

Seasonal Variations in the Loosely Sorbed Phosphorus Fraction of the Sediment of a Shallow and Hypereutrophic Lake

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ABSTRACT / On the basis of selective extractions, loosely sorbed phosphorus (ADS-P) has been shown to constitute much of the total phosphorus in the P-rich near-surface sediments of Lake Søbygaard, Denmark. The concentrations of ADS-P are seasonally variable, ranging from 0.2 mg Pg⁻¹ DW in the winter to more than 2 mg Pg⁻¹ DW in the summer.

The variations can be observed as deep as 10 cm into the sediment but are most pronounced in the upper few centimeters.

During the summer, lake and pore water pH levels are very high, and photosynthetic activity causes elevation to pH 10-11 in the lake. Laboratory experiments demonstrated a strong association between ADS-P and high pore water pH.

It is likely that Lake Søbygaard represents an extreme example of pH control on sediment/water phosphorus equilibria in which high concentrations of internal ADS-P contribute significantly to the total P load of the Lake.

Introduction

Lake eutrophication has become a major problem worldwide, and many attempts have been made to stop its development over the past decade. In Denmark, this has been done mainly by reducing the phosphorus input. However, in spite of a successful phosphorus reduction program, many lakes continue to be eutrophic, and the expected lake recovery delayed. Often, this is caused by a continued release of phosphorus from the sediments where it has been accumulating as a result of excessive external loading. Phosphorus can be released from sediments under both anaerobic and aerobic conditions (Boström and others 1985). This is of importance especially in shallow and nonstratified lakes. Investigations concerning phosphorus adsorption and dynamics in sediments of these lakes, therefore, may help to predict how long internal phosphorus loading from the sediment will continue.

This article describes some investigations in shallow and hypereutrophic Lake Søbygaard, in Denmark. They concern seasonal variation in phosphorus release rates from sediment and how this variation seems to be coupled to seasonal variation in lake water pH and concentrations of loosely sorbed phosphorus in sediment.

Lake Description

Lake Søbygaard is a small, hypereutrophic lake situated in the central part of Jutland, Denmark. The lake area is 0.4 km²; it has a mean depth of 1.0 m and a maximum depth of 1.9 m (Søndergaard and others 1987). Because of a high nutrient level, the phytoplankton biomass is very high. The summer secchi depth is usually between 0.3 and 0.5 m, and chlorophyll *a* concentrations are between 500 and 1000 µg l⁻¹. Tot-P is between 0.2 and 0.8 mg l⁻¹ and tot-N between 3 and 6 mg l⁻¹. Water retention time is short, about 20 days.

Mechanical and biological treatment of influent waters continued until 1982; since then, additional chemical treatment has been applied and external phosphorus loadings have been reduced by more than 90 percent. Phosphorus concentrations in the lake, however, have not decreased correspondingly, due to a continuing phosphorus release from the sediment. This internal phosphorus loading now dominates the phosphorus loading of the lake. Since 1982 the internal phosphorus load has been about 8 g P m⁻² yr⁻¹ while the external load has been about 5 g P m⁻² yr⁻¹ (Table 1). The net phosphorus release rate from the sediment shows a distinct seasonal pattern as indicated in the data of the 1985 phosphorus mass budget (Table 2).

During the winter, phosphorus concentrations at the outlet from the lake are more or less equal to the inlet concentrations; during the rest of the year, outlet concentrations are much higher than inlet concentra-

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Table 1. Changes in phosphorus loading and retention, Lake Søbygaard.

P in $\text{g m}^{-2}\text{yr}^{-1}$	1978	1982	1983	1984
Σ Inlet	27.8	33.7	6.7	4.9
Σ Outlet	11.8	27.8	14.7	13.1
Retention	15.9	5.9	-8.0	-8.2

Table 2. Net phosphorus release rates from sediment 1985 ($\text{mg P m}^{-2} \text{d}^{-1}$).

	Winter	Spring	Summer	Autumn	Yearly
Mean	-5	15	35	25	20
Range	-10-0	0-30	20-100	0-50	-10-100

tions and this difference corresponds to the internal phosphorus loading. On a yearly basis the internal phosphorus loading is about $20 \text{ mg P m}^{-2} \text{d}^{-1}$ but, during some periods in summer, the phosphorus release rate can be as high as $100 \text{ mg P m}^{-2} \text{d}^{-1}$ (Søndergaard and others 1986).

The internal phosphorus load has its origin in a large phosphorus pool which was built up in the sediment during the period prior to chemical wastewater treatment. Phosphorus concentrations are high in the upper 20–25 cm of the sediment, ranging from about $8 \text{ mg P g}^{-1} \text{DW}$ near the surface of the sediment to almost $12 \text{ mg P g}^{-1} \text{DW}$ at 15-cm depth (Fig. 1); background levels are about $2 \text{ mg P g}^{-1} \text{DW}$.

Most of the phosphorus in the sediment can be extracted by NH_4Cl or NaOH , and is likely in the form of loosely sorbed P or as Fe and Al bound P (as defined by Hietjes and Lijklema 1980). Organic bound phosphorus decreases significantly with sediment depth, and calcium bound phosphorus is generally of minor importance. The sediment is very iron rich, concentrations are typically $50\text{--}70 \text{ mg Fe g}^{-1} \text{DW}$, corresponding to a P:Fe ratio of about 1:5 or 1:6 in the upper 10 cm of the sediment.

Primary production in the lake is very high, from 1500 to $1700 \text{ g C m}^{-2} \text{yr}^{-1}$ (Jeppesen and others in prep.), and, during summer, lakewater pH may rise to between 10 and 11. These very high pH levels influence pore water pH in the sediment as well, thereby increasing pH in the upper 8–10 cm of the sediment (Søndergaard in prep.).

Materials and Methods

Sediment was collected with a core-sampler from a central part of the lake, and previous sampling demonstrated that there is little horizontal variation in the

sediment composition (Søndergaard 1987). On each sampling date, four sediment cores were recovered from the middle of the lake. The cores were cut into 1- or 2-cm sections. These were stored at 5°C until the following day, and then analyzed for dry weight, organic matter, total iron, and phosphorus. Phosphorus was fractionated into loosely sorbed phosphorus (ADS-P), iron and aluminum bound phosphorus, calcium bound phosphorus, and organic bound phosphorus (calculated as $\text{tot-P} - (\text{ADS-P} + \text{Fe and Al-P} + \text{Ca-P})$, according to the procedure of Hietjes and Lijklema (1980). Total phosphorus was measured as MRP after extraction with 1 M HCl of ash-free sediment. Dry weight was determined by drying at 105°C for 24 h, and organic matter by drying to constant weight at 550°C . Iron was measured in acid solution by bipiridyl complex formation. Pore water was sampled in situ by use of ceramic cups incubated at different depths (0–40 cm) in the sediment, as described by Søndergaard (in preparation). Pore water was sampled weekly or more frequently during July–September, and every fortnight during October–December; pH in the pore water was measured potentiometrically.

During April 1986, when natural ADS-P concentrations were low, sediment was sampled for pH-manipulated laboratory experiments. The procedure was as follows: samples from three different sediment depths were used (0–1, 1–2, and 2–4 cm). To each of five subsamples from these depths, small but different amounts of 0.1 M NaOH were added to adjust pH to different levels between 7 and 11. The addition of NaOH did not change the dry weight of the sediment. After the addition of NaOH, the sediment samples were placed in the dark at 5°C . ADS-P and pH were measured in each of the samples after 2, 5, and 12 days; pH was measured potentiometrically and ADS-P as described previously.

Results and Discussion

Field Observations

Typical profiles of pore water pH during summer and winter are shown in Figure 2. Relative to winter profiles, summer pH values were higher in the upper 10 cm of sediment. The increase was especially pronounced in the top 5 cm of sediment, where pH increased to between 9 and 10. Below 10 cm depth pH did not change seasonally; it was constantly about 8.5 at 10–12 cm depth and 7.6 at 40 cm depth.

The increased pH in the upper part of the sediment during summer is interpreted as a reflection of the photosynthetically increased pH in the lake water. Seasonal variations in pore water chemistry have been

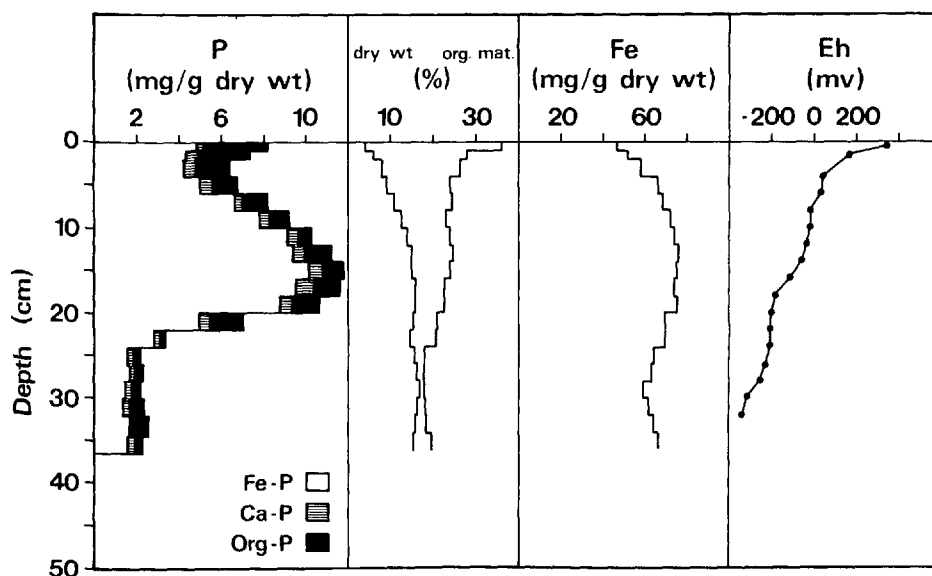


Figure 1. Phosphorus, dry weight, organic matter, iron, and redox potential (Eh) in the upper 36 cm of sediment, Lake Søbygaard.

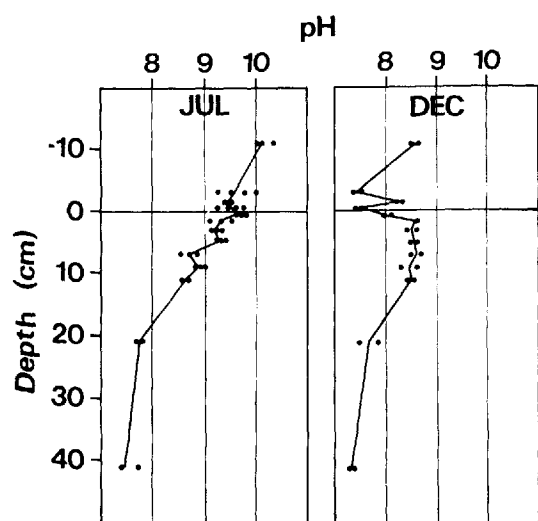


Figure 2. Typical summer (July) and winter (December) profiles of pH in pore waters from the upper 40 cm of sediment, Lake Søbygaard. (From Søndergaard, in preparation).

reported in other lakes (Carignan 1985, Holdren and others 1977) but usually not in pore water pH. In Lake Søbygaard, the influence of acidification due to degradation of organic matter near the sediment surface seems to have only limited effect as a means of suppressing high pH in the upper part of the sediment. The pH measured at a given time in pore water is thereby seen as an equilibrium pH determined largely by the balance between lake water alkalinity and acidification in the sediment due to decomposition.

Changes in pore water also may be induced during frequent resuspensions of the lake bottom (Sønder-

gaard 1986, Jensen and Kristensen 1986). Resuspension increases the contact between sediment and lake water, and thereby facilitates P release and the incorporation of lake water to erosional depths within the sediment.

Concentrations of loosely sorbed phosphorus (ADS-P) were measured once or twice a month in the upper 12 cm of sediment from May 1985 to May 1986 (Figs. 3 and 4). Increased sediment ADS-P was noted first in June at depths of 0–2 cm. At depths of 2–8 cm the effect was more apparent in September. An increase in the deeper parts of the sediment occurred after a violent storm which resulted in considerable resuspension of the upper sediment. Sediment reworking is considered an important mechanism for the increase of ADS-P at depths below about 2 cm (Søndergaard 1986). ADS-P levels decreased during October and reached minimum values between December and April. In winter, ADS-P at 2–4 cm depths was between 0.2 and 0.4 mg P g⁻¹ DW; during summer it was between 1.5 and 2.0 mg P g⁻¹ DW. The summer increase was greater near the sediment surface. At depths below 10 cm, ADS-P was constantly less than 0.1 mg P g⁻¹ DW.

Redox potential and pH are believed to be major factors controlling the adsorption of phosphorus in sediments rich in iron (Lijklema 1977, Andersen 1978, Jacobsen 1978). Therefore it would be expected that the large phosphorus pool, most of which is bound to iron in the sediment of Lake Søbygaard, would be influenced by the seasonal variations recorded in pore water pH. When pH is increased in the sediment it creates an increased competition between hydroxyl ions and phosphate ions, thereby decreasing the sorp-

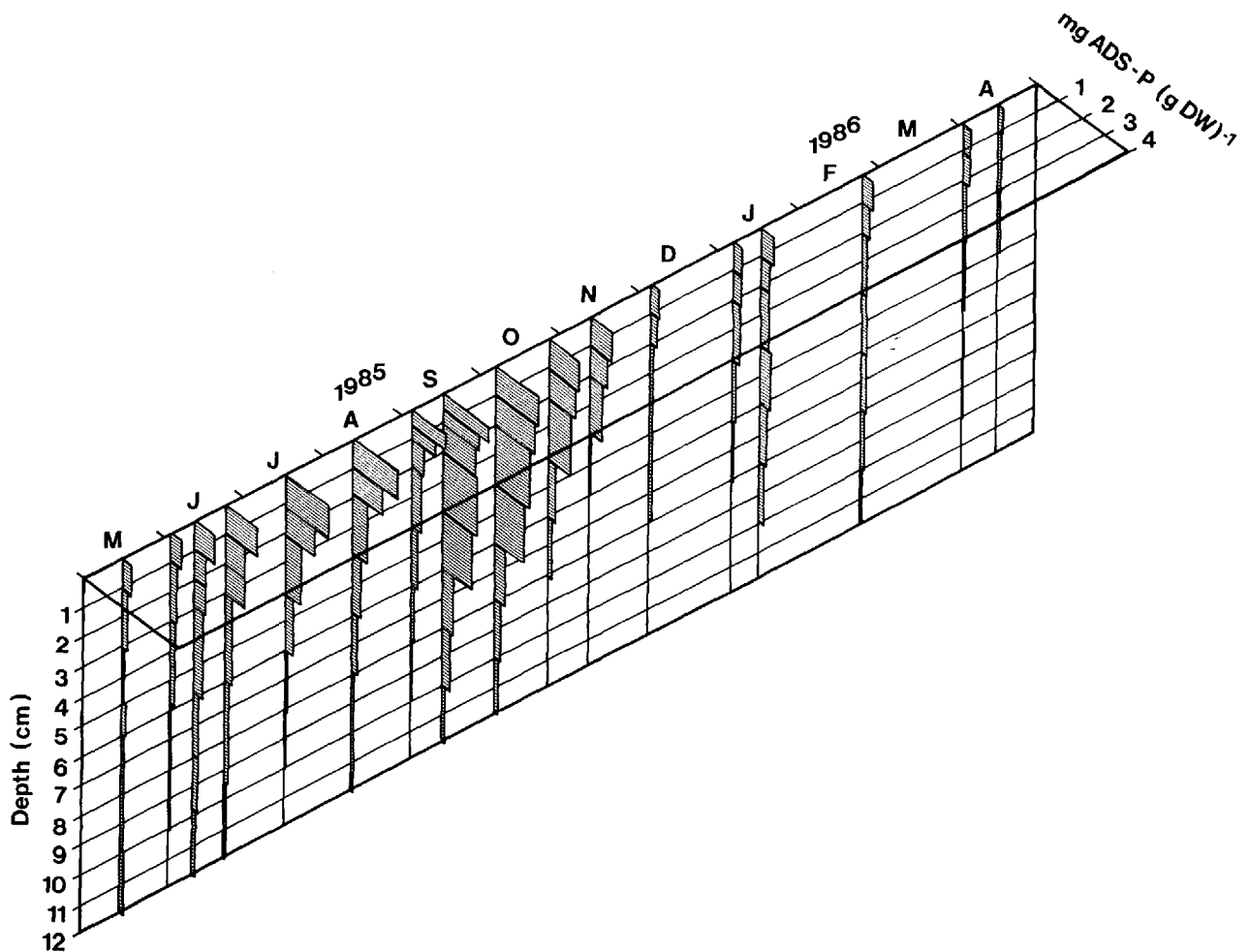


Figure 3. The seasonal variation of ADS-P concentrations in the upper 12 cm of sediment, Lake Søbygaard.

tion of phosphate on iron. Thus the seasonal variations in ADS-P which were observed can be explained by changed phosphate binding capacity due to the variations in pore water pH, as suggested by Lijklema (1977). Further, it is conjectured that the iron-phosphorus bond may weaken so that it becomes possible to partially extract this form of P by NH_4Cl (ADS-P). Part of the Fe-P might be transferred to ADS-P in response to increasing pH.

The seasonal variations of near-surface ADS-P concentrations thus appear to be coincident with variations in pore water pH. Although both variations are related, they may not be directly so. Sediment resuspension, diffusion, and changes in redox potential may be additional and contributory factors. Seasonal variations in sediment parameters have been reported in other lakes (Boström and others 1985, Carignan 1985), but usually not to the extent recorded from Lake Søbygaard and, hitherto, rarely in ADS-P concentrations (Boström and others 1982). In shallow

Lake Søbygaard, many conditions such as phytoplankton biomass and production, pH and phosphorus concentrations are considered to be extreme and they sometimes change dramatically (Jeppesen and others, in prep.).

Laboratory Experiments

In laboratory incubator experiments, it was demonstrated that artificially increased pH resulted in increased ADS-P concentrations in the sediment (Fig. 5). The increase was near linear and effects were greatest in the range from pH 8 to 10; only minor changes occurred between pH 7 and 8. There was no significant difference between sediment samples from 0–1, 1–2 and 2–4 cm depths. An increase in pH to 10.7 within 2 days increased ADS-P from about 0.2 to about 1.2 mg P g^{-1} DW. Within 5 days the maximum pH had decreased to about 9, but ADS-P was still between 1.2 and 1.5 mg P g^{-1} DW. After 12 days incu-

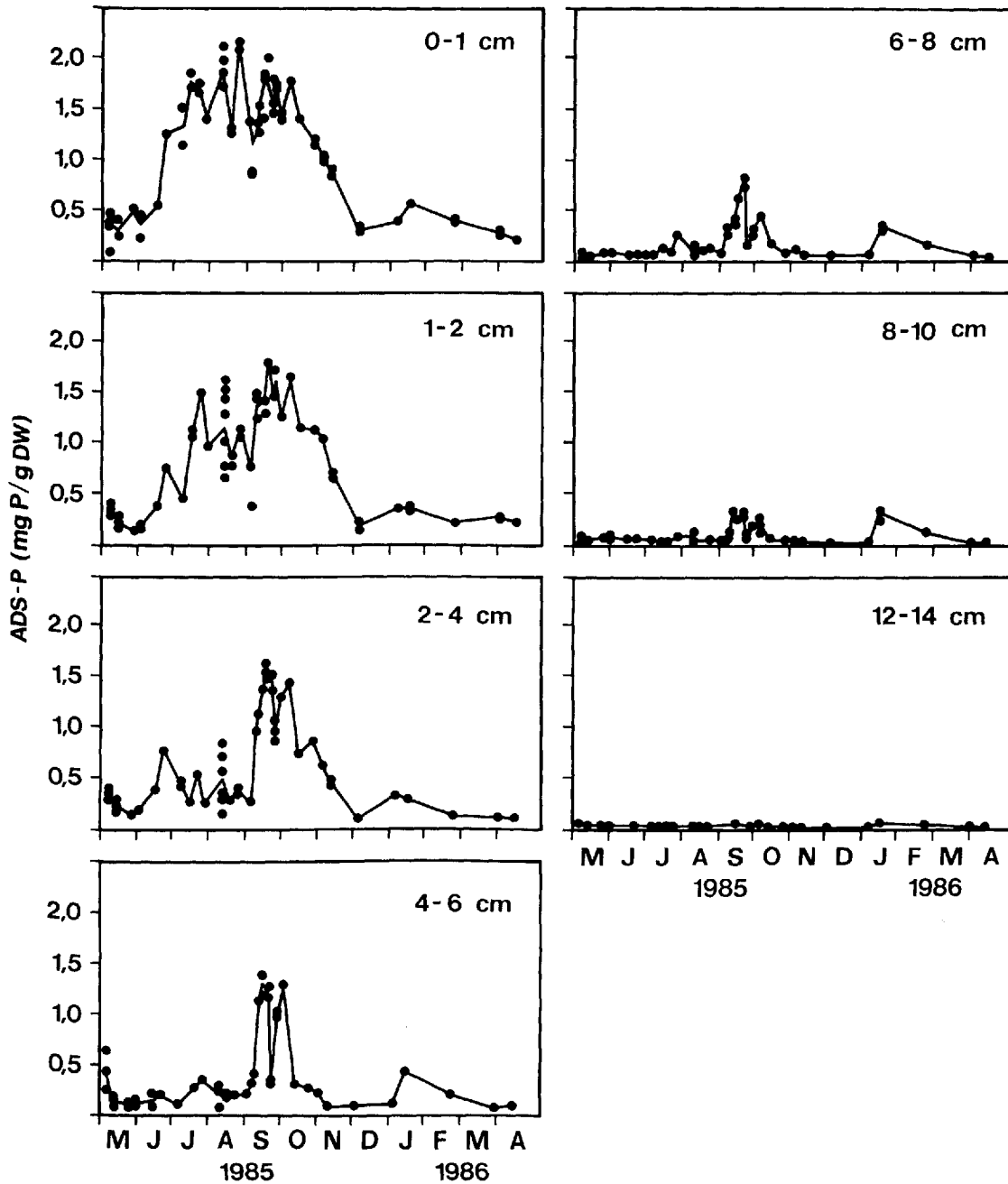


Figure 4. Seasonal variations of ADS-P in different sections of sediment, Lake Søbygaard.

bation maximum pH had decreased to 7.8 and ADS-P to between 0.6 and 0.8 mg P g⁻¹ DW.

The increase in ADS-P after the experimental increase of pH was comparable to the natural increase observed in the sediments of the lake. At pH 9.2–9.6, ADS-P in the experiments increased to between 0.5 and 1.5 mg P g⁻¹ DW, depending on the incubation time. This compares with the summer pore water pH increase in the lake to between 9.2–9.6 and ADS-P to 1.0–2.0 mg P g⁻¹ DW. There is a reasonable agree-

ment between experimental and observed variations in ADS-P due to increase pH.

The effect of increased pH was most pronounced between 8 and 10, although some effect could also be observed between 7.5 and 8.0, when the sediment was incubated for 12 days. When pH was increased to more than 10, the increase in ADS-P was less pronounced. These observations are interpreted as a stepwise substitution reaction with OH⁻ on iron hydroxides as proposed by Andersen (1975) and Lijk-

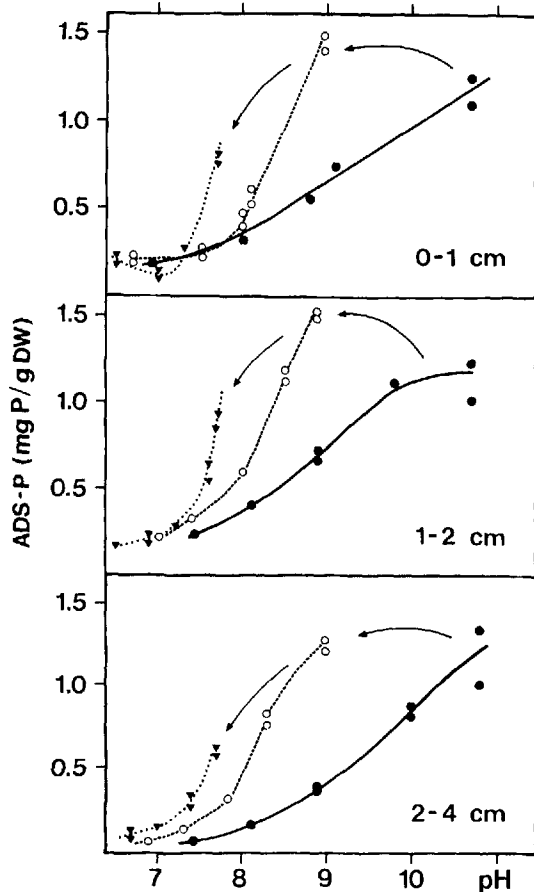


Figure 5. ADS-P concentrations of different sample depths after experimental pH-manipulation. Subsamples incubated for 2 (●), 5 (○), and 12 (△) days.

lema (1977). At pH 7–8, OH^- concentrations are not high enough to cause any change in the adsorption of phosphorus, but at higher pH the adsorption is affected and ADS-P concentrations increase (and Fe-P decrease). At pH 10–11, iron hydroxides probably start to near saturation with respect to OH^- , although some phosphorus (Fe-P) is still adsorbed; the increase in ADS-P is less pronounced.

Although phytoplankton biomass and lake water pH increased in April–May, ADS-P did not increase until June. Probably this delayed response in ADS-P concentration can be explained by the buffering processes in the sediment (Jacobsen 1978) but, unfortunately, pH in pore water was not measured until July.

During the experiments, ADS-P concentrations did not respond immediately to changing pH; rather, they exhibited a distinct hysteresis. Hysteresis effects are not unusual with these types of experiments (Kamp-Nielsen 1979, Lijklema 1977), and they probably indicate the occurrence of other less reversible processes when pH is changed. The adsorption and desorption

of phosphate due to changes in pH are believed to be reversible (Lijklema 1977). The hysteresis effect is important in describing the nature of the adsorption processes but it is not expected to influence the overall pattern of phosphorus release in the lake, where the sediment is not usually exposed to sudden changes in pH.

The results of these experiments indicate a strong association between increased sediment pore water pH and ADS-P. Field observations confirm that variations follow a seasonal cycle. The relationships suggest that high phytoplankton production causes high pH in lake water and in the pore water, and this leads to an increase of ADS-P concentrations in the near-surface sediment. Do increased concentrations of ADS-P lead to increased rates of phosphorus release? Strong relationships between internal phosphorus loading and ADS-P concentrations observed in Lake Søbygaard make this seem very likely. If this is so, high primary productivity, achieved by raising pH, adds to positive feedback mechanisms which accelerate phosphorus release from some sediments. Boström (1984) has concluded that sediments in many lakes receiving loads of poorly treated sewage contain considerably more ADS-P than unpolluted lakes, and that differences in phosphorus release rates from sediments can be explained largely by differences in the fractional composition of the sediment phosphorus. Thus seasonal variations in ADS-P have the potential to dominate internal P loading mechanisms in some very shallow lakes where concentrations of P in pore water are substantially greater than in overlying lake water.

It is recognized that other factors, particularly redox conditions, are likely to influence P release from the iron-rich sediments of Lake Søbygaard (Jeppesen and others 1986). It is most probable that peaks in P release reflect the combined effects of periodic physical mixing of bottom sediments and overlying water and/or the development of occasional anoxic conditions. However, it is probably only the sustained period of high pH which most effectively characterizes the conditions of seasonally continuous internal loading.

Conclusions

Although the phosphorus concentrations in the sediment of Lake Søbygaard are unusually high compared to most other lakes, the mechanisms which drive internal phosphorus loading in this lake may apply to other shallow and highly eutrophic lakes. It is thought that Lake Søbygaard represents an extreme example of pH influence on sediment/water P-equilibria under the influence of high productivity.

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