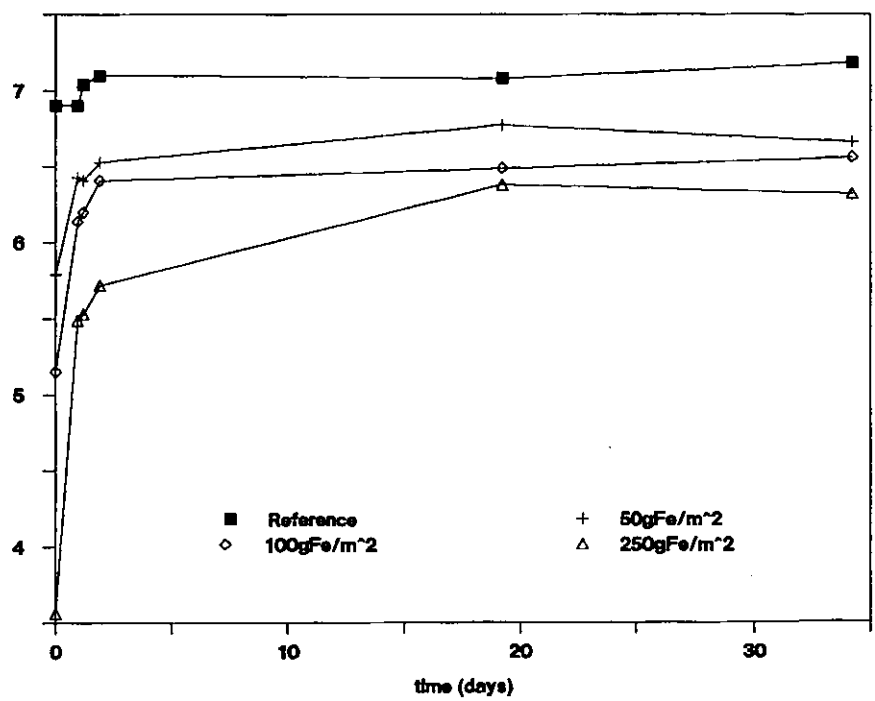


Fig. 21 (d): pH changes in the sediment Anoxic columns

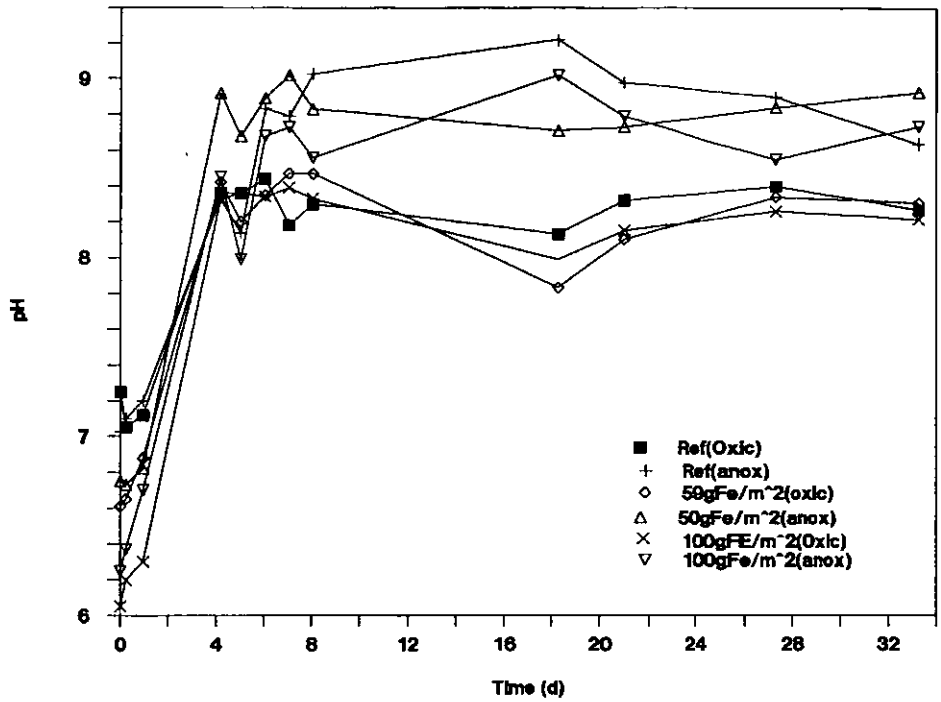


Fig. 22(a) : pH variations of release reactors
(Water phase, Column 1A, 1B, 2A, 2B, 3A, 3B)

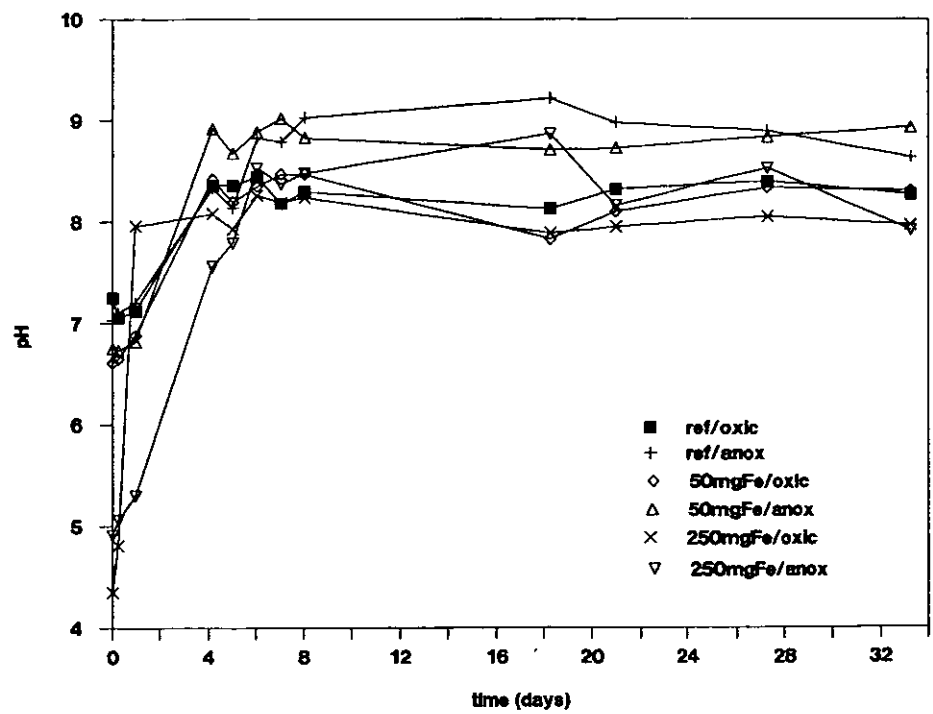


Fig. 22(b) : pH variations of release reactors
(Water phase Çolumn 1A, 1B, 2A, 2B, 4A, 4B)

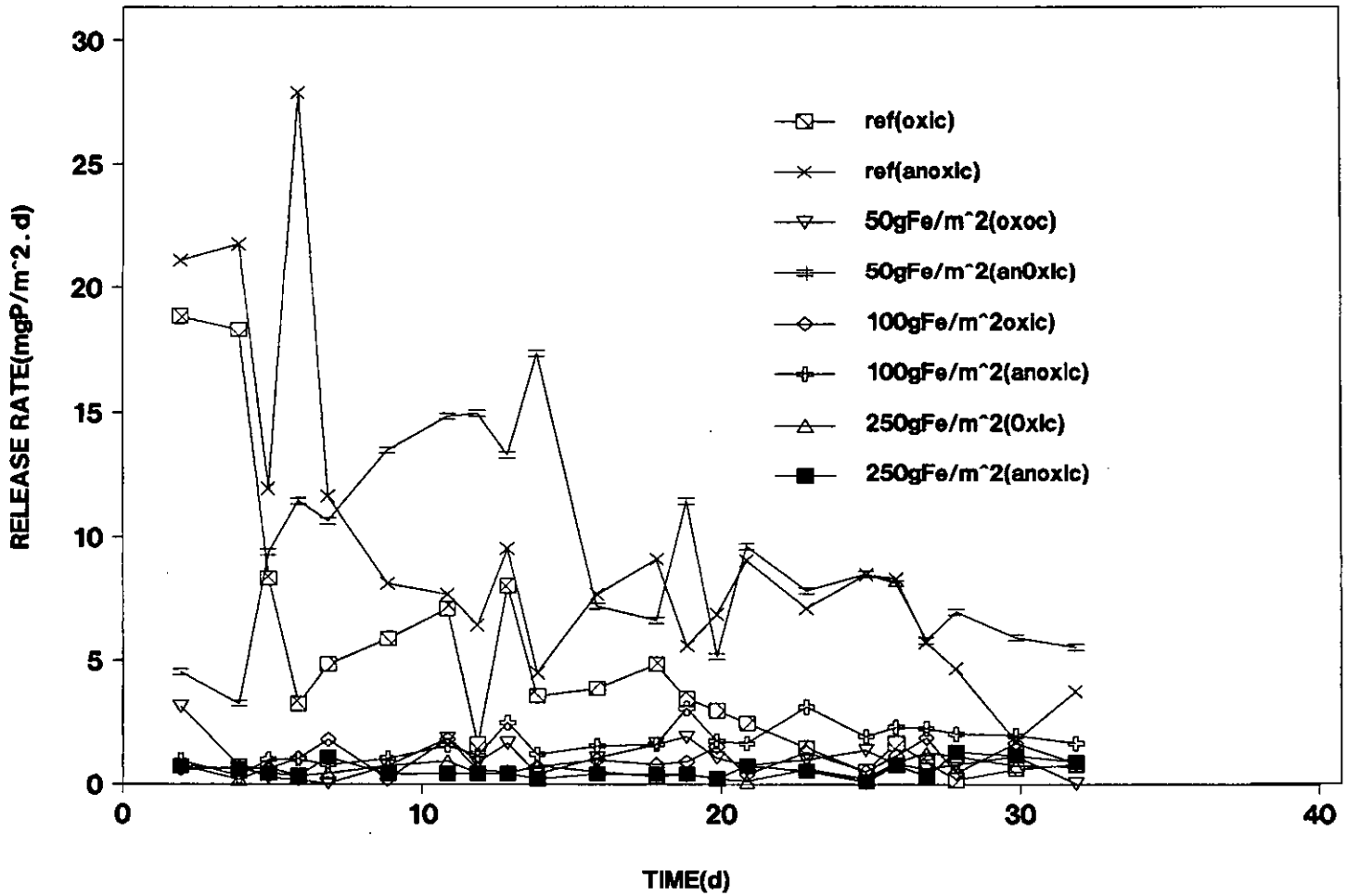


Fig. 23(a) : Variation of Phosphorus Release Rates With Time

(continus flow reactors)

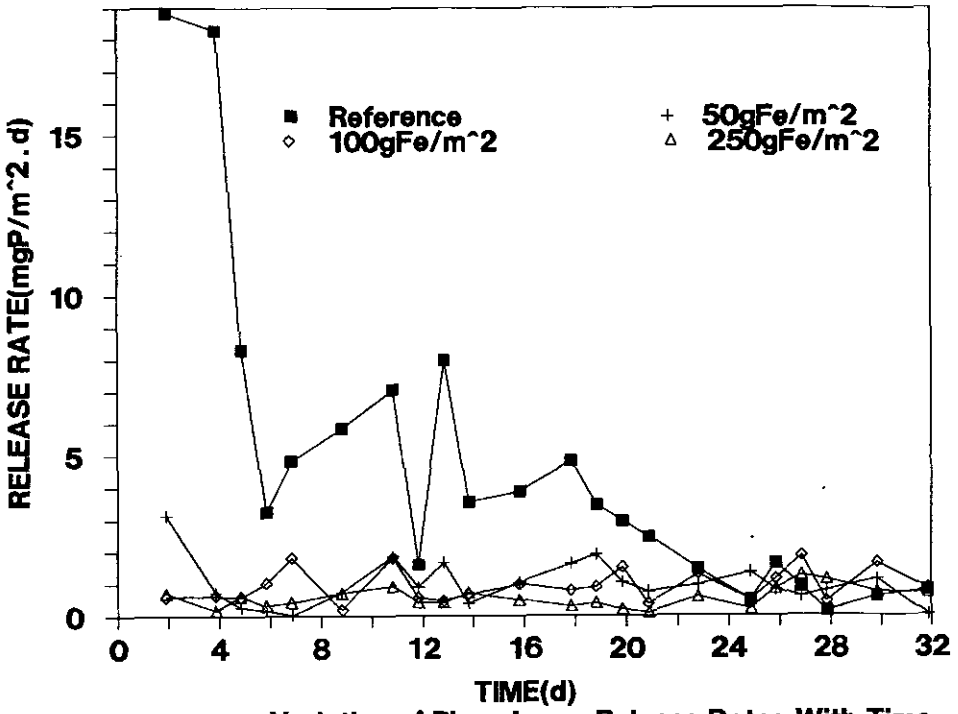


Fig. 23(b) : Variation of Phosphorus Release Rates With Time (continus flow reactors – oxic columns)

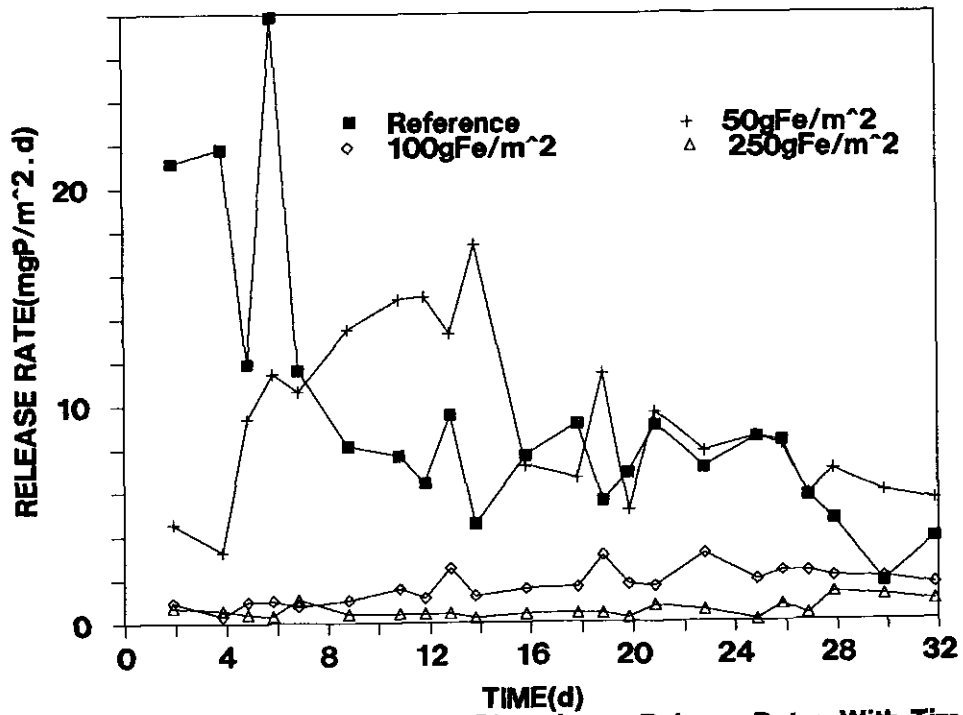
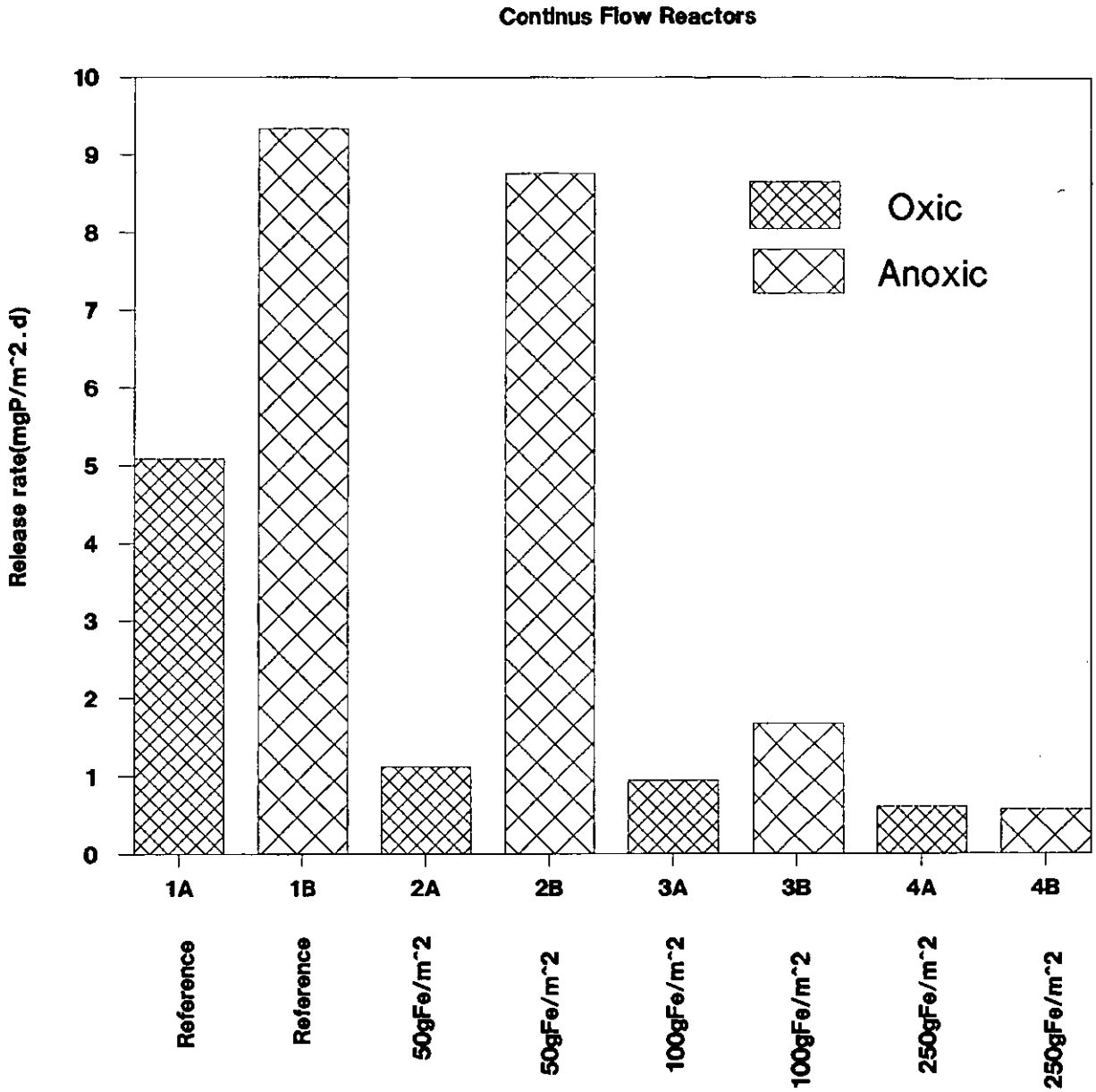


Fig. 23(c) : Variation of Phosphorus Release Rates With Time (continus flow reactors – anoxic columns)

Fig. 24 : **Average (time weighted) Phosphorus release rates**



7. CONCLUSIONS.

1. Aluminum salts can be used for the control of P release in deep lakes, subject to some restrictions. Most of the adverse effects do not exist if the pH of the treated lake water does not fall below 6. At this pH, harmful Al^{3+} species do not predominate and the dissolved Al concentration is less than 50 µg/L. That is the maximum acceptable Al concentration for drinking water. Aluminum salts should not be used for phosphorus inactivation in shallow lakes.

2. NO_3^- addition could cause some environmental damages due to the following reasons:

i). NO_3^- is a plant nutrient.

ii). NO_3^- addition could enhance the P release in sediments with high amounts of organically bound Phosphorus, by dissimilation.

iii). Iron bound phosphorus also can be released, when NO_3^- is depleted in the sediment. NO_3^- reducing bacteria can utilize iron(III) as an electron acceptor.

3. When comparing the three ferric chloride doses, on the basis of P inactivation efficiency and the initial pH change, the 100 gFe^{3+}/m^2 dose can be taken as a reasonable treatment for the sediment tested. This treatment suppressed the P release rate about 80%, both in oxic and anoxic conditions, compared to the corresponding non treated sediments. The pH reduction after mixing is only about 1.5 pH units from the initial sediment pH, and it also recovered within two days. There is no necessity to add NO_3^- to the sediment if a reasonable amount of iron is added to the sediment.

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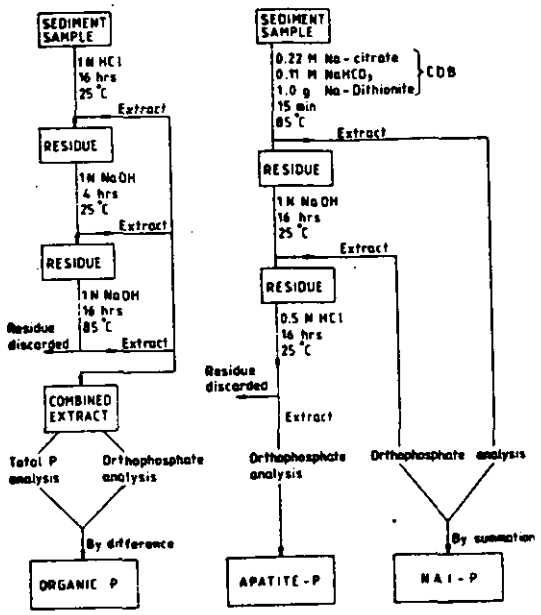
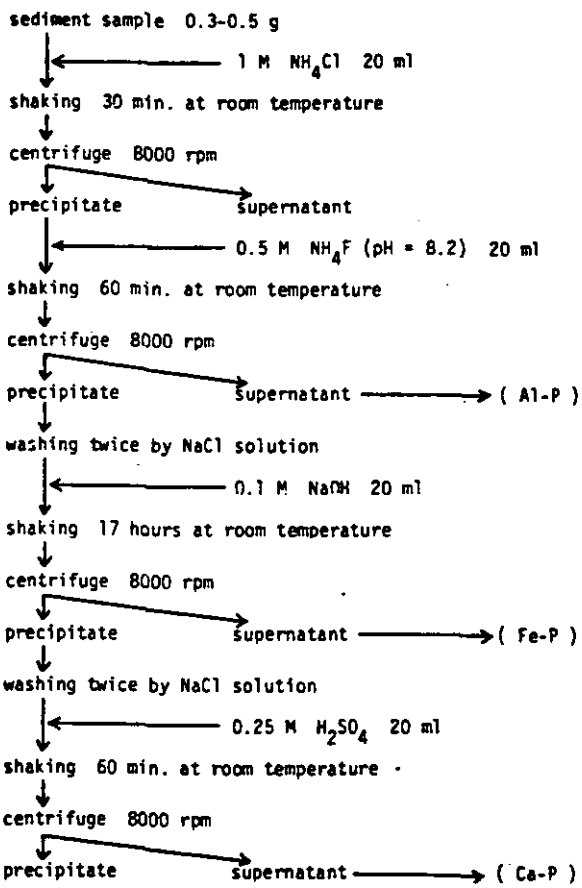
APPENDIX 1.



A. Outline of analytical procedure to determine apatite-P, NAI-P and organic-P. (source: Williams et. al. 1976, Modified)



B. Inorganic phosphorus fractionation in lake sediments (source: Hosomi, 1982)

APPENDIX 2.

Computer programme in BASIC for calculating the amounts of chemicals need for preparing artificial lake water.

```
10 REM RECIPE FOR PREPARING SYNTHETIC WATER
20 REM WRITTEN BY W.A.D.D.WIJESOORIYA
30 REM INPUT DATA
40 INPUT "Volume of synthetic water need, in L = ";N
50 PRINT:PRINT
60 LPRINT:LPRINT
70 INPUT "Give K concentration in lake water mg/L ";K
80 INPUT "Give Na concentration in lake water mg/L";NA
90 INPUT "Give Ca concentration in lake water mg/L";CA
100 INPUT "Give Mg concentration in lake water mg/L";MG
110 INPUT "Give Cl concentration in lake water mg/L";CL
120 INPUT "Give SO4concentration in lake water mg/L";SO4
130 INPUT "Give HCO3 mg/L,If unknown press ENTER ";HCO3
140 IF HCO3 = 0 THEN 150 ELSE 170
150 HCO3 = ((K/39.1)+(NA/23)+(CA*2/40)+(MG*2/24.3)-(CL/35.5)-(SO4*2/96))*61
160 IF HCO3 < 0 THEN GOTO 330 ELSE 170
170 REM CALCULATION
180 A = 110*CA/40
190 B = MG*248.48/24.3
200 C = K*74.56/39.1
210 E = HCO3*84/61
220 F = ((CL/35.5)-(A*2/110)-(C/74.56))*58.44
230 D = ((SO4/96)-(B/246.48))*322.19
240 G=A*N/1000
250 H=B*N/1000
260 I=C*N/1000
270 J=D*N/1000
280 L=E*N/1000
290 M=F*N/1000
300 REM OUTPUT PART
310 PRINT:PRINT:PRINT
320 LPRINT:PRINT
330 LPRINT "INPUT DATA"
340 LPRINT "----------"
350 PRINT "INPUT DATA"
360 PRINT "----------"
370 LPRINT:PRINT
380 LPRINT "K+ Concentration      =";K;"mg/L"
390 PRINT "K+ Concentration      =";K;"mg/L"
400 LPRINT "Na+Concentration      =";NA;"mg/L"
410 PRINT "Na+Concentration      =";NA;"mg/L"
420 LPRINT"Ca++ Concentration     =";CA;"mg/L"
430 PRINT"Ca++ Concentration     =";CA;"mg/L"
440 LPRINT"Mg++ Concentration     =";MG;"mg/L"
450 PRINT"Mg++ Concentration     =";MG;"mg/L"
460 LPRINT"Cl-  Concentration     =";CL;"mg/L"
470 PRINT"Cl-  Concentration     =";CL;"mg/L"
480 LPRINT"SO4= Concentration     =";SO4;"mg/L"
490 PRINT"SO4= Concentration     =";SO4;"mg/L"
500 LPRINT"HCO3-Concentration     =";HCO3;"mg/L"
510 PRINT"HCO3-Concentration     =";HCO3;"mg/L"
520 IF HCO3 < 0 THEN GOTO 920 ELSE 530
530 IF A<0 OR B<0 OR C<0 OR D<0 OR E<0 OR F<0 THEN GOTO 920 ELSE 540
540 LPRINT:PRINT
```

```
550 PRINT "AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER"
560 PRINT "-------------------------------------------"
570 LPRINT "AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER"
580 LPRINT "-------------------------------------------"
590 LPRINT:PRINT:PRINT
600 PRINT "Amount Calcium Chloride  =";A      ;"mg"
610 LPRINT "Amount Calcium Chloride  =";A      ;"mg"
620 PRINT "Amount Magnesium sulphate=";B      ;"mg"
630 LPRINT "Amount Magnesium sulphate=";B      ;"mg"
640 PRINT "Amount Potasium Chloride =";C      ;"mg"
650 LPRINT "Amount Potasium Chloride =";C      ;"mg"
660 PRINT "Amount Sodium Sulphate   =";D      ;"mg"
670 LPRINT "Amount Sodium Sulphate   =";D      ;"mg"
680 PRINT "Amount Sodium bicarbonate=";E      ;"mg"
690 LPRINT "Amount Sodium bicarbonate=";E      ;"mg"
700 PRINT "Amount sodium chloride   =";F      ;"mg"
710 LPRINT "Amount sodium chloride   =";F      ;"mg"
720 PRINT:PRINT
730 LPRINT:PRINT:PRINT
740 PRINT "RECIPE FOR PREPARING";N;"L SYNTHETIC WATER"
750 PRINT "-----------------------------------------"
760 LPRINT "RECIPE FOR PREPARING";N;"L SYNTHETIC WATER"
770 LPRINT "-----------------------------------------"
780 LPRINT:PRINT:PRINT
790 PRINT "Amount Calcium Chloride  =";G      ;"g"
800 LPRINT "Amount Calcium Chloride  =";G      ;"g"
810 PRINT "Amount Magnesium sulphate=";H      ;"g"
820 LPRINT "Amount Magnesium sulphate=";H      ;"g"
830 PRINT "Amount Potasium Chloride =";I      ;"g"
840 LPRINT "Amount Potasium Chloride =";I      ;"g"
850 PRINT "Amount Sodium Sulphate   =";J      ;"g"
860 LPRINT "Amount Sodium Sulphate   =";J      ;"g"
870 PRINT "Amount Sodium bicarbonate=";L      ;"g"
880 LPRINT "Amount Sodium bicarbonate=";L      ;"g"
890 PRINT "Amount sodium chloride   =";M      ;"g"
900 LPRINT "Amount sodium chloride   =";M      ;"g"
910 GOTO 960
920 PRINT:PRINT
930 LPRINT:PRINT
940 PRINT "ERROR: PLEASE CHECK INPUT DATA"
950 LPRINT "ERROR: PLEASE CHECK INPUT DATA"
960 END
```

```
INPUT DATA
----------

K+ Concentration      = 7.1 mg/L
Na+Concentration      = 75 mg/L
Ca++ Concentration    = 59 mg/L
Mg++ Concentration    = 11.1 mg/L
Cl-  Concentration    = 129 mg/L
SO4= Concentration    = 72 mg/L
HCO3-Concentration    = 132.5062 mg/L
```

```
AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER
-------------------------------------------

Amount Calcium Chloride  = 162.25 mg
Amount Magnesium sulphate= 113.5032 mg
Amount Potasium Chloride = 13.53903 mg
Amount Sodium Sulphate   = 93.27509 mg
Amount Sodium bicarbonate= 182.4676 mg
Amount sodium chloride   = 29.34957 mg

RECIPE FOR PREPARING 50 L SYNTHETIC WATER
-----------------------------------------

Amount Calcium Chloride  = 8.1125 g
Amount Magnesium sulphate= 5.675161 g
Amount Potasium Chloride = .6769515 g
Amount Sodium Sulphate   = 4.663755 g
Amount Sodium bicarbonate= 9.123377 g
Amount sodium chloride   = 1.467479 g
```

APPENDIX 3.

Phosphate Release Experiment : Column 1A

Condition:	reference oxic	INPUT DATA Vol. sampl	75.00	(ml)	Calculations
		Hight colu	15.00	(cm)	average release rate: 5.10
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	220.000	0	0.46			
4	9.40	221.000	550	3.39	1.93	18.8438	55.2750
5	8.40	192.000	190	4.35	3.87	18.3016	72.8140
6	8.45	135.000	183	5.35	4.85	8.3059	81.1372
7	8.45	82.000	183	6.35	5.85	3.2472	84.3844
8	8.45	64.000	183	7.35	6.85	4.8336	89.2180
11	8.30	58.000	680	10.35	8.85	5.8529	106.7400
12	8.30	65.000	170	11.35	10.85	7.0770	113.8170
13	8.30	41.000	170	12.35	11.85	1.5940	115.4110
14	8.30	61.000	170	13.35	12.85	7.9980	123.4090
15	8.50	49.000	170	14.35	13.85	3.5603	126.9990
18	8.05	40.000	650	17.34	15.84	3.8759	138.5540
19	8.30	44.000	180	18.35	17.84	4.8336	143.4380
20	8.45	39.000	180	19.35	18.85	3.4614	146.9210
21	8.45	34.000	180	20.35	19.85	2.9730	149.8940
22	8.45	29.000	180	21.35	20.85	2.4630	152.3570
25	8.35	15.000	660	24.35	22.85	1.4580	156.7250
26	8.40	10.000	175	25.35	24.85	0.4990	157.2250
27	8.40	13.000	185	26.35	25.85	1.6460	158.8710
28	8.20	11.000	170	27.34	26.85	0.8834	159.7470
29	8.40	6.000	190	28.35	27.85	0.1498	159.8980
32	8.35	6.000	670	31.35	29.85	0.5964	161.6860
33	8.30	7.000	170	32.35	31.85	0.7886	162.4730

Phosphate Release Experiment : Column 1B

Condition:	reference anoxic	INPUT DATA Vol. sampl	75.00	(ml)	Calculations
		Hight colu	14.00	(cm)	average release rate: 9.44
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	220.000	0	0.46			
4	9.40	226.000	610	3.39	1.93	21.1166	61.9420
5	8.40	239.000	130	4.35	3.87	21.7930	82.8270
6	8.45	176.000	175	5.35	4.85	11.9052	94.7570
7	8.45	230.000	175	6.35	5.85	27.8600	122.6170
8	8.45	170.000	175	7.35	6.85	11.6000	134.2170
11	8.30	77.000	680	10.35	8.85	8.1092	158.4940
12	8.30	76.000	180	11.35	10.85	7.6630	166.1570
13	8.30	69.000	180	12.35	11.85	6.4150	172.5720
14	8.30	82.000	180	13.35	12.85	9.5210	182.0930
15	8.50	62.000	180	14.35	13.85	4.5064	186.6370
18	8.05	79.000	650	17.34	15.84	7.6562	209.4620
19	8.30	85.000	180	18.35	17.84	9.1091	218.6660
20	8.45	69.000	180	19.35	18.85	5.5791	224.2800
21	8.45	68.000	180	20.35	19.85	6.8470	231.1270
22	8.45	79.000	180	21.35	20.85	9.0370	240.1640
25	8.35	72.000	660	24.35	22.85	7.0822	261.3810
26	8.40	78.000	180	25.35	24.85	8.4723	269.8710
27	8.40	79.000	185	26.35	25.85	8.3040	278.1750
28	8.20	68.000	170	27.34	26.85	5.7106	283.8380
29	8.40	55.000	190	28.35	27.85	4.6602	288.5370
32	8.35	35.000	660	31.35	29.85	3.4791	298.9670
33	8.30	26.000	170	32.35	31.85	2.1114	301.0740

Posohate Release Experiment : Column 2A

					Calculations		
Condition:	Fe(50)/oxic	INPUT DATA					
		Vol. sampl	75.00	(ml)			
		Hight colu	14.50	(cm)	average release rate		1.10
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	38.000	0	0.46			
4	9.40	38.000	530	3.39	1.93	3.1350	9.1960
5	8.40	25.000	130	4.35	3.87	0.7283	9.8940
6	8.45	15.000	140	5.35	4.85	0.2694	10.1640
7	8.45	9.000	140	6.35	5.85	0.1620	10.3260
8	8.45	5.000	140	7.35	6.85	0.0220	10.3480
11	8.30	7.000	720	10.35	8.85	0.7342	12.5460
12	8.30	13.000	170	11.35	10.85	1.8500	14.3960
13	8.30	11.000	170	12.35	11.85	0.8860	15.2820
14	8.30	14.000	170	13.35	12.85	1.6600	16.9420
15	8.50	9.000	170	14.35	13.85	0.3987	17.3440
18	8.05	11.000	630	17.34	15.84	1.0432	20.4540
19	8.30	14.000	165	18.35	17.84	1.6181	22.0890
20	8.45	17.000	165	19.35	18.85	1.9111	24.0120
21	8.45	14.000	165	20.35	19.85	1.0530	25.0650
22	8.45	11.000	165	21.35	20.85	0.7650	25.8300
25	8.35	10.000	650	24.35	22.85	0.9680	28.7300
26	8.40	12.000	170	25.35	24.85	1.3652	30.0980
27	8.40	10.000	175	26.35	25.85	0.8100	30.9080
28	8.20	8.000	170	27.34	26.85	0.5970	31.5000
29	8.40	8.000	170	28.35	27.85	0.7775	32.2840
32	8.35	9.000	630	31.35	29.85	0.8479	34.8260
33	8.30	6.000	170	32.35	31.85	0.3006	35.1260

Phosphate Release Experiment :Column 2B

					Calculations		
Condition:	Fe(50)/anoxic	INPUT DATA					
		Vol. sampl	75.00	(ml)			
		Hight colu	14.00	(cm)	average release rate:		8.76
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	50.000	0	0.46			
4	9.40	50.000	590	3.39	1.93	4.5341	13.3000
5	8.40	49.000	90	4.35	3.87	3.2630	16.4270
6	8.45	74.000	165	5.35	4.85	9.3844	25.8310
7	8.45	97.000	165	6.35	5.85	11.4280	37.2590
8	8.45	104.000	165	7.35	6.85	10.6280	47.8870
11	8.30	138.000	660	10.35	8.85	13.4727	88.2210
12	8.30	145.000	170	11.35	10.85	14.8470	103.0680
13	8.30	149.000	170	12.35	11.85	14.9660	118.0340
14	8.30	142.000	170	13.35	12.85	13.2790	131.3130
15	8.50	161.000	170	14.35	13.85	17.3623	148.8200
18	8.05	74.000	640	17.34	15.84	7.1866	170.2450
19	8.30	71.000	170	18.35	17.84	6.6161	176.9300
20	8.45	95.000	170	19.35	18.85	11.4226	188.4240
21	8.45	73.000	170	20.35	19.85	5.1520	193.5760
22	8.45	86.000	170	21.35	20.85	9.6110	203.1870
25	8.35	83.000	630	24.35	22.85	7.8139	226.5960
26	8.40	85.000	170	25.35	24.85	8.4943	235.1080
27	8.40	83.000	175	26.35	25.85	8.1200	243.2280
28	8.20	72.000	160	27.34	26.85	5.7933	248.9730
29	8.40	72.000	168	28.35	27.85	6.9406	255.9714
32	8.35	60.000	660	31.35	29.85	5.9121	273.6954
33	8.30	58.000	170	32.35	31.85	5.5135	279.1974

Phosphate Release Experiment : Column 3A

Conditions Fe(100)/oxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	15.50	(cm)	average release rate:	0.94
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	7.000	0	0.46			
4	9.40	7.000	550	3.39	1.93	0.5966	1.7500
5	8.40	6.000	220	4.35	3.87	0.6386	2.3620
6	8.45	6.000	180	5.35	4.85	0.6107	2.9740
7	8.45	8.000	180	6.35	5.85	1.0240	3.9980
8	8.45	6.000	680	7.35	6.85	1.8040	5.8020
11	8.30	6.000	170	10.35	8.85	0.1964	6.3900
12	8.30	12.000	170	11.35	10.85	1.8120	8.2020
13	8.30	9.000	170	12.35	11.85	0.5640	8.7660
14	8.30	7.000	170	13.35	12.85	0.4740	9.2400
15	8.50	7.000	170	14.35	13.85	0.6803	9.9260
18	8.05	10.000	650	17.34	15.84	0.9828	12.8560
19	8.30	9.000	175	18.35	17.84	0.7868	13.6510
20	8.45	9.000	175	19.35	18.85	0.8944	14.5510
21	8.45	12.000	175	20.35	19.85	1.5150	16.0660
22	8.45	8.000	175	21.35	20.85	0.3800	16.4460
25	8.35	13.000	670	24.35	22.85	1.3031	20.3500
26	8.40	9.000	180	25.35	24.85	0.5010	20.8520
27	8.40	10.000	185	26.35	25.85	1.1430	21.9950
28	8.20	14.000	180	27.34	26.85	1.8595	23.8390
29	8.40	9.000	190	28.35	27.85	0.4403	24.2830
32	8.35	16.000	690	31.35	29.85	1.6378	29.1930
33	8.30	12.000	185	32.35	31.85	0.8377	30.0290

Phosphate Release Experiment : Column 3B

ConditionsFe(100)/anoxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	13.00	(cm)	average release rate:	1.67
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	10.200	0	0.46			
4	9.40	10.000	610	3.39	1.93	0.9346	2.7414
5	8.40	6.000	180	4.35	3.87	0.3089	3.0374
6	8.45	8.000	185	5.35	4.85	0.9859	4.0254
7	8.45	9.000	185	6.35	5.85	1.0140	5.0394
8	8.45	8.000	185	7.35	6.85	0.7540	5.7934
11	8.30	10.000	710	10.35	8.85	1.0308	8.8794
12	8.30	13.000	180	11.35	10.85	1.5630	10.4424
13	8.30	12.000	180	12.35	11.85	1.1450	11.5874
14	8.30	19.000	180	13.35	12.85	2.4910	14.0784
15	8.50	15.000	180	14.35	13.85	1.2040	15.2924
18	8.05	16.000	650	17.34	15.84	1.5514	19.9174
19	8.30	16.000	180	18.35	17.84	1.6152	21.5494
20	8.45	24.000	180	19.35	18.85	3.0609	24.6294
21	8.45	20.000	180	20.35	19.85	1.7240	26.3534
22	8.45	18.000	175	21.35	20.85	1.6400	27.9934
25	8.35	32.000	680	24.35	22.85	3.1277	37.3634
26	8.40	24.000	190	25.35	24.85	1.9240	39.2914
27	8.40	22.000	205	26.35	25.85	2.3160	41.6074
28	8.20	21.000	200	27.34	26.85	2.2538	43.8424
29	8.40	20.000	190	28.35	27.85	2.0261	45.8854
32	8.35	19.000	695	31.35	29.85	1.9600	51.7614
33	8.30	17.000	190	32.35	31.85	1.6514	53.4094

Phosphate Release Experiment : Column 4A

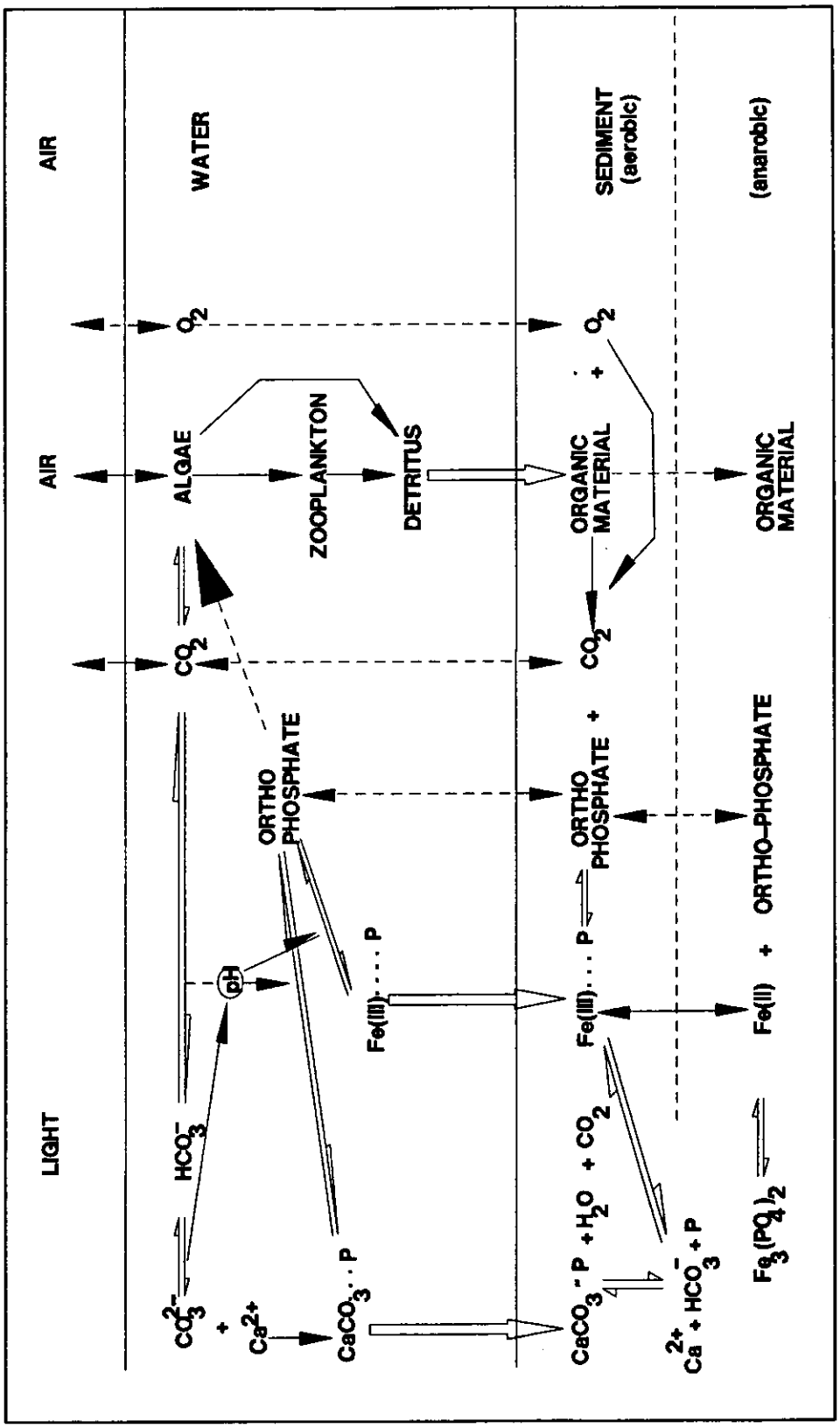
Conditions Fe(250)/oxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	15.00	(cm)	average release rate:	0.59
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	6.000	0	0.46			
4	9.40	6.000	790	3.39	1.93	0.7077	2.0760
5	8.40	4.000	160	4.35	3.87	0.1774	2.2460
6	8.45	5.000	190	5.35	4.85	0.6257	2.8730
7	8.45	4.000	190	6.35	5.85	0.3270	3.2000
8	8.45	4.000	190	7.35	6.85	0.4240	3.6240
11	8.30	7.000	690	10.35	8.85	0.7125	5.7570
12	8.30	8.000	185	11.35	10.85	0.9300	6.6870
13	8.30	6.000	185	12.35	11.85	0.4280	7.1150
14	8.30	5.000	185	13.35	12.85	0.4220	7.5370
15	8.50	6.000	185	14.35	13.85	0.7160	8.2590
18	8.05	5.000	670	17.34	15.84	0.4995	9.7480
19	8.30	4.000	180	18.35	17.84	0.3058	10.0570
20	8.45	4.000	180	19.35	18.85	0.4055	10.4650
21	8.45	3.000	175	20.35	19.85	0.2000	10.6650
22	8.45	2.000	175	21.35	20.85	0.1000	10.7650
25	8.35	6.000	670	24.35	22.85	0.5982	12.5570
26	8.40	4.000	180	25.35	24.85	0.2096	12.7670
27	8.40	6.000	200	26.35	25.85	0.8500	13.6170
28	8.20	9.000	190	27.34	26.85	1.2555	14.8620
29	8.40	10.000	185	28.35	27.85	1.1286	16.0000
32	8.35	7.000	698	31.35	29.85	0.7266	18.1782
33	8.30	7.000	175	32.35	31.85	0.7015	18.8782

Phosphate Release Experiment : Column 4B

Condition:Fe(250)/anoxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	16.50	(cm)	average release rate:	0.57
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	6.000	0	0.46			
4	9.40	6.000	790	3.39	1.93	0.7077	2.0760
5	8.40	6.000	160	4.35	3.87	0.5885	2.6400
6	8.45	5.000	190	5.35	4.85	0.4171	3.0580
7	8.45	4.000	190	6.35	5.85	0.3120	3.3700
8	8.45	7.000	190	7.35	6.85	1.0780	4.4480
11	8.30	4.000	690	10.35	8.85	0.3968	5.6360
12	8.30	4.000	185	11.35	10.85	0.4160	6.0520
13	8.30	4.000	185	12.35	11.85	0.4160	6.4680
14	8.30	4.000	185	13.35	12.85	0.4160	6.8840
15	8.50	3.000	185	14.35	13.85	0.1974	7.0830
18	8.05	4.000	670	17.34	15.84	0.4052	8.2910
19	8.30	4.000	180	18.35	17.84	0.4038	8.6990
20	8.45	4.000	180	19.35	18.85	0.4055	9.1070
21	8.45	3.000	180	20.35	19.85	0.1920	9.2990
22	8.45	5.000	180	21.35	20.85	0.7380	10.0370
25	8.35	5.000	695	24.35	22.85	0.5140	11.5770
26	8.40	3.000	180	25.35	24.85	0.0778	11.6550
27	8.40	5.000	190	26.35	25.85	0.7540	12.4090
28	8.20	4.000	180	27.34	26.85	0.2965	12.7030
29	8.40	8.000	190	28.35	27.85	1.2853	13.9990
32	8.35	11.000	698	31.35	29.85	1.1449	17.4314
33	8.30	10.000	175	32.35	31.85	0.8868	18.3164



APPENDIX 4 : Phosphorus cycling in lake eco-system.

G L O S S A R Y.

ADVANCED WASTE TREATMENT : Often abbreviated AWT and also referred to as tertiary treatment. Wastewater treatment usually directed at major plant nutrients, results in a high quality effluent.

AEROBIC : Environment in which oxygen is present. Also refers to processes occurring in presence of oxygen.

ALGAE : Simplest green plants having neither roots, stems, nor leaves; those in fresh water are usually microscopic in size.

ALGAE BLOOM OR ALGAL BLOOM : Very rapid growth of algae with formation of large concentrations which sometimes form floating mats or distinct coloration of the water.

ANAEROBIC: Environment in which oxygen is absent. Also refers to processes occurring in absence of oxygen.

AQUATIC PLANTS: Plants that grow in water. Some aquatic plants are rooted, some are free floating.

CULTURAL EUTROPHICATION: The acceleration by human activities of the natural aging processes in a lake.

D.O. Dissolved oxygen required for the maintenance of aerobic aquatic organisms. Low D.O. levels approach anaerobic conditions.

ECOLOGY: A branch of science concerned with the interrelationship of organisms to one another and to their environment.

EFFLUENT: Treated or untreated wastewater that flows from sewers, treatment plants, or industrial plants.

ENVIRONMENT: All the external conditions that surround living, such as soil, water, and air.

EPILIMNION: Upper warm circulating layer in a stratified lake.

DECOMPOSITION: Breakdown of materials into simpler forms by action of aerobic or anaerobic microorganisms.

DETRITUS: Minute particles of the decaying remains of dead plants and animals.

EROSION: Process by which soils are loosened and moved from one place to another.

EUTROPHIC: Waters with high rate of nutrient supply and resulting high levels of organic production.

EUTROPHICATION: The addition of inorganic nutrients organic matte and/or silt to a lake, leading to decreased volume and increased biological material. This can occur either as a natural stage in lake maturation or in an accelerated fashion due to human activities. (Cultural eutrophication).

FLUSHING RATE: Time it takes for the total volume of a lake to be replaced. Also known as retention time.

HYPOLIMNION: The deep, cold, lower level of a stratified lake.

LITTORAL ZONE: Shallow water interface area between the land of the drainage basin and the open waters of the lake.

LIMNOLOGY: the study of freshwater systems.

MACROPHYTE: Large, rooted aquatic plant.

MESOTROPHIC: Waters with a moderate supply of nutrients and moderate level of organic production.

NUTRIENT: A chemical element or compound which promotes the growth and development of organisms.

PHOTOSYNTHESIS: Synthesis of organic compounds with the aid of light by chlorophyll-containing cells.

PLANKTON: Microscopic free floating plants and animals.

POLLUTANT: A substance, medium, or agent that causes physical impurity. Official EPA definition is: dredged spoil, solid waste, incinerator residue, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials, heat, wrecked or discarded equipment, rock, sand, cellar dirt, and industrial, municipal, and agricultural waste discharged into water.

RESIDENCE TIME: Amount of time a substance will remain in a lake before being flushed or settled out.

SECCHI DISK: A white disk 20 centimeters (8 inches) in diameter used to measure transparency of water.

SEDIMENT: Particles of material transported to a lake or suspended in its water. Also refers to bottom material in lakes that result from its formation, the remains of organisms, erosion from land.

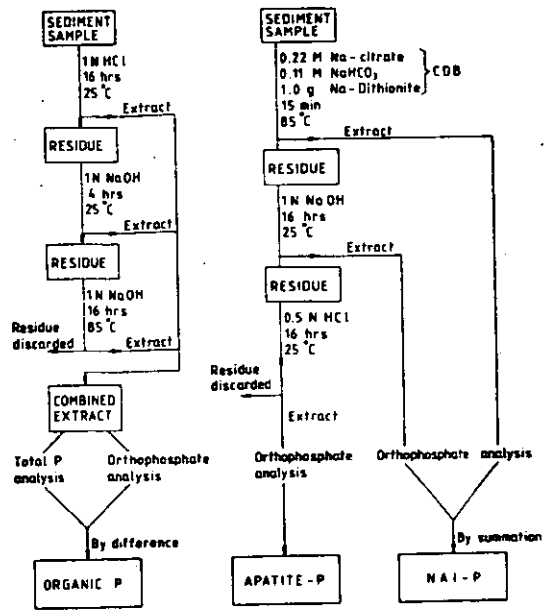
STRATIFICATION: Thermal layering of a lake in which the water column is divided by density into a cold lower region and a warm upper region with a relatively thin boundary area between.

THERMOCLINE: Region of rapid temperature transition in a stratified lake that separates the epilimnion.

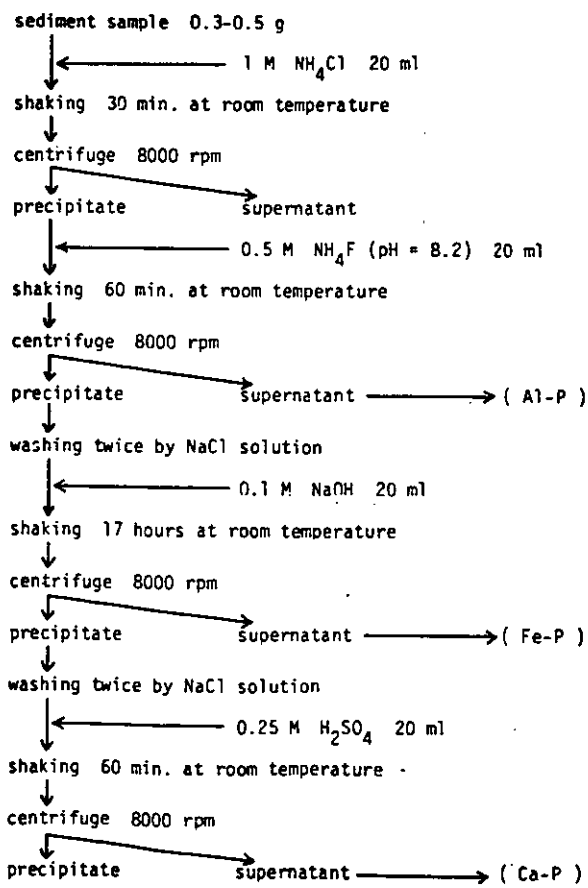
TRIBUTARY: Stream or river that flows into a lake.

TURBIDITY: Condition of opacity or muddiness in water resulting from particles in suspension.

APPENDIX 1.



A. Outline of analytical procedure to determine apatite-P, NAI-P and organic-P. (source: Williams et. al. 1976, Modified)



B. Inorganic phosphorus fractionation in lake sediments (source: Hosomi, 1982)

APPENDIX 2.

Computer programme in BASIC for calculating the amounts of chemicals need for preparing artificial lake water.

```
10 REM RECIPE FOR PREPARING SYNTHETIC WATER
20 REM WRITTEN BY W.A.D.D.WIJESOORIYA
30 REM INPUT DATA
40 INPUT "Volume of synthetic water need, in L = ";N
50 PRINT:PRINT
60 LPRINT:LPRINT
70 INPUT "Give K concentration in lake water mg/L ";K
80 INPUT "Give Na concentration in lake water mg/L";NA
90 INPUT "Give Ca concentration in lake water mg/L";CA
100 INPUT "Give Mg concentration in lake water mg/L";MG
110 INPUT "Give Cl concentration in lake water mg/L";CL
120 INPUT "Give SO4concentration in lake water mg/L";SO4
130 INPUT "Give HCO3 mg/L,If unknown press ENTER ";HCO3
140 IF HCO3 = 0 THEN 150 ELSE 170
150 HCO3 = ((K/39.1)+(NA/23)+(CA*2/40)+(MG*2/24.3)-(CL/35.5)-(SO4*2/96))*61
160 IF HCO3 < 0 THEN GOTO 330 ELSE 170
170 REM CALCULATION
180 A = 110*CA/40
190 B = MG*248.48/24.3
200 C = K*74.56/39.1
210 E = HCO3*84/61
220 F = ((CL/35.5)-(A*2/110)-(C/74.56))*58.44
230 D = ((SO4/96)-(B/246.48))*322.19
240 G=A*N/1000
250 H=B*N/1000
260 I=C*N/1000
270 J=D*N/1000
280 L=E*N/1000
290 M=F*N/1000
300 REM OUTPUT PART
310 PRINT:PRINT:PRINT
320 LPRINT:PRINT
330 LPRINT "INPUT DATA"
340 LPRINT "-----------"
350 PRINT "INPUT DATA"
360 PRINT "----------"
370 LPRINT:PRINT
380 LPRINT "K+ Concentration      =";K;"mg/L"
390 PRINT "K+ Concentration      =";K;"mg/L"
400 LPRINT "Na+Concentration      =";NA;"mg/L"
410 PRINT "Na+Concentration      =";NA;"mg/L"
420 LPRINT"Ca++ Concentration    =";CA;"mg/L"
430 PRINT"Ca++ Concentration    =";CA;"mg/L"
440 LPRINT"Mg++ Concentration    =";MG;"mg/L"
450 PRINT"Mg++ Concentration    =";MG;"mg/L"
460 LPRINT"Cl- Concentration    =";CL;"mg/L"
470 PRINT"Cl- Concentration    =";CL;"mg/L"
480 LPRINT"SO4= Concentration    =";SO4;"mg/L"
490 PRINT"SO4= Concentration    =";SO4;"mg/L"
500 LPRINT"HCO3-Concentration    =";HCO3;"mg/L"
510 PRINT"HCO3-Concentration    =";HCO3;"mg/L"
520 IF HCO3 < 0 THEN GOTO 920 ELSE 530
530 IF A<0 OR B<0 OR C<0 OR D<0 OR E<0 OR F<0 THEN GOTO 920 ELSE 540
540 LPRINT:PRINT
```

```
550 PRINT "AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER"
560 PRINT "-----------------------------------------"
570 LPRINT "AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER"
580 LPRINT "-----------------------------------------"
590 LPRINT:PRINT:PRINT
600 PRINT "Amount Calcium Chloride  =";A      ;"mg"
610 LPRINT "Amount Calcium Chloride  =";A      ;"mg"
620 PRINT "Amount Magnesium sulphate=";B      ;"mg"
630 LPRINT "Amount Magnesium sulphate=";B      ;"mg"
640 PRINT "Amount Potasium Chloride =";C      ;"mg"
650 LPRINT "Amount Potasium Chloride =";C      ;"mg"
660 PRINT "Amount Sodium Sulphate   =";D      ;"mg"
670 LPRINT "Amount Sodium Sulphate   =";D      ;"mg"
680 PRINT "Amount Sodium bicarbonate=";E      ;"mg"
690 LPRINT "Amount Sodium bicarbonate=";E      ;"mg"
700 PRINT "Amount sodium chloride   =";F      ;"mg"
710 LPRINT "Amount sodium chloride   =";F      ;"mg"
720 PRINT:PRINT
730 LPRINT:PRINT:PRINT
740 PRINT "RECIPE FOR PREPARING";N;"L SYNTHETIC WATER"
750 PRINT "-----------------------------------------"
760 LPRINT "RECIPE FOR PREPARING";N;"L SYNTHETIC WATER"
770 LPRINT "-----------------------------------------"
780 LPRINT:PRINT:PRINT
790 PRINT "Amount Calcium Chloride  =";G      ;"g"
800 LPRINT "Amount Calcium Chloride  =";G      ;"g"
810 PRINT "Amount Magnesium sulphate=";H      ;"g"
820 LPRINT "Amount Magnesium sulphate=";H      ;"g"
830 PRINT "Amount Potasium Chloride =";I      ;"g"
840 LPRINT "Amount Potasium Chloride =";I      ;"g"
850 PRINT "Amount Sodium Sulphate   =";J      ;"g"
860 LPRINT "Amount Sodium Sulphate   =";J      ;"g"
870 PRINT "Amount Sodium bicarbonate=";L      ;"g"
880 LPRINT "Amount Sodium bicarbonate=";L      ;"g"
890 PRINT "Amount sodium chloride   =";M      ;"g"
900 LPRINT "Amount sodium chloride   =";M      ;"g"
910 GOTO 960
920 PRINT:PRINT
930 LPRINT:PRINT
940 PRINT "ERROR: PLEASE CHECK INPUT DATA"
950 LPRINT "ERROR: PLEASE CHECK INPUT DATA"
960 END
```

```
INPUT DATA
----------

K+ Concentration      = 7.1 mg/L
Na+Concentration      = 75 mg/L
Ca++ Concentration    = 59 mg/L
Mg++ Concentration    = 11.1 mg/L
Cl-  Concentration    = 129 mg/L
SO4= Concentration    = 72 mg/L
HCO3-Concentration    = 132.5062 mg/L
```

```
AMOUNTS OF SALTS PRESENT IN 1.0L SYNTHETIC WATER
-----------------------------------------

Amount Calcium Chloride  = 162.25 mg
Amount Magnesium sulphate= 113.5032 mg
Amount Potasium Chloride = 13.53903 mg
Amount Sodium Sulphate   = 93.27509 mg
Amount Sodium bicarbonate= 182.4676 mg
Amount sodium chloride   = 29.34957 mg

RECIPE FOR PREPARING 50 L SYNTHETIC WATER
-----------------------------------------

Amount Calcium Chloride  = 8.1125 g
Amount Magnesium sulphate= 5.675161 g
Amount Potasium Chloride = .6769515 g
Amount Sodium Sulphate   = 4.663755 g
Amount Sodium bicarbonate= 9.123377 g
Amount sodium chloride   = 1.467479 g
```

Phosphate Release Experiment : Column 1A

Condition:	reference oxic	INPUT DATA Vol. sampl	75.00	(ml)	Calculations
		Hight colu	15.00	(cm)	average release rate: 5.10
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	220.000	0	0.46			
4	9.40	221.000	550	3.39	1.93	18.8438	55.2750
5	8.40	192.000	190	4.35	3.87	18.3016	72.8140
6	8.45	135.000	183	5.35	4.85	8.3059	81.1372
7	8.45	82.000	183	6.35	5.85	3.2472	84.3844
8	8.45	64.000	183	7.35	6.85	4.8336	89.2180
11	8.30	58.000	680	10.35	8.85	5.8529	106.7400
12	8.30	65.000	170	11.35	10.85	7.0770	113.8170
13	8.30	41.000	170	12.35	11.85	1.5940	115.4110
14	8.30	61.000	170	13.35	12.85	7.9980	123.4090
15	8.50	49.000	170	14.35	13.85	3.5603	126.9990
18	8.05	40.000	650	17.34	15.84	3.8759	138.5540
19	8.30	44.000	180	18.35	17.84	4.8336	143.4380
20	8.45	39.000	180	19.35	18.85	3.4614	146.9210
21	8.45	34.000	180	20.35	19.85	2.9730	149.8940
22	8.45	29.000	180	21.35	20.85	2.4630	152.3570
25	8.35	15.000	660	24.35	22.85	1.4580	156.7250
26	8.40	10.000	175	25.35	24.85	0.4990	157.2250
27	8.40	13.000	185	26.35	25.85	1.6460	158.8710
28	8.20	11.000	170	27.34	26.85	0.8834	159.7470
29	8.40	6.000	190	28.35	27.85	0.1498	159.8980
32	8.35	6.000	670	31.35	29.85	0.5964	161.6860
33	8.30	7.000	170	32.35	31.85	0.7886	162.4730

Phosphate Release Experiment : Column 1B

Condition:	reference anoxic	INPUT DATA Vol. sampl	75.00	(ml)	Calculations
		Hight colu	14.00	(cm)	average release rate: 9.44
		Area.colu	25.00	(cm^2)	(mgP/m^2.d)

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	220.000	0	0.46			
4	9.40	226.000	610	3.39	1.93	21.1166	61.9420
5	8.40	239.000	130	4.35	3.87	21.7930	82.8270
6	8.45	176.000	175	5.35	4.85	11.9052	94.7570
7	8.45	230.000	175	6.35	5.85	27.8600	122.6170
8	8.45	170.000	175	7.35	6.85	11.6000	134.2170
11	8.30	77.000	680	10.35	8.85	8.1092	158.4940
12	8.30	76.000	180	11.35	10.85	7.6630	166.1570
13	8.30	69.000	180	12.35	11.85	6.4150	172.5720
14	8.30	82.000	180	13.35	12.85	9.5210	182.0930
15	8.50	62.000	180	14.35	13.85	4.5064	186.6370
18	8.05	79.000	650	17.34	15.84	7.6562	209.4620
19	8.30	85.000	180	18.35	17.84	9.1091	218.6660
20	8.45	69.000	180	19.35	18.85	5.5791	224.2800
21	8.45	68.000	180	20.35	19.85	6.8470	231.1270
22	8.45	79.000	180	21.35	20.85	9.0370	240.1640
25	8.35	72.000	660	24.35	22.85	7.0822	261.3810
26	8.40	78.000	180	25.35	24.85	8.4723	269.8710
27	8.40	79.000	185	26.35	25.85	8.3040	278.1750
28	8.20	68.000	170	27.34	26.85	5.7106	283.8380
29	8.40	55.000	190	28.35	27.85	4.6602	288.5370
32	8.35	35.000	660	31.35	29.85	3.4791	298.9670
33	8.30	28.000	170	32.35	31.85	2.1114	301.0740

APPENDIX 3.

Posohate Release Experiment : Column 2A

Condition: Fe(50)/oxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	14.50	(cm)	average release rate (mgP/m^2.d)	1.10
	Area.colu	25.00	(cm^2)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	38.000	0	0.46			
4	9.40	38.000	530	3.39	1.93	3.1350	9.1960
5	8.40	25.000	130	4.35	3.87	0.7283	9.8940
6	8.45	15.000	140	5.35	4.85	0.2694	10.1640
7	8.45	9.000	140	6.35	5.85	0.1620	10.3260
8	8.45	5.000	140	7.35	6.85	0.0220	10.3480
11	8.30	7.000	720	10.35	8.85	0.7342	12.5460
12	8.30	13.000	170	11.35	10.85	1.8500	14.3960
13	8.30	11.000	170	12.35	11.85	0.8860	15.2820
14	8.30	14.000	170	13.35	12.85	1.6600	16.9420
15	8.50	9.000	170	14.35	13.85	0.3987	17.3440
18	8.05	11.000	630	17.34	15.84	1.0432	20.4540
19	8.30	14.000	165	18.35	17.84	1.6181	22.0890
20	8.45	17.000	165	19.35	18.85	1.9111	24.0120
21	8.45	14.000	165	20.35	19.85	1.0530	25.0650
22	8.45	11.000	165	21.35	20.85	0.7650	25.8300
25	8.35	10.000	650	24.35	22.85	0.9680	28.7300
26	8.40	12.000	170	25.35	24.85	1.3652	30.0980
27	8.40	10.000	175	26.35	25.85	0.8100	30.9080
28	8.20	8.000	170	27.34	26.85	0.5970	31.5000
29	8.40	8.000	170	28.35	27.85	0.7775	32.2840
32	8.35	9.000	630	31.35	29.85	0.8479	34.8260
33	8.30	6.000	170	32.35	31.85	0.3006	35.1260

Phosphate Release Experiment :Column 2B

Condition: Fe(50)/anoxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	14.00	(cm)	average release rate: (mgP/m^2.d)	8.76
	Area.colu	25.00	(cm^2)		

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	50.000	0	0.46			
4	9.40	50.000	590	3.39	1.93	4.5341	13.3000
5	8.40	49.000	90	4.35	3.87	3.2630	16.4270
6	8.45	74.000	165	5.35	4.85	9.3844	25.8310
7	8.45	97.000	165	6.35	5.85	11.4280	37.2590
8	8.45	104.000	165	7.35	6.85	10.6280	47.8870
11	8.30	138.000	660	10.35	8.85	13.4727	88.2210
12	8.30	145.000	170	11.35	10.85	14.8470	103.0680
13	8.30	149.000	170	12.35	11.85	14.9660	118.0340
14	8.30	142.000	170	13.35	12.85	13.2790	131.3130
15	8.50	161.000	170	14.35	13.85	17.3623	148.8200
18	8.05	74.000	640	17.34	15.84	7.1866	170.2450
19	8.30	71.000	170	18.35	17.84	6.6161	176.9300
20	8.45	95.000	170	19.35	18.85	11.4226	188.4240
21	8.45	73.000	170	20.35	19.85	5.1520	193.5760
22	8.45	86.000	170	21.35	20.85	9.6110	203.1870
25	8.35	83.000	630	24.35	22.85	7.8139	226.5960
26	8.40	85.000	170	25.35	24.85	8.4943	235.1080
27	8.40	83.000	175	26.35	25.85	8.1200	243.2280
28	8.20	72.000	160	27.34	26.85	5.7933	248.9730
29	8.40	72.000	168	28.35	27.85	6.9406	255.9714
32	8.35	60.000	660	31.35	29.85	5.9121	273.6954
33	8.30	58.000	170	32.35	31.85	5.5135	279.1974

Phosphate Release Experiment : Column 3A

Conditions Fe(100)/oxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	15.50	(cm)	average release rate:	0.94
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	7.000	0	0.46			
4	9.40	7.000	550	3.39	1.93	0.5966	1.7500
5	8.40	6.000	220	4.35	3.87	0.6386	2.3620
6	8.45	6.000	180	5.35	4.85	0.6107	2.9740
7	8.45	8.000	180	6.35	5.85	1.0240	3.9980
8	8.45	6.000	680	7.35	6.85	1.8040	5.8020
11	8.30	6.000	170	10.35	8.85	0.1964	6.3900
12	8.30	12.000	170	11.35	10.85	1.8120	8.2020
13	8.30	9.000	170	12.35	11.85	0.5640	8.7660
14	8.30	7.000	170	13.35	12.85	0.4740	9.2400
15	8.50	7.000	170	14.35	13.85	0.6803	9.9260
18	8.05	10.000	650	17.34	15.84	0.9828	12.8560
19	8.30	9.000	175	18.35	17.84	0.7868	13.6510
20	8.45	9.000	175	19.35	18.85	0.8944	14.5510
21	8.45	12.000	175	20.35	19.85	1.5150	16.0660
22	8.45	8.000	175	21.35	20.85	0.3800	16.4460
25	8.35	13.000	670	24.35	22.85	1.3031	20.3500
26	8.40	9.000	180	25.35	24.85	0.5010	20.8520
27	8.40	10.000	185	26.35	25.85	1.1430	21.9950
28	8.20	14.000	180	27.34	26.85	1.8595	23.8390
29	8.40	9.000	190	28.35	27.85	0.4403	24.2830
32	8.35	16.000	690	31.35	29.85	1.6378	29.1930
33	8.30	12.000	185	32.35	31.85	0.8377	30.0290

Phosphate Release Experiment : Column 3B

ConditionsFe(100)/anoxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	13.00	(cm)	average release rate:	1.67
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	10.200	0	0.46			
4	9.40	10.000	610	3.39	1.93	0.9346	2.7414
5	8.40	6.000	180	4.35	3.87	0.3089	3.0374
6	8.45	8.000	185	5.35	4.85	0.9859	4.0254
7	8.45	9.000	185	6.35	5.85	1.0140	5.0394
8	8.45	8.000	185	7.35	6.85	0.7540	5.7934
11	8.30	10.000	710	10.35	8.85	1.0308	8.8794
12	8.30	13.000	180	11.35	10.85	1.5630	10.4424
13	8.30	12.000	180	12.35	11.85	1.1450	11.5874
14	8.30	19.000	180	13.35	12.85	2.4910	14.0784
15	8.50	15.000	180	14.35	13.85	1.2040	15.2924
18	8.05	16.000	650	17.34	15.84	1.5514	19.9174
19	8.30	16.000	180	18.35	17.84	1.6152	21.5494
20	8.45	24.000	180	19.35	18.85	3.0609	24.6294
21	8.45	20.000	180	20.35	19.85	1.7240	26.3534
22	8.45	18.000	175	21.35	20.85	1.6400	27.9934
25	8.35	32.000	680	24.35	22.85	3.1277	37.3634
26	8.40	24.000	190	25.35	24.85	1.9240	39.2914
27	8.40	22.000	205	26.35	25.85	2.3160	41.6074
28	8.20	21.000	200	27.34	26.85	2.2538	43.8424
29	8.40	20.000	190	28.35	27.85	2.0261	45.8854
32	8.35	19.000	695	31.35	29.85	1.9600	51.7614
33	8.30	17.000	190	32.35	31.85	1.6514	53.4094

Phosphate Release Experiment : Column 4A

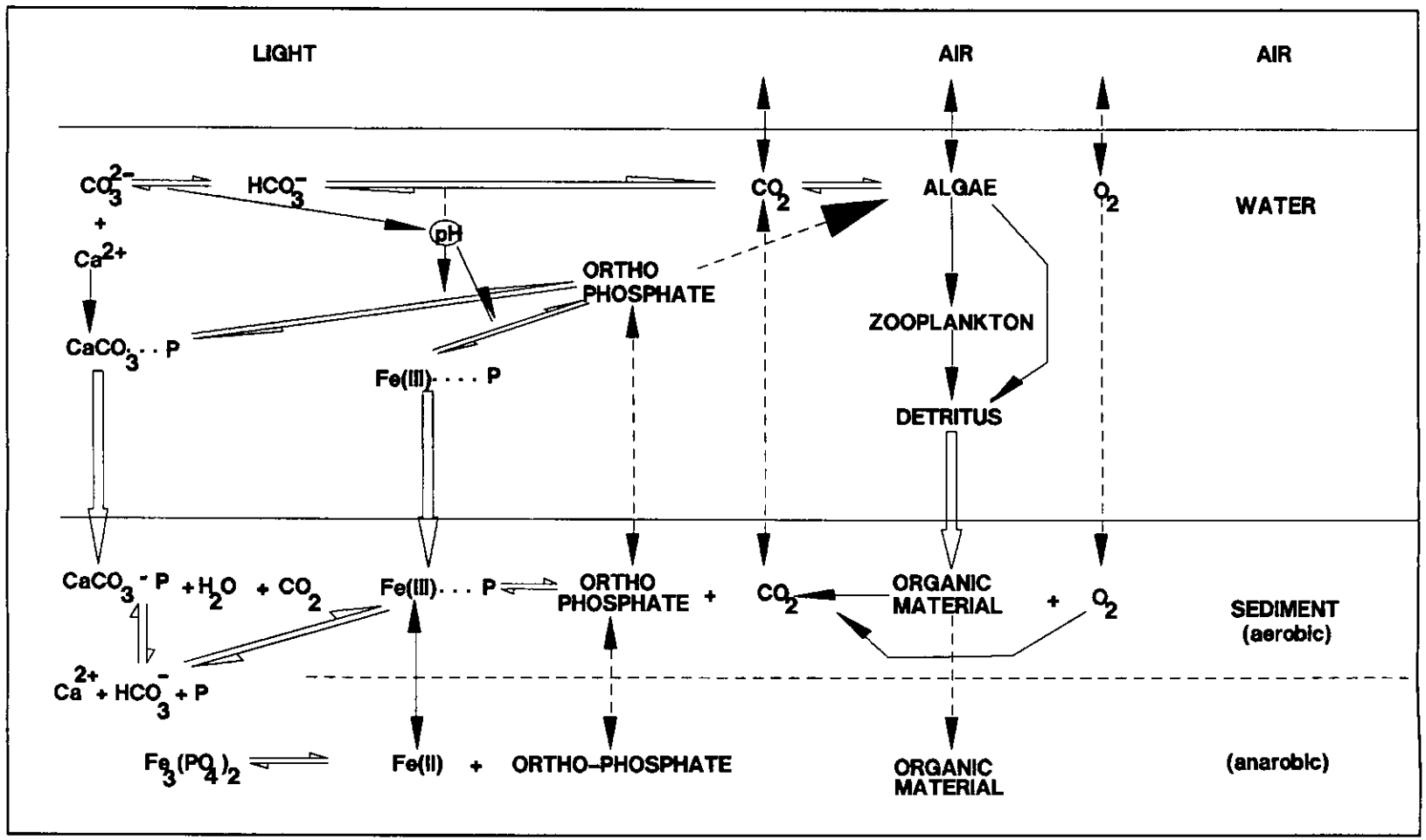
Conditions Fe(250)/oxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	15.00	(cm)	average release rate:	0.59
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	6.000	0	0.46			
4	9.40	6.000	790	3.39	1.93	0.7077	2.0760
5	8.40	4.000	160	4.35	3.87	0.1774	2.2460
6	8.45	5.000	190	5.35	4.85	0.6257	2.8730
7	8.45	4.000	190	6.35	5.85	0.3270	3.2000
8	8.45	4.000	190	7.35	6.85	0.4240	3.6240
11	8.30	7.000	690	10.35	8.85	0.7125	5.7570
12	8.30	8.000	185	11.35	10.85	0.9300	6.6870
13	8.30	6.000	185	12.35	11.85	0.4280	7.1150
14	8.30	5.000	185	13.35	12.85	0.4220	7.5370
15	8.50	6.000	185	14.35	13.85	0.7160	8.2590
18	8.05	5.000	670	17.34	15.84	0.4995	9.7480
19	8.30	4.000	180	18.35	17.84	0.3058	10.0570
20	8.45	4.000	180	19.35	18.85	0.4055	10.4650
21	8.45	3.000	175	20.35	19.85	0.2000	10.6650
22	8.45	2.000	175	21.35	20.85	0.1000	10.7650
25	8.35	6.000	670	24.35	22.85	0.5982	12.5570
26	8.40	4.000	180	25.35	24.85	0.2096	12.7670
27	8.40	6.000	200	26.35	25.85	0.8500	13.6170
28	8.20	9.000	190	27.34	26.85	1.2555	14.8620
29	8.40	10.000	185	28.35	27.85	1.1286	16.0000
32	8.35	7.000	698	31.35	29.85	0.7266	18.1782
33	8.30	7.000	175	32.35	31.85	0.7015	18.8782

Phosphate Release Experiment : Column 4B

Condition:Fe(250)/anoxic	INPUT DATA			Calculations	
	Vol. sampl	75.00	(ml)		
	Hight colu	16.50	(cm)	average release rate:	0.57
	Area.colu	25.00	(cm^2)	(mgP/m^2.d)	

Day nr (--)	Time (h)	conc. (µg P/l)	Volume (ml)	Cal.time (d)	Time (d)	Rel.rate (mgP/m^2.d)	Tot.release (mgP/m^2)
1	11.00	6.000	0	0.46			
4	9.40	6.000	790	3.39	1.93	0.7077	2.0760
5	8.40	6.000	160	4.35	3.87	0.5885	2.6400
6	8.45	5.000	190	5.35	4.85	0.4171	3.0580
7	8.45	4.000	190	6.35	5.85	0.3120	3.3700
8	8.45	7.000	190	7.35	6.85	1.0780	4.4480
11	8.30	4.000	690	10.35	8.85	0.3968	5.6360
12	8.30	4.000	185	11.35	10.85	0.4160	6.0520
13	8.30	4.000	185	12.35	11.85	0.4160	6.4680
14	8.30	4.000	185	13.35	12.85	0.4160	6.8840
15	8.50	3.000	185	14.35	13.85	0.1974	7.0830
18	8.05	4.000	670	17.34	15.84	0.4052	8.2910
19	8.30	4.000	180	18.35	17.84	0.4038	8.6990
20	8.45	4.000	180	19.35	18.85	0.4055	9.1070
21	8.45	3.000	180	20.35	19.85	0.1920	9.2990
22	8.45	5.000	180	21.35	20.85	0.7380	10.0370
25	8.35	5.000	695	24.35	22.85	0.5140	11.5770
26	8.40	3.000	180	25.35	24.85	0.0778	11.6550
27	8.40	5.000	190	26.35	25.85	0.7540	12.4090
28	8.20	4.000	180	27.34	26.85	0.2965	12.7030
29	8.40	8.000	190	28.35	27.85	1.2853	13.9990
32	8.35	11.000	698	31.35	29.85	1.1449	17.4314
33	8.30	10.000	175	32.35	31.85	0.8868	18.3164



APPENDIX 4 : Phosphorus cycling in lake eco-system.