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PHOSPHORUS EXCHANGE BETWEEN LAKE
SEDIMENT AND THE OVERLYING WATER

by

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1. Introduction

Lake sediments can play an important role as a reservoir of nutrients like phosphate (P) and nitrogen (N) (9). In the Netherlands, huge amounts of phosphate, which is often the most important nutrient for algal growth, already enter the lakes from human, agricultural and industrial sources. In many Dutch lakes the situation worsens because of the influence of the river Rhine and because most of the lakes do not have a significant outflow of phosphate.

Lake IJssel, for example, receives about 10 gr./m² (3 gr./m³/yr) of total phosphate; only about 10% of the phosphate-load leaves the lake (15). Undoubtedly this phosphate-load has contributed significantly to the eutrophication of Lake IJssel; it exceeds the "critical level" of 0.05 gr.P./m², yr* considerably

The trophic states of a lake are determined by the amount or rate of algal growth which can be limited by phosphate, nitrate/ammonium and other macro- and micronutrient concentrations, light penetration, dissolved oxygen and also the entire biomass (2-6). The trophic states of lakes can range from oligotrophic conditions - low concentrations of nutrients and thus few algae, high concentration and small fluctuations of dissolved oxygen and high light penetration - to an eutrophic state with a high concentration of algae due to increasing concentrations of nutrients, low light penetration, increase of the entire biomass and considerable fluctuations in dissolved oxygen, with sometimes low or even zero dissolved oxygen concentrations (3).

This change is often mainly caused by the increase in the concentration of phosphate in the lakewater. At the moment, in several Dutch lake areas, efforts are made or planned to reverse this process through a reduction of the phosphate-load of the lakes. Since sediments interact strongly with the overlying water, especially in lakes that are shallow (which most Dutch lakes are), P can be released back into the water from the sediment, when its loading is reduced. This is due to the buffering effect of sediments on P solutions (22, 3, 21), a process, in which the sediment removes phosphate from the overlying water when its concentration is high and releases phosphate back into the water when the concentration is low. Besides, other chemical and/or biological processes can contribute to a release of phosphates from the sediment. The purpose of the studies in this field has been to understand the mechanism and find a proper system to measure the release of phosphate from sediment to the overlying water (4).

2. Algal growth

There are about 15-20 elements that are necessary for the growth of freshwater plants, the most important of which are the nutrients carbon, nitrogen, oxygen and phosphorus.

Carbon usually occurs as CO₂, H₂CO₃ or HCO₃⁻. CO₂ supply from the air or from bottom sediments (breakdown of organisms), will be sufficient to maintain growth of relatively large algal crops (2-6). Controlling eutrophication by limiting carbon, is suggested to be ineffective, mainly because in a lake that becomes eutrophic, the green algae are replaced by blue-green algae, a replacement which is accompanied by an increase in pH in solution and an increase in water temperature, both decreasing CO₂ concentration (3).

Nitrogen usually occurs as nitrate (NO₃⁻). NO₃-N concentrations increase with an increasing amount of fertilizer, applied to the lake

* According to Vollenweider, it is only below this level that a lake can be oligotrophic.

especially from farm areas (2-6).

Nitrogen can be a limiting factor for algal growth, unless blue-green algae that can utilize nitrogen gas from the air are present (3). Besides, it is difficult to remove the supplied nitrates artificially because of their sources (rain, rural runoff); partly this removal is realized already through the process of denitrification in the sediment.

Oxygen. In lakes, a diurnal fluctuation of dissolved oxygen can be observed. During daylight, O_2 is produced in the photosynthesis of algae (3). While its consumption, as Fillos and Swanson (1975) suggest, is a result of the oxygen demand of the aerobic bacteria in the mud surface and of the immediate chemical demand by products of anaerobic decomposition (4). This is a sediment surface process (3) with sediments acting as a sink for oxygen which is supplied to the sediment surface at a rate controlled by:

1. Biological oxygen demand (BOD) - respiration and metabolic activities in the sediment by organisms like algae and bacteria (20),
2. mineralization of algae by zooplankton and by bacteria (2-9),
3. Chemical Oxygen demand (COD) - inorganic elements, like Fe^{+2} , released into the sediment from decomposing biological matter, accumulate in reduced form (20),
4. diffusion, which regulates transport.

Animals and higher plants account for only a small part of the total oxygen uptake, so that they do not minimize algal biomass (2-6).

Another important factor is the depth to which oxygen can penetrate into the sediment. This will be controlled by the rate of O_2 supply to a unit area of the sediment surface and by the oxygen demand per unit volume of the sediment (20). When, as a result, anaerobic conditions near the sediment - water interface occur, this indicates that the lake is eutrophic.

Phosphorus is the nutrient which can be most easily limited to reduce eutrophication in lakes (3), where it appears as particulate phosphorus and dissolved phosphate.

The total P concentrations of most eutrophic surface waters are found to be between 10 to 50 $g P l^{-1}$. When variations are recorded due to different geochemical structures of lake sediments (7), it was also found that the patterns of phosphate found in sediments also occur in water (2-9).

Particulate P includes: 1. P in organisms which are nucleic acids (DNA, RNA and phosphoproteins), low molecular weight esters, vitamins etc. and nucleotide phosphate (ATP, ADP) 2. mineral phases of rock and soil (for example hydroxyapatites), inorganic complexes on which P can be adsorbed (clays) and ferric hydroxide. 3. P adsorbed onto dead particulate organic matter.

dissolved P includes: 1. orthophosphate PO_4^{-3} , 2. polyphosphates, 3. organic colloids or P combined with adsorptive colloids (7).

The distribution of phosphate in a water column of a lake is generally not homogeneous. Although the dissolved phosphate tends to reach uniform concentration through the column, this tendency is counteracted by the various particulate phosphate compounds (1).

When separating total phosphate into organic and inorganic fractions it is found that the majority of the total P is in the organic form (15). Although inorganic phosphate is only a small fraction of the total phosphate, Chang and Javkson (1957) developed a fractionation method for inorganic phosphate in soil into calcium-phosphate, aluminium-phosphate, iron-phosphate and reductant soluble phosphate (10).

It was also found that the phosphorus content of the sediment can be several orders of magnitude higher than that of the water (7), Stumm and Leckie (1970) found in marine sediments (in the U.S.A.) that phosphate concentrations in the interstitial water were about 50 times higher than in the overlying water (25) and Bengtsson (1975) found that the P-content of dry sediment is about ten times higher in the 0-5 cm layer than in the deeper layers (17).

Phosphate is an available nutrient for algal growth by taking part in the photosynthesis of algae. There is also a rapid accumulation of more phosphate than is needed (luxury uptake in the cells of up to 60%). The combination of algal excretion and bacterial degradation tends to recycle this phosphate, weakly bound as polyphosphate within the cells, back into the lake system (enzymatic release), to sustain an algal bloom.

Due to the low limit of phosphate concentration, at which algal growth is limited by it, usually $10-20 \mu\text{gP l}^{-1}$, the condition described above can easily produce eutrophication in lakes.

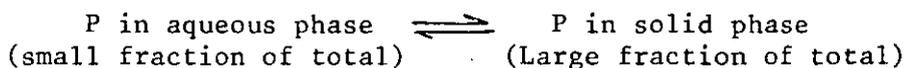
3. The exchange processes

Since, in many cases, phosphorus rather than nitrogen limits biomass synthesis (21), the exchange of phosphorus has been mainly studied. The mechanism by which phosphorus is exchanged between sediments and the overlying water is not understood, yet, it is considered as a major component of the phosphorus cycle in natural waters (7). Snow and DiGiano (1976) indicated that the deposition of P onto the bottom of a lake is mainly due to algal uptake and subsequent settling as well as adsorption onto either iron (Fe) or aluminium (AL) complexes or surface exchange on clay minerals, while the release back into the water (as a result of desorption, surface exchange, mineralization), controlled by various factors as redox potential, pH and temperature, enables P to be transported back into the overlying water (3).

Kamp Nielsen (1974) investigated the exchange rates of P during anoxic conditions and concluded that the concentration gradient of NH_4^+ CL-extractable phosphate in the upper centimeters of the sediment and the bottom water controls this exchange (19).

Rippey (6) suggested the ligand exchange of OH for PO_4 in the basis iron phosphate compound is the reverse of the equation:

$\text{Fe-OH} + \text{PO}_4^{3-} \rightleftharpoons \text{Fe-PO}_4 + \text{OH}^-$ as the mechanism of P-release due to pH-increase
According to Hayes and Phillips, the dynamic equilibrium of P in a surface water may be represented by:



Thus heterogeneous equilibrium, characterized by the solubility of AlPO_4 (variscite), FePO_4 (strengite) and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (hydroxy-apatite) and the adsorption of phosphate on clays, determine the distribution between the aqueous phase and the solid phase in the sediments (20,8).

Stumm and Leckie (1970) studied the mechanism of phosphorus exchange and made a steady state model of a natural water system including a kinetic interpretation of the exchange process; they indicated that an unbalance between photosynthesis and respiration functions leads to pollutional effects (21).

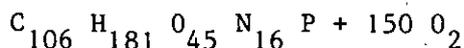
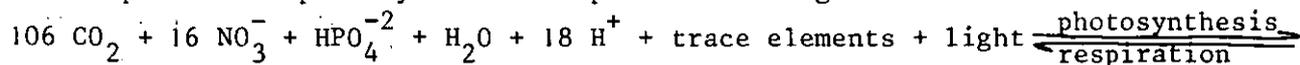
It seems that the effectiveness of the net phosphate sink to the sediments and the velocity of processes regenerating phosphate to the wa-

ter, indicate the mechanisms involved in the process of exchange of phosphate between sediments and lake water to be of a biological, chemical and physical nature. The important factors in these processes are the ability of the sediments to retain phosphate and the conditions of the overlying water and the sediment, causing the transport of phosphate back to the lake water (1).

The biological processes contain two parameters pertinent for the synthesis of biomass in lakes where phosphorus is a growth limiting nutrient: 1. capacity for photosynthesis 2. productivity (rate of biomass production). The biological processes involve phosphorus uptake by algae (conversion of inorganic P into cell P) (1) and mineralization which is the decomposition of algal cells by zooplankton or bacteria (2-9), a process through which, ultimately, phosphate can be released back into the water (or retained by the sediments) (4). Since bacteria cannot penetrate the living cell, autolysis makes the cells susceptible to bacterial attack so that, just before death, the cells become permeable to bacterial enzymes (2-9).

Mineralization in the waterphase is strongly temperature-dependent and can be measured through O_2 consumption in darkness (2-9).

In the process of photosynthesis-respiration of algae:



as a result of mineralization, occurring mainly in the deeper water-layers and in the sediment, phosphate and nitrate were found to be liberated in the same fixed ratio (21).

The chemical processes involve trapping mechanisms in the superficial oxidized mud sediment that can remove inorganic P from water and prevent its transport (20). The removal of inorganic P is supposed to be a precipitation process by calcium, aluminium and iron phosphate or an adsorption one by iron or aluminium oxides and by positive-charged sites of organic particles and clay minerals (3).

The mechanism whereby iron and phosphate combine is believed to be surface adsorption onto hydroxide gels of iron (3); this occurs when lake stratification is destroyed, then dissolved Fe^{2+} is oxidized (by O_2) and the Fe^{3+} ions formed (pH>6), precipitate as $Fe(OH)_3$. Under aerobic conditions, the amorphous hydroxide gels can adsorb phosphate from the water and release it back under anaerobic conditions (23) by the breakdown of the ferric hydroxometal complexes (3). Kamp-Nielsen suggested that iron phosphate controls the anaerobic phosphate exchange (19).

The aluminium phosphates where the hydrate amorphous aluminium-P or aluminium hydroxide-P is considered to be one of the dominant adsorbents of phosphate in anaerobic, slightly acidic sediments (3). In alkaline hard water, often the Calcium-content of the water controls the phosphate concentration (1). Andersen (1975) found that phosphate has been precipitated together with Calcium in the same ratio as in hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). This precipitation carries phosphate into the sediment due to the very low solubility of this compound (5). Addition of $CaCO_3$, generally, increases eutrophication because of increasing pH and carbon supply (2-17) and because soils with $CaCO_3$ have a lower phosphate binding capacity (1).

Clays are small colloidal minerals, that have been found to have not only negative, but also positive charges at the edges of the lattice so that they are able to adsorb PO_4^{3-} ions, following Langmuir isotherm

and forming $Al_4(Si_4O_{10})(OH)_8 PO_4$. Clays, entering a lake, tend to settle to the bottom, adsorbing PO_4^{3-} and removing it from the lake water and thus increasing the phosphate stored in sediment (3).

The physical processes involve, generally, the diffusion transport through the interstitial water, which is generally considered to be the rate determining step for the transfer of phosphate from the solid phase to the overlying water through an undisturbed water-sediment interface (24).

In all but the upper few millimeters of sediment, diffusion is controlled by motion on molecular scale with corresponding low diffusion rate, while in the water, exchange is regulated by much higher variable turbulent diffusion rates (7, 20, 19).

The data demonstrated (18) that the release of phosphates (also Fe and Si) from mud is a result of continuous diffusion, the intensity of which depends on concentration gradients.

The concentration gradient is defined as the difference between the phosphate concentration in the water and the NH_4Cl extractable phosphate in the upper centimeters in the sediment (19).

According to Kamp-Nielsen, under anaerobic conditions, the diffusion process leads to an impoverishment of phosphate (and Fe) in the uppermost layer and under aerobic conditions it leads to a displacement of phosphate (and Fe) from the reduced lower mud into the oxidized mud surface. For aerobic phosphate-binding, diffusion was found to be not an important process, since under those conditions phosphate has to move against a large concentration gradient which does not have a great seasonal variation (19).

Hydrological conditions (turbulence) of the sediment due to wind (especially in shallow lakes) cause the phosphate near the sediment-water interface to be released into the lake water (7, 16). When the whole water column is well mixed, the oxygen supply from the atmosphere is continually delivered by turbulent water movements to the sediment surface and the concentration is maintained close to full saturation at all depths in the water (20), but during the calm warm periods in summer the lake stratifies and can become anoxic below about 2 m depth (17) with an impact on P-exchange like described above.

Controlling factors. The exchange of P in the lake sediments is controlled by various factors. These factors allow phosphate to be released into the interstitial water where it can be transported into the overlying water.

1. pH. Andersen (1975) indicated that phosphate liberation from lake sediments does not generally follow the same pattern from lake to lake but will depend on pH relationships and sediment composition (5). The most pronounced influence of pH is observed on the exchange of P, Fe and Ca (20). This difference in pH was used in soil researches for extracting phosphate selectively from sediments (10,11,12,13,14).

The adsorption of phosphate on clay particles decreases as pH is increasing and phosphate, that may have been originally adsorbed, is released from the solid phase in the sediment (7).

2. Redoxpotential. The difference between reduced and oxidized soils in release and sorption of phosphate suggests that under reducing conditions there is an increase of the solid material that reacts with the phosphate (22), so the amount of phosphate desorbed generally increases with a decrease in the redox potential (3).

Patrick and Khalid suggest that this difference is due to the difference in the capacity of oxidized and reduced forms of iron oxide to sorb and release orthophosphate (22).

This indicates that phosphate is released from sediments at low redox potentials (19) which are caused by decomposition of plankton (4).

3. Temperature. Temperature affects the rate of adsorption of phosphate and the equilibria between sediment and interstitial water (3) in such a way that the rate of adsorption decreases with increasing temperature. The seasonal periodicity of both primary production and thermal stratification means that the exchange of phosphates is strongly influenced by seasons (1). Thus, in shallow eutrophic lakes, during the winter when temperature is low, the sediment adsorbs or retains phosphate and as temperature increases during the summer, also pH increases near the sediment-water interface, the redox potential decreases and the sediments release phosphate back into the interstitial water where it can be transported to the overlying water (3).
4. An example of an experimental system of measuring phosphate-release (as has been developed at T.H. Twente)

Mortimer (1971) indicated that in order to be able to predict the dynamics of nutrient availability from sediments, information on the nutrient concentration in the interstitial water is more important than data on the total nutrient content of sediments (20).

Many experiments have been done on measuring the phosphate exchange between undisturbed sediments and the overlying water. For example, in order to evaluate the phosphate flux from the sediment and its oxygen demand, a series of experiments were conducted (1969) using large underwater chambers that isolated sections of lake bottom (16). Snow and Digiano (1976) used the same idea and built a special fiberglass caisson, simulating a lake volume with bottom sediments exposed to the overlying water but hydraulically separated from the lake itself, only allowing flow of water into and out the caisson passing first through an ion exchanger and an activated carbon, column which reduced the concentration of phosphate in the overlying water (3).

Since turbulence in the overlying water increases release from the sediments and dispersion of phosphate from the overlying water (16) there has been a need for developing a method for undisturbed sampling for laboratory experiments. Mortimer (1942) described the sampling of undisturbed mud cores using the Jenkin surface-mud sampler (20). The center of this apparatus is a glass tube of 6 cm diameter and 60 cm length Bengtsson (1975) used the Jenkin sampler in his experiments for calculating the release rate of phosphate, taking to each experiment 5 cm samples by pressing the sediment down from the tube by a rubber stopper (17).

Fillos and Swanson (1975), although not taking undisturbed samples (all samples were mixed before placement into the reactors), built a specific apparatus for measuring the oxygen uptake rate of benthic deposits (4). This was a continuous flow system (for the overlying water) without disturbing the deposits, consisting of eight airtight reactors in two mixed water baths and a tank from which the water flowed to an activated carbon column, then, through a 25-l glass jug, where the oxygen concentration could be controlled by N_2 gas, to the reactors.

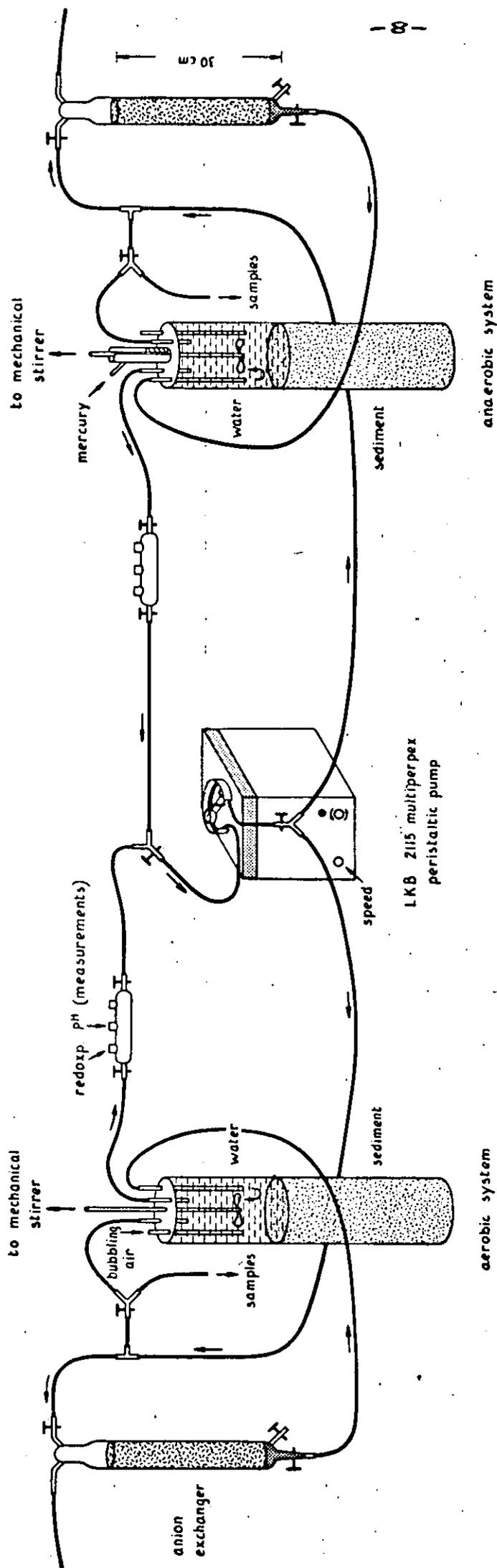
At T.H. Twente, preliminary experiments have been done for the measurement and calculation of the release rate of P from Brielsemeer sediments.

A Jenkin sampler has been used for sampling undisturbed cores. The center of the apparatus is a plexiglas cylinder of 12 cm diameter and 40 cm length. Sediment is filled up to about 30 cm height. The system described in figure 1 consists of: (1) two plexiglas cylinders, one kept under aerobic and the other under anaerobic conditions. Each cylinder contains the sediment and the overlying water as taken from the lake and is sealed with a top plate with openings for inlet-outlet of water, mechanical stirrer and in the aerobic system one more opening for air bubbling. On each cylinder's wall there are special holes, covered with rubber stoppers for inserting the platinum microelectrodes for measuring the redox potentials of different layers of the sediment. (2). LKB pump which can produce a constant flow rate of water through the system. (3) Anion-exchangers which are responsible for reducing the concentration of phosphate in the overlying lake water (4) pipes and valves system for directing properly the flow of water (for the anaerobic system it was suggested to use glass pipes to prevent O_2 leaking into the system). (5) three-necked tubes for measuring pH and redox potentials. Preliminary preparations have to be done: (1) the minimum weight of anion exchanger needed to adsorb the phosphate in the overlying lake water should be calculated (2). The exchanger should be washed first with base and brought to neutral pH in order that the water passing through it would not lower the pH of the whole system. (3) pH, redox potential, orthophosphate, iron (Fe^{+2} , Fe^{+3}) Magnesium, Calcium, Manganese and iron- and calciumbound phosphate-concentration in the sediment should be measured. (4) Producing anaerobic conditions just by closing tightly the system; then, the oxygen disappears because it is reduced by the organic matter in the sediment. (When O_2 is removed by bubbling N_2 gas it was found to lower CO_2 concentration and thus lower pH of the system).

The experiment has to be carried on for about 3 weeks. In the beginning the water is circulated through the anion exchanger for 2-3 hrs. to reduce the original phosphate concentration of the lake water. Then each day the system operates for only one hour.

50 ml. samples are taken in the beginning once a day and when proceeding, once in two days, from a sample pipe, replacing the sampled water by new lake water by pumping it through the same pipe (but in the opposite direction).

The analyses daily done are orthophosphate (ascorbic acid analysis) and iron (Fe^{+2} , Fe^{+3}). In sediments the fractionation method of Chang and Jackson has been used. Besides, efforts have been made to measure the (membrane-) exchangeable phosphate.



capacity of anion exchanger AG 1 - X 4 (20-50 mesh, chloride form) 3^5 meq/gr. dry weight
 1^2 meq/ml. resin bed
 length of anion exchanger column : 40 cm, diameter : 5 cm, filled : 30 cm.
 size of the container (cylinder) : length : 50 cm, diameter : 12 cm, sediment height : ~ 30 cm
 pump - maximal capacity : 100 μ l/min.

Fig. 1 Experimental system for measuring phosphate - release.

LITERATURE

1. J. Griffith, A. Beton, J.M. Spencer and D.T. Mitchell, "Environmental Phosphorus Handbook".
2. H.L. Golterman, "Physiological Limnology - Development in water science (2)".
3. P.D. Snow and F.A. Digiano, "Mathematical Modeling of Phosphorus Exchange Between Sediments and Overlying water In Shallow Eutrophic Lakes", Report to the division of water pollution control, Massachusetts Water Resources Commission. Department of Environmental Quality Engineering (1976).
4. J. Fillos and W.R. Swanson, "The Release of Nutrients from River and Lake sediments". WPCF 47(5) p. 1032 (1975).
5. J. Møller Andersen, "Influence of pH on release of Phosphorus from Lake Sediments", Arch. Hydrobiol. 76(4) p. 411-419 (1975).
6. B. Rippey, "The Behaviour of Phosphorus and Silicon in Undisturbed Cores of Lough Neagh Sediments".
7. R.G. Wetzel, "Limnology".
8. F.R. Hayes and J.E. Phillips, "Lake water and sediment- Radiophosphorus Equilibrium with Mud, Plants and Bacteria Under Oxidized and Reduced Conditions", Limno. Oceanogr. 3 p. 459-475 (1958).
9. A.C. Hendricks and J.K.G. Silver, "Nutrient Ratio Variation in Reservoir Sediments", JWPCF 45 (3) p. 490-497 (1973).
10. S.C. Chang and M.L. Jackson, "Fractionation of soil Phosphorus", Soil science Vol. 84 (1957).
11. A.N. Smith, "Fractionation of Inorganic Phosphorus in soil", AGRI Digest. 17 (1969).
12. J.K. Syers, R. Shah and T.W. Walker, "Fractionation of Phosphorus in Two Alluvial Soils and Particle Size Separates", Soil Science 108 (4) (1969).
13. C.R. Frink, "Fractionation of Phosphorus in Lake Sediments, Analytical Evaluation", Soil Science Soc. Amer. Proc. 33 (1969)
14. K. Vahtras and L. Wiklander, "Phosphate Studies in Soil", Lantbruks-högskolans analen 36 p. 115-134 (1970).
15. H.L. Golterman, C.C. Bakels and J. Jakobs-Mögelin", Availability of Mud Phosphates for the Growth of Algae". Verh. Internat. Limnol 17 p. 467-479 (1969).
16. W.C. Sonzogni, D.P. Larken, K.W. Malveg and M.D. Schudt, "Use of large submerged Chambers to measure sediment-water Interaction", Water Research 14 p. 461-464 (1977).
17. L. Bengtsson, "Phosphorus Release from a Highly Eutrophic Lake Sediment", Verh. Internat. Verein. Limnol. 19 p. 1107-1116 (1975).
18. V.U. Tessenow, "Lösungs-, Diffusions- und Sorptionsprozesse in der Oberschicht von Seesedimenten", Arch. Hydrobiol./suppl. 38 (4) p. 353-398(1972).
19. L. Kamp-Nielsen, "Mud-Water Exchange of Phosphate and Other Ions in Undisturbed Sediment Cores and Factors Affecting the Exchange Rate", Arch. Hydrobiol. 73(2) p. 218-237 (1974).

20. C.H. Mortimer, "Chemical Exchange Between Sediments and Water in the Great Lakes. Speculations on Probable Regulatory Mechanisms", *Limn. and oceanog.* 16(2) p. 387-404 (1971).
21. W. Stumm and J.O. Leckie, "Phosphate Exchange with Sediments: Its Role in the Productivity of Surface Waters".
22. W.H. Patrick and R.A. Khalid, "Phosphate Release and Sorption by Soils and Sediments: Effect of Aerobic and Anaerobic Conditions", *science* 186 p. 53-55 (1974).
23. H.B.N. Hynes and B.J. Greibs, "Movement of Phosphate and Other Ions from and Through Lake Muds", *journal fisheries board of Canada* 27 (4) 1970.