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# Phosphorus in interstitial water: methods and dynamics

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## Abstract

Interstitial (pore) water is important for phosphorus dynamics in limnic ecosystems. This review summarizes the most important processes influencing the generation and transport of pore-water P from, to and within the sediment. Sampling methodology is discussed thoroughly in combination with what little information is available on various P species in the pore water.

Pore water P concentrations in various trophic systems and the spatial and temporal distributions are also described. The last sections of the article deal with diffusive P flux calculations and comparison with measured P fluxes. Factors influencing P fluxes, such as adsorption, possible precipitation mechanisms, advection and bioturbation, are discussed.

The general conclusion drawn from this review is that pore-water P investigations (concentrations and gradients) are an underestimated ecological tool in studying and describing trophic status, redox conditions,spatial and temporal distribution of P-sediment release, potential precipitation mechanisms on a long-term basis and ground-water inflow areas, as well as lake-water seepage.

## Introduction

Organic surface sediments usually have a water content of 95–99% in freshwater ecosystems. Only a minor part of this water is bound to solid chemical substances. The major part of the water content constitutes the mobile liquid medium, which surrounds the sediment particles. This mobile water fraction is named interstitial water or pore water and is a highly important transition medium for the movement of solute species across the sediment-water interface. The volume of pore water from the sediment layer 0–20 cm in a lake can be significant when compared with the volume of the lake. Lindmark & Bengtsson (1979) calculated the pore-water volume (0–20 cm) of Lake Södra Bergundasjön ($A = 4.3$ km$^2$, $Z_{Mean} = 2.4$ m) to be about 5% of the total lake volume. The composition of pore water is therefore an important factor in considering the structure and function of a lake.

Transport of dissolved materials across the sediment-water interface, as well as within the sediment, is an important factor affecting the chemical characteristics of lake. Accordingly, interstitial water concentrations and concentration gradients in the sediment have to be known when exchange processes are studied (Ohle, 1964; Holdren *et al.*, 1977; Brinkman. *et al.*, 1982; Håkansson & Jansson, 1983).

Mechanisms for transport of chemical species across the sediment-water interface were grouped into the following categories by Lerman (1978):

1. sedimentation flux of solids,
2. dissolved material and water flux into the sediment, owing to the growth of the sediment column,
3. dissolved material and pore water flow upwards, caused by a hydrostatic pressure gradient of ground water in aquifers on land,
4. molecular diffusional fluxes in the pore water,
5. mixing of sediment and water at the interface (bioturbation and water turbulence).

Processes 1–3 are advective fluxes, in contrast to the molecular diffusion responsible for process 4 and the mainly random processes in 5. Compaction of the sediment may also cause an advective flux of pore water upwards.

Syers *et al.* (1973) stated that 'interstitial P is the sediment fraction most sensitive to environmental conditions and highest in chemical mobility'. Information on the P level in the interstitial water of lake sediments is therefore more important than information on the sediment total P for predicting the trophic state of the lake and the dynamics of the sediment-P release.

Since, the interstitial P concentration generally exceeds the P concentration in the overlying water, a simple diffusion model and the concentration gradient between pore water and overlying water can be used for calculating the minimum P release across the sediment-water interface (Holdren *et al.*, 1977; Lerman, 1978; Berner, 1980). Other mechanisms, such as water turbulence, bioturbation and gas ebullition, always increase the P flux, compared with values obtained from molecular diffusion considerations. In McCaffrey *et al.*, (1980), Elderfield *et al.* (1981) Callander & Hammond (1982) and Hall (1984), excellent comparative discussions are focused on the use of pore-water gradients and directly measured benthic fluxes in chambers for predicting the P release from marine sediments.

The composition of the interstitial water is controlled by complex interactions between the ground-water recharge system, mineralogical dissolution and precipitations, biological activity, and by physical interactions between sediment and water (Harriss, 1967). The phosphorus concentration in the pore water and in the sediment particles regulate the adsorption-desorption and other exchange processes. The pore water, in turn, influences the dissolved inorganic-P levels in the overlying water (Li *et al.*, 1972).

## Sampling and speciation

### *Sampling*

Limited information is available on the levels of P in sediment pore waters and on the relationships between interstitial P and rates of P release from sediments. One reason for the relatively few detailed studies on pore-water composition probably lies in the methodological problems of separating the pore water or substances dissolved in the pore water from sediment particles. Interstitial water characteristics are determined by the sampling method and handling of the sediments, and these factors should be taken into concideration in comparing the results obtained from various investigations.

According to Brinkman *et al.* (1982), the most important requirements of a pore water sampler are:

1. minimal disturbance of the sediment-water interface and sediment structures,
2. prevention of oxidation of anoxic pore water,
3. little or no change in temperature or pressure,
4. sufficient sample volume,
5. minimal water flow (streaming) through the sediments,
6. high depth resolution. Gradients, especially those close to the interface or the redox boundary, can be rather steep.

There are four main techniques for separating the interstitial water from the sediment particles:

1. separation by centrifugation,
2. separation by pressure or vacuum filtration,
3. separation by dialysis,
4. separation by direct suction.

The separation procedures may also be divided into laboratory methods (1–3) and *in situ* techniques (3–4).

*Centrifugation*

Centrifugation is the simplest way of separating pore water from the sediment. The method is useful for rapid processing of samples when the demands for accuracy and reproducibility are low (Håkansson & Jansson, 1983). The centrifugation rate normally varies between 3000–20000 r.p.m., with a separation time between 15–60 min. Of the separation techniques, the centrifugation method gives the highest values for concentrations of substances, since fine particulate matter is not completely sedimentated. This can, however, be reduced to a certain extent by a subsequent filtration through a 0.2 $\mu$m membrane filter. Chemical changes during sampling and centrifugation will reduce the amount of dissolved P due to adsorption by Fe(III) hydroxides (Bray *et al.*, 1973) and/or an alteration of the gas equilibria. All samples and analytical procedures must then be carried out in an inert atmosphere.

*Pressure filtration*

The filtration is probably the most commonly used method for obtaining pore water. Several devices for pressure and vacuum filtration have been described (Siever, 1962; Reeburgh, 1967; Robbins & Gustini, 1976; Enell, 1979a). Some examples of pressure filtration apparatuses are given in Fig. 1. Some of the devices are made for both laboratory and field use. The pressure filtration apparatus is usually operated with $N_2$ gas, but Ar and He may also be used. In gas operation, the apparatus has no piston or moving parts. The use of an inert gas makes it possible to avoid oxidation during processing of the samples. Filtration is usually performed through a 0.45 $\mu$m membrane filter.

Enell (1979a) studied the influence of several parameters on the sampling and analysis of pore water phosphorus obtained by pressure filtration and concluded that the following factors were crucial for the results (Table 1):

- time between sampling and processing or analysis,
- temperature during storage or processing,
- redox conditions during sampling, storage and processing,
- filtration pressure during processing.

The pore-water separation must be performed immediately after sampling (if possible within some minutes), at *in situ* temperature of the sediment, under nonoxidizing conditions and at an adequate pressure.

Bishoff *et al.* (1970) and Fanning & Pilson (1971) showed that warming marine sediment samples to room temperature, prior to the pressure filtration of the pore water results in enrichment of K, Cl and silica, and depletion of Mg and Ca. These results are due to the change in the ion-change as a function of temperature. Thus, for an accurate analysis of the pore water, separation must be performed at the *in situ* temperature of the sediment.

*Table 1.* Molybdate reactive phosphorus (MRP) concentrations in pore water removed at different temperatures and pressures. Sediment taken from Lake Bysjön.

A. Concentration of MRP in the first 2 ml of pore water.
B Mean concentration of the 2–20 ml portions of pore water (n = 9).
C Range for the concentration of the 2–20 ml portions of pore water (n = 9).
(Modified from Enell, 1979a).

| Sediment depth cm | Temperature °C | Pressure atm | A MRP $\mu$g/l | B MRP $\mu$g/l | C MRP $\mu$g/l |
|---|---|---|---|---|---|
| 0–1 | 4 | 0.5 | 180 | 275 | 260–280 |
| 0–1 | 4 | 2 | 230 | 300 | 280–310 |
| 0–1 | 20 | 0.5 | 480 | 640 | 610–670 |
| 0–1 | 20 | 2 | 280 | 380 | 370–420 |
| 1–2 | 4 | 2 | 200 | 310 | 290–320 |
| 1–2 | 20 | 2 | 310 | 480 | 460–510 |
| 2–3 | 4 | 2 | 260 | 315 | 310–320 |
| 2–3 | 20 | 2 | 420 | 670 | 640–680 |

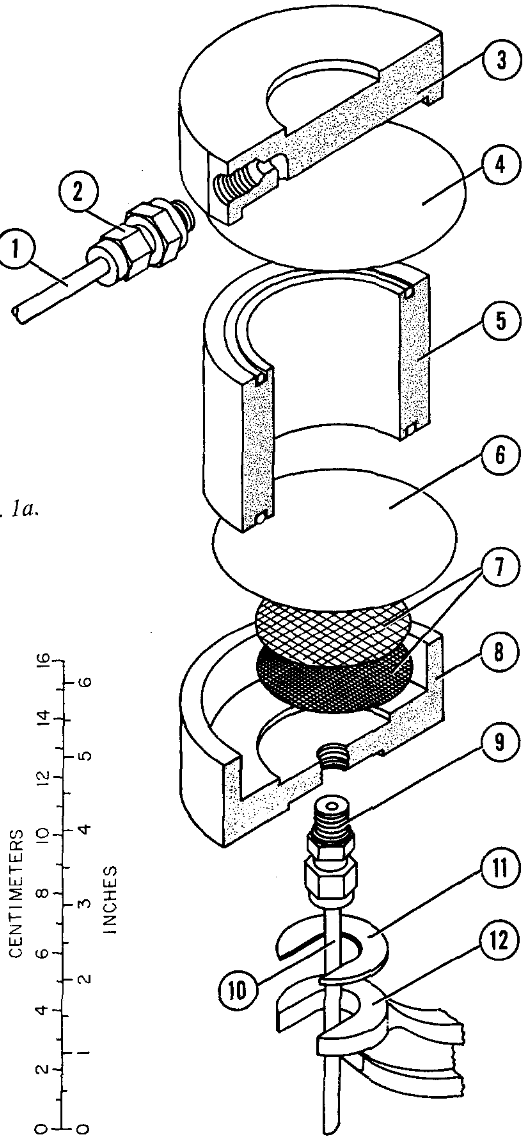

*Fig. 1a.*

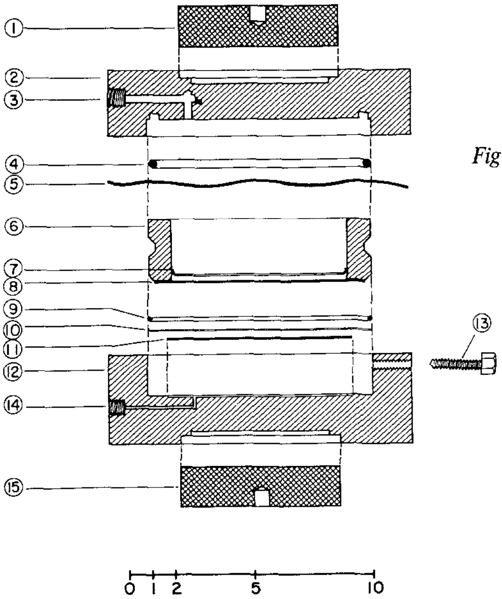

*Fig. 1b.*

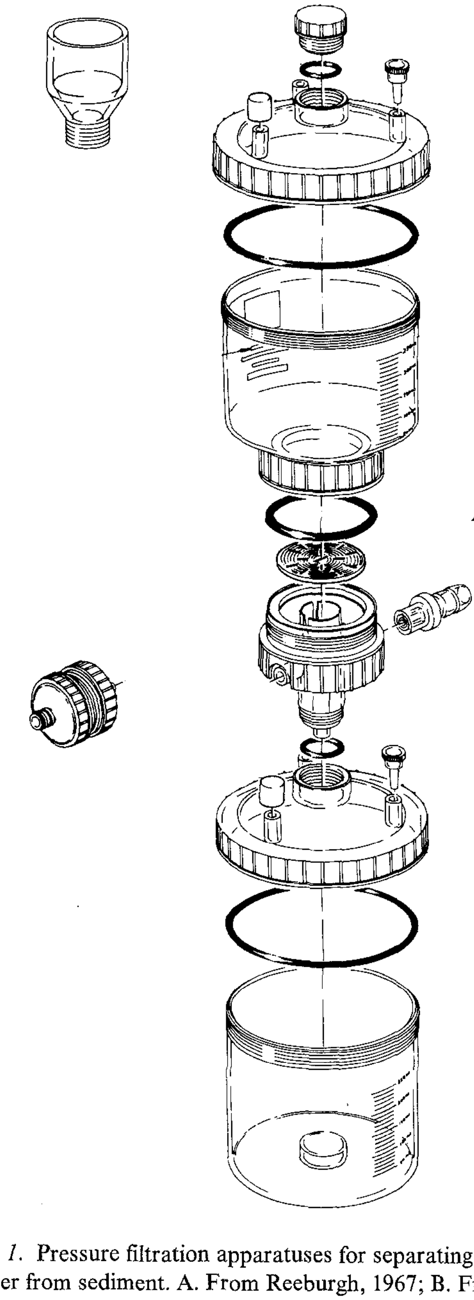

*Fig. 1c.*

*Fig. 1.* Pressure filtration apparatuses for separating pore water from sediment. A. From Reeburgh, 1967; B. From Robbins & Gustini, 1976; C. From Enell, 1979.

### *Dialysis*

One of the main problems associated with pressure techniques is the disturbance caused by the difference between laboratory and *in situ* conditions.

To minimize this source of error, it may be advantageous to carry out the pore-water separation in intact sediment-water cores or *in situ*. This can be done by inserting a probe, glass rod or chamber into the sediment.

Different kinds of dialysis techniques have been designed (Norvell, 1974; Mayer, 1976; Hesslein, 1976; Winfrey & Zeikus, 1977; Ripl, 1978; Bottomley & Bayly, 1984; Yoshida, 1985; van Ech & Smits, 1985). Some apparatuses are shown in Fig. 2 in the dialysis technique, the sampler is initially filled with distilled water, for example, and then coated with a dialysis membrane. A diffusion equilibrium between the pore water outside the sampler and the distilled water inside is reached after an incubation period of about 2–10 days, depending on the temperature, sample volume (radius of the sampler), porosity of the

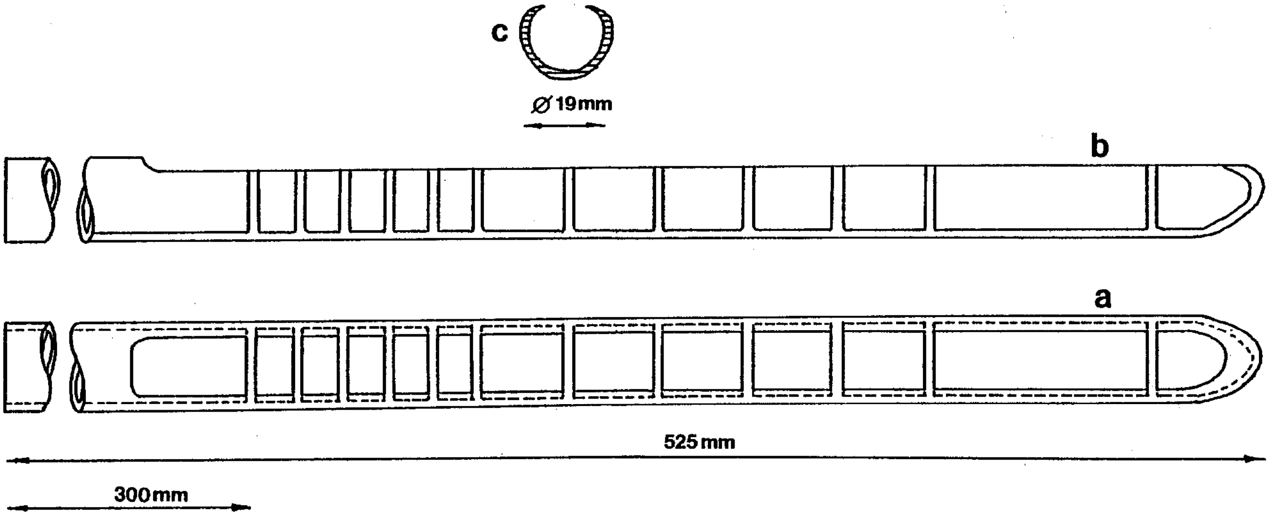

Fig. 2a.

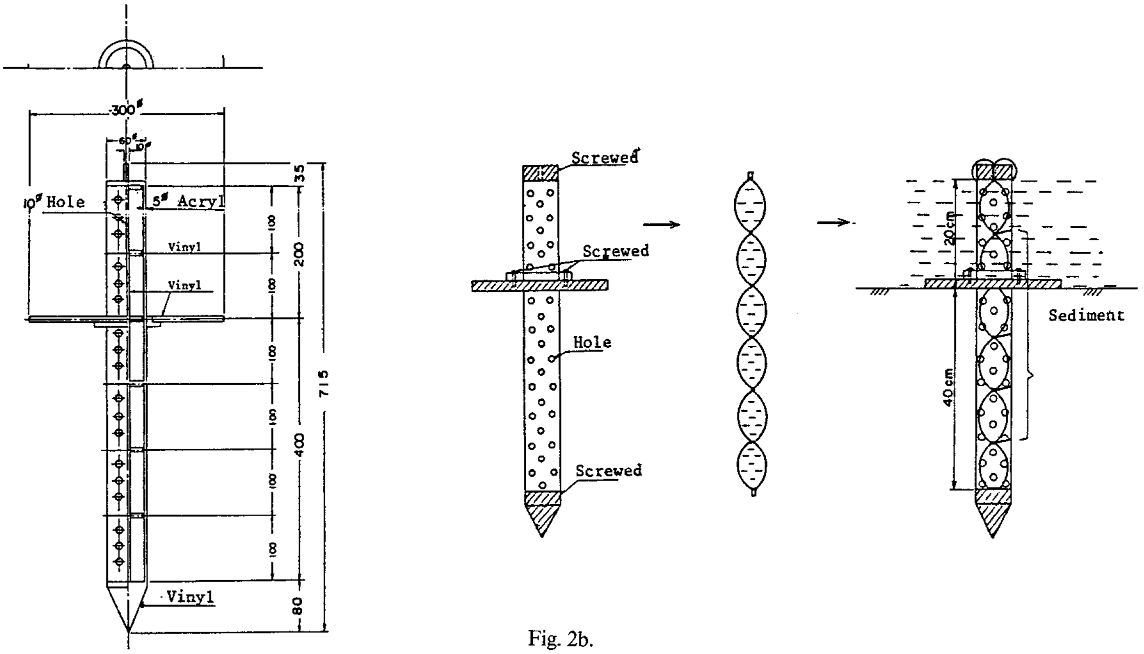

Fig. 2b.

*Fig. 2.* Examples of pore-water samplers using the dialysis technique. A. From Ripl, 1978; B. From Yoshida, 1985; C. From van Eck & Smits, 1985.

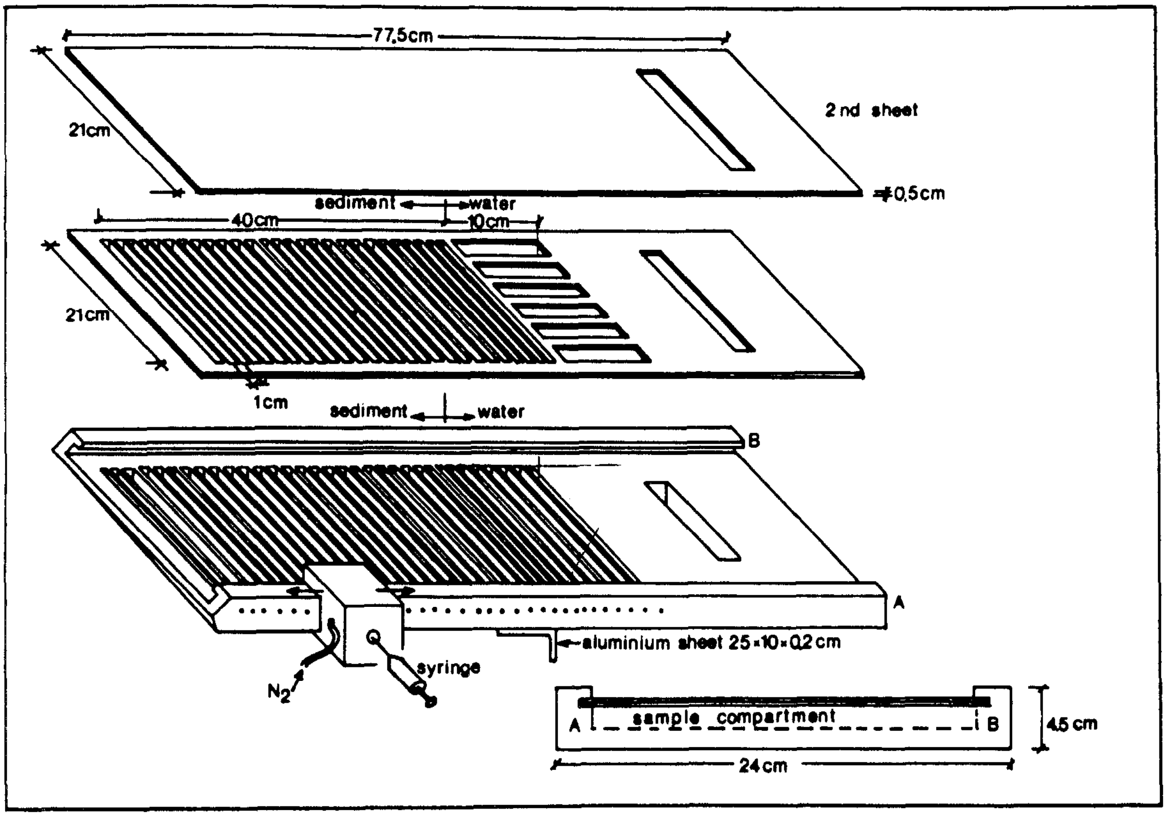

Fig. 2c.

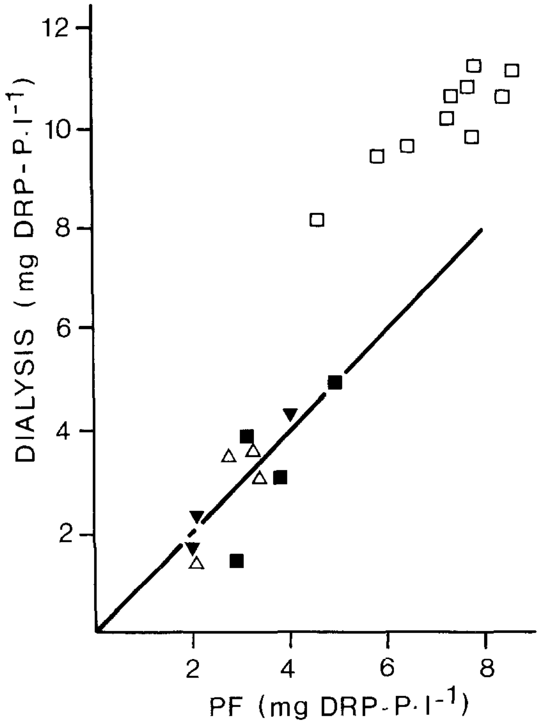

*Fig. 3.* Concentration of $PO_4$-P in the pore water obtained by pressure-filtration (PF, X-axis) and the dialysis method (Y-axis) for various gyttja sediments. The four symbols designate four different sediments. (Modified from Ripl, 1978).

membrane, and the porosity and adsorptive capacity of the sediment.

The results described by Ripl (1978) and Yoshida (1985) show that the P concentrations obtained by the dialysis technique are lower than those obtained by pressure filtration (Fig. 3). Carignan (1984a) found that cellulose-based membranes may lead to underestimations or overestimations of pore-water solutes. Polycarbonate samplers were found to be unsuitable because of iron precipitation. Carignan (1984b) suggests the use of a biological inert dialysis membrane (*e.g.* Gelman HT-450) to avoid destruction of the membrane during incubation. He also found (1984a) that the initial presence of dissolved $O_2$ in the compartments can significantly affect sample composition. The oxidation problem is obviously most pronounced when the dialysis technique is used in oligotrophic lake sediments, and not so important in eutrophic, more microbially active environments, where reduced conditions rapidly develop.

*Suction*

Hertkorn-Obst *et al.* (1982), Brinkman *et al.* (1982) and Howes *et al.* (1985) described apparatuses that collect pore water from sediments by a direct suction sampling techniques (Fig. 4). This

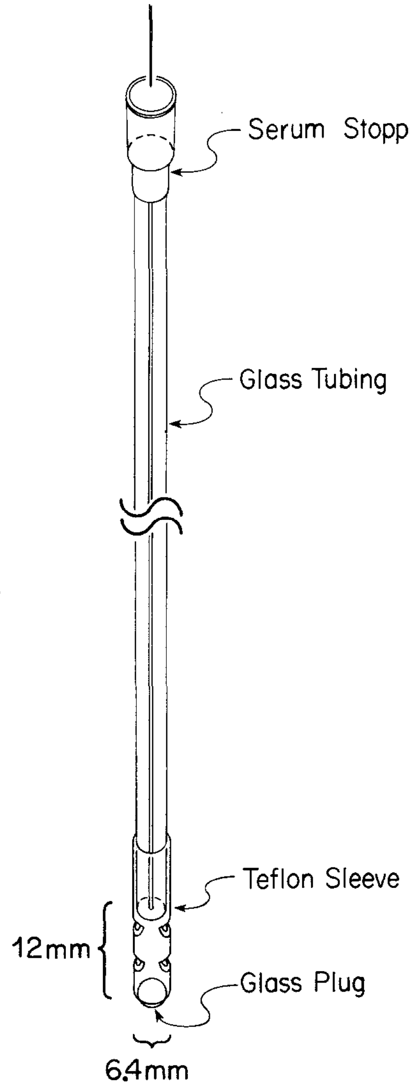

*Fig. 4a.*

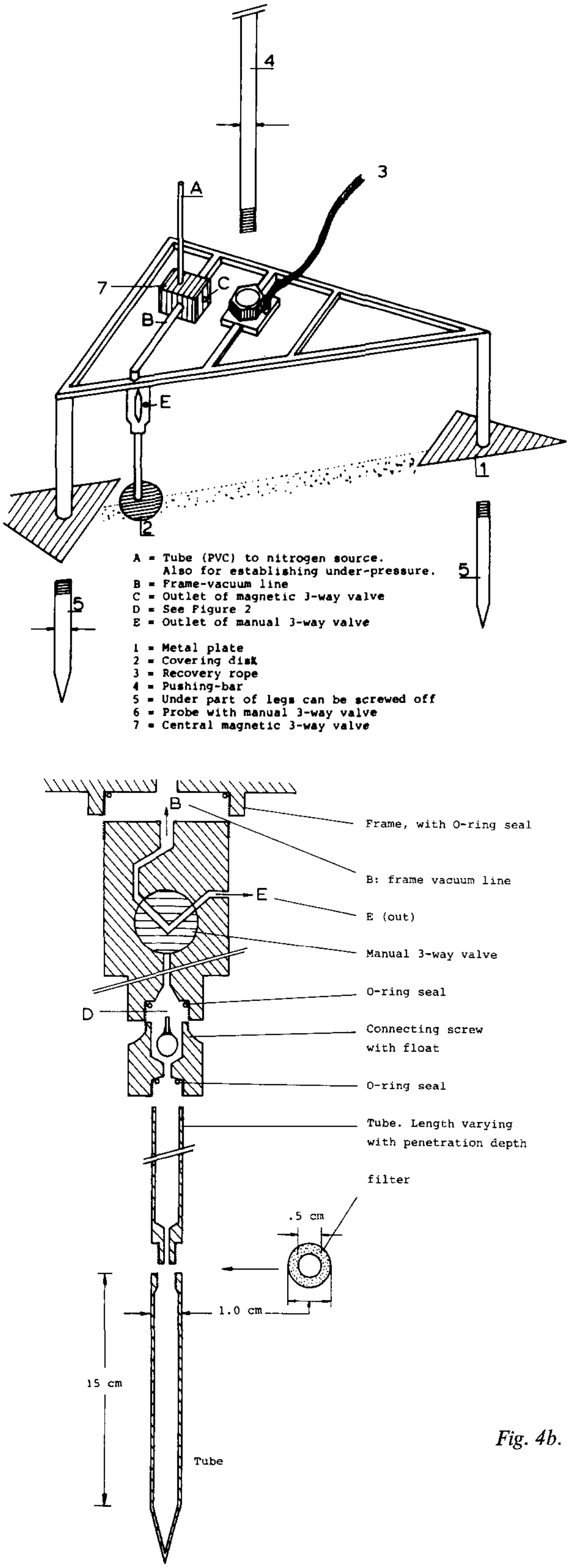

*Fig. 4b.*

*Fig. 4.* Apparatuses for direct suction sampling. A. From Howes *et al.*, 1985; B. From Brinkman *et al.*, 1982.

technique allows interstitial water to be obtained from sediments without serious disturbances of the sediment structure even at quite large sample volumes. Oxidation effects can be excluded. The sampling time is about one day. The technique is, however, not suitable in extremely soft sediments and is also limited to shallow lakes ($< 10$ m).

The pressure needed to force the interstitial water through the probe is simply provided by the hydrostatic pressure at the lake bottom or, alternatively, by vacuum equipment connected to the sampler.

Howes *et al.* (1985) compared the results obtained from three different pore-water separation techniques: centrifugation, squeezing and suction. The sediment core-sectioning techniques (centrifugation and squeezing) significantly increased the concentration of total organic carbon (P not measured). He concluded that the suction technique was the only method giving reliable *in situ* results.

The information above clearly indicates the problems encountered when comparing results obtained from various investigations involving different techniques and sample treatments.

*Speciation*

Generally, the phosphorus in the pore water constitutes a rather small part of the total sediment fraction, $< 1\%$. It must also be stressed that rather sparse information is available concerning the chemical composition of pore water phosphorus.

Most pore-water investigations have focused on the analysis of inorganic P, usually expressed as $PO_4$-P. Methodological studies (Rigler, 1973) have shown, however, that the molybdate-reactive P-analysis often overestimates the orthophosphate concentration because, for example, of hydrolysis of some easily degraded organic substances (Broberg & Persson, this volume).

Surprisingly, few investigators have analysed both soluble reactive phosphorus (SRP) and total dissolved phosphorus (TDP). The reason for this is probably a restricted pore-water volume. Löfgren & Ryding (1985a) concluded that the TDP-fraction and the SRP-fraction were approximately equal in 12 sediments from nine different Swedish lakes. Enell (1980) found that the TDP-fraction in a hypertrophic sediment consisted to about 90–100% of SRP. The percentage of SRP decreased with increasing sediment depth.

Fleischer (1978), however, found in laboratory experiments that the dominant, and only labelled P compound (after $^{33}PO_4$ incubation) had separation characteristics different from SRP and concluded that the compound was of organic nature.

Using gel molecular exlusion chromatography (GEC), Wang *et al.* (1985) made a speciation study of P in the pore water from Lake Geneva sediments. The dominant P from in the uppermost part (0–10 cm) of the sediment was confirmed as being orthophosphate, while condensed P forms dominated in the lower parts ($> 20$ cm). Boers *et al.* (1985) investigated the pore-water composition and the P release from an organic rich lake sediment in The Netherlands. They found that most of the P releases was in dissolved organic form (DOP). The dominant part of the DOP fraction had a molecular weight of 20000–30000.

## Pore-water phosphorus concentrations

The interstitial P concentration generally exceeds the P concentration in the overlying water. Boström *et al.* (1982) concluded that pore-water concentrations are very approximately 5–20 times higher than those in the overlying waters. There is a large deviation in the pore-water P concentration between oligotrophic and eutrophic lakes and the temporal and spatial variation of the interstitial P concentration within lakes is large owing to changes in chemical, physical and biological processes during the year.

*Characteristic concentrations*

In spite of the difficulties encountered when comparing interstitial P concentrations obtained from various investigations with the use of different

*Table 2.* Phosphorus concentrations in sediment pore water (approx. 0–5 cm) from different aquatic systems of different trophic states.

| Local | Trophic state | Method | Minimum mg/l | Mean mg/l | Maximum mg/l | Sampling period | Reference |
|---|---|---|---|---|---|---|---|
| Fegen 6–38 m | O | PF | 0.01 | 0.05 | 0.11 | Su, A | Enell (1975) |
| Hinnasjön | O | PF | 0.02 | | 0.04 | | Graneli (1975) |
| Fiolen | O | PF | <0.01 | 0.04 | 0.07 | W, Sp, Su | Enell (unpubl.) |
| Sörmogen | O | D | <0.01 | 0.09 | 0.20 | Su, A | Enell (unpubl.) |
| Skärsjön 1) 8 m | O | D | 0.01 | 0.05 | 0.08 | Y | Enell & Löf (1983, 1984) |
| Skärsjön 2) 8 m | O | D | | 2.83 | | Y | Enell & Löf (1983, 1984) |
| Viaeredssjön | O–M | PF | 0.07 | 0.29 | 0.54 | Su, A | Enell & Karlberg (1975) |
| Öresjö | M | PF | 0.10 | 0.56 | 1.9 | Y | Enell (1979b) |
| Byasjön 1) 8 m | M–E | D | | 0.46 | | Y | Enell & Löf (1983, 1984) |
| Byasjön 2) 8 m | M–E | D | | 2.20 | | Y | Enell & Löf (1983, 1984) |
| Lillesjön 3) | E | D | | 0.80 | | Y | Ripl (1978) |
| Lillesjön 4) | E | D | | 0.73 | | Y | Ripl (1978) |
| Laduviken | E | D | 0.62 | 0.7 | 0.77 | Sp, Su, W | Enell (1984) |
| Trekanten | E | D | 0.16 | 1.01 | 2.66 | Y | Enell & Lundqvist (1983) |
| Vallentunasjön 2 m | E | D | <0.03 | | 2.82 | Y | Löfgren (unpubl.) |
| Vallentunasjön 4 m | E | D | 1.45 | | 3.45 | Y | Löfgren (unpubl.) |
| Trummen 3) | E | PF | | 2.39 | | W, Su | Bengtsson *et al.* (1975) |
| Trummen 4) | E | PF | | 0.05 | | W, Su | Bengtsson *et al.* (1975) |
| Södra Bergundasjön 1973 | HE | PF | 2.2 | 9.3 | 15.2 | Y | Bengtsson (1975) |
| 1974 | HE | PF | 6.2 | 9.7 | 12.9 | Y | Lindmark & Bengtsson (1979) |
| Bysjön 1974–1977 | HE | PF | 0.33 | 5.3 | 8.7 | Y | Enell (1980) |
| L. Woahink | O | C | | | <0.01 | | Gahler (1969) |
| L. Leman 300 m | O–M | C | 1.06 | | 1.47 | Sp, Su | Nembrini *et al.* (1982) |
| L. 227 in the Experimental Lake Area | O–M | D | | | >0.001 | Y | Schindler *et al.* (1977) |
| L. Minoqua 4.5 m | M | C | 0.01 | | 0.14 | Sp, A | Holdren & Armstrong (1985) |
| L. Minoqua 12 m | M | C | 0.13 | | 0.43 | Sp, A | Holdren & Armstrong (1985) |
| L. Piburger See | M | C | 0.02 | | 0.24 | Y | Psenner (1984) |
| L. Kinneret | E | C | 0.02 | | 0.80 | Y | Serruya *et al.* (1974) |
| L. Mendota 5 m | E | C | 0.14 | | 0.56 | Sp, A | Holdren & Armstrong (1985) |
| L. Mendota 19 m | E | C | 3.27 | | 4.24 | Sp, A | Holdren & Armstrong (1985) |
| L. Wingra 3.5 m | E | C | 0.03 | | 1.6 | Y | Holdren *et al.* (1977) |
| L. Wingra | E | C | 0.25 | | 2.7 | Y | Holdren *et al.* (1977) |
| L. Plussee | E | C | 0.67 | | 3.6 | Y | Golachowska (1979) |
| Stone Lake | HE | ? | 0.21 | | 3.7 | Sp, Su, A | Theis & McCabe (1978) |
| L. Charles East | HE | ? | 0.15 | | 2.5 | Sp, Su, A | Theis & McCabe (1978) |
| Funka Bay, Japan | Mar | PF | <0.7 | | >7.7 | Y | Watanabe & Tsunogai (1984) |
| Mikawa Bay, Japan | Mar | D | 0.01 | | 1.86 | A, W, Sp | Yoshida (1985) |
| Narrangansett Bay, USA | Mar | C | 0.9 | | 24.8 | W, A, Su | Elderfield *et al.* (1981) |

1) at a reference station
2) under a cage fish farm
3) before restoration
4) after restoration

O = oligotrophic
M = mesotrophic
E = eutrophic
HE = hypertrophic
Mar – marine

PF = pressurefiltration
D = dialysis
C = centrifugation

Su = summer value
A = autumn value
W = winter value
Sp = spring value
Y = year value

separation techniques (see section 2), pore-water P concentrations in lakes of different trophic status are given in Table 2.

Table 2 shows that the interstitial P concentration is usually significantly lower in oligotrophic environments (0.01–0.5 mg/l), compared with eutrophic systems (0.1–> 10 mg/l). The range between the minimum and maximum concentrations are also greater in the eutrophic environments.

We have found that in calculating a characteristic interstitial P concentration for a lake sediment, it is necessary to have results from observations made during all four seasons.

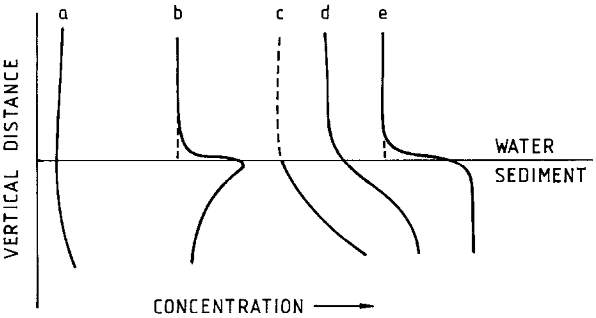

*Fig. 5.* Schematic representation of profile shapes of soluble reactive P (SRP) in the water-sediment column. The water-sediment interface is usually equal to the redox boundary. Broken lines denote turnover periods. The individual shapes a–e are discussed in the text.
(Modified from Davison, 1982).

## *Generalized vertical profiles*

Vertical pore-water P profiles, obtained in different trophic environments, exhibit various shapes. In order to understand the different processes involved in creating a profile, a good conceptual understanding may be obtained by reading the discussion of different iron and manganese profiles provided, in generalized terms, by Davison (1982). As a result of the strong interrelation between iron and phosphorus, it can be stated that many of the processes controlling the iron system also affect phosphorus. Manganese may also be important for the adsorption of P in the presence of divalent cations (Kawashima *et al.*, 1986).

Figure 5 shows a generalized picture of some pore-water P gradients in different trophic environments. The following gradients were recorded:

a) in most of the oligotrophic lakes, with a more or less homogeneous SRP concentration throughout the sediment and water column (Lake Skärsjön, Enell & Löf, 1984).
b) at shallow water depths in eutrophic sediments (L. Vallentunasjön, Löfgren, unpubl.), in eutrophicated surface sediments caused, for example, by cage fish farming (Lake Skärsjön, Enell & Löf, 1984), after a shift from oxidized to reduced conditions in eutrophic sediments (Tessenow & Frevert, 1977), after a collapsed *Myriophyllum* bloom in eutrophic littoral sediments (Lake Buckhorn, Carignan, 1984b), and after the collapse and sedimentation of a dense phytoplankton bloom (Funka Bay, Watanabe & Tsunogai, 1984).
c) in eutrophic sediments during turnover (Lake Årungen, Skogheim, 1978).
d) in eutrophic sediments during stratification (Lake Årungen, Skogheim, op. cit.).
e) in hypertrophic sediments during both stratified and circulating periods (Lake Bysjön, Enell, 1980).

The broken lines in the water phase in the figure represents a circulating water mass.

## *Temporal variation*

Temporal variations are particularly pronounced in shallow and eutrophic systems. This results in increased P concentrations especially during summer and autumn periods (Fig. 6), in connection with the degradation of plant debris (Carignan, 1984b, 1985), and following the sedimentation of a phytoplankton bloom (Watanabe & Tsunogai, 1984). In addition, short term variations within days are found in these upper sediment layers (Fig. 7, Kawai *et al.* 1985).

*Fig. 6a.*

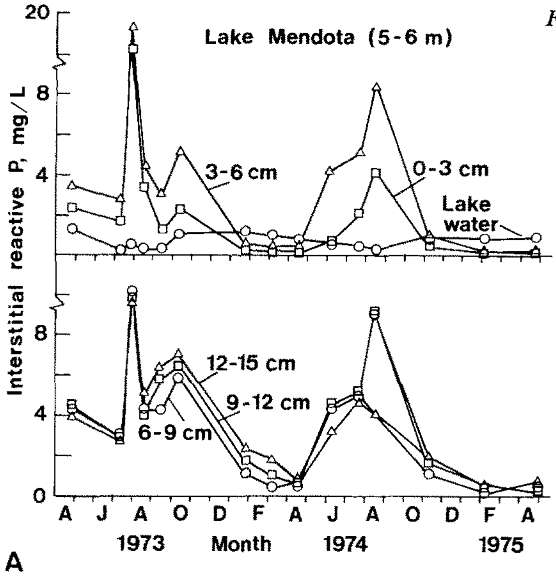

*Fig. 6c.*

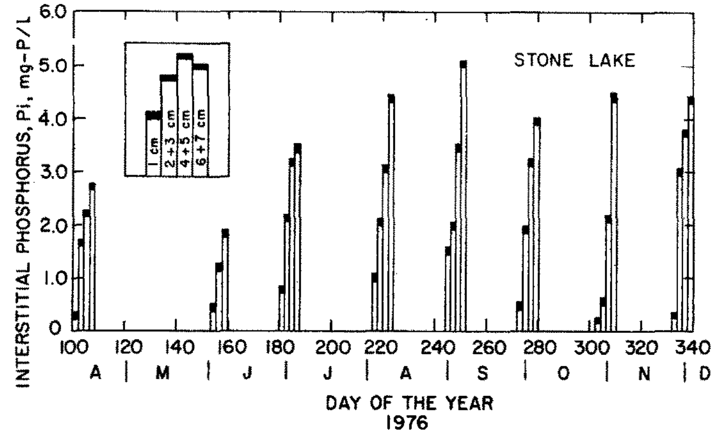

*Fig. 6b.*

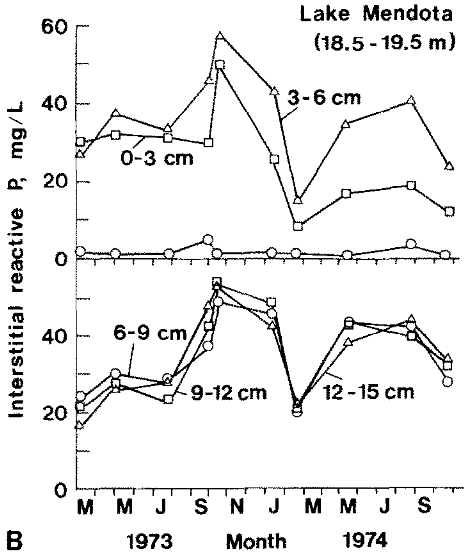

*Fig. 6d.*

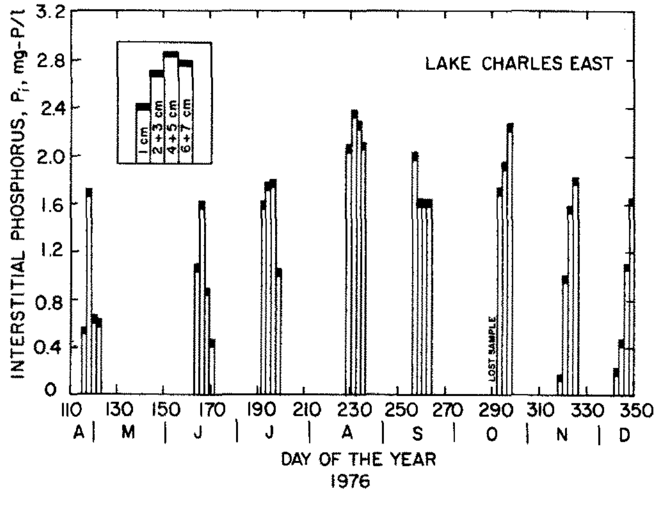

*Fig. 6.* Seasonal variation in the concentration of P in pore water from A. Lake Mendota, water depth 5–6 m. B. Lake Mendota, water depth 18–19 m. C. Stone Lake, water depth 18 m. D. Lake Charles East, water depth 3.2 m. (A and B from Håkansson & Jansson (1983), modified from Holdren *et al.*, 1977, and C and D reprinted with permission from Water Res., 12, Theis a McCabe, Phosphorus dynamics in hypereutrophic lake sediments, Copyright 1978, Pergamon Journals Ltd.)

Hourly changes can be expected in shallow regions in view of the rapid changes in oxygen gradients recorded in marine environments by microelectrode measurements (Revsbech *et al.*, 1983; Jörgensen & Revsbech, 1985). Deeper sediment strata (usually below 20–30 cm) show small seasonal changes (Fig. 8).

Temporal changes in the surface-sediment pore-water chemistry are mainly caused by microbial activity, but the hydrodynamics of the water column and seasonal variations in benthic populations may also have a great influence. Microorganisms rapidly change their activity in response to environmental changes, such as input of

*Fig. 7a.*

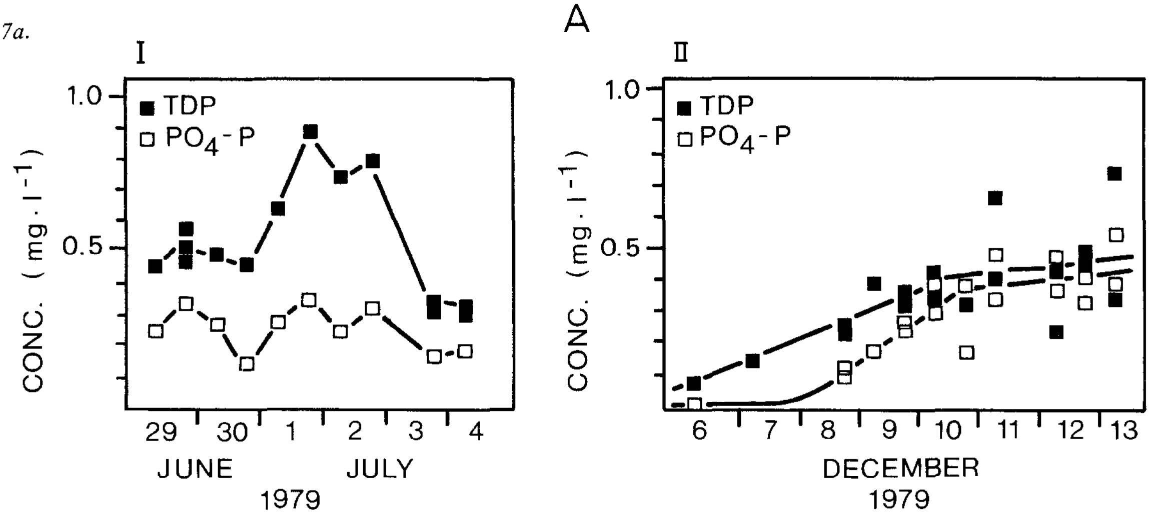

*Fig. 7b.*

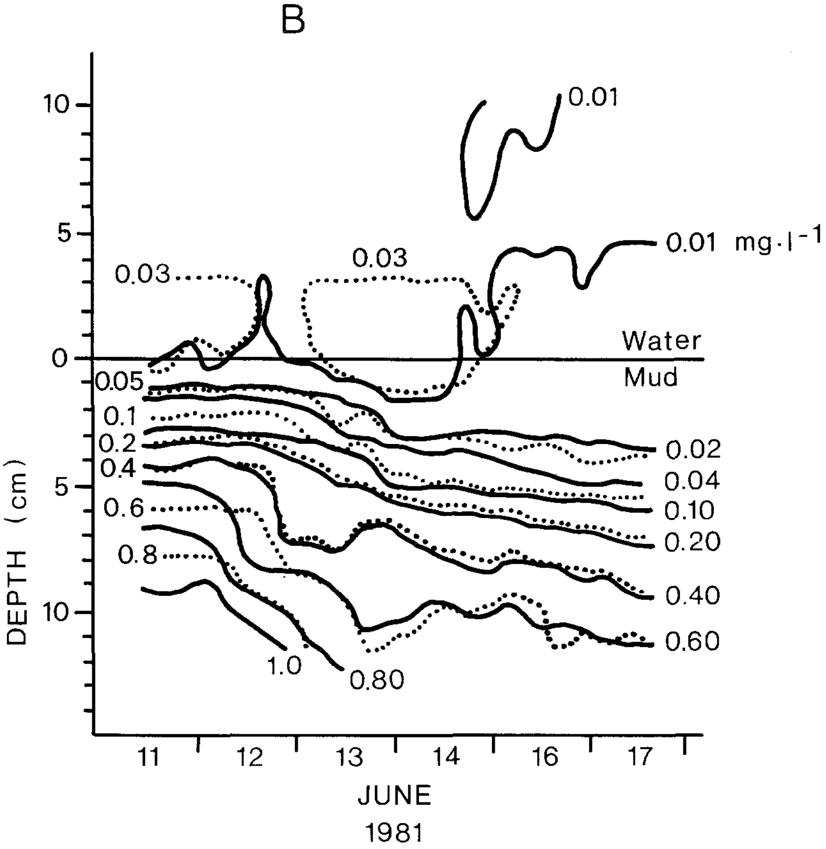

*Fig. 7.* A. Changes in the concentration of TDP and $PO_4$-P in the pore water at Station 1 in Takahamairi Bay. I: 29/6–4/7 1979; II: 6–13/12 1979. B. Vertical and temporal change in TDP (broken line) and $PO_4$-P (solid line) concentrations in overlaying and pore waters at Station 3 in Takahamairi Bay. (Modified from Kawai *et al.*, 1985).

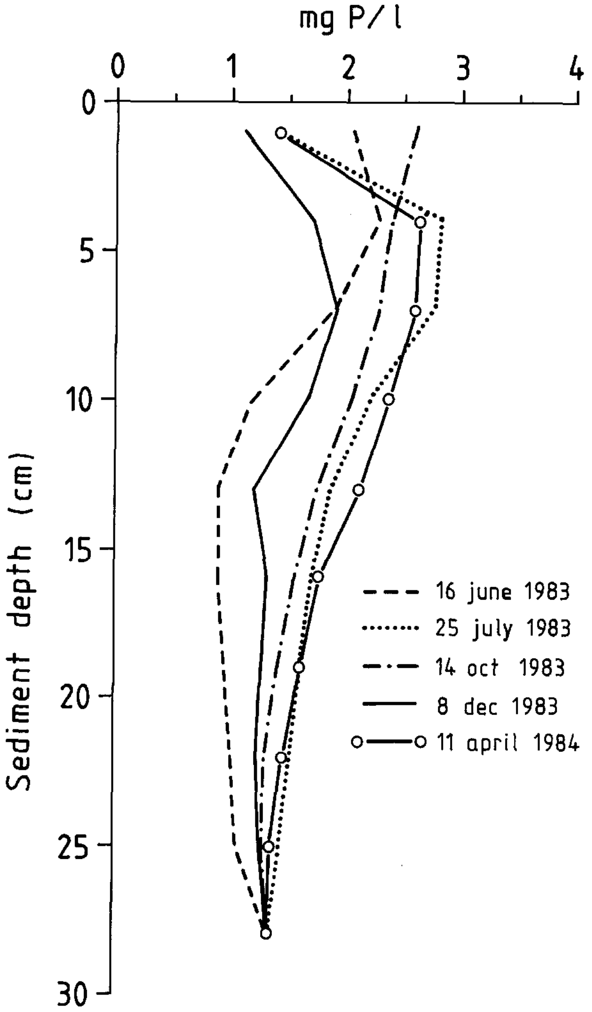

*Fig. 8.* Seasonal and vertical variation of pore water reactive P (SRP) in Lake Vallentunasjön, Sweden. (Löfgren, unpubl.)

organic matter, fluxes of electron acceptors and changes in temperature. This creates changes in redox potential and thereby in the adsorption-desorption characteristics of the iron-phosphorus system. Simultaneously, there is a biological uptake or release. A diffusive flux, directed downwards and/or upwards from this biological active layer also leads to a slow change in this more biological inert zone.

The seasonal variation in the ground-water inflow may also be of interest (Vanek, 1985a & b; Enell, 1985a).

### *Spatial variation*

Factors creating different spatial distribution patterns of the pore-water P concentrations show a great diversity. In general, the variations are determined by the chemical composition and amount of sedimentating material, in combination with bottom dynamics. Higher concentrations are usually found at accumulation bottoms with sediments rich in organic material and phosphorus (Holdren *et al*, 1977; Frevert, 1979; Enell, 1980, 1985b).

Point sources, such as sewage treatment plants and industries can also create sediment areas with high interstitial-P concentrations (Fig. 9, Frevert, 1979). Ground-water inflow to a lake-water seepage through the organic sediment can also create strange distribution patterns. The latter process results in a more or less homogeneous concentration throughout the water and pore water column (Enell, 1985a). A high oxygen content in the lake water can result in a well-oxidized surface sediment with low P concentrations in the pore water down to considerable depth.

## Physical and chemical transformations

### *Adsorption-desorption*

The distribution of P between solids and solution in sediment-water systems has been investigated in numerous adsorption-desorption studies, where interest has been focused on the capacity of the sediments to fix or liberate P.

Adsorption in a solid-solution system is caused by surface reactions, where solute species attach to solid surfaces by either chemical bonds, steric effects or electrostatic forces (Stumm & Morgan, 1981). In sediment adsorption studies, however, the results obtained are dependent upon the experimental technique used. Adsorption or sorption is often synonymous with uptake, which may include biological processes as well as precipitation of discrete solid phases.

The sorption capacity of a sediment is strongly influenced by its mineral composition. Inorganic

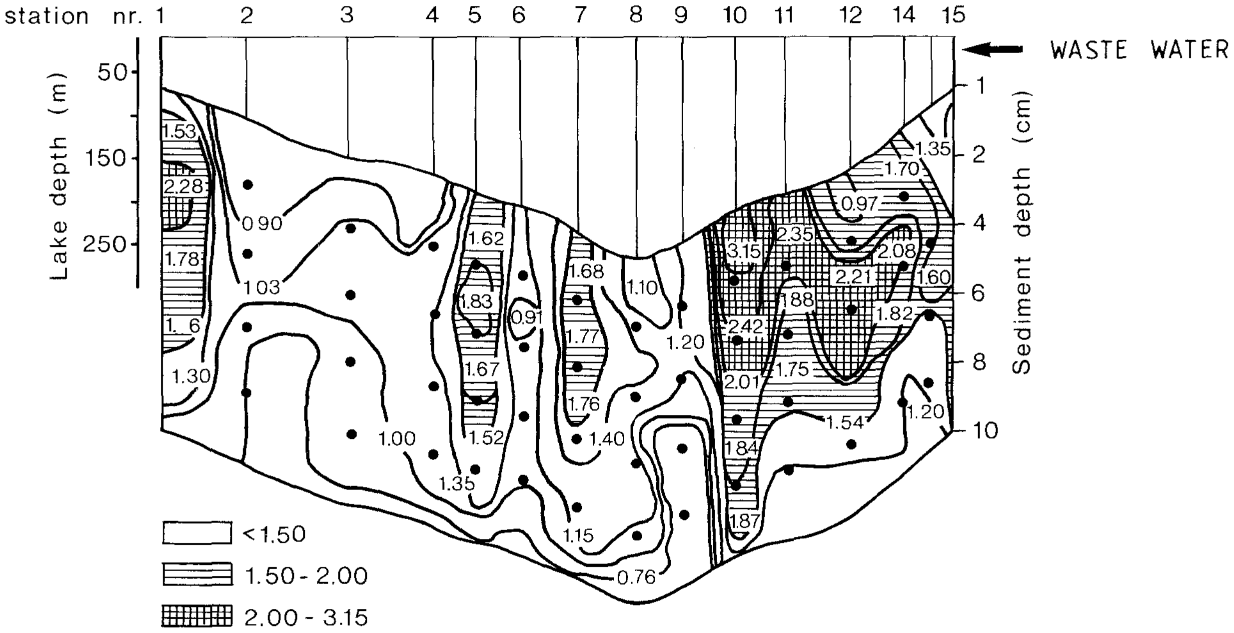

*Fig. 9.* Isoconcentration diagram vs. sediment layers (cm) for TDP in the pore water of station KN-LA in Lake Constance. Concentration in mg/l. (Modified from Frevert, 1979).

solids, such as ferric oxyhydroxides, aluminium oxyhydroxides, calcium compounds (*e.g.* calcite and aragonite) and clay minerals (*e.g.* illite, montmorillonite and kaolinite) have a high affinity for phosphate (Cole *et al.*, 1953; Stumm & Leckie, 1971; Edzwald *et al.*, 1976; Lijklema, 1977; 1980, deKanel & Morse, 1978; Stumm & Sigg, 1979). These compounds can serve as adsorption sites in sediments (Stumm & Leckie, 1971; Tessenow, 1974; Jacobsen, 1977; 1978a,b, Ku *et al.*, 1978; Krom & Berner, 1980a). With the exception of humic-iron complexes (Ohle, 1937; 1964), the organic matrix, however, seems to be less efficient in adsorbing phosphate. Boström *et al.* (1982) in fact state that 'the organic matter itself cannot bind phosphate, but that the adsorption of P is entirely dependent on the amount of associated metals such as iron and aluminium'.

By changing the surface charge of the solids, pH greatly affects the adsorption capacity. A positive correlation is found between a decrease in pH and an increased binding of P to iron, aluminium and clay compounds (not for montmorillonite). On the contrary, the calcium compounds, calcite and montmorillonite increase their phosphate reduction capacity at high pH and as a result of the precipitation of an insoluble calcium phosphate phase, possibly apatite (Stumm & Leckie, 1971; Edzwald *et al.*, 1976; Jacobson, 1978a).

Sediment desorption experiments at different pH values show increased release with increased pH (Boström *et al.*, 1982). However, extrapolation of results obtained from exchange experiments at pH 8–10 to lake conditions may be somewhat hazardous, since sediments are generally extremely well-buffered systems with approximately neutral pH. High pH might possibly release phosphate attached to iron and aluminium compounds at the sediment surface. It has been shown, however, that the internal P load rises during periods of high pH in the lake water (Ryding 1985).

Ever since the studies of Einsele (1936, 1938) and Mortimer (1941, 1942) the importance of the redox-dependent sediment-phosphorus release has been well established among limnologists. Under oxidized conditions, phosphate is adsorbed and coprecipitated with amorphous ferric oxohydroxides, while reduced conditions cause dissolution of the ferric-oxyhydroxide-phosphate complexes, resulting in a release of ferrous iron and phosphate.

Equilibrium models such as the Langmuir of Freundlich equations are most frequently used to describe the adsorption-desorption properties of different sediments, but empirical models have also been used (*e.g.* Logan 1982). Krom & Berner (1980a) used a linear isotherm to describe adsorption between sediment particles and pore water (Fig. 10), and described two estuarine sediments with a simple linear adsorption coefficient both at oxidized and reduced conditions (Table 3). Their study is the only one, as far as we know, in which the changes in P concentration both in pore water and bottom water are followed so as to permit the amount of P adsorbed to be calculated.

It is difficult to make a quantitative comparison of adsorption isotherms reported in the literature because the experimental designs are not standardized. Table 3 shows, however, a summary of some reported values of phosphate adsorbed per equilibrium concentration for different substances. Figure 11 shows the adsorption of isotherms for eight Danish lake sediments.

No general conclusions can be drawn on the adsorption capacity of calcareous as compared with non-calcareous sediments. Williams *et al.* (1970) and Shukla (1971) found that non-calcareous sediments were more efficient in sorbing phosphate than calcareous, but Berner (1974) and Morse & Cook (1978) have shown large phosphate fixation also in calcareous sediments. These contradicting results are not unexpected because the adsorption capacity is dependent not only on the type of substrate, but also on the number of adsorption sites, which can differ greatly as a result of varying amounts of adsorbent, competition between phosphate and other ligands or be reduced as a result of organic coatings on the surfaces. Jacobsen (1978a) strongly emphasizes the importance of the ferric iron system for the adsorption of phosphate at the sediment surface. He also emphasized the fact that calcium-bound phosphate is more abundant in the reduced sediment strata.

To some extent, the pore-water P concentration reflect the adsorption characteristics within the sediment. It seems reasonable to conclude that sediments with a large reduction in P concentration between oxidized and reduced layers have a high adsorption capacity, caused by the iron system.

### *Precipitation of solid phases*

Formation of discrete P mineral phases within sediments (authigenic formation) have been intensively studied for a long time. Interest has been focused on whether there are any equilibrium reactions which can 'buffer' high pore water P concentrations by precipitation of solid phases. It has been proposed that a number of mineral species control the pore-water P concentration in sediments, but empirical evidence for such a buffering system is not available, except for minerals formed during geological time perspectives (Altschuler, 1973). The formation of vivianite ($Fe_3(PO_4)_2\ 8H_2O$), which has been reported to have a short response time (1–20 days) for phosphate with respect to iron phosphate precipitation, must also be considered as a potential buffering system (Emerson & Widmer, 1978).

Environments suitable for authigenic phosphate mineral formation are mostly found in highly reduced sediments, where mineralization and reduction have created high concentrations of such elements as iron, calcium and phosphate (Gulbrandsen, 1969; Jones & Bowser, 1978). Vivianite crystals, suggested to be authigenically formed, have been identified by X-ray diffraction in limnic sediments from such reduced environments (Dell, 1973; Tessenow, 1974; Nriagu & Dell, 1974; Postma, 1981; Nembrini *et al.*, 1982; Merkt, 1985). Poorly crystalline or amorphous vivianite has also been reported (Emerson & Widmer, 1978; Siebers *et al.*, 1982). Apatite ($Ca_5(PO_4)_3(F,OH)$) and carbonate apatite ($Ca_{10}(PO_4)_5CO_3F_2(OH)$) crystals, authigenically formed, have been identified in marine environ-

*Table 3.* Values of mass of phosphate adsorbed/equilibrium concentration for different substrates. Data should be used for approximate comparisons. Experimental conditions varied between studies and data have often been fitted to more complex isotherms than the linear model used. From Krom & Berner (1980a, references in the table can be found in the original paper).

| Substrate | Oxygen status in exp. | K* | Reference |
|---|---|---|---|
| Iron oxide (goethite) | oxic | 3000 | Hingston *et al.* 1974 |
| Illite | oxic | 250 | Edzwald *et al.* 1976 |
| Montmorillonite | oxic | 100 | Edzwald *et al.* 1976 |
| Calcium carbonate (syn. powder) | oxic | 20 | Edzwald *et al.* 1976 |
| Calcite | oxic | 20 | Cole *et al.* 1953 |
| Aragonite | oxic | 10 | deCanel & Morse 1978 |
|  | oxic | 175 | deCanel & Morse 1978 |
| Soil | oxic | 15–70 | Olsen and Watanabe 1957 |
| Soils | oxic and anoxic | 80 | Khalid *et al.* 1977 |
| Lake sidement | oxic | 40 | Hwang *et al.* 1976 |
| Lake sediment |  |  |  |
| calcareous | oxic | 35 | Li *et al.* 1972 |
| noncalcareous | oxic | 25–35 | Li *et al.* 1972 |
| Lake sediment |  |  |  |
| calcareous | anoxic | 5 | Li *et al.* 1972 |
| noncalcareous | anoxic | 1–5 | Li *et al.* 1972 |
| Estuarine sediment | oxic | 3750 | Jitts 1959 |
| Estuarine sediment | oxic | 250 | Pomeroy *et al.* 1965 |
| Estuarine sediment | oxic | 50 | This study |
| Oceanic sediment | oxic | 500–5000 | Berner 1973 |
| Estuarine sediment | anoxic | 1 | This study |

K* = linear adsorption coefficient

ments (Gulbrandsen, 1969; Altschuler, 1973). The presence of poorly crystalline particles in limnic sediments has also been suggested (Emerson & Widmer, 1978), but the precipitation kinetics at least for the crystallized apatite, seem to be slow (Frevert, 1979).

As a result of the findings of authigenically formed P minerals in sediments, thermodynamic equilibrium models have been tested in a search for possible phosphate 'buffering' systems. This approach assumes that the system is in thermodynamic equilibrium and that the solid phase is well characterized and present in the sediment. This is obviously not always true, but the approach indicates which minerals might be formed and definitively rules out those that cannot be formed.

Supersaturation with respect to vivianite, apatite and other minerals is frequently reported and

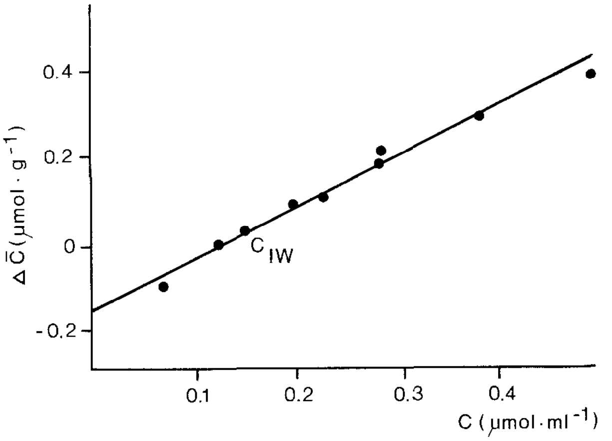

*Fig. 10.* Representative plot of mass of phosphate adsorbed during experiment ($\Delta C$) in μmol/g against equilibrium concentration of dissolved phosphate (C) in umol/ml. $C_{IW}$ is concentration of phosphate in original pore water. (Redrawn from Krom & Berner, 1980a.)

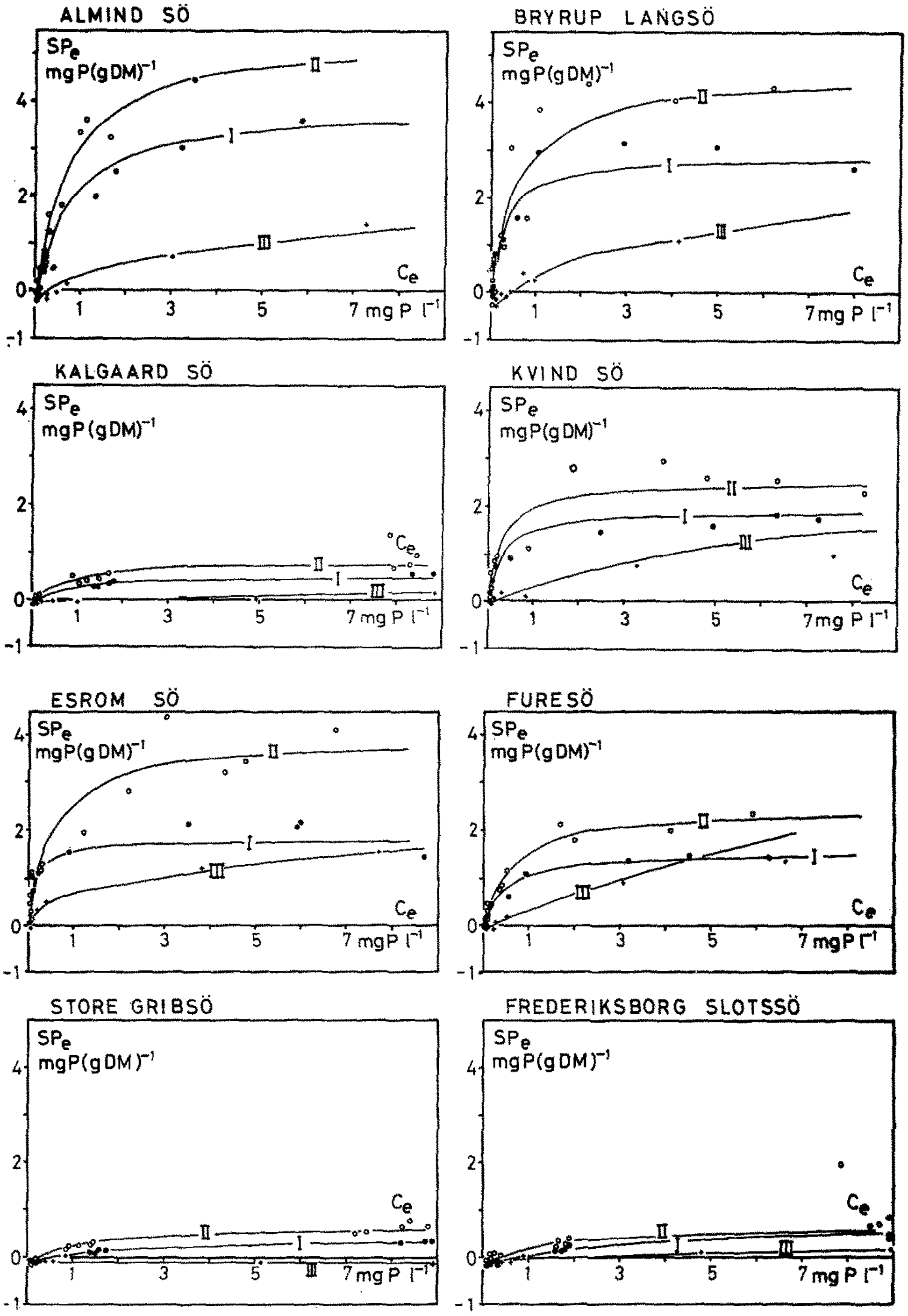

*Fig. 11.* Results of sorption experiments with eight Danish lake sediments and calculated isotherms. I: oxidized mud and demineralized water, II: oxidized mud and lake water, and III: reduced mud and demineralized water. (From Jacobsen, 1977).

is explained by slow kinetics for the precipitation reactions. Crystal growth of vivianite is controlled by a slow process at the grain surface rather than by diffusion to the surface (Emerson & Widmer, 1978). Postma (1981) showed that processes tending to increase pH were much more rapid than the precipitation reaction. Accordingly, it may be concluded that high supersaturation with respect to vivianite is to be expected at higher pH, and that many other processes which tend to change the pore-water phosphate and ferrous iron concentration more rapidly than within 1-20 days may affect the saturation level. Saturation or supersaturation with respect to vivianite in marine environments was reported by Elderfield *et al.* (1981) and Martens *et al.* (1978) and in limnic systems by Dell (1973), Emerson (1976), Emerson & Widmer (1978), Frevert (1979), Holdren & Armstrong (1985), Löfgren & Ryding (1985a), Nembrini *et al.* (1982, 1983), Norvell (1974), Nriagu & Dell (1974), Postma (1981) and Tessenow (1974).

Apatites can be directly precipitated on surfaces of biogenic silica and/or inorganic phases, such as calcite (Burnett, 1977; Stumm & Leckie, 1971) or be deposited in place of $CaCO_3$ (D'Anglejon, 1968; Manheim *et al.*, 1975). Formation is, however, greatly inhibited by $Mg^{2+}$-ions and the reaction rate is strongly reduced at high $CO_3^{2-}/PO_4^{3-}$ ratios (Stumm & Leckie, 1971). Supersaturation has also been found for apatite in many sediments (Burnett, 1977; D'Anglejon, 1968; Gaudette & Lyons, 1980; Korm & Berner, 1980b, Manheim, 1974; Carignan, 1984b; Emerson, 1976; Holdren & Armstrong, 1985; Löfgren & Ryding, 1985a,b; Norvell, 1974).

Other minerals in pore-water systems reported as saturated or supersaturated (indicating slow reaction kinetics) are struvite $MgNH_4PO_46H20$ (Elderfield *et al.*, 1981; Martens *et al.*, 1978, McCaffrey *et al.*, 1980), anapaite $Ca_2Fe(PO_4)_24H_2O$ (Holdren & Armstrong, 1985; Nriagu & Dell, 1974), proapatite $Ca_2(HPO_4)(OH)_2$ (Frevert, 1979) and whitlockite $Ca_3(PO_4)_2$ (Holdren & Armstrong, 1985; Matisoff *et al.*, 1980; Norvell, 1974).

From these kinetic considerations it may be concluded that phosphate precipitation reactions are slow processes and that the kinetics of many other physical, chemical and biological processes are much more rapid. Formation of discrete minerals can hardly 'buffer' pore-water P changes to any great extent in biological active sediments in which the environmental conditions can change within hours. In biologically more inert sediments and below the active biological surface layer, however, minerals can form and act as a phosphate 'buffer' system over the long term.

## Fluxes of phosphate in the sediment column and across the sediment-water interface

Pore-water P compounds are directly exchangeable with the water column (Syers *et al.*, 1973; Boström *et al.*, 1982) and the often very steep concentration gradients at the sediment-water interface, create a driving force for a diffusive flux towards the lower concentration in the overlying water. Phosphorus release from sediments is caused by this concentration gradient, but the rate-determining process does not have to be of molecular diffusive origin. Bioturbation, gas ebullition, currents, etc., are other processes which can significantly increase the P flux (Boström *et al.*, 1982). From a P concentration maximum (Fig. 12) in the pore water, a diffusive flux is directed both upwards and downwards in the sediment column (Berner, 1980; Davison, 1982; Watanabe & Tsunogai, 1984).

### *Fluxes within the sediment column*

Sediments may be regarded as liquids containing high concentrations of solids (Davison, 1982). Accordingly, Fick's First Law of diffusion in aqueous solution may be applied to the system with some modifications. Theories for mathematical modelling of diffuse fluxes within sediments have been described by Lerman (1978) and, more recently, by Berner (1980).

Solid particles in the sediment hinder the

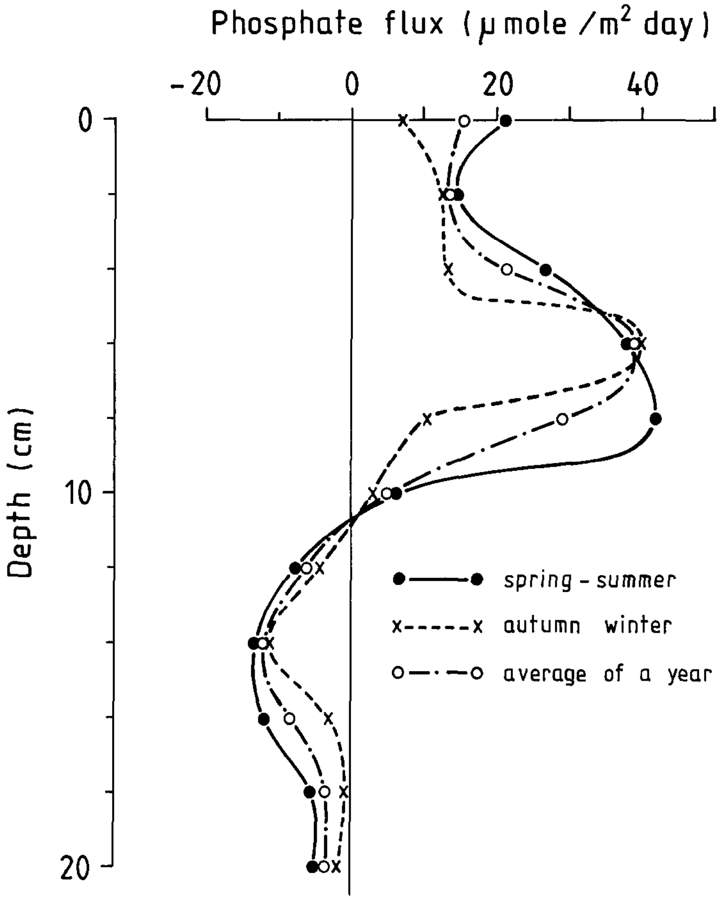

*Fig. 12.* Vertical profiles of the calculated interstitial phosphate flux ($\mu$mol/m$^2$ d) in the top 20 cm. The three curves relate respectively to the spring-summer (Aug. and Sept. 1980 and Mar.–July 1981) and autumn-winter (Oct. 1980–Feb. 1981) period and the annual mean (Aug. 1980–July 1981). Positive and negative values indicate the upward and downward fluxes, respectively. (Modified from Watanabe & Tsunogai, 1984).

mobility of ions and molecules and suppress free diffusion in all directions, causing a lower diffusive flux than in aqueous solution. To correct for this, Berner (1980) has suggested the introduction of a sediment diffusion coefficient ($D_S$) dependent on the diffusion coefficient of the investigated component at infinite dilution (D) and turtuosity ($\theta$).

$$D_S = \frac{D}{\theta^2} \quad \text{where} \quad \theta > 1$$

Turtuosity can be calculated from the measurements of porosity ($\phi$) and formation factor (F) where:

$$\phi = \frac{\text{volume of pore water}}{\text{volume of total sediment}}$$

$$F = \frac{\text{electrical resistivity of sediment}}{\text{electrical resistivity of pore water}}$$

$$\theta^2 = \phi \cdot F$$

The modified Fick's First Law of diffusion in sediments is then expressed by the equation:

$$J_S = -\phi \cdot D_S \cdot \left(\frac{dC_i}{dx}\right)$$

where

$J_S$ = diffusive flux in sediment (mass/area*time)

$\frac{dC_i}{dx}$ = concentration gradient of substance i in the x direction (mass/volume · distance

The sediment diffusion coefficient is multiplied by the porosity in order to obtain the correct unit of $J_S$. $C_i$ is the concentration of dissolved species per unit volume in the interstitial water and not of the total sediment. Multiplication by porosity corrects for this (Berner, 1980).

Diffusion is also influenced by adsorption, which has a retarding effect on the diffusive propagation of tracers. This is corrected for by introducing a linear equilibrium adsorption term (K) in the sediment diffusion coefficient (Krom & Berner 1980b), where K can be calculated from:

$$K = K^* \cdot \frac{\bar{\rho}_s \cdot (1 - \phi)}{\phi}$$

$K^*$ = linear adsorption constant, independent of porosity

$\bar{\rho}_s$ = average density of sediment solids

The final expression for the sediment diffusion coefficient corrected for adsorption ($D_{SA}$) is:

$$D_{SA} = \frac{D_S}{1 + K}$$

The general model of sediment diffusion, according to a modified Fick's First Law equation, cannot be rendered operative when discrete mineral formation takes place in the system (Krom & Berner, 1980b, Davison, 1982), but this is probably a less important process in most sediments (see section 4.2).

Few determinations of $D_{SA}$ have been performed to take account of the influence of adsorption, advection, bioturbation, currents, etc. Krom & Berner (1980b) calculated a sediment diffusion coefficient for the composite of the diffusivities $HPO_4^{2-}$ and $H_2PO_4^-$ in anaerobic marine sediments to $D_{SA(20\,°C)} = 3.6 \pm 1.1 \times 10^{-6}$ cm²/s, which is slightly lower than the diffusion coefficient for these ions at infinite dilution $D_{(20\,°C)} = 7.0 \times 10^{-6}$ cm²/s (recalculated by Krom & Berner from Li & Gregory, 1974).

From the pore-water P profile in a reduced lake sediment, Tessenow (1972) calculated the maximal diffusion coefficient '$D_{SA}$' = $4.4 \times 10^{-6}$ cm²/s, which is in good agreement with $D_{SA}$ calculated by Krom & Berner (1980b). The theoretical model for the determination of '$D_{SA}$' was, however, based on an exponential function.

Sediment diffusion coefficients cannot be transferred from one system to another without correcting for differences in temperature and porosity (Krom & Berner, 1980a). The diffusion coefficient can, however, be modified for different temperatures by the Stoke-Einstein relation. Applications of the model are also restricted to environments with low bioturbation and turbulence caused by other processes. Diffusion coefficients from measurements in this type of environment must be considered as 'apparent diffusion coefficients' ($D_{app}$) which reflect the sum of physical, chemical and biological processes involved in the vertical transport of phosphate.

### *Fluxes across the sediment-water interface*

Vertical transports across the sediment-water interface are much more complicated than fluxes within the sediment. This complexity is increased if the redox potential shifts from reduced to oxidized conditions in this boundary (Davison, 1982), where the adsorption characteristics of phosphate changes drastically. Bioturbation, gas ebullition and currents are frequently more pronounced in this region too, which means that measurements of $D_{app}$ must be made in order to calculate diffusive fluxes.

Flux measurements at the sediment-water interface have been performed in numerous studies both with intact cores in laboratory and with bell jars and similar equipment *in situ*. Table 4 and 5 show the results obtained from some of these studies where the diffusive flux has also been calculated from the pore-water P profiles. The results show large discrepancies, often up to more than one order of magnitude, between calculated and measured fluxes. The general pattern, however, is that the measured fluxes are correlated to the pore-water P concentrations (Fig. 13, Callander & Hammond, 1982; Carignan & Flett, 1981; Elderfield *et al.*, 1981; Holdren *et al.*, 1977; McCaffrey *et al.*, 1980; Psenner, 1984). A temporal pattern is often shown with larger fluxes during high temperature during the summer (Table 5, Fig. 6), when the pore-water P concentration is usually higher near the sediment surface (Theis & McCabe, 1978; Watanabe & Tsunogai, 1984).

Table 5 also shows that measured fluxes across the sediment-water interface are in closer agreement with the diffusive fluxes during reduced conditions (measured/calculated = 0.15–3.6), compared with oxidized environments (measured/calculated = 0.7–20). The lower ratio obtained under reduced conditions might be explained by a steeper pore-water P concentration gradient at the sediment-water interface, caused by dissolution of ferric phosphate complexes during anaerobic conditions, as outlined by Tessenow & Frevert (1977). They stated that anaeroby simultaneously causes a liberation of phosphate from

*Table 4.* 'Apparent' diffusion coefficients and the ratio of measured to calculated diffusive phosphorus fluxes (Meas/Cal) across the sediment-water interface in different aquatic systems.

| Local | Technique$^{+}$ | Redox state | $D_{app}$ cm$^2$/s | $\frac{\text{Meas. flux}}{\text{Cal. flux}}$ | Reference |
|---|---|---|---|---|---|
| L. Furesø<br>L. Esrom sø<br>L. St Gribsø<br>L. Grane Langsø<br>L. Trummen | Lab | Red | $0.6 \cdot 10^{-6}$ | 0.15* | Kamp-Nielsen (1974) |
| L. Piburger See | Lab | Ox + Red | – | 10–50 | Psenner (1984) |
| L. Brielle | Lab | ? | $10 \cdot 10^{-6}$ | 2.5* | Lijklema & Hieltjes (1982) |
| L. Mendota | Mass balance | Ox + Red | – | 2.8·3.4 | Holdren *et al.* (1977) |
| L. Constance (obersee) | Lab | Red | $14.6 \cdot 10^{-6}$ | 3.6* | Frevert (1982) |
| Baltic Sea | In situ | Ox | $58 \cdot 10^{-6}$ | 5–20 | Holm (1978) |
| | In situ | Red | $25 \cdot 10^{-6}$ | | |
| Potomac River Estuary | In situ | Ox + Red | – | 5–10 | Callander (1982) |
| Potomac River Estuary | In situ | Ox | – | 3.3–7 | Callander & Hammond (1982) |
| Narragansett Bay | In situ | Ox | – | 2.7–3.9 | McCaffrey *et al.* (1980) |
| Narragansett Bay | In situ 20 °C | Ox | – | 1.3–3.8 | Elderfield *et al.* (1981) |
| | In situ 5 °C | Ox | – | 0.7–0.9 | |
| Great Bay Estuary | In situ | Ox | – | 6.6 | Lyons *et al.* (1982) |

* We have made a rough estimation of the measured/calculated fluxes by calculating the $D_{app}/D_{SA}$-ratios. At a constant concentration gradient across the sediment-water interphase, this ratio reflects the influence of advective and random processes on the phosphorus flux. $D_{SA} = 4 \cdot 10^{-6}$ cm$^2$/s (Krom & Berner 1980b) was used in the calculations.

$^{+}$ Technique refers to how the measured flux have been obtained.

*Table 5.* Calculate diffusive and measured fluxes across the sediment-water interface in different aquatic systems.

| Local | Sediment depth (cm) | Temperature (°C) | $D_s$ (cm²/s) | Calculated diffusive flux (mg P/m² · d) | Measured flux (mg P/cm² · d) | Reference |
|---|---|---|---|---|---|---|
| Narragansett Bay, | SWI | | | 5.6 | 15–22 | McCaffrey *et al.* |
| Rhode Island, USA | | 19 | $4 \cdot 10^{-6}$ | | | (1980) |
| | >20 | | | 0.2 | – | |
| Narragansett Bay, | SWI | 20 | | 5–62 | 19–81 | Elderfield *et al.* |
| Rhode Island, USA | | | $3.3 \cdot 10^{-6}$ | | | (1981) |
| Oxic-suboxic | SWI | 5 | | 3.4–40 | 3.1–28 | |
| Potamac River Estuary, | | | | | | Callender & Ham- |
| Cheasapeake Bay, | SWI | – | $7 \cdot 10^{-6}$ | 1.9–6.2 | 6.2–43 | mond (1982) |
| USA | | | | | | |
| Oxic-suboxic | | | | | | |
| Great Bay Estuary, | | | | | | Lyons *et al.* (1982) |
| New Hampshire, | SWI | 20–24 | $4 \cdot 10^{-6}$ | 1.3 | 8.6 | |
| USA | | | | | | |
| Oxic-suboxic | | | | | | |
| Lake Mendota, USA | SWI | Summer | $1.10 \cdot 10^{-6}$ | 2.9 | 8–10 | Holdren *et al.* |
| Sum of oxic-anaerobic | SWI | Winter | | 1.3 | | (1977) |
| Gullmarsfjorden, | | | | | | Sundby *et al.* |
| Sweden, Oxic | SWI | 10 + − 1 | $10.7 \cdot 10^{-6}$ | 4.0 | 0 | (1986), Hall P. |
| Anoxic | SWI | 10 + − 1 | $4 \cdot 10^{-6}$ | 1.5 | 9.3 | (pers. com.) |

SWI = Sediment-Water Interface

the sediment interface and increases the diffusive gradient across the sediment-water boundary (Fig. 14). Sometimes, this 'surface' liberation leads to higher fluxes than those calculated from pore-water P gradients, which are almost invariably the results of investigations with sampling intervals too large for this phenomenon to be detected.

Another explanation for a closer fitness to diffusive fluxes during anaerobic conditions might be greatly reduced bioturbation activity. Substancially increased benthic fluxes can occur in aerobic environments (Petr, 1977; McCaffrey *et al.*, 1980; Graneli, 1979; Matisoff *et al.*, 1985). Graneli (op.cit.) showed a 2–4 times larger flux with the presence of chironomid larvae (1 000 ind/m²) at oxidized conditions. The bioturbation effect was negligible under anaerobic conditions. The same results have been observed in marine environments (van der Loeff *et al.*, 1984).

The effects of benthic organisms on the P flux to the water mass are mainly due to active transport of sediment particles and water across the sediment-water interface and by alteration of the physical environment, for example, pH and redox properties (Petr, 1977; Matisoff *et al.*, 1985; Berner, 1980; McCaffrey *et al.*, 1980).

Increased P fluxes to the water mass are commonly observed, but Davis *et al.* (1975) found that tubificids could decrease the pore water P concentration in the upper sediment layer as a result of inflow of oxygenated water into the worm burrows. Jörgensen & Revsbech (1985) arrived at the same results. Davis *et al.* (op.cit.) state, however, that both liberation and fixation can occur, depending on the amount of redox-sensitive P.

Different ways of modelling the influence of

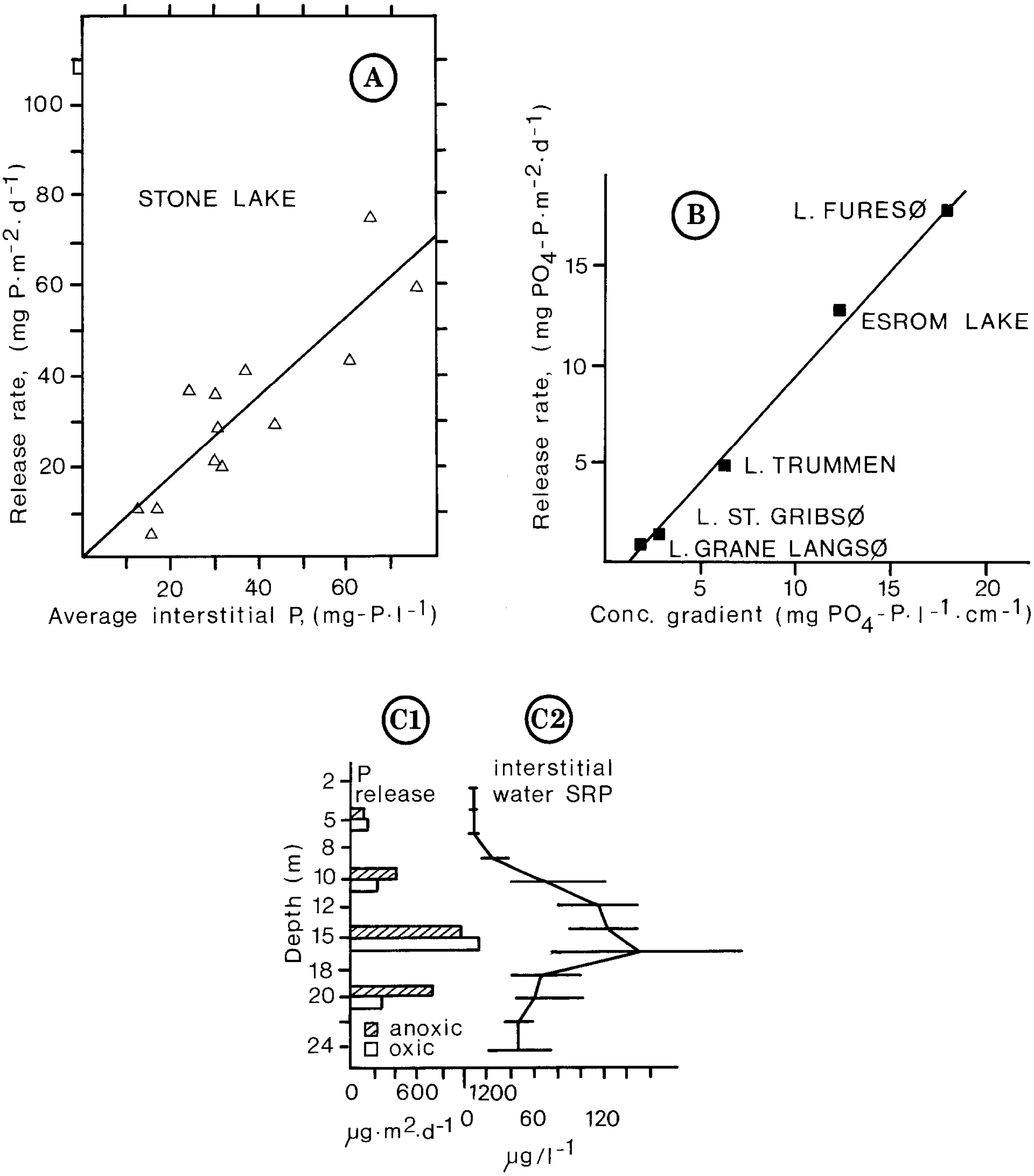

*Fig. 13.* A. Release rate of phosphorus from Stone Lake sediments as a function of average pore-water phosphorus concentrations. (Modified from Theis & McCabe, 1978). B. Anaerobic phosphorus release rate as a function of the concentration gradient across the sediment-water interface. Concentration gradient = difference between phosphate concentration in water and $NH_4$-Cl-extractable phosphorus in the topmost centimetre in the sediment, for Lake Trummen between lake water and pore water. (Modified from Kamp-Nielsen, 1974). C1. Average phosphorus release rates at 4, 8 and 12 °C under aerobic and anaerobic conditions in laboratory experiments with Lake Piburger See sediments. C2. Mean and extreme values of the pore-water phosphorus concentrations (Oct. 1980–Aug. 1981) in Lake Piburger See sediments. (C1 and C2, modified from Psenner, 1984).

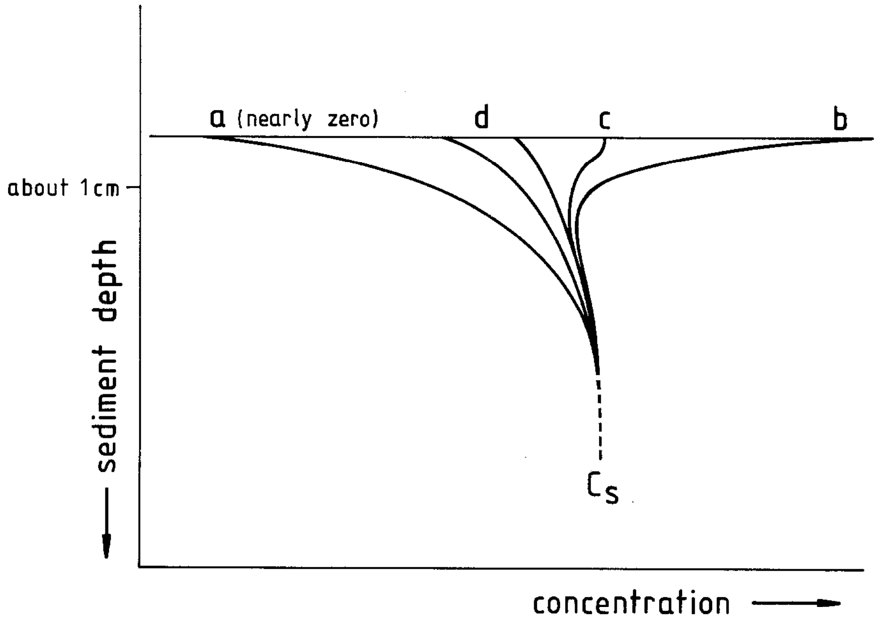

*Fig. 14.* Probable concentration gradients of Fe, Mn and P in the sediment pore water during the breakdown of an oxidized sediment surface by reduction (a-b-c-d is the time order, a = oxic, b-c-d- = anoxic). $C_s$ = saturation (equilibrium) concentration of low, permanently reduced sediment (Modified from Tessenow a Frevert, 1977).

bioturbation on fluxes in sediments and across the sediment-water interface are given by Håkansson & Källström (1978), Berner (1980), McCaffrey *et al.* (1980), Aller (1980) and Kamp-Nielsen *et al.* (1982).

Increased diffusive flux caused by stirring effects, such as water action, has been shown by Hesslein (1980). He presented clear evidence for an increased mixing of pore waters to a depth of 10 cm during autumn overturn and also higher diffusive fluxes in sediments in contact with water from the mixed layer, compared with hypolimnion bottoms. These advective movements can cause either liberation or fixation of P as a result of the influence on redox potential. A positive correlation between P-release and mixing energy was found in laboratory experiments by Holdren & Armstrong (1980), and in lake studies by Ryding & Forsberg (1977) and Ahlgren (1980).

Very little is known of the impact of macrophytes on the pore water P flux. Carignan (1985) found a decreased P concentration in the pore water during summer as a result of root assimilation activity. The trend was reversible, with higher concentrations in spring and autumn, caused by root decay. Possible effects on the pore-water composition were suggested as resulting from changed sedimentation patterns, alteration of redox potential, pH, sorption of P and release of organic compounds, such as root exudates (Carignan, 1985).

## Conclusions and applications

The use of pore-water investigations (concentrations and gradients of phosphorus) have been restricted to a few research projects. One reason for this has been the lack of an appropriate method for separating the pore water from the sediment.

The commonly used separation techniques, employing centrifugation and/or pressure filtration, have been found in a number of methodological studies, to overestimate or underestimate the actual concentrations of different substances in the pore water. The reasons for this are, for example, increased temperature during separation, oxidation of the sediment, excessively high filtration pressure, excessively long time between sampling and separation etc. During the late 1970s the development of separation techniques resulted in methods which allow *in situ* sampling. These *in situ* techniques are dialysis and suction.

It is, however, difficult to state that these *in situ* techniques really permit the actual composition of pore water to be determined. Since these techniques are based on *in situ* incubation, the discrepancies arising from the actual interstitial composition will be dependent, for example, on time of incubation, porosity of the dialysis membrane, equilibration medium, etc. The influence of these factors can, however, be measured qualitatively and quantitatively by the investigator. Factors that are difficult to measure are, for example, changed porosity caused by microbial degradation of the dialysis membrane and Donnan effects. The suction technique can be superior to the dialysis technique when rapid sampling is necessary for studying short-term changes.

It must also be stressed that the equipment used for *in situ* separation is inexpensive and the sampler can easily be constructed by the investigator.

It is possible to describe the trophic state of a lake ecosystem on the basis of the total P concentration in the sediment. In eutrophicated lakes, however, an increased total P is often registered in the surface sediment (gyttja of domestic origin).

Chemical extraction of the total P content of sediment into different fractions increases the chances of classifying the trophic level.

Pore water investigations (P concentrations) are excellent, however, for describing the trophic status of a lake ecosystem. Large differences in pore-water P concentrations occur between oligotrophic, mesotrophic and eutrophic systems (Table 2). This technique also provides an opportunity for following seasonal changes (Fig. 6) and, in eutrophic ecosystems, even short-term variations (Fig. 7). In connection with the discussion of these temporal variations in the pore-water P concentration, it may be stated that potential precipitation mechanisms of solid phases are probably of minor importance. Discrete minerals are only formed in the long term.

The use of traditional P-budget calculations (input-output models) has provided data on internal P loads for many lakes. Mechanisms regulating this sediment-P release were reviewed thoroughly by Boström *et al.* (1982). They concluded that for the release of P, two different mechanisms have to occur simultaneously or within a short period of time: (i) mobilization of particulate P to the pore-water P, and (ii) transport to the water body (Fig. 15).

Pore-water phosphorus concentrations and gradients can be used for diffusion flux calculations for evaluating the quantitative impact of internal P loading.

However, results from calculated and measured diffusive flux studies have shown relatively large discrepancies between the calculated and measured values, although mixing processes, such as bioturbation, gas ebullition and currents, have

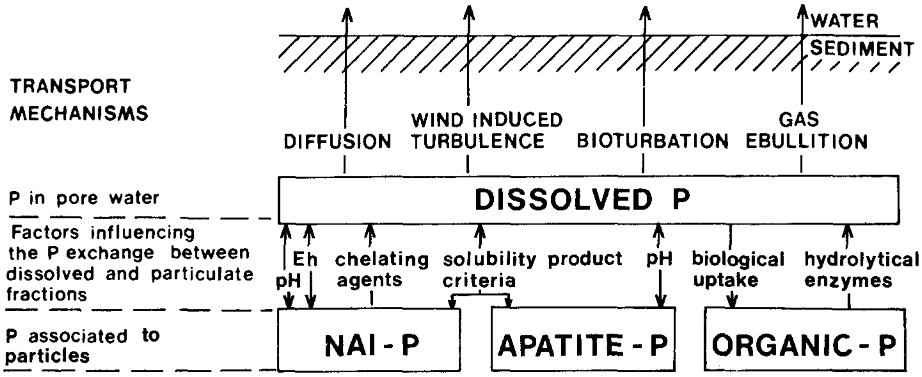

*Fig. 15.* Illustration of the dominating processes regulating the release of phosphorus from lake sediments. (From Håkansson & Jansson, 1983, modified from Boström *et al.*, 1982).

been low. This leads us to suggest that a direct release of particulate P, mainly bound to iron oxyhydroxides in the top layer on the surface, can also occur, as a result of high pH or of partly reduced conditions (see Fig. 14).

Although the theoretically calculated diffusive fluxes do not equal measured fluxes, a good estimation of the importance of sediment-P release may be obtained. Further investigations are necessary before reliable quantitative P-release rates can be calculated. In this respect, studies in marine environments are much more common and better developed than in freshwater systems (Table 5).

Studies of different P forms in the interstitial water, their vertical distribution, pH- and redox-dependence, transformations, etc., are other important aspects of sedimentological research.

Finally, pore-water investigations have obviously been underestimated as an ecological tool for collecting information and data on:

- trophic status of lakes,
- redox conditions in the sediment,
- spatial and temporal distribution of P in lake sediments (mapping point and diffusive sources),
- sediment P release (internal P load),
- potential precipitation mechanisms on a long-term basis,
- ground-water inflow areas and lake-water seepage.

## References

Ahlgren, I., 1980. A dilution model applied to a system of shallow eutrophic lakes after diversion of sewage effluents. Arch. Hydrobiol. 89: 17–32.

Aller, R. C., 1980. Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average microenvironment. Geochim. Cosmochim. Acta 44: 1955–1965.

Altschuler, Z. S., 1973. The weathering of phosphate deposits – Geochemical and environmental aspects. In E. J. Griffith, A. Beeton, J. M. Spencer & D. T. Mitchell (eds.), Environmental phosphorus handbook. J. Wiley & Sons, NY: 33–96.

Bengtsson, L., 1975. Lake Trummen restoration project. I. Water and sediment chemistry. Verh. int. Ver. Limnol. 19: 1080–1087.

Bengtsson, L., S. Fleischer, G. Lindmark and W. Ripl., 1975. Lake Trummen restoration project. I. Water and sediment chemistry. Verh. int. Ver. Limnol. 19: 1080–1087.

Berner, R. A., 1974. Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus and silica in anoxic marine sediments. In E. D. Goldberg (ed.), The Sea. Vol. 5. J. Wiley & Sons, NY: 427–449.

Berner, R. A., 1980. Early diagenesis. A Theoretical approach. Princeton Series in Geochemistry. Princeton Univ. Press. Princeton, 241 pp.

Bishoff, J. L., R. E. Greer & A. D. Luistro, 1970. Composition of interstitial waters of marine sediments: temperature of squeezing effect. Science 167: 1245–1246.

Boers, P. C. M., O. van Hese, F. de Bles & Th. E. Cappenberg, 1985. The release of dissolved organic phosphorus from the peaty sediments of the shallow eutrophic Loosdrecht Lakes (The Netherlands). 3rd International Symposium. Interactions between Sediments and Waters. Geneva – August 1984. In press.

Boström, B., M. Jansson & C. Forsberg, 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. Beih. Ergebn. Limnol. 18: 5–59.

Bottomley, E. Z. & J. L. Bayly, 1984. A sediment porewater sampler used in root zone studies of the submerged macrophyte, *Myriophyllum spicatum*. Limnol. Oceanogr. 29: 671–673.

Bray, J. T., O. P. Bricker & B. N. Troup, 1973. Phosphate in interstitial waters of anoxic sediments: oxidation effect during sampling procedure. Science 180: 1362–1364.

Brinkman, G. A., W. van Raaphorst & L. Lijklema, 1982. In situ sampling of interstitial water from lake sediments. Hydrobiologia 92: 659–663.

Broberg O.& K. Pettersson, 1987. This volume. Burnett, W. C., 1977. Geochemistry and origin of phosphorite deposits from off Peru and Chile. Geol. Soc. Am. Bull. 88: 813–823.

Callander, E., 1982. Benthic phosphorus regeneration in the Potomac River Estuary. Hydrobiologia 91/92: 431–446.

Callander, E. & D. E. Hammond, 1982. Nutrient exchange across the sediment-water interface in the Potomac River Estuary. Estuar. coast. Shelf Sci. 15: 395–413.

Carignan, R., 1984a. Interstitial water sampling by dialysis: Methodological notes. Limnol. Oceanogr. 29: 667–670.

Carignan, R., 1984b. Sediment geochemistry in a eutrophic lake colonized by the submersed macrophyte *Myriophyllum spicatum*. Verh. Int. Ver. Limnol. 22: 355–370.

Carignan, R., 1985. Nutrient dynamics in a littoral sediment colonized by the submersed macrophyte *Myriophyllum spicatum*. Can. J. Fish. aquat. Sci. 42: 1303–1311.

Carignan, R. and Flett, R. J., 1981. Postdepositional mobility of phosphorus in lake sediments. Limnol. Oceanogr. 26: 361–366.

Cole, C. V., S. R. Olsen & C. O. Scott, 1953. The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Am. Proc. 17: 352–356.

D'Anglejan, B. F., 1986. Phosphate diagenesis of carbonate sediments as a mode of *in situ* formation of marine phosphorites: observations in a core from the eastern Pacific. Can. J. Earth Sci. 5: 81–87.

Davis, R. B., D. L. Thurlow & F. E. Brewster, 1975. Effects of burrowing tubificid worms on the exchange of phosphorus between lake sediment and overlaying water. Verh. int. Ver. Limnol. 19: 382–394.

Davison, W., 1982. Transport of iron and manganese in relation to the shapes of their concentration-depth profiles. Hydrobiologia 92: 463–481.

deKanel, J. & J. W. Morse, 1978. The chemistry of orthophosphate uptake from seawater on to calcite and aragonite. Geochim. Cosmochim. Acta 42: 1335–1340.

Dell, C. I., 1973. Vivianite: An authigenic phosphate mineral in Great Lakes sediments. Proc. 16th Conf. Great Lakes Res. Int. Ass. Great Lakes Res., Ann Arboour, Michigan: 1027–1028.

Edzwald, J. K., D. C. Toensing & M. Chi-Yew Leung, 1976. Phosphate adsorption reactions with clay minerals. Envir. Sci. Technol. 10: 485–490.

Einsele, W., 1936. Uber die Beziehungen des Eisenkreislaufs zum Phosphatkreislauf im eutrophen See. Arch. Hydrobiol. 29: 664–686.

Einsele, W., 1938. Uber chemische und kolloidchemische Vorgänge in Eisen-Phosphat-Systemen unter limnochemischen und limnogeologischen Gesichtspunkten. Arch. Hydrobiol. 33: 361–387.

Elderfield, H. R. J. McCaffrey, N. Luedtke, M. Bender & V. W. Truesdale, 1981. Chemical diagenesis in Narragansett Bay sediments. Am. J. Sci. 281: 1021–1055.

Emerson, S., 1976. Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochim. Cosmochim. Acta 40: 925–934.

Emerson, S. & G. Widmer, 1978. Early diagenesis in anaerobic lake sediments – II. Thermodynamic and kinetic factors controlling the formation of iron phosphate. Geochim. Cosmochim. Acta 42: 1307–1316.

Enell, M., 1975. Sedimentundersökningar i Fegen och Kalvsjön. Limnologisk undersökning. In I. Lundqvist (ed.), Fegen, Kalvsjön. Limnologisk undersökning 1974-1975. Inst. of Limnology, Univ. Lund: 174-216 (in Swedish).

Enell, M., 1979a. Critical analysis of a method for removal of interstitial water from lake sediment. In M. Enell & G. Gahnström (eds), 7th Nordic Symposium on Sediments. Aneboda. ISSN 0348-0798: 183–192.

Enell, M., 1979b. Sedimentundersökningar i Öresjö. In C. Gelin (ed.), Limnologisk undersökning i Öresjö (Borås kommun). Inst. of Limnology, Univ. Lund.: 55–105 (in Swedish).

Enell, M., 1980. The phosphorus economy of a hypertrophic seepage lake in Scania, South Sweden, Inst. of Limnology, Univ. Lund. Ph. D thesis. ISSN 0348–0798. 190 pp.

Enell, M., 1984. Restaurering av Laduviken i Stockholms kommun Redovisning och utvärdering av limnologiska undersökningar. Inst. of Limnology, Univ. Lund. ISSN 0348–0798: 116 pp (in Swedish).

Enell, M., 1985a. Does seepage influence the exchange of phosphorus between sediment and water? In M.Enell, W. Graneli & L.-A. Hansson (eds), 13th Nordic Symposium on Sediments. Aneboda. In press.

Enell, M., 1985b. Fosfor- och kvävebelastningen fran fiskodlingar-skillnaden mellan sjöar av olika trofigrad. In Akvakultur-Miljöproblem, Nordforsk, Helsinki, Publ. 1985: 2: 55–65 (in Swedish).

Enell, M. & S. Karlberg, 1975. Viaredssjön. En limnologisk undersökning. Inst. of Limnology, Univ. Lund 39 pp. (in Swedish).

Enell, M. & I. Lundqvist, 1983. Restaurering av Trekanten i Stockholms kommun. Redovisning och utvärdering av limnologiska undersökningar. Inst. of Limnology, Univ. Lund. ISSN 0348–0798. 141 pp. (in Swedish).

Enell, M. & J. Löf, 1983. Miljökonsekvenser av akvakultur. Sedimentation från fiskkasseodlingar. Forskningsredogörelse till SNV. Inst. of Limnology, Univ. Lund. ISSN 0348-0798. 46 pp. (in Swedish).

Enell, M.& J. Löf, 1984. Miljökonsekvenser av akvakultur. Sedimentation från fiskkasseodlingar. Forskningsredogörelse för BÅ 1983/1984. Inst. of Limnology, Univ. Lund. ISSN 0348–0798. 28 pp. (in Swedish).

Fanning, K. A. & M. E. Pilson, 1971. Interstitial silica and pH in marine sediments: some effects of sampling procedures. Science 173: 1228–1231.

Fleischer, S., 1978. Evidence for the anaerobic release of phosphorus from lake sediments as a biological process. Naturwissenschaften 65: 109–110.

Frevert, 1979. Phosphorus and iron concentrations in the interstitial water and dry substances of sediments of Lake Constance (Obersee). Arch. Hydrobiol/Suppl. 55: 298–323.

Frevert, T., 1982. Phosphorus and iron concentrations in the interstitial water and dry substances of sediments of Lake Constance (Obersee). III. Mobility of phosphorus, iron and manganese in profundal sediment. Arch. Hydrobiol. Suppl. 59: 319–329.

Gahler, A. R., 1969. Sediment-water nutrient interchange. Proceedings of the Eutrophication-Biostimulation Assesment Workshop. Berkely, California: 243–257.

Gaudette, H. E. & W.-B. Lyons, 1980. Phosphate geochemistry in nearshore carbonate sediments: a suggestion of apatite formation. Soc. Econ. Pal. Min. 29: 215–225.

Golachowska, J. B., 1979. Phosphorus forms and their seasonal changes in water and sediments of Lake Plussee. Arch. Hydrobiol. 86: 217–241.

Graneli, W., 1975. Fosforomsättning – sedimentens roll. Nordforsk, Helsinki, Publ., 1975: 1: 213–222 (in Swedish).

Graneli, W., 1979. The influence of *Chironomus plumosus* larvae on the exchange of dissolved substances between sediment and water. Hydrobiologia 66: 149–159.

Gulbrandsen, R. R., 1969. Physical and chemical factors in the formation of marine apatite. Econ. Geol. 64: 365–382.

Hall, P., 1984. Chemical fluxes at the sediment-seawater interface; In situ investigations with benthic chambers. Ph. D. thesis. Univ. Göteborg and Chalmers Univ. of Technology, Göteborg. ISBN 91-7032-164-7, 183 pp.

Harriss, R. C., 1967. Silica and Chloride in interstitial waters of rivers and lake sediments. Limnol. Oceanogr. 12: 8–12.

Hertkorn-Obst. U., H. Wendeler, T. Feuerstein & W. Schmitz, 1982. A device for sampling interstitial water out of river and lake beds. Environ. Tech. Letters 3: 263–266.

Hesslein, R. H., 1976. An *in situ* sampler for close interval pore water studies. Limnol. Oceangr. 21: 912–914.

Hesslein, R. H., 1980. In situ measurements of pore water diffusion coefficients using tritiated water. Can. J. Fish. aquat Sci. 37: 545–551.

Holdren, G. C. & D. E. Armstrong, 1980. Factors affecting phosphorus release from intact lake sediment cores. Envir. Sci. Technol. 14: 79–87.

Holdren, G. C. & D. E. Armstrong, 1985. Interstitial concentrations as an indicator of phosphorus release and mineral formation in lake sediments. 3rd international Symposium. Interactions between sediment and waters. Geneva – August 1984. In press.

Holdren, G. C., D. E. Armstrong & R. F. Harris, 1977. Interstitial inorganic phosphorus concentrations in Lakes Mendota an Wingra. Wat. Res. 11: 1041–1047.

Holm, N. G., 1978. Phosphorus exchange through the sediment-water interface. Mechanism studies of dynamic processes in the Baltic Sea Ph. D. thesis, Univ. Stockholm. ISBN 91-7146-023-3, 149 pp.

Howes, B. L., J. W. H. Dacey, S. G. Wakeman, 1985. Effects of sampling technique on measurements of pore water constituents in salt mash sediments. Limnol. Oceanogr. 30: 221–227.

Håkansson, L. & M. Jansson, 1983. Principles of Lake Sedimentology Springer-Verlag, Berlin, 316 pp.

Håkansson, L. & A. Källström, 1978. An equation of state for biologically active lake sediments and its implications for interpretations of sediment data. Sedimentology 25: 205–226

Jacobsen, O.-S, 1977. Sorption of phosphate by Danish lake sediments Vatten 3: 290–298.

Jacobsen, O.-S, 1978a. Sorption, adsorption and chemosorption of phosphate by Danish lake sediments. Vatten 4: 230–243.

Jacobsen, O.-S, 1978b. A descriptive model for phosphate sorption by lake sediments. In O. Skogheim, B. Faafeng & M. Laake (eds), 6th Nordic Symposium on Sediments. Hurdal, Norway. ISBN-82-990528-0-7: 127–136.

Jones, B. F. & C. J. Bowser, 1978. The mineralogy and related chemistry of lake sediments. In A. Lerman (ed.), Lakes, chemistry, geology, physics. Springer-Verlag, NY: 179–236.

Jörgensen, B. B. & N. P. Revsbech, 1985. Diffuse boundary layers and the oxygen uptake of sediments and detritus. Limnol. Oceangr. 30: 111–122.

Kamp-Nielsen, L., 1974. Mud-water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting the exchange rates. Arch. hydrobiol. 73: 218–237.

Kamp-Nielsen, L., H. Meyer & S. E. Jörgensen, 1982. Modelling the influence of bioturbation on the vertical distribution of sedimentary phosphorus in Lake Esrom. In P. G. Sly (ed.). Sediment/freshwater interaction. Dr W. Junk, The Hague: 197–206.

Kawai, T., A. Otsuki, M. Aizaki & M. Nishikawa, 1985. Phosphate release from sediment into aerobic water in a eutrophic shallow lake, L. Kasumigaura. Verh. int. Ver. Limnol. 22: 3316–3322.

Kawashima M., Y. Tainaka, T. Hori, M. Koyama & T. Takamatsu, 1986. Phosphate adsorption onto hydrous manganese (IV) oxide in the presence of divalent cations. Wat. Res. 20: 471–475.

Krom, M. D. & R. A. Berner, 1980a. Adsorption of phosphate in anoxic marine sediments. Limnol. Oceanogr. 25: 797–806.

Krom, M. D. & R. D. Berner, 1980b. The diffusion coefficient of sulfate, ammonium and phosphate ions in anoxic marine sediments. Limnol. Oceanogr. 25: 327–337.

Ku, W. C., F. A. DiGiano & T. H. Feng, 1978. Factors affecting phosphate adsorption equilibria in lake sediments. Wat. Res. 12: 1069–1074.

Lerman, A., 1978. Chemical exchange across sediment-water interface. Ann. Rev. Earth Planet. Sci. 6: 281–303.

Li, W. C., D. E. Armstrong, J. D. H. Williams, R. F. Harris, & J. K. Syers, 1972. Rate and extent of inorganic phosphate exchange in lake sediments. Proc. Soil. Sci. Amer. 36: 279–285.

Li, V. H. & S. Gregory, 1974. Diffusion of ions in sea water and in deep sea sediments. Geochim. Cosmochim. Acta 38: 703–714.

Lijklema, L, 1977. The role of iron in the exchange of phosphate between water and sediment. In H. L. Golterman (ed.), Interactions between sediments and fresh water. Dr. W. Junk. The Hague: 313–317.

Lijklema, L, 1980. Interaction of orthophosphate with iron (III) and aluminium hydroxides. Envir. Sci. Technol. 14: 537–541.

Lijklema, L. and A. H. M. Hieltjes, 1982. A dynamic phosphate budget model for a eutrophic lake. Hydrobiologia 91/92: 227–233.

Lindmark, G. & L. Bengtsson, 1979. Influence of interstitial water on growth of *Selenastrum capricornutum* in water from Lake Södra Bergundasjön. Vatten 35: 222–235.

Logan, T. J., 1982. Mechanisms for release of sediment bound phosphate to water and the effect of agricultural land management on fluvial transport of particular and dissolved phosphate. Hydrobiologia 91/92: 519–530.

Lyons, W. B., T. C. Loder & S. M. Murray, 1982. Nutrient pore water chemistry, Great Bay, New Hampshire: Benthic fluxes. Estuaries 5: 230–233.

Löfgren, S & S.-O. Ryding, 1985a. Apatite ionic products in different eutrophic sediments. Verh. int. Ver. Limnol. 22: 3323–3328.

LÖfgren, S. & S.-O Ryding, 1985b. Apatite solubility and microbial activities as regulators of internal loading in shallow, eutrophic lakes. Verh. int. Ver. Limnol. 22: 3329–3334.

Manheim, F. T., 1974. Studies on marine interstitial waters with special reference to marine drilling. Dept. of Geology. Univ. Stockholm, Ph. D. Thesis. 378 pp.

Manheim, F., G. T. Rowe & A. Jipa, 1975. Marine phosphorite formation off Peru. J. Sed. Pet. 45: 243–251.

Martens, C. S., R. A. Berner, & J. K. Rosenfield, 1978. Interstitial water chemistry of anoxic Long Island Sound sediments. 2. Nutrient regeneration and phosphate removal. Limnol. Oceanogr. 23: 605–617.

Matisoff, G., A. H. Lindsay, S. Matis & F. M. Soster, 1980. Trace model equilibria in Lake Erie sediments. J. Great Lakes Res. 6: 353–366.

Matisoff, G., J. B. Fisher & S. Matis, 1985. Effects of benthic macroinvertebrates on the exchange of solutes between sediments and freshwater. Hydrobiologia 122: 19–33.

Mayer, L. M., 1976. Chemical water sampling in lakes and sediments with dialysis bags. Limnol. Oceanogr. 21: 909–912.

McCaffrey, R. J., A. C. Meyers, E. Davey, G. Morrison, M. Bender, N. Luedtke, D. Cullen, P. Froelich & G. Klinkhammer, 1980. The relation between pore water chemistry and benthic fluxes of nutrients and manganese in Narrangansett Bay, Rhode Island. Limnol. Oceanogr. 25: 31–44.

Merkt, J., 1985. On the geochemistry of iron in the sediments of small lakes. (Abstract). In H. Löffler (ed.), IV Int. Symposium on Paleolimnology. Ossiach, Austria, September 1985. In press.

Morse, J. W. & N. Cook, 1978. The distribution and forms of phosphorus in North Atlantic Ocean deep-sea and continental slope sediments. Limnol. Oceanogr. 23: 825–830.

Mortimer, C. H., 1941. The exchange of dissolved substances between mud and water in lakes. I. J. Ecol. 29: 280–329.

Mortimer, C. H., 1942. The exchange of dissolved substances between mud and water in lakes. II. J.Ecol. 30: 147–201.

Nembrini, G., J. A. Capobianco, J. Garcia & J.-M. Jacquet, 1982. Interaction between interstitial water and sediment in two cores of Lac Leman, Switzerland. Hydrobiologia 91/92: 363–375.

Nembrini, G., J. A. Capobianco, M. Viel & F. Williams, 1983. A Mössbauer and chemical study of the formation of vivianite in sediments of Lago Maggiore (Italy). Geochim. Cosmochim. Acta 47: 1459–1464.

Norvell, W. A., 1974. Insolubilization of inorganic phosphate by anoxic lake sediments. Proc. Soil. Sci. Soc. Amer. 38: 441–445.

Nriagu, J. O. & C. I. Dell, 1974. Diagenetic formation of iron phosphate in recent lake sediments. Am. Mineral. 59: 934–946.

Ohle, W., 1937. Kolloidgele als Nährstoffregulanten der Gewässer. Naturwissenschaften. 25: 471–474.

Ohle, W., 1964. Interstitiallösung der Sedimente, Nährstoffgehalt des Wassers und Primärproduktion des Phytoplanktons in Seen. Helgoländer wiss. Meeresunters. 10: 411–429.

Petr, T., 1977. Bioturbation and exchange of chemicals in the mud-water interface. In. H. L. Golterman (ed.). Interactions between Sediments and Fresh water. Dr. W. Junk, The Hague,: 216–226.

Postma, D., 1981. Formation of siderite and vivianite and the porewater composition of a recent bog sediment in Denmark. Chem. Geol. 31: 225–244.

Psenner, R., 1984. Phosphorus release patterns from sediments of a meromictic mesotrophic lake (Piburger See, Austria). Verh. int. Ver. Limnol. 22: 219–228.

Reeburgh, W. S., 1967. An improved interstitial water sampler. Limnol. Oceanogr. 12: 163–165.

Revsbech, N. P., B. B. Jörgensen,T. H. Blackburn & Y. Cohen 1983. Microelectrode studies of the photosynthesis and $O_2$, $H_2S$ and pH profiles of a microbial mat. Limnol. Oceanogr. 28: 1062–1074.

Rigler, F. H., 1973. A dynamic view of the phosphorus cycle in lakes. In E. J. Griffith, A. Beeton, J. M. Spencer & D. T. Mitchell (eds), Environmental Phosphorus Handbook. J. Wiley & Sons, NY: 539–568.

Ripl, W., 1978. Oxidation of lake sediments with nitrate – A restoration method for former recipients. Inst. of Limnology, Univ. Lund. Ph. D. thesis. ISSN 0348-0798, 151 pp.

Robbins, J. A. & J. Gustini, 1976. A squeezer for efficient extraction of pore water from small volumes of anoxic sediment – Limnol. Oceanogr. 21/ 905–909.

Ryding. S.-O., 1985. Chemical and Microbiological processes as regulators of the exchange of substances between sediments and water in shallow, eutrophic lakes. Int. Revue ges. Hydrobiol. 70: 657–702.

Ryding, S.-O. & C. Forsberg, 1977. Sediments as a nutrient source in shallow polluted lakes. In H. L. Golterman (ed.), Interactions between sediments and fresh water. Dr. W. Junk, The Hague: 227–234.

Schindler, D. W., R. Hesslein & G. Kipphut, 1977. Interactions between sediments and overlaying waters in an experimentally eutrophicated Precambrian Shield Lake. In H. L. Golterman (ed.), Interactions between sediments and fresh waters. Dr. W. Junk, The Hague: 235–243.

Serruya, C. M. Edelstein, U. Pollinger & S. Serruya, 1974. Lake Kinneret sediments: Nutrient composition of pore water and mud water exchanges. Limnol. Oceanogr. 19: 489–508.

Shukla, S. S., J. K. Syers, J. D. H. Williams, D. E. Armstrong & R. F. Harris, 1971. Sorption of inorganic phosphate by lake sediments. Soil. Sci. Soc. Am. Proc. 35: 244–249.

Siebers, H. H., Van der Kraan & M. Donze, 1982. The fractionation of iron-phosphorus compounds in sediments studied by Mössbauer spectroscopy. Hydrobiologia 91/92: 697–700.

Siever, S., 1962. A squeezer for extracting interstitial water from modern sediments. J. Sediment. Petrol. 32: 329–331.

Skogheim, O., 1978. Tid/dyp-variasjon i interstitialvannets kjemiske sammensetning i Åringen. In D. Hongve, O.

Skogheim, B. Faafeng & M. Laake (eds), 6th Nordic Symposium on Sediments. Hurdal, Norway. ISBN-82-990528-0-7: 39–50. (in Norwegian).

Stumm, W. & J. O. Leckie, 1971. Phosphate exchange with sediments; its role in the productivity or surface waters. Proc. 5th Int. Water Poll. Res. Conf., Pergamon Press. Dubendorf-Zurich, Separatum 406: 1–26.

Stumm, W. & J. J. Morgan, 1981. Aquatic Chemistry, 2. J. Wiley & Sons, NY: 605–606.

Stumm, W. & L. Sigg, 1979. Kolloidchemische Grundlagen der Phosphor-Elimination in Fällung, Flockung und Filtration. Z. Wasser u. Abwasser Forsch. 2: 73–83.

Sundby, B., L. Anderson, P. Hall, Å. Iverfeldt, M. Rutgers van der Loeff & S. Westerlund, 1986. The effect of oxygen on release and uptake of cobolt, manganese, iron and phosphate at the sediment-water interface. Geochim. Cosmochim. Act in press.

Syers, J. K., R. F. Harris & D. E. Armstrong, 1973. Phosphate chemistry in lake sediments. J. envir. Qual. 2: 1–14.

Tessenow, U., 1972. Lösungs-, Diffusions- und Sorptionsprozesse in der Oberschicht von Seesedimenten. I. Ein langzeit experimenten unter aeroben und anaeroben bedingungen im fliessgleichgewicht. Arch. Hydrobiol. Suppl. 38: 353–398.

Tessenow, U., 1974. Lösungs-, Diffusions- und Sorptionsprozesse in der Untersicht von Seesedimenten. IV. Arch. Hydrobiol. Suppl. 47: 1–79.

Tessenow, U. & T. Frevert, 1977. Reaction and migration in sediment-water interactions. Preprint of a paper presented at the Jubilee Symposium on Lake Metabolism and Lake Management. Uppsala. August 1977.

Theis, T. L. & P. J. McCabe, 1978. Phosphorus dynamics in hypereutrophic lake sediments. Wat. Res. 12: 677–685.

van der Loeff R. M., L. Andersson, P. Hall, Å. Iverfeldt, A. Josefsson, B. Sundby & S. Westerlund, 1984. The asphyxiation technique: An approach to distinguishing between molecular diffusion and biologically mediated transport at the sediment-water interphase. Limnol. Oceanogr. 29: 675–686.

van Eck, G. Th. M. & J. G. C. Smits, 1985. Calculation of nutrient fluxes across the sediment-water interface in shallow lakes. 3rd international Symposium. Interactions between sediments and waters. Geneva – August 1984. In press.

Vanek, V., 1985a. Groundwater and Lakes. A literature review. Inst. of Limnology, Univ. Lund. ISSN 0348-0798. 56 pp.

Vanek, V., 1985b. The role of groundwater in lake ecosystems. In M. Enell, W. Graneli & L.-A. Hansson (eds.), 13th Nordic Symposium on Sediments. Aneboda. In press.

Wang, Z.-J., F. Giovanoli, H. El-Ghobary & J.-P. Vernet, 1985. A speciation study of phosphorus in the interstitial water from Lake Geneva (Switzerland). 3rd International Symposium. Interactions between Sediments and Waters. Geneva – August 1984. In press. Watanabe, Y. & S. Tsynogai, 1984. Adsorption-desorption control of phosphate in anoxic sediment of a coastal sea, Funka Bay, Japan. Mar. Chem. 15: 71–83.

Williams, D. H. J., J. K. Syers, R. F. Harris & D. E. Armstrong, 1970. Adsorption and desorption of inorganic phosphorus by lake sediments in a 0.1 M NaCl system. Envir. Sci. Technol. 4: 517–519.

Winfrey, M. R. & J. G. Zeikus, 1977. The effect of sulfate on carbon and electron flow during microbial methanogenesis in fresh water sediments. Appl. envir. Microbiol. 33: 275–281.

Yoshida, T, 1985. On the behaviour of nutrients in sediment pore water and on sediment surface. 3rd International Symposium. Interactions between sediments and waters. Geneva – August 1984. In press.