THE RELEASE OF DISSOLVED PHOSPHORUS FROM LAKE SEDIMENTS

BIBLIOTHEEK
LANDBOUWUNIVERSITEIT
WAGENINGEN

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NN08201, 1405

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THE RELEASE OF DISSOLVED PHOSPHORUS FROM LAKE SEDIMENTS

academisch proefschrift ter verkrijging van de graad van
doctor in de landbouw- en milieuwetenschappen,
op gezag van de rector magnificus,
dr. H.C. van der Plas,
in het openbaar te verdedigen
op vrijdag 22 maart 1991
des namiddags te vier uur in de aula
van de Landbouwuniversiteit te Wageningen.

ISN: 536148

The research described in this thesis was carried out at the Limnological Institute, "Vijverhof" laboratory (Nieuwersluis, the Netherlands) and the Institute for Inland Water Management and Waste Water Treatment (Lelystad, the Netherlands). Additional financial support was by STW (Technical Science branch of the Dutch Organization for Scientific Research) and the European Community.

NN08201, 1403

STELLINGEN

1 Soluble Reactive Phosphorus wordt vaak aangeduid als orthofosfaat. Het verschil tussen deze twee is echter veel groter dan vaak wordt gemeend.

2 De basis waterkwaliteitsnorm van 0,15 mg totaal fosfaat per liter sluit niet aan bij de omschrijving van de gewenste basiskwaliteit (..er is geen permanente dominantie van blauwalgen...).
Derde nota Waterhuishouding, Rijkswaterstaat 1989.

3 Om de eutrofiëring van de Nederlandse oppervlaktewateren werkelijk terug te dringen zijn dan ook veel verder gaande maatregelen nodig dan een convenant om tot 75% defosfatering op de afvalwaterzuiveringsinstallaties te komen. In dit opzicht kan een voorbeeld worden genomen aan de effluenteis van 0,5 mg P l^{-1} die in Zweden wordt gehanteerd.

4 Net als fosfaatfixatie, moet de bruikbaarheid van baggeren als methode om interne fosfaatbelasting in ondiepe meren in Nederland te bestrijden nog worden aangetoond.

5 De bijdrage van bodemwoelende vis aan de nalevering van nutriënten door de waterbodem wordt vaak sterk overschat. Brasem is dan ook een gevolg en géén oorzaak van eutrofiëring.
dit proefschrift

6 Van integrale proefprojecten om de eutrofiëring te bestrijden kan alleen worden geleerd, indien ze ook worden vergezeld door gedegen onderzoek.

7 Vooralsnog hebben waterkwaliteitsmodellen géén grotere voorspellende waarde dan de weermodellen van het KNMI. Beide zijn slechts geschikt om binnen een nauwe marge van randvoorwaarden en over een korte tijdsperiode verwachtingen uit te spreken. Naast die modellen blijft "de natte vinger" een uiterst belangrijk instrument.

8 De stelling dat een hoge pH in de waterkolom de nalevering van fosfaat door de waterbodem bevordert, berust grotendeels op een experimenteel artefact.
dit proefschrift

9 Meer aandacht voor de stikstofbelasting van de Nederlandse oppervlaktewateren is geen overbodige luxe. Dit mag echter niet leiden tot een evenredige afname van de aandacht voor het terugdringen van de fosfaatbelasting.

10 De Verenigde Staten kunnen hun energie beter steken in maatregelen om de emissie van kooldioxide te verminderen dan in pogingen de rest van de wereld duidelijk te maken dat zij toch echt hun best doen.

11 Waterkwaliteit is in meer dan één opzicht een kwestie van kwantiteit.

12 De conclusie van Drake en Haney dat door hen gemeten fosfaatfluxen overeenkomen met uit poriënwaterprofielen berekende fluxen, berust op een rekenfout.
Drake, J.C. and I. Haney (1987). Freshw. Biol. 17: 513 - 523.

13 Een ieder die een rapport uitgeeft zonder duidelijk een auteur te vermelden, geeft hiermee impliciet te kennen dat hij of zij geen prijs stelt op opname van dit produkt in literatuur opslagsystemen.

14 In sommige kringen hebben nieuwere en snellere personal computers de rol van snelle auto's als belangrijkste gespreksonderwerp overgenomen.

Lelystad, 26 november 1990 Paul Boers

Stellingen, behorend bij het proefschrift:
The release of dissolved phosphorus from lake sediments.

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

1.1 EUTROPHICATION: A GLOBAL PROBLEM

Excessive loading of lakes with nutrients often leads to increased algal growth and biomass. This phenomenon is known as eutrophication. Increased loadings with nitrogen and phosphorus are considered to be the prime causes of eutrophication (Vollenweider, 1968).

Although in a number of cases nitrogen has been identified to be the primary nutrient limiting algal growth (Schmidt-Van Dorp, 1978; Klapwijk, 1988; Ryding, 1981), eutrophication is usually combatted by decreasing the phosphorus loadings. The reasons are that phosphate is considered to be the natural growth limiting nutrient in freshwater lakes and that reduction of nitrogen loads might lead to dominance of nitrogen-fixing cyanobacteria.

Worldwide, and also in the Netherlands, reduction of phosphorus loading is the common strategy (Rijkswaterstaat, 1989a, 1989b). In spite of considerable efforts, the results of this policy so far have not been very encouraging. It is expected that general measures, as a 75% P removal at wastewater treatment plants, the use of phosphorus free detergents and a gradual decrease of manure supply will lower phosphate concentrations in the Dutch lakes insufficiently to decrease algal biomass as well (Rijswaterstaat, 1989a). Additional measures, such as flushing, diversion of nutrient rich water, dephosphorization of inlet water, biomanipulation, dredging, compartmentalization, are needed to combat eutrophication successfully. These additional measures are highly lake-specific.

Examples of such tailor-made lake restoration programmes in the Netherlands are: Reeuwijk Lakes area (Klapwijk, 1988), Loosdrecht Lakes (Van Liere et al., 1986 and 1990), Lake Veluwemeer (PER, 1986; Hosper & Meijer, 1986). However, even in these lakes, the success of the efforts has been only limited. Probably only in lake Veluwemeer the phosphate concentrations decreased to a level where the algal biomass and composition were affected.

1.2 WHY DO EUTROPHIC LAKES NOT RECOVER?

Several reasons for the often only limited success of lake restoration programmes have been given. A first reason is, that drastic reductions of the external phosphorus loading are needed to force a lake into another trophic category (Cullen & Forsberg, 1988). It is very difficult to bring about such a decrease of the phosphorus loading. A second reason may be the resistance of the foodweb to changes (Van Donk & Gulati, 1989). Measures to overcome this problem are in development. They are known as foodweb manipulation. Such measures have proven to be quite successful in small lakes (Van Donk & Gulati, 1989). The usefulness in large lakes is still a matter of research.

A third reason is a release of phosphorus from the sediments, a phenomenon known as internal loading.

1.3 INTERNAL LOADING

This process is the subject of this thesis. As early as 1941, Mortimer recognized the relevance of this process in deep, stratifying lakes (Mortimer, 1941 and 1942). For a long time, however, this process was not considered to be of any importance for shallow lakes, as their surface sediments are not anoxic. It is the merit of Golterman, that this point of view was abandoned. He claimed that also in shallow lakes sediment phosphorus can be an excellent source for algal growth and that this sediment phosphorus might cause a delayed response of a lake to a decreased external phosphorus loading (Golterman et al., 1969). Since that time, numerous papers on this subject have been published, symposiums have been organized and in the Netherlands at least seven Ph. D. theses deal with this subject (Hieltjes, 1980, Kelderman, 1985; Brinkman & Van Raaphorst, 1986; Siebers, 1985; Van Straten, 1986; Klapwijk, 1988). This thesis is the eighth and certainly not the last.

Without any doubt, internal loading may delay an improvement of the water quality. Maybe the best known examples are the Swedish Lake Trummen (Bengtsson et al., 1975) and the Danish Lake Søbygard (Søndergaard, 1989). There is also little doubt, that the fear for internal loading has delayed many lake restoration projects.

A major problem with respect to sediment-water exchange processes of phosphorus compounds is that the knowledge of this subject is still fragmentary and rather qualitative. Much is known of the chemical processes governing the dissolved phosphate concentrations in the interstitial waters, but we do not know exactly by what mechanism and to what extent phosphate is ultimately immobilized in the sediments. It is known that microbial processes are important in the phosphorus cycling in sediments, but the determination of the various fractions of organic phosphorus in sediments, that might be relevant in this respect, is not well possible. Phosphorus release rates from sediment cores can be measured in the laboratory and bio-available phosphorus in the sediments can be quantified, but we can not relate these measurements to the expected behavior of the lake after a reduction of the external loading. Several dynamic models that describe the sediment-water interactions have been constructed (e.g. Jørgensen et al., 1982), but their predictive power is questionable.

This poses a problem for lake restoration programs: measures to decrease internal loading are very costly, but it is difficult to assess the necessity of such measures.

1.4 SCOPE OF THIS THESIS

This thesis deals with quantification of internal loading and with measures to combat internal loading.

In the first four chapters a study of the sediment-water exchange of phosphorus in the shallow Loosdrecht Lakes is described. The external phosphorus loading to this lake was decreased in 1984. The chapters focus on the distribution of phosphorus in the sediments (chapter 2), the exchange of particulate organic matter between the sediments and water (chapter 3) and the phosphorus release processes in the sediments (chapters 4 and 5).

The next three chapters deal with the quantification of the sediment-water exchange of phosphorus under different conditions. Chapter 6 focusses on the often mentioned influence of pH on the phosphorus release. Chapter 7 presents an overview sediment-water exchange rates in a number of shallow lakes with a reduced external loading in relation to the sediment composition.

In chapter 8, the first results of a new and economic method to combat internal phosphorus loading are reported. Chapter 9 describes changes in the phosphorus cycling through the food web due to biomanipulation. This includes sedimentation and release from the sediments. Chapter 10 contains a summary and the general conclusions.

Scientific research is often a cooperative occupation, and the research leading to this thesis is no exception to the rule. Most chapters have been written in close cooperation with one or several co-authors.

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CHAPTER 2

DISTRIBUTION AND FORMS OF PHOSPHORUS IN THE SEDIMENTS OF THE LOOSDRECHT LAKES

Paul Boers, Ad Wisselo & Tom Cappenberg

A part of this chapter was also published in:
Verh. int. Ver. Limnol. 22: 842 - 847

ABSTRACT- The sediments of the Loosdrecht Lakes consist mainly of organic matter with a C:N ratio of about 20. The organic matter originates probably from macrophytes.

In most parts of the lakes, the upper 18 cm of the sediments contain 10 - 15 g P m^{-2}*. Only near the former inlet of phosphorus rich water from the river Vecht this amount is higher. The phosphorus accumulation in the sediments is much lower than can be expected from the high external loading. This may be due to a transport of phosphorus from the sediments downwards by infiltration.*

Desorption experiments and bio-assays both indicate that about 5% of the sediment phosphorus is "available". This compares well with the amount of loosely bound phosphorus, as determined with selective extractions. These same extractions indicate that a major part of the sediment phosphorus is associated with organic matter.

2.1 INTRODUCTION

The Loosdrecht Lakes are situated in the centre of the Netherlands and are man-created by peat-excavation. The lakes' area is 18.3 km^2, the average depth is about 2 m. The lakes are highly eutrophic, with chlorophyll-a maxima up to 240 mg m^{-3}. The main source of pollution of the lakes is an external phosphorus loading of about 1 g P m^{-2} y^{-1}, mainly from the river Vecht. In summer, water from this river is let into the lakes to maintain the desired water level. In order to reduce the external phosphorus loading, Vecht water will be replaced by water from the Amsterdam-Rhine Canal, in which the phosphorus concentration will be lowered by coagulation with ferrichloride. This will diminish the external P loading to about 0.3 g P m^{-2} y^{-1}. For a further description of the Loosdrecht Lakes and hydrological data, see Van Liere et al. (1984), Kal et al. (1984).

After reduction of the external loading an internal phosphorus loading from the sediments might delay an improvement of the water quality and therefore this process is included in the research to the lakes' response to the decreased phosphorus loading. In this chapter some background data on the composition of the sediments are described, including the distribution of phosphorus in the Loosdrecht lakes sediment, some results of experiments of chemical properties and availability of the sediment phosphorus for autotrophic growth.

2.2 METHODS

Undisturbed mud cores were taken with a cylindrical stainless steel bottom sampler, provided with a steel cutter head and a separate perspex inner core of 40 cm height and 5 cm inner diameter (Van Raaphorst & Brinkman, 1984). The sampler is driven into the bottom by hand and then closed with a rubber stopper. After sampling, the inner core can be closed with a separate rubber stopper and removed without disturbing the sample. In the laboratory, the sample is cut into segments, 0-2, 2-4, 4-6, 6-10, 10-14 cm, etc. which are kept at 4 °C in the dark for analysis.

For mapping the P distribution in the lake sediments, about 40 cores were taken, covering the whole lake area with its different bottom types. Of all core segments, dry weight was determined by drying at 105 °C overnight, organic matter as loss on ignition upon heating at 550 °C during 2 h. Total sediment-P was determined by boiling the ash in diluted sulfuric acid after Andersen (1976), followed by a soluble reactive phosphorus (SRP) determination on a Technicon AA II auto-analyser, with a modified molybdate-blue method after Murphy & Riley (1962).

The various phosphorus fractions in the 0-2 cm layers of a selected number of samples were determined after Hieltjes & Lijklema (1980). 1M NH_4Cl was used to determine "adsorbed and loosely bound P", 0.1 M NaOH to determine "Fe- and Al-bound P" and 0.5 M HCl to determine "Ca-bound P". The remainder P is called "resistant P". Humic acids present in the NaOH extracts, preventing proper SRP determination, were precipitated with diluted H_2SO_4, followed by filtration. The filtrate is used for SRP determination. A subsample from the complete NaOH extract was used for total P determination. The difference between total P and SRP is called "humic acid bound P". In the segments of one core from the centre of the lake organic C, N and carbonate C were determined with a Perkin-Elmer 240 elemental analyser, using dried and ashed samples. In these segments Ca, Fe, and Al were determined with a Perkin-Elmer 560 AAS after digestion with HNO_3 and HCl.

Bioassays with 4g of wet sediment as the sole phosphorus source were carried out, using 200 ml of two weeks old phosphorus starved *Scenedesmus quadricauda* cultures. Medium: modified Skulbergs Z-8 50% medium (Bolier et al., 1981). Light: 30 W m^{-2}, 20 °C, day/night regime 12h/12h. Maximum yields, measured as chlorophyll-a, were compared with those of control cultures with known amounts of K_2HPO_4 as the sole phosphorus source.

Exchangeable sediment phosphorus was measured in a dual-chamber system (Hieltjes, 1980). The lower chamber contained a suspension of 10 g wet sediment in 500 ml water and the upper chamber a suspension of 10 g anion exchange resin of the type BIO-RAD AG1-X4, 20-50 mesh in demi water. The two chambers were separated by 2μm zooplankton gauze and both suspensions were stirred. The phosphate on the ion exchange resin was removed at regular intervals by washing the resin with 0.1 M HCl and determined as described above. The experiments were done with the 0-2, 2-4 and 4-6 cm segments of a sediment sample from station 4 (Fig. 1) and were run for 25 - 40 days.

2.3 RESULTS

Sediment characteristics

At most sampling stations the lower layers of the bottom consist of firm peat, covered by variable amounts of very loose brown mud, that accumulates at wind sheltered places. The sediments contain up to 80% organic matter, reflecting the peat origin of the area, except where sand is the main bottom constituent. Here very low amounts of organic matter are found. Total phosphorus and average organic matter content in the top 18 cm of the sediments were mapped (Fig. 1).

This accumulated P is rather constant (10-15 g m^{-2}) except in the Kievitsbuurt near the inlet of phosphorus rich Vechtwater, where it is higher than average and

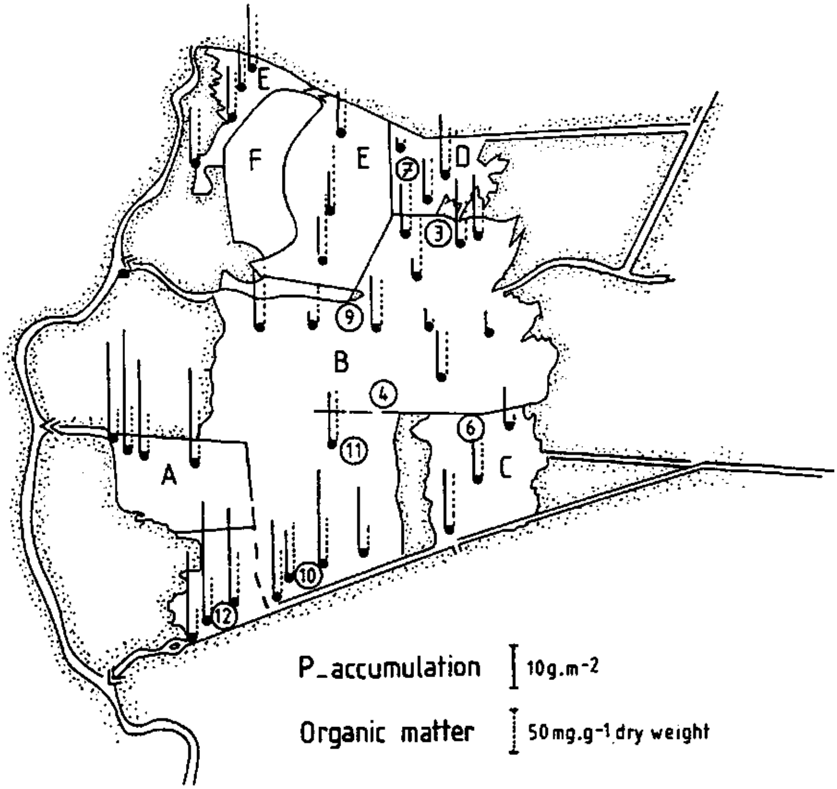

Fig. 1. Map of Loosdrecht Lakes. Bars indicate accumulated P, and organic matter content in upper 18 cm. Encircled numbers are the main sampling stations used for other sediment experiments (see text). In capitals: sections of the lake area; A: Kievitsbuurt; B: Main lakes; C: Lake Breukeleveen; D: Vuntus; E: Lake Loenderveen, eastern part and western part; F: Drinking water reservoir.

at some stations near islands and in the eastern part of the lakes, where the bottom consists mainly of sand, not capable of binding high amounts of P. Probably, the relatively high accumulation of P in the sediments of the Kievitsbuurt is caused by retention of part of the P present in the water of the river Vecht.

The gross elemental composition of a typical sample from the middle of the lakes is given in Table 1. The C:N ratio is high and fairly constant (20-25), indicating that the organic matter originates from macrophytes. Such a type of sediment is called dy (see Wetzel, 1975). The amount of carbonate-C is low.

Table 1. Composition (mg g dry weight^{-1}) of a sample from station 11 (see Fig. 1), sampled 5-7-1982. Dry weight expressed as mg g wet weight^{-1}.

depth (cm)	dry weight	org. matter	C-org.	C-$CaCO_3$	N	Fe	Ca	Al	P
0- 2	80	570	270	3	14	20	26	8.8	1.09
2- 4	100	720	390	3	18	16	26	8.9	0.69
4- 6	100	780	420	3	19	15	24	9.5	0.54
6-10	110	770	430	3	19	15	24	9.2	0.45
10-14	100	870	490	4	22	12	23	3.8	0.38
14-18	100	930	530	5	26	11	22	0	0.43

Bio-assays

Results of the algal bio-assays are given in Table 2. The percentages of available P are very low. These results agree well with those of Klapwijk et al. (1982). These authors found comparable or even lower percentages of bio-available P in peaty sediments from lakes situated in the western part of the Netherlands.

Chemical extractions

The results of the chemical extractions are given in Table 3. From these figures it is obvious that the NaOH extracts often contain more humic acid bound P than other forms of P. Almost no P is extracted with NH_4Cl.

Table 2. Phosphorus available for algal growth (% of total sediment P) in the 0-2 cm layers of sediment samples from different sampling stations in the Loosdrecht lakes (means of duplicate determinations).

station	bio-available P
4	4
6	3
8	4
9	3
11	6

Table 3. Results of chemical extractions of the 0 - 2 cm layer of sediments from different sampling stations (see Fig. 1). Figures are in mg P g dry weight^{-1}, with percentage of total in parentheses.

Station	l. bound	Fe&Al-P	humic acid P	Ca-P	resist. P	sum
11	0.03(3)	0.34(30)	0.25(22)	0.21(19)	0.30(27)	1.13
3	0.03(5)	0.12(20)	0.09(15)	0.09(15)	0.27(45)	0.60
6	0.05(5)	0.19(20)	0.36(38)	0.09(10)	0.25(27)	0.94
7	0.05(4)	0.25(20)	0.53(42)	0.07(6)	0.35(28)	1.25
Loend.-W	0.06(5)	0.30(24)	0.36(28)	0.19(15)	0.36(28)	1.27
Loend.-E	0.04(4)	0.22(24)	0.22(24)	0.13(14)	0.30(33)	0.91
12	0.20(6)	1.55(43)	1.04(28)	0.37(10)	0.46(13)	3.62

Furthermore, up to 47% of the sediment P is not extracted at all with the method used. This phosphorus fraction is attributed to other organic compounds, as stated by Hieltjes & Lijklema (1980).

This means that in the sediments 41% to 70% of the P is bound to humic acids or other organic compounds, an unusually high amount. However, it should be stated that this amount is only an estimate, as it is possible that P is liberated from the humic acids during dissolution with NaOH or precipitated with the acid later on.

Exchangeable phosphorus

The results of the measurement of exchangeable phosphorus on a sediment sample from station 4 are summarized in Fig. 2. The highest amount of exchangeable phosphorus was measured in the 0-2 cm layer and decreased with sediment depth. Even in the 0-2 cm layer, only 4% of the sediment phosphorus was exchangeable. The desorption process took over a month in the 0-2 cm layer and about a fortnight in the deeper layers.

2.4 DISCUSSION AND CONCLUSIONS

According to the phosphate concentration profile in the sediments (see Table 1), the enrichment with phosphorus is restricted to a sediment layer of less than 10 cm thick. Therefore, viewed in the light of the P loading of about 1 g P m^{-2} y^{-1} on the Loosdrecht Lakes during the past decades, an average accumulation of 10 - 15 g P m^{-2} in a layer of 18 cm is not very high. This may be due to the infiltration of lake water in the sediments, carrying away pore water with

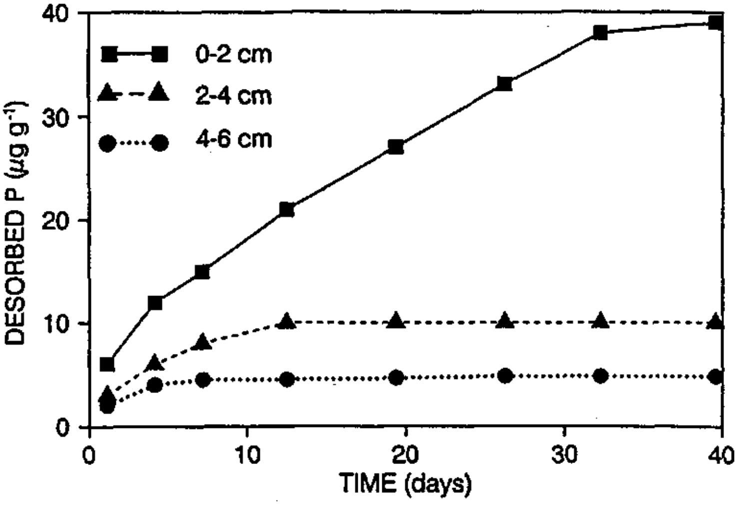

Fig. 2. Desorption of P from sediment suspensions from station 4.

dissolved P concentrations of about 1 mg P l^{-1} (Chapter 5). With an average infiltration rate of 2 mm d^{-1}, about 0.75 g P m^{-2} y^{-1} or 75 % of the external loading is transported to the groundwater.

From our results it is clear that the chemical extractions according to Hieltjes & Lijklema (1980) and bio-assays are not comparable. Hieltjes (1980) claims that the combined NH_4Cl and NaOH extractions give bio-available phosphorus. We find much lower amounts of bio-available phosphorus. Perhaps the NH_4Cl extraction alone gives the best results, but the phosphorus liberated with this extraction is difficult to estimate, because of the low SRP concentration in the NH_4Cl-solution obtained. Klapwijk et al. (1982) found that the NH_4Cl step, nor the NaOH step, nor the sum of the two steps was comparable with algal available phosphorus.

According to Bruning & Klapwijk (1984), the extent to which sediment phosphorus is available for algal growth depends on the pH in the bio-assays. A possible explanation may be a partial extraction of the NaOH fraction at high pH. Williams et al. (1980) found an extraction with NTA to give results that are comparable with bio-assays. However, some experiments indicated that with this technique about 50 % of the phosphorus in the sediments of the Loosdrecht Lakes was extracted. The amount of exchangeable phosphorus was in the same order of magnitude as the amount of bio-available phosphorus and the amount of NH_4Cl-P. These three methods all indicate that only a small proportion, namely about 5%, of the sediment phosphorus is readily available.

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CHAPTER 3

UNMASKING THE PARTICULATE ORGANIC MATTER IN A LAKE ECOSYSTEM:
Origin and fate of POM in the shallow eutrophic Loosdrecht Lakes (the Netherlands)

Paul Boers & Jaap Boon

Arch. Hydrobiol. Beih. 31: 27 - 34

ABSTRACT- Pyrolysis mass spectrometry, pyrolysis gas chromatography and pyrolysis gas chromatography mass spectrometry were used to study interactions between seston, surface sediments and peat in the shallow and eutrophic Loosdrecht Lakes. The bulk of the surface sediments consists of refractory macrophyte debris, most likely originating from the peat. Significant amounts of this material are also present in the seston in wintertime, while in summer algal material dominates the seston. Only trace amounts of the algal material are present in the surface sediments.

Keywords: surface sediments, peat, seston composition, pyrolysis-mass spectrometry, pyrolysis-gas chromatography, pyrolysis-gas chromatography mass spectrometry, lignin.

3.1 INTRODUCTION

Production and degradation of particulate organic matter (POM) are the key processes in aquatic ecosystems. The POM in the water may result not only from production by the phytoplankton, but also from resuspension of the bottom sediments, especially in large, shallow lakes. Knowledge of the relative amounts from both sources enables to interpret measurements of primary production and respiration. Sedimentary POM may originate from the sedimentation of algal material, allochtonous macrophyte debris or, in some cases, old macrophyte debris which is already present in the lake basin. This is the case in so-called peat lakes. Mineralization by the microbial community drives all microbial and chemical processes in the sediments. It is well known nowadays, that these processes may greatly influence the quality of the overlying waters. A topic of special interest in this respect is the release of nutrients by the sediments (Boers & Van Hese, 1988). These nutrients may accelerate the production of POM by the phytoplankton in the water.

The lakes under study, the Loosdrecht Lakes in the Netherlands are a series of shallow lakes, manmade by the excavation for peat. Their morphology, the high average wind speeds in the Netherlands and the organic nature of their sediments strongly favour resuspension of the surface sediments. On the other hand, the organic nature of the sediments makes resuspension difficult to detect. In the sediments, the nature of the POM is impossible to trace. Overall chemical parameters may give only some vague indications about the possible origin of the POM. Only techniques that give insight in the molecular structure of the organic compounds may give more information. With such tools it is possible to trace compounds that are characteristic for POM of a certain origin and to use such marker compounds for quantification of the relative contributions in the different pools. This paper describes the application of pyrolysis, a depolymerization technique, in combination with capillary gas chromatography and mass spectroscopy to samples of seston, surface sediments and peat from the Loosdrecht Lakes. Some of the results obtained with these techniques are discussed briefly.

Table 1. Some characteristics of the Loosdrecht Lakes.

Surface area	16.8	km^2
Average depth	1.8	m
Maximum depth	3.5	m
Primary Production	500	$g\ C\ m^{-2}\ y^{-1}$
Max. chlorophyll-a	250	$\mu g\ l^{-1}$
Sediment (0 - 2 cm):		
Dry weight	10	% of wet weight
Organic Matter	60	% of dry weight
C/N ratio of organic matter	19	w/w
P	0.11	% of dry weight

3.2 MATERIAL AND METHODS

study area

The Loosdrecht Lakes, their history and sediment chemistry have been described elsewhere (Van Liere, 1986 and Boers et al., 1984). Sampling station 9 is situated in the Northern part of the lakes, station 4 in the middle and station 5 in the South. Table 1 summarizes some important characteristics of the lakes.

analytical procedures

Pyrolysis by fast inductive heating of the sample on a ferromagnetic wire in an inert atmosphere has proven to be a very useful technique for depolymerization of organic macromolecules (Meuzelaar et al., 1982). The pyrolysis of complex samples inevitably results in the production of hundreds of compounds. The application of pyMS, that is a quadrupole mass spectrometer connected directly to the pyrolyser (Boon et al., 1984), results in combined mass spectra of hundreds of different compounds. These spectra are therefore very complex. They can be used for fingerprinting only. Comparison of pyMS data from different samples was done by means of multivariance analysis with a modification of the numerical computer programme ARTHUR (Boon et al., 1984). This procedure results in so-called discriminant functions (D-functions), which describe the differences in a set of samples. D-functions can be used in different ways. For each sample, the D-scores, that are the contributions of the different D-functions to the spectra of the samples, can be calculated. These D-scores show the relative differences between the samples. They can be plotted against each other or against another variable. The D-functions themselves are combinations of mass peaks and therefore mass spectra. As they describe the differences between the samples, these mass spectra contain information about the compounds, responsible for these differences. Chemical interpretation of the D-functions gives information on these compounds. Although the D-functions are less complicated than the original fingerprints, their interpretation still is only provisional.

Separation of the pyrolysis products with capillary gas chromatography leads to complex chromatograms. Detection of the peaks was done with a mass spectrometer, which allows identification of the peaks (pygcMS; Boon et al., 1986). This knowledge improves the interpretation of the pyMS data. The use of a FID-detector and a peak integrating system (Nelson analytical 4000) permits quantification of the peak areas in the individual chromatograms.

PyMS was applied to a series of samples, consisting of seston, peat and surface sediments. The seston samples were collected monthly from September 1982 till August 1983 by filtration of about 10 l of surface water from stations 5 and 9 in the lakes over a 0.2 μm polycarbonate filter (Nucleopore, USA) under nitrogen pressure. The surface sediments were taken by pipetting the upper 2 - 3 mm from undisturbed sediment cores, sampled at the same stations as the seston. The peat was obtained from the same cores by removing all sediments above the peat. All samples were kept at -24 °C until analysis. Based upon the pyMS data we choose some seston, sediment and peat samples for more detailed analysis with pygcMS and pygc.

For interpretation of the results from the seston samples, other water parameters, such as temperature, concentrations of nutrients and chlorophyll-a were available.

3.3 RESULTS AND DISCUSSION

The multivariance analysis of pyMS data of all samples shows the most characteristic differences between the samples. In Table 2 some scores on the first D-function are depicted. The D1 function describes 60 % of the characteristic differences between the samples.

Three types of samples resemble closely: peat (Fig. 1A), surface sediments (Fig. 1B) and seston from winter and spring (Fig. 1C). The fourth group consists of seston from summer and early autumn (Fig. 1D) and differs greatly from the others. The positive part of the first D-function contains characteristics for algal material (e.g. M/z 59, 74, 92, 98, 117). These peaks are also found in the mass spectra of the summer and early autumn seston samples. The negative part contains characteristics for macrophyte detritus (e.g. M/z 94, 108, 120, 122, 124,

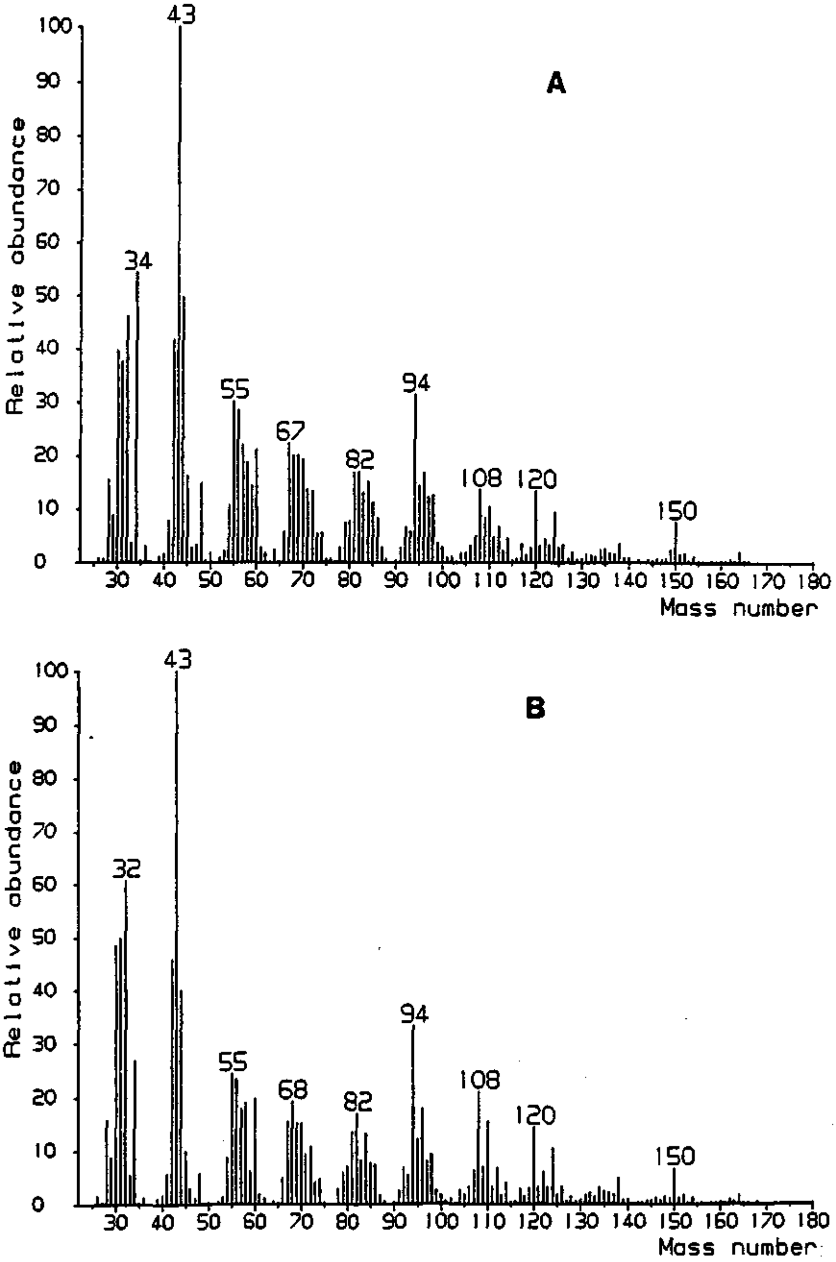
Table 2. D1-scores of some representative samples

Seston from October, 1982	+1.01
Seston from November, 1982	- 0.47
Seston from April, 1983	+0.08
Seston from July, 1983	+1.35
Sediment from station 9	- 1.19
Peat from station 9	- 1.70

150). These peaks are also found in the mass spectra of the peat, sediment and winter and spring seston samples. The close resemblance of peat, sediment and winter seston shows that the peat is the primary source of the macrophyte detritus. The D1- scores show furthermore that, under the assumption that the summer seston is composed of pure algal matter, the november seston contains about 25 % algal matter.

A subfile of seston samples only was examined in more detail with multivariance analysis. The D1-scores and the chlorophyll-a concentrations of these samples are given in Fig. 2. The differences between the two stations are small. The chlorophyll-a concentrations follow a normal pattern for this type of lakes: high concentrations in summer and much lower in winter. The D1-scores roughly follow the same pattern: positive scores in summer and negative ones in winter. The D1- function describes about 59 % of the variance between the samples. The positive part contains mass peaks, characteristic for algal material and the negative part those for macrophyte debris. This implies that algae are more important in the summer seston and macrophyte detritus dominates the winter seston. These differences are only relative: with pyMS data of these samples only, the amounts of peat in the seston cannot be quantified.

A more detailed analysis of some peats, sediments, winter, spring and summer seston, with pygcMS revealed six groups of compounds in the samples: fatty acids, pigments, carbohydrates, proteins, lignins and natural aliphatic polyethylenes (N.A.P., see Nip et al., 1986). The last two originate from macrophyte debris. The other four are synthesized mainly by algae, although the peat also contains some pigments, proteins and fatty acids. Table 3 gives the relative amounts of five of the six groups of compounds in the different samples. Carbohydrate peaks are difficult to quantify and therefore omitted. The pygcMS results confirm the provisional conclusions based on analysis with pyMS.


A
B
Relative abundance
Mass number
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10
20
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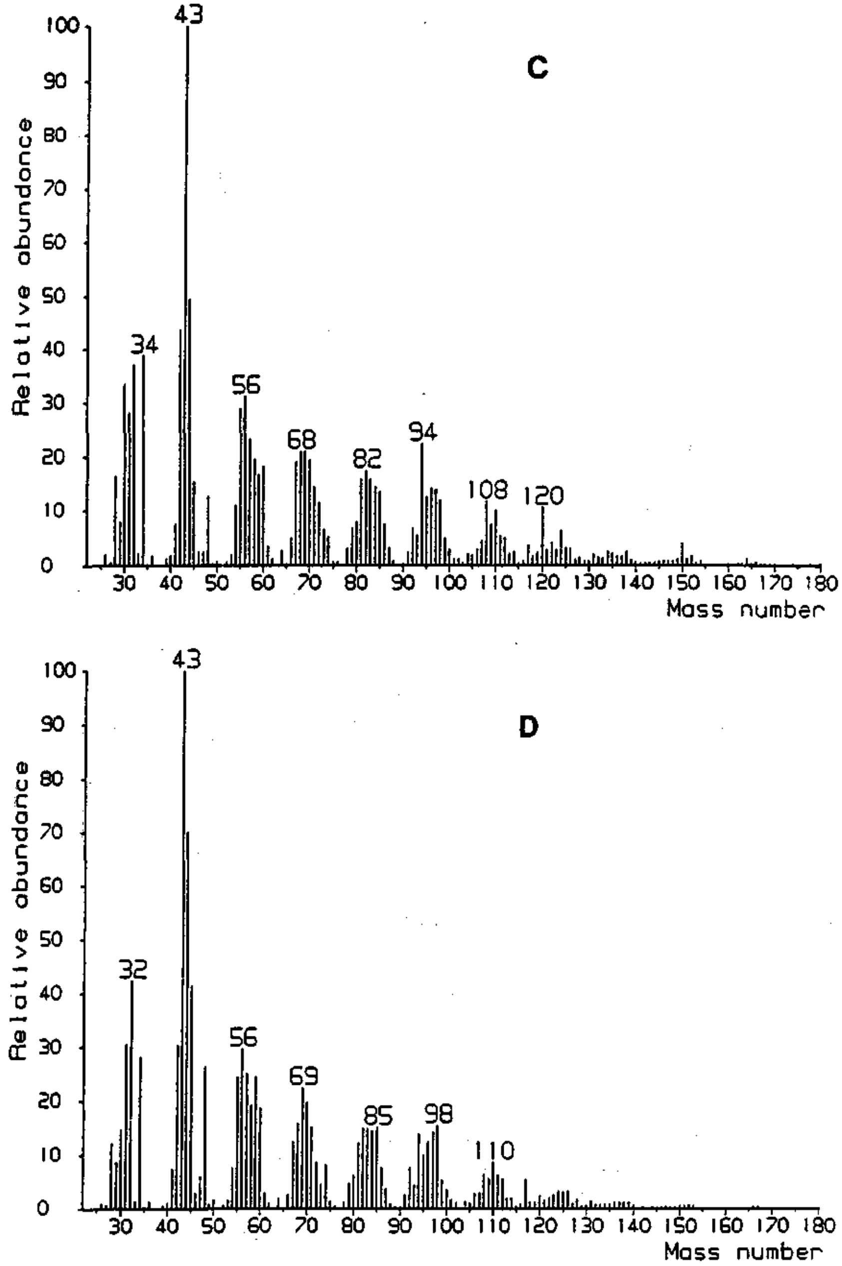

Fig 1. Pyrolysis Mass Spectra of peat from station 4 (A), surface sediments from station 9 (B), seston from station 9 sampled November, 1982 (C) and seston from station 9, sampled August 1983 (D).

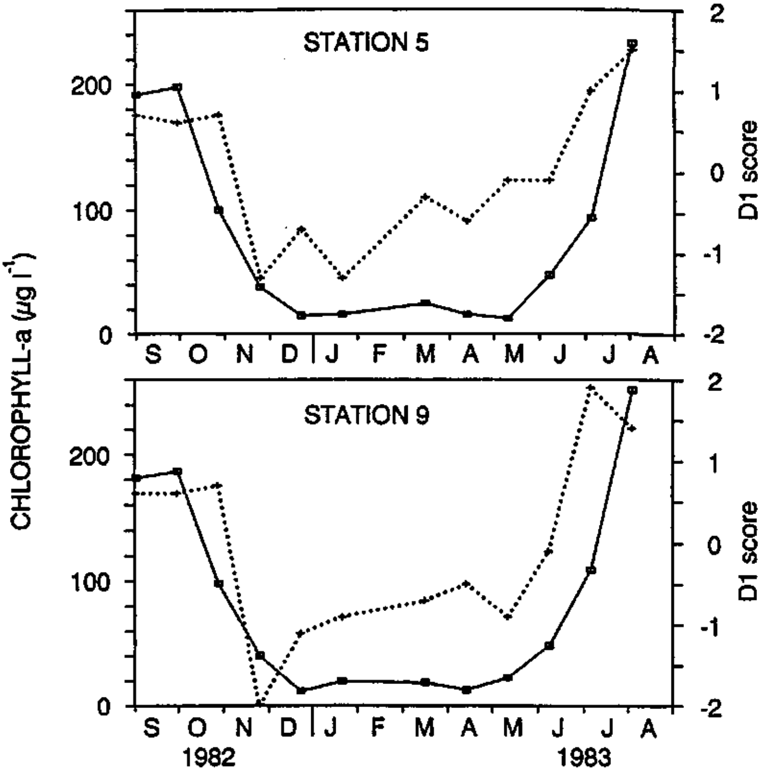

Fig 2. D1 scores (+·····+) and chlorophyll-a concentrations (□——□) of seston from stations 5 (upper) and 9 (lower). The correlation coefficient (R^2) between D1 score and chlorophyll-a concentration is 0.66 for station 5 and 0.57 for station 9 (N = 12).

Table 3. Abundance (% of total peak area) of five groups of compounds in seston, peat and sediment.

	Samples				
Compounds	Sediment 1-9-'82	Seston 29-9-'82	Seston 19-1-'83	Seston 2-8-'83	Peat stat. 4
Fatty acids	1.43	12.0	3.5	10.6	1.16
Proteins	0.71	1.20	1.30	3.00	0.36
Pigments	0.82	3.87	1.63	4.34	0.45
N.A.P.	2.51	0.00	1.70	0.00	2.77
Lignins	11.5	2.85	5.31	3.00	13.1

Table 4. Correlation coefficients (R^2) of peak areas of 42 main peaks in the gc's of peat, sediment and winter seston.

	peat st. 4	peat st. 9	sediment 1-9-'82	sediment 27-10-'82	seston 19-1-'83
peat 4	x	0.72	0.97	0.98	0.49
peat 9		x	0.81	0.80	0.25
sedim. 1-9			x	0.97	0.37
sedim. 27-10				x	0.32

Table 4 gives correlation coefficients between the peak areas of the 42 most important compounds in the chromatograms of peat from two locations, two sediment samples and a winter seston. The table shows that the two peat samples resemble. It also makes clear that the sediments are almost identical and that the sediments are made up from peat material.

The peat from station 4 closely resembles this peat. Most likely the material originates from the eastern part of the lakes. This high correlation shows again, that recognizable algal material is almost completely lacking in the sediments. And finally, the winter seston differs from the surface sediments.

The algal populations in the water phase may be very dense in summer. Our data on the surface sediments show that hardly any of this algal material reaches the surface sediments. Instead, these sediments are essentially identical to the peats under the sediments. This implies that the degradation of the algal material in the water phase must be very efficient. Consequently, the recycling of the nutrients also takes place largely in the water phase. For the microbial community in the sediments this implies that their diet contains only very limited amounts of algal material and mainly much more refractory macrophyte remains, originating from the peats in the eastern parts of the lakes. The surface sediments contribute significantly to the seston composition. The whole year, except in summer, significant amounts of sediment material are present in the seston. In winter, and especially during storm events, this is even the main component of the seston. The presence of such relatively refractory material in the seston will significantly affect the specific production and respiration properties.

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CHAPTER 4

PHOSPHORUS RELEASE FROM THE PEATY SEDIMENT OF THE LOOSDRECHT LAKES (THE NETHERLANDS)

Paul Boers & Olaf Van Hese

Water Research 22: 355 - 363

ABSTRACT- Seasonal patterns in phosphorus release from sediments of the Loosdrecht Lakes were studied in the laboratory in a continuous flow system. The highest release rates (up to 4 mg P m^{-2} d^{-1}) were found in August and the lowest (0.2 mg P m^{-2} d^{-1}) in winter. Temperature was found to be the most important factor controlling release; only temperatures above 13 °C allowed release in summer. An infiltration rate of 10 mm d^{-1} suppressed the P-release effectively. A pH of 9.5 instead of 8.2 in the overlying water had only a minor effect on release rates. Release rates based on a preliminary phosphorus budget calculated for 1984 and those measured in the laboratory were comparable. A conceptual model based upon mineralization and precipitation processes was employed to explain the results obtained. The observed influences of temperature, infiltration and pH of the water column were explained qualitatively by the model. An effect of changes in oxygen penetration depth on phosphorus release rates cannot be excluded.

Key words: internal load, eutrophication, release experiments, phosphorus, sediments.

4.1 NOMENCLATURE

Symbol	Meaning	Dimensions
α	Conversion factor between oxygen consumption and phosphorus mineralization	(-)
C	Dissolved phosphorus concentration in the pore water	(μg P ml^{-1})
C_0	Dissolved phosphorus concentration at sediment-water interface	(μg P ml^{-1})
C_{eq}	Equilibrium concentration of precipitation process	(μg P ml$^{-1)}$
C_n,C_{n+1}	Dissolved phosphorus concentrations in overlying water of release reactor at t_n and t_{n+1}	(mg P m^{-3})
D	Effective molecular diffusion constant for oxygen	(cm^2 d^{-1})
D_e	Effective molecular diffusion constant for phosphate in the sediment	(cm^2 d^{-1})
D_b	Bioturbation diffusion constant	(cm^2 d^{-1})
F	Phosphorus flux across sediment-water interface	(mg P m^{-2} d^{-1})
h	Height of water column of release reactor	(m)
$[O_2]$	Oxygen concentration at the sediment-water interface	(μg O_2 ml^{-1})
k	Mineralization rate constant for degradable phosphorus	(d^{-1})
K_a	Partition coefficient for phosphate in the sediment	(-)
K_p	Precipitation rate for phosphate in the sediment	(d^{-1})
P(x)	Degradable organic phosphorus concentration in sediment at depth x	(μg P ml^{-1})
P(0)	Degradable organic P concentration in sediment at $x = 0$	(μg P ml^{-1})
R	Residence time	(d)
$R(O_2)$	Oxygen consumption rate	(μg O_2 cm^{-3} d^{-1})
SOD	Sediment oxygen demand	(μg O_2 cm^{-2} d^{-1})
t	Time	(d)
t_n,t_{n+1}	Successive sampling days for the release reactor	(d)
u	Infiltration rate	(cm d^{-1})
w	Sedimentation rate	(cm d^{-1})
x	Depth in sediment	(cm)
X	Oxygen penetration depth	(cm)

4.2 INTRODUCTION

The Loosdrecht Lakes are a series of shallow, interconnected lakes, formed originally by peat mining. Water from the river Vecht was periodically let in the lakes to maintain water level. Until recently the external phosphorus loading averaged approx. 1.1 g P m^{-2} y^{-1} (Kal et al., 1984), causing chlorophyll-a concentrations of up to 240 mg m^{-3}. To reduce the external phosphorus load, the inlet of water from the River Vecht was replaced in 1984 by dephosphorized water from the nearby Amsterdam-Rhine Canal. This decreased the external loading to 0.3 g P m^{-2} y^{-1}.

In such cases, a phosphorus release from the sediments may delay the reduction of the total phosphorus concentrations in the water column. This study is aimed at assessing the contribution of the internal phosphorus loading to the phosphorus cycling in the Loosdrecht Lakes and at studying the influence of pH, temperature and groundwater infiltration on the release from the sediments. For interpreting the results, a simple, conceptual model that describes the dissolved phosphorus concentrations in the pore water as a function of depth is presented. Also, the possible effects of changes in oxygen penetration depths on release rates are evaluated.

Phosphorus fluxes between water and sediments have been measured using sediment suspensions (Boström & Petterson, 1982) and batch experiments with intact cores (Holdren & Armstrong, 1980; Psenner, 1984). We chose a continuous flow system with intact cores (Hieltjes, 1980; Van Liere & Mur, 1982; Boers et al., 1984a; Brinkman & Van Raaphorst, 1986). In intact cores concentration gradients of phosphate and electron acceptors in the sediment are more or less maintained. In suspensions this is impossible. The impact of these gradients on both sediment chemistry and transport processes is great. In a continuous flow system the phosphorus released is removed with the effluent. This prevents a build-up of high phosphorus concentrations in the overlying water, which may decrease the release rates. In the lakes, such a build-up is prevented by consumption of the released phosphorus by the phytoplankton. Also, a continuous flow system allows easy control of pH, temperature and infiltration.

Table 1. Some characteristics of the Loosdrecht Lakes.

Water:		
Catchment area	44.4	km^2
Water area	18.3	km^2
Average depth	1.8	m
Mean hydraulic retention time	1	year
Average total P concn (1979 - 1982)	94	mg m^{-3}
Average total N concn (1979 - 1982)	521	mg m^{-3}
Chl.-a Average (1979 - 1982)	153	mg m^{-3}
Summer max. (1983)	240	mg m^{-3}

Sediment (0 - 2 cm top layer):		
Dry weight	9	% wet wt
Org. matter	540	mg g^{-1} dry wt
Fe	22	mg g^{-1} dry wt
Ca	43	mg g^{-1} dry wt
$CaCO_3$	45	mg g^{-1} dry wt
P	1.1	mg g^{-1} dry wt
C/N	19	w/w

4.3 MATERIALS AND METHODS

Sampling Area

Van Liere et al. (1984) and Kal et al. (1984) described the lakes and their origin. Boers et al. Table 1 contains some data on water and sediments.

Release Reactor

Undisturbed cores of the lake sediments were taken with a hand-driven steel core sampler, having a detachable perspex inner core of 5 cm inner diameter and 40 cm length (Van Raaphorst & Brinkman, 1984). The inner cores were installed in the laboratory in a continuous flow reactor (Fig. 1) within 6 hours after sampling. Artificial lake water, with an ion composition similar to that of the lake water, was used to continuously replace the overlying water using a Gilson Minipuls 2 peristaltic pump; residence time was one day and was checked regularly. Wetted air was bubbled through at a rate of 0.8 l h^{-1} for aerating the water. The overlying water was sampled for analysis three times a week.

Boers et al. (1984a, 1984b) have demonstrated that a significant proportion of the dissolved phosphorus released from the Loosdrecht Lakes sediments is not

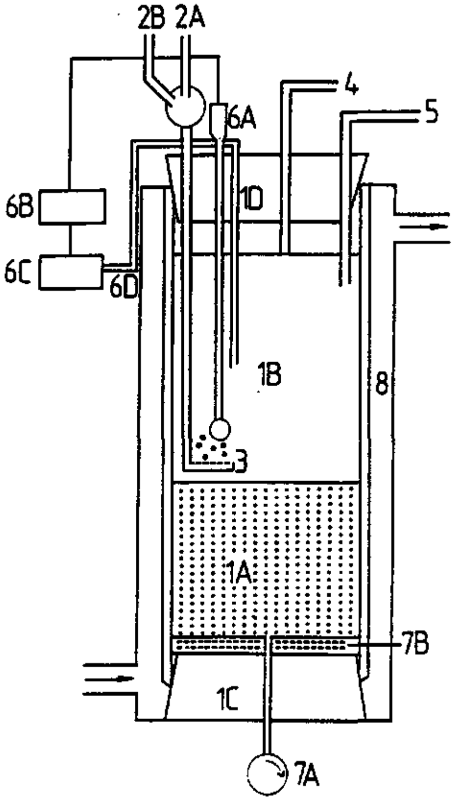

Fig. 1. Flow diagram of release reactor. 1: reaction vessel (1A sediment compartment; 1B water compartment [13 cm high]; 1C and 1D: neoprene stoppers); 2: inlet for 2A: medium; 2B: wetted air; 3: sintered glass filter; 4: outlet for air and water; 5: sampling tube; 6: pH-stat (6A: pH electrode; 6B: pH meter; 6C: pH controller; 6D: inlet for NaOH); 7: outlet for infiltration (7A: peristaltic pump; 7B: polyether tissue, to avoid clogging of the pumping system); 8: circulating water bath.

soluble reactive phosphorus (SRP), but dissolved organic phosphorus (DOP). Therefore, the released phosphorus was measured as total dissolved phosphorus (TDP) in the filtrate after membrane filtration (Millipore HA 0.45 μm) and wet digestion with potassium persulfate (Eisenreich et al., 1975). The phosphorus release rate in the reactor was calculated by measuring the TDP concentrations in the overlying water at two sampling times. A mass balance of phosphorus was calculated using the equation:

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

The experiments were usually done at pH 8.3, 20 °C and without simulated infiltration. A pH of 8.3 was maintained by the buffering capacity of the sediment. A pH of 9.5, which is the maximum pH value in the lakes, was obtained by addition of NaOH (0.01 M), using a pH-stat (Radiometers PHM61 and TTT60). Temperature was controlled with a circulating water bath in which the reactors were placed. Influence of infiltration (upward seepage appears to be of minor importance in the Loosdrecht Lakes: Kal et al., 1984) was studied by pumping water out at the lower end of the reactor. The infiltration rate was set at 10 mm d^{-1}, a rate that is comparable with the maximum rate in the lakes. For extrapolating the laboratory findings to the lakes, data on the pH, temperature and total phosphorus concentration in the lakes were available.

4.4 RESULTS AND DISCUSSION

Release experiments

Phosphorus release patterns from the sediment (Fig. 2) show the rate to vary with time. For an evaluation of the results, release rates were averaged over the first 28 days to give the average release rate (ARR).

Phosphorus release rates from the sediments, measured at a temperature of 20 °C, varied with season and were influenced by temperature (Fig. 3). In 1983, the highest release was measured in July. The seasonal release pattern differed between 1983 and 1984.

Shallow lakes like the Loosdrecht Lakes react quickly on changing air temperatures. As mineralization is very sensitive to temperature, the high temperature sensitivity of summer release rates may result from an important contribution of mineralization. The winter releases are much less influenced by temperature and may be controlled mainly by desorption.

In 1983 high releases were found until the end of September, but in 1984 it happened in April, June and August. Release rates from cores sampled in winter appear to be independent of temperature. In summer samples, when ARR is high anyway, a decrease in temperature is very effective in decreasing release rates in the laboratory (Fig. 3). So, a phosphorus release in the lakes is not the result of changed sediment properties or temperature alone, but of both. During certain periods dissolved phosphorus may be liberated and the temperature determines if the release occurs and at what rate. Seasonal variations in temperature (Fig. 4), together with the laboratory findings (Fig. 3), show that release can be expected during the summer.

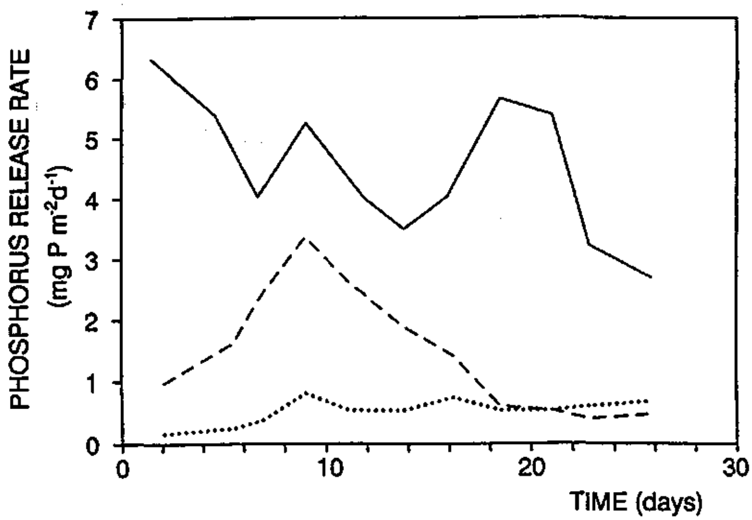

Fig. 2. Phosphorus release patterns of some experiments on different sampling dates: ——, *8 August 1984;* - - - -, *6 June 1984;* ·····, *9 May 1984.*

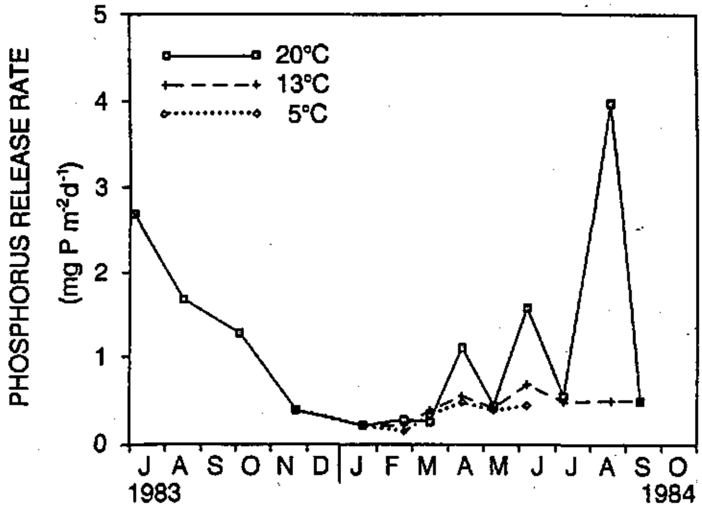

Fig. 3. Influence of temperature on average release rate between July 1983 and September 1984 in mg P m^{-2} d^{-1}*. Symbols indicate the sampling dates of the cores.*

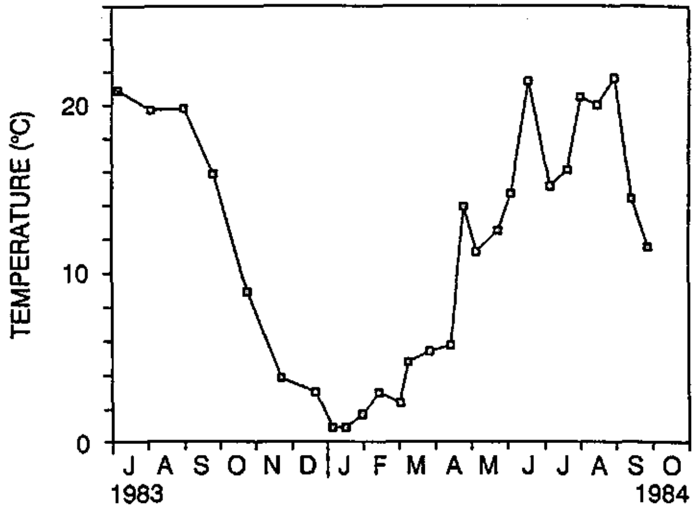

Fig. 4. Seasonal variations in temperature (°C) in the Loosdrecht Lakes.

The observed influence of temperature on release rates in the Loosdrecht Lakes differs from experiences elsewhere. Although Kelderman & Van der Repe (1982) found that the temperature is an important controlling factor for P-release patterns in cores from Lake Grevelingen, Holdren & Armstrong (1980) reported that the temperature has little influence on aerobic P-release from noncalcareous sediments, while the impact on release from calcareous sediments is great. For the deep stratified Piburger See, Psenner (1984) found the effect of temperature to vary with depth, impact being the largest at a depth of 15 m. Probably temperature effects should be interpreted in terms of their effect upon reaction rates of chemical and microbial processes, as well as their mutual interaction, e.g. the redox conditions affecting the adsorptive properties of sediments.

A second factor affecting phosphorus release rate is infiltration. Its influence on release rates shows a similar pattern as temperature: in winter samples it has only minor influence, but release from summer samples is strongly suppressed (Fig. 5). The lakes lose much water to the nearby polders, the average loss being about 3 mm d^{-1}. These rates vary strongly from north to south with a maximum of up to 10 mm d^{-1} in the extreme south of the lakes (Kal, unpublished data). As we found that an infiltration rate of 10 mm d^{-1} very effectively prevents release (Fig. 5), a result also found by Van Liere & Mur (1982) in some other Dutch lakes, it is probable that the field release rates are lower than in the laboratory experiments without simulated infiltration. The infiltration affects the-phosphorus

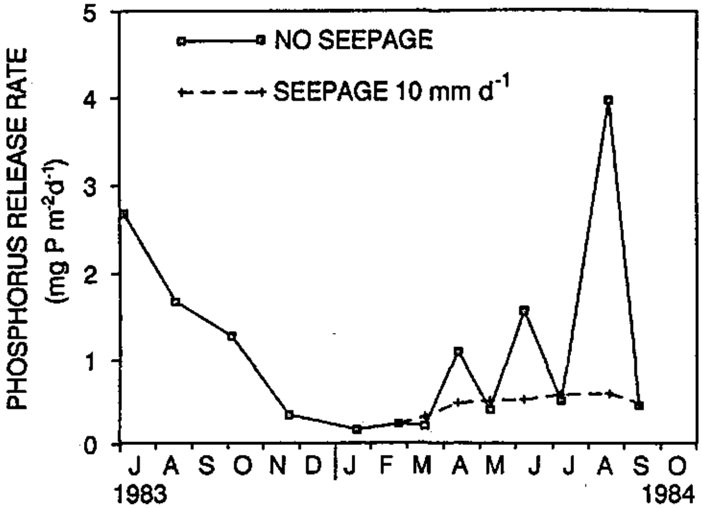

Fig. 5. Average release rate (mg P m^{-2} d^{-1}) in 1983 and 1984 with and without simulated downward seepage of 10 mm d^{-1} at pH 8.3 and 20 °C. Symbols indicate the sampling dates of the cores.

concentration profile in the pore water and increases the oxygen penetration depth in the sediment. Both may affect the release rate. This will be discussed in more detail in a next section.

A third factor affecting phosphorus release rate is the pH in the water column. The results show a small increase in rates due to a rise in pH from 8.2 to 9.5 (Fig. 6). The latter value is often reached in summer during high algal productivity in the lakes. This pH effect differs from those reported by others, such as Rippey (1977) and Ryding & Forsberg (1977). They reported strongly enhanced phosphorus release rates at pH of 9.0 and higher. This is commonly attributed to a decreased adsorption capacity for phosphate at high pH of iron(III) hydroxides precipitating at the sediment water interface (Lijklema, 1980).

For evaluation of the extent of the phosphorus release from the sediments, total P concentrations in the main lakes during 1984 were also monitored. In this period virtually no inflow of P from the River Vecht occurred; therefore, any increase in total phosphorus concentration must be due to release from the sediments. From Fig. 7 it is clear that when release rates were high in the laboratory, net release also occurred in the lakes; both rates being in the same order of magnitude. However, in the laboratory only release is measured, whereas in the lakes the changes in concentrations are the results of both release from

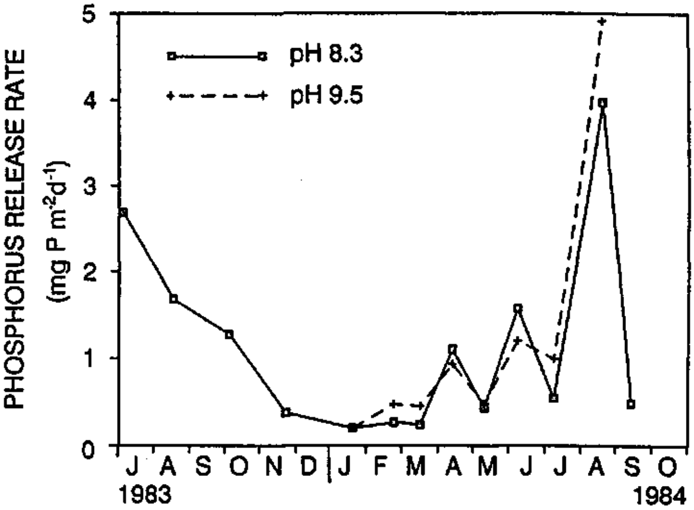

Fig. 6. Average release rate (mgP m^{-2} d^{-1}) in 1983 and 1984 at 20 °C at pH 8.3 and at pH 9.5. Symbols indicate the sampling dates of the cores.

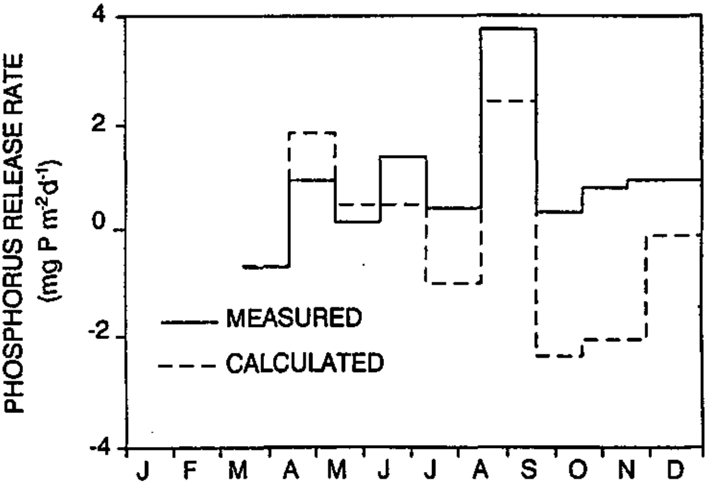

Fig. 7. Comparison of ARR at 20 °C and changes in total phosphorus concentration (mg P m^{-2} d^{-1}) in the lakes in 1984.

the sediments and loss by sedimentation. Therefore, the gross release rates in the lakes will be higher than those measured in the laboratory. This, according to Boström et al. (1982) is often observed.

A source of deviation is the use of ARR. ARR as used in this study, a 4 week average, implies that during the experiment the conditions in the sediment change gradually. Especially under conditions where mineralization contributes significantly, the degradable phosphorus pool will decrease. The August sample (Fig. 2) may examplify this. Maximum release rates would be about 1.6 times higher than ARR. Although a complete phosphorus budget for the Loosdrecht Lakes was not possible, internal loading as calculated from the budget and as measured in the laboratory fit fairly well.

A conceptual model

Different processes play a role in the early diagenesis of phosphorus in sediment. Berner (1976, 1980) described these processes in detail. The processes are input of degradable material by sedimentation, slow mixing of the upper sediment strata, e.g. by bioturbation, mineralization of the degradable material, transport of dissolved compounds through molecular diffusion, transport of dissolved compounds through infiltration, fast equilibrium adsorption and slow precipitation of inorganic phosphorus compounds.

Van Raaphorst & Brinkman (1984) proposed a model in which fast desorption processes drive the release, resulting in a very thin (0.1 cm) active sediment layer, in which infiltration hardly influences the release rate. Lijklema (1985, 1986) formulated some mineralization-driven release models, leading to a much thicker (1 cm) active sediment layer and infiltration having a much stronger effect on release rate. The latter statement agrees with conclusions based on our laboratory results. In his models an increase in sediment thickness due to sedimentation was not included.

As a first assumption we will consider only a steady-state situation, in which the sedimentation rate is constant. The mineralization process, which triggers the release process, includes a series of oxidation steps, using different electron acceptors. We assume that mineralization is a first order process in respect to the degradable phosphorus concentration.

Physico-chemical interactions between the sediment matrix and dissolved phosphorus are numerous and complex. They involve a whole range of processes, varying from very fast equilibrium adsorption to the formation of minerals as apatite, with a time constant in the order of years. A discussion of these processes is beyond the scope of this article. Here, the slow reactions are described as a first order reaction with a certain equilibrium concentration. Fast equilibrium adsorptions are described with a simple linear distribution coefficient.

Finally, sediment compaction is neglected. With these assumptions the mass balance for the degradable organic phosphorus concentration in the sediment is:

$$\delta P(x)/\delta t = 0 = D_b[\delta^2 P(x)/\delta x^2] - w[\delta P(x)/\delta x] - kP(x) \qquad (2)$$

The solution is:

$$P(x) = P(0)\exp(ax) \qquad (3)$$

where

$$a = [w - \sqrt{(w^2 + 4kD_b)}]/2D_b \qquad (4)$$

The mass balance for dissolved phosphorus in the pore water is:

$$\begin{aligned}\delta C/\delta t = 0 = {} & D_e(\delta^2 C/\delta x^2)/(1+K_a) - w(\delta C/\delta x) - u(\delta C/\delta x)/(1+K_a) \\ & + kP(x)/(1 + K_a) - K_p(C - C_{eq})/(1+K_a) \qquad (5)\end{aligned}$$

Substitution of equation (3) in equation (5) gives the differential equation to be solved. With the boundary conditions:

$x = 0$ ---> $C = C_o$
$x = \infty$ ---> $C = C_{eq}$

the solution is:

$$C(x) = (A - C_{eq} + C_o)\exp(Bx) - A\exp(ax) + C_{eq} \qquad (6)$$

where

$$A = kP(0)/[D_e a^2 - (1+K_a)wa + ua - K_p] \qquad (7)$$

$$B = \{(1+K_a)w + u - \sqrt{([(1+K_a)w+u]^2 + 4K_pD_e)}\}/2D_e \qquad (8)$$

The flux across the sediment-water interface is calculated from the concentration gradient at the sediment water interface according to Fick's first law of diffusion, corrected for transport by infiltration:

$$F = -uC_o - D_e[A(B - a) + B(C_o - C_{eq})] \qquad (9)$$

Our data set is not complete and some parameters can not be measured, rate, the bioturbation coefficient and the sedimentation rate. The mineralization parameters were estimated from the composition of the sediment top layer and some sediment oxygen demand measurements with undisturbed sediment cores. The total phosphorus concentration at the sediment water interface [P(0)] was assumed to be equal to the total phosphorus content of the seston during strong resuspension (1.2 mg P g^{-1} dry weight), corrected for the porosity of the sediment (92 - 93 %). Organic phosphorus, that was assumed to be completely degradable, was taken as the sum of the humic acid bound and the not extractable fractions (22 and 29 % respectively, Boers et al., 1984a). The mineralization rate constant at the sediment-water interface was calculated from the sediment oxygen demand:

$$kP(0) = \alpha R(O_2) \qquad (10)$$

α is made up of the P:C and the $C:O_2$ ratios of the mineralization reaction and a correction for the differences in molecular weight of O_2 and P. Considering an overall mineralization reaction of:

$$CH_2O + O_2 \dashrightarrow CO_2 + H_2O$$

the $C:O_2$ ratio is 1 (M/M). The P:C ratio is quite a problem. As a first assumption we used the P:C ratio of the seston, which is about 0.0073 (w/w) or 0.0028 (M/M) (Van Liere, unpublished results). The correction factor for the molecular weights is 31/32. So, $\alpha = 0.0027$.

$R(O_2)$ was calculated from the sediment oxygen demand, assuming that the mineralization process is zero-order in the oxygen concentration, using the equations given by Bouldin (1968):

$$R(O_2) = (SOD)^2/(2D[O_2]) \qquad (11)$$

Substitution of equation (11) in equation (10) results in:

$$k = \alpha(SOD)^2/(2D[O_2]P(0)) \qquad (12)$$

Values for $[O_2]$ and P(0) are given in Table 2. The only parameter left is the diffusion coefficient for oxygen. The molecular diffusion coefficient is 0.86 $cm^2\ d^{-1}$, but Lindeboom et al. (1985) reported apparent values of 8.2 - 10.5 $cm^2\ d^{-1}$. These values apparently include contributions of turbulence in the boundary layer. With a measured SOD of about 60 $\mu g\ O_2\ cm^{-2}\ d^{-1}$, k is in the range of 0.0012 - 0.014 d^{-1}. We choose an average value of 0.006 d^{-1}. The sedimentation rate was calculated as a yearly average, assuming that the net external phosphorus loading of 1.1 g P $m^{-2}\ y^{-1}$ or 0.3 μg P $cm^{-2}\ d^{-1}$ accumulates in the sediment by

Table 2. Values of parameters used for the calculation of a pore water profile.

Symbol	Value	units
C_0	0.005	μg P ml^{-1}
$[O_2]$	10	μg O_2 ml^{-1}
w	0.003	cm d^{-1}
u	0.01	cm d^{-1}
P(0)	40	μg P ml^{-1}
D_e	0.3	cm^2 d^{-1}
D_b	0.003	cm^2 d^{-1}
k	0.006	d^{-1}
K_a	1	(-)
K_p	0.1	d^{-1}
C_{eq}	0.05	μg P ml^{-1}

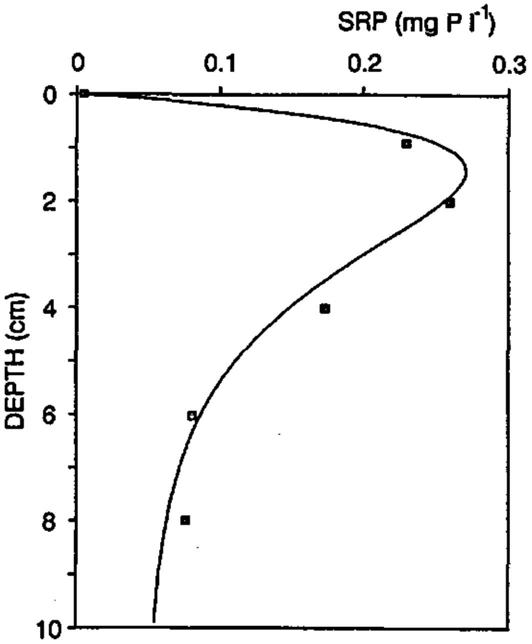

Fig. 8. Simulation of SRP concentrations in pore water. ——, simulation; □ measured concentrations. See text for details.

Table 3. Sensitivity analysis of the conceptual sediment phosphorus model with the parameter values from Table 2. Release rate is 1.6 mg P m^{-2} d^{-1}. Results of changes in values of the various parameters as fraction of original flux are given.

Parameter	change	result
P(0)	x2	1.94
w	x0.1	0.83
	x10	1.74
u	x10	0.88
	x50	0.34
	x100	0.34
D_e	x2	1.14
D_b	x0.5	0.88
	x2	1.15
K_p	x0.5	1.09
	x2	0.89
	x0	1.47
k	x0.11	0.27
	x0.33	0.53
	x2	1.46
K_a	x0	1.00
	x10	0.97

sedimentation. This results in the sedimentation rate of about 0.003 cm d^{-1}. The infiltration rate and molecular diffusion constant are available from literature. The latter should be corrected for porosity, but this is over 90 %, and the correction is small compared to the uncertainty in the value of the diffusion constant (Berner, 1980). The values of the various variables and parameters, reflecting summer conditions, used for model calculations and the construction of Fig. 8 are given in Table 2. The pore water profile, measured in the laboratory, fits in well. A release rate of 1.60 mg P m^{-2} d^{-1}, calculated according to equation (9) is in the range of those measured (Fig 3).

As the model is conceptual, analysis of the effects of changes in the values of the parameters may provide insight into effects of changing conditions in the sediment on release rates and into the sensitivity for inaccurate parameter values and other assumptions. Impact of changes of the values of the various parameters on the release rate is summarized in Table 3. Changes in the resulting pore water concentrations, although they may be substantial, are not presented here.

Sedimentation and mineralization rate are the most important. It is clear from

Table 3 that not the quantity of the sedimenting material, but the portion of degradable phosphorus in it is important. Even a doubling of the sediment growth rate does not affect the flux, but an increase in the input of degradable phosphorus in it, which is reflected in an increase in P(0), leads to an almost proportional rise in the flux. Secondly, changes in the mineralization rate are of great importance. On the contrary, the physico-chemical parameters influence the release rates much less. The exact value of the adsorption coefficient is unimportant, the same is true for the precipitation rate. Only if the precipitation rate is much slower than modelled here, release rates are significantly higher. The values for the precipitation process given here are in the range of those reported for the formation of vivianite (Emerson & Widmer, 1978). Also, the exact values of the two diffusion coefficients are not very important. As the sediments of the Loosdrecht Lakes are very porous, the molecular diffusion coefficient may be used for D_e. The situation is different for the bioturbation coefficient; the chosen value is only a very rough estimate. In the model presented here, a higher coefficient yields a higher release rate, because we choose a fixed value for P(0). However, an increased mixing of the sediment will result in a lower value for P(0) and thus in a lower release rate.

The model described above is certainly too simple. Slow and fast interactions between dissolved phosphorus and the sediment matrix are taken as constant over the depth. Differences in characteristics of the different aerobic and anaerobic mineralization processes are not taken into account. A model that contains all these details is much more complex and would require a multi-layer structure with different boundary conditions and process parameters. The resulting equations are too complicated for analytical solutions and the required additional efforts are considerable. Yet we believe that the simple model describes the interactions between the different processes quite satisfactorily and may be used for interpretation of the laboratory results. Therefore, an important question is to what extent these results agree with the outcomes of the model described. The most important are the influence of pH, season, temperature and infiltration rate on release rates.

First, there is a lack of influence of pH on release rate. High pH promotes the desorption of phosphates, especially from iron- and aluminum hydroxides (Lijklema, 1980). This is simulated by lowering the value of the adsorption constant K_a in the model, and K_a does not affect the calculated flux. This agrees well with our experimental findings.

Secondly, the release rates vary temporally, there is a trend towards higher release rates in summer, with a maximum in August. According to the model this can be caused only by a higher portion of degradable organic P in the sedimentating material. This seems quite likely because in summer large amounts of algal material will be present in the sedimentating material. However, until now no evidence could be found for this hypothesis. In contrary, in a pilot study to the chemical composition of the 0 - 1 mm toplayer of the sediments no differences between the summer and winter samples were found (Boers & Boon, 1988). Thus, the conclusion that other factors must at least partly be responsible for seasonal variations in release rates is inevitable. Possibly the seasonal changes in the microbial flora in the sediment are caused by slow adaptations to the changing environment. This would result in systematically lower mineralization rates in winter and consequently, small influence of temperature on this rate in winter.

Thirdly, temperature may affect the release rate. We assume that a 10 °C rise in temperature leads to a three-fold increase in k. This, according to the model, will cause a two-fold increase in the flux. Qualitatively, this agrees with the results of the release experiments, as temperature affects release rate much less at low release rates. However, the effect of temperature is sometimes much greater than a factor 2 per 10 °C. This is partly due to the assumption of steady state conditions. A lower value for k will result in a higher pool of degradable phosphorus. This compensates partly for the lower mineralization rate. A sudden increase in temperature, which is of course not a steady state condition, then leads to strongly increased release rates.

Fourth, as regards infiltration, the model predicts a four-fold decrease in response to an infiltration rate of 10 mm d^{-1}, independent of the value of P(0). We found this infiltration rate to decrease release rates strongly, but the extent to which this is the case depends on the actual release rate. At high release rates the effect tends to be more than a factor of 4 and at low release rates, less or even absent. Knowledge of influence of infiltration on release rates at lower infiltration rates is needed, not only to improve the model, but also for good extrapolation of the laboratory data.

The steady-state approach certainly has its limitations as changes in environmental conditions may also be important. For example, changes in oxygen penetration depth, caused by differences in sediment oxygen demand, may drastically affect the phosphorus binding capacity of the sediment layers involved. The model presented here does not take such effects into account, because we assumed the phosphate binding properties to be constant with depth and assumed a steady-state in mineralization rate. Modelling of the oxygen penetration depths under different steady state conditions may give an impression of the possible effects of changes in the oxygen penetration depth on the phosphorus release. Temperature and infiltration are the most important factors, influencing the penetration depth.

In the absence of infiltration and assuming that the mineralization process is zero order in oxygen, Bouldin (1968) gave a simple relation between the sediment oxygen demand, the oxygen consumption rate and the oxygen concentration at the sediment-water interface:

$$SOD = \sqrt{2[O_2]R(O_2)D} \tag{13}$$

and for the oxygen concentration as a function of depth:

$$C(x) = [R(O_2)/2D]x^2 - x\sqrt{2[O_2]R(O_2)/D} + C(0) \tag{14}$$

From these equations, relations between the oxygen penetration depth, SOD and the oxygen consumption rate are obtained:

$$X = \sqrt{2D[O_2]/R(O_2)} \tag{15}$$

$$R(O_2) = SOD^2/2D[O_2] \tag{16}$$

$$X = 2D[O_2]/SOD \tag{17}$$

In case infiltration is involved, another mass balance for oxygen in the pore water must be solved:

$$\delta C/\delta t = 0 = D\delta^2C/\delta x^2 - u\delta C/\delta x - R(O_2) \tag{18}$$

With the boundary conditions:

$x = 0 ===> C = [O_2]$
$x = X ===> C = 0$ and $\delta C/\delta x = 0$

the solution is:

$$C(x) = [O_2] - \{[R(O_2)D/u^2)\exp(-uX/D)]1 - \exp(ux/D)]\} - R(O_2)x/u \tag{19}$$

$$X = (D/u)\ln\{R(O_2)D\} - (D/u)\ln\{u^2[O_2] + R(O_2)D - R(O_2)Xu\} \tag{20}$$

Equation (20) cannot be solved explicitly, but X must be estimated with a starting value obtained from equation (15).

Equations (15), (16), (17) and (20) may be used for assessment of the influences of changes in temperature and infiltration rate on X. The amount of sediment phosphorus involved in changes in X can be estimated from the dry weight of the sediment (Table 1), its phosphorus content (Table 1), the thickness of the layer involved and the Fe-bound fraction of the sediment phosphorus (approx. 25%, Boers et al., 1984). Furthermore, a SOD of 60 $\mu g\ O_2^-\ cm^{-2}\ d^{-1}$ at 20

°C and in the absence of infiltration is assumed. Depending on the value of D, which is very uncertain, this SOD results in oxygen penetration depths of 0.33 cm ($D = 1$ cm^2 d^{-1}) to 3.3 cm ($D = 10$ cm^2 d^{-1}). An infiltration rate of 1 cm d^{-1} increases the penetration depth with 6% for both values of D, corresponding with 5 ($D = 1$ cm^2 d^{-1}) to 50 ($D = 10$ cm^2 d^{-1}) mg P m^{-2}.

Assuming that a 10 °C rise in temperature leads to a threefold increase in $R(O_2)$, impact of changes in temperature on the oxygen penetration depth is much larger. According to equation (20), such difference in temperature will cause a change in X by 75%, corresponding with 62 ($D = 1$ cm^2 d^{-1}) to 620 ($D = 10$ cm^2 d^{-1}) mg P m^{-2}. Due to the large uncertainty in the value for the diffusion constant, as stated before, an exact evaluation of the impact of changes in oxygen penetration depth on phosphorus release rates is impossible. Changes in temperature are certainly much more important than those in infiltration rate. Probably, differences in oxygen penetration depth due to changes in temperature are responsible for part of the large impact of temperature on release rates observed in summer (Fig. 3).

4.5 CONCLUSIONS

In 1984, the first year with reduced external phosphorus load, the internal loading in the Loosdrecht Lakes seemed to be enough for maintaining high total phosphorus concentrations in the water column. Laboratory studies on P-release indicated the existence of seasonal patterns in this internal load. The laboratory experiments also showed a marked influence of temperature and an infiltration rate of 10 mm d^{-1} on release rates, whereas an increase of pH from 8.2 to 9.5 in the overlying water had only minor influence.

Our study using a steady-state model shows that phosphorus release from the Loosdrecht Lakes is driven by mineralization. According to this model, only the portion of degradable organic P in the organic loading on the sediment can be responsible for high release rates in summer. Deviations from this process may be caused by variations in sediment mixing rate and sedimentation rate. Seasonal variations in composition of the microbial flora in the sediment may also cause seasonal variations in the release rates. Finally, non-steady-state conditions like a changing oxygen penetration depth may cause variations in release rates.

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CHAPTER 5

ION CONCENTRATIONS IN INTERSTITIAL WATER AS INDICATORS FOR PHOSPHORUS RELEASE PROCESSES AND REACTIONS

Paul Boers & Frans De Bles

Water Research, in press

ABSTRACT- Sediment composition and interstitial water concentrations of soluble reactive phosphorus (SRP), dissolved iron, ammonia nitrogen and DOC and pH were monitored at five sampling stations in the shallow Lake Loosdrecht (the Netherlands). The differences in concentrations between the sediments were much larger than the differences in overall sediment composition. The concentrations of SRP and ammonia were strongly correlated, the ratio between them was close to that predicted from a mineralization model.

Possibly, the high concentrations of refractory organic material in the sediments affect the availability of iron. The pore water was calculated to be frequently supersaturated with respect to vivianite. This, however, did not seem to affect the phosphate concentrations in the pore water.

Keywords: sediments, phosphate, interstitial water, mineralization, organic matter.

5.1 NOMENCLATURE

Symbol	Meaning	Dimensions
A	$=1.825 \times 10^6 (\epsilon T)^{-3/2}$	
C	concentration	(mg l^{-1})
C_{eq}	equilibrium concentration	(mg l^{-1})
C_x	concentration at depth x	(mg l^{-1})
C_∞	concentration at infinite depth	(mg l^{-1})
D_b	bioturbation mixing coefficient	(cm^2 d^{-1})
D_e	effective diffusion coefficient	(cm^2 d^{-1})
$D_{n,p}$	effective diffusion constant of ammonia, phosphate	(cm^2 d^{-1})
DOC	Dissolved Organic Carbon	
IAP	Ion Activity Product	
I	ionic strength	(mol l^{-1})
K	equilibrium constant	
k_m	mineralization rate constant	(d^{-1})
pK	$-\log_{10}K$	
POC	Particulate Organic Carbon	
N(x)	particulate organic N concentration in sediment	(mgN l^{-1})
P(x)	particulate organic P concentration in sediment	(mgP l^{-1})
Q	linear adsorption constant	(-)
SRP	Soluble Reactive Phosphorus	
T	absolute temperature	(K)
TDFe	Total Dissolved Iron	
TDP	Total Dissolved Phosphorus	
t	time	(d)
w	sedimentation rate	(m d^{-1})
x	depth in sediment	(m)
Z	ionic charge	(-)
γ	activity coefficient	(-)
ϵ	dielectric constant of water	(-)
μ	conductivity	(μS)

5.2 INTRODUCTION

Retention in and release from the sediments is an important part of the phosphorus cycling in shallow lakes. Several processes control the phosphorus retention and release, such as mineral formation (e.g. Emerson, 1976 and Holdren & Armstrong, 1986), mineralization, transport, complexation of metal ions and phosphate by DOC (Emerson, 1976; Boers et al., 1984a) or adsorption by POC.

We studied the phosphorus release processes in the Loosdrecht Lakes, a series of interconnected, shallow eutrophic lakes. In 1984 the external phosphorus loading of the lakes was decreased to combat the eutrophication. The release of phosphorus from the sediments was one of the processes investigated. Previous research indicated that phosphorus release from Lake Loosdrecht sediments is to a large extent controlled by mineralization processes (Boers & Van Hese, 1988). The sediments consist mainly of macrophyte detritus, rich in lignin derivates (Boers & Boon 1988). Hence, processes involving POC and DOC might be relatively important in these sediments.

The concentrations of certain ions in pore water are sensitive indicators for processes controlling the concentrations of these ions. Therefore we monitored the concentrations in the pore waters at five sampling stations in Lake Loosdrecht and the interconnected Lake Breukeleveen from April until November 1985. We have used these data to evaluate the different processes governing the behavior of phosphate in the Loosdrecht lakes sediments.

In this paper, we will present and discuss the results for ammonia, as it reflects the role of mineralization processes; for iron, because its relationship with the chemistry of phosphate (e.g. Syers et al., 1973); for DOC, possibly of importance for the complexation of iron, and for the pH, influencing many equilibria.

5.3 MATERIALS AND METHODS

Sampling area

Lake Loosdrecht and the interconnected lakes Vuntus, Breukeleveen and Kievitsbuurt (Fig. 1) are shallow eutrophic lakes situated in the Netherlands. Their average depths are 1.5 to 1.8 meters and summer chlorophyll-a concentrations are about 200 $\mu g\ l^{-1}$. They are manmade by peat mining. In 1984 the inlet of phosphate rich water from the river Vecht was replaced by dephosphorized water from the Amsterdam-Rhine Canal, thus decreasing the overall external phosphorus loading from 1.1 to about 0.3 $g\ P\ m^{-2}\ y^{-1}$ (Van Liere, 1986 and Kal et al., 1984). Boers et al. (1984b) reported the chemical

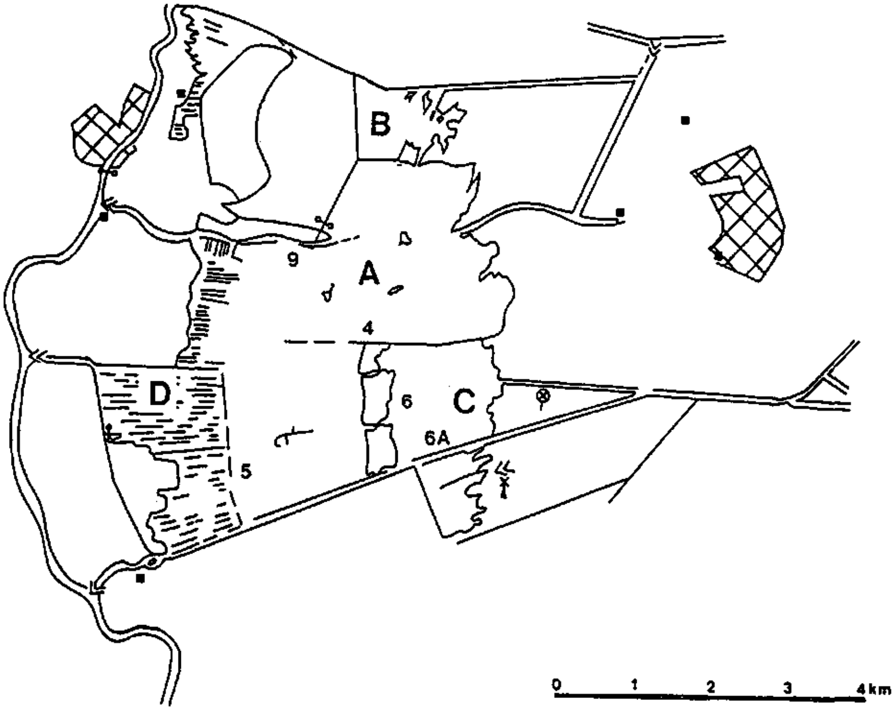

Fig. 1. Map of the Loosdrecht Lakes area, indicating sampling stations.
A: Lake Loosdrecht; B: Lake Vuntus; C: Lake Breukeleveen; D: Lake Kievitsbuurt.

composition of the sediments. Three stations (4, 5 and 9) are situated in Lake Loosdrecht, the two others (6 and 6A) in the interconnected Lake Breukeleveen. The local water depth at the stations was between 1.5 and 1.75 m.

Sampling procedure

Sampling of the pore water was performed with dialysis chambers, according to Hesslein (1980). Sampling depths were 1, 3, 5, 8 and 12.5 cm in the sediment. The chambers, two at each location, were inserted in the sediments and collected fourteen days later by a SCUBA diver. Laboratory experiments had revealed an equilibration time of about ten days. Due to the high turbidity of the lakes

(Secchi depth in summer of about 25 cm) visual inspection on proper placing of the samplers was impossible. From April - November every four weeks new samplers were installed. On the day of collection a sample of the overlying water was taken just above the bottom. This sample was also used to measure temperature and conductivity. At each sampling station a sediment sample was taken by pushing a perspex core into the sediment by hand.

Analytical methods

Immediately after collection, the chambers were emptied by means of a syringe. A part of the sample was acidified to pH = 1 with sulfuric acid in order to prevent oxidation and precipitation of iron, although in the non-acidified samples such a precipitate was never observed. Upon arrival at the laboratory the pH was measured with a combined pH electrode and a pH meter. Immediately after that, SRP and ammonia were determined on auto-analysers according to standard procedures. Part of the sample was destructed with persulfate and sulfuric acid (Eisenreich et al., 1975) for determination of TDP and TDFe. The remaining sample was stored at -24 °C for analysis of DOC. This was analysed with a TOC-SIN II phase separation analyser.

The sediment cores were cut in slices of 0-2, 2-4, 4-6, 6-8 and 8-14 cm. Dry weight, loss on ignition and total phosphorus were determined. Analytical procedures were as described by Boers et al. (1984b). Except for Fe at station 9, local variations in sediment composition are small. Therefore, other sediment characteristics (iron, calcium, aluminum, calciumcarbonate, C/N ratios) were used as available from an earlier sediment sampling programme.

5.4 RESULTS

Sediment characteristics

The general sediment characteristics (Table 1) indicate the resemblances and differences between the sampling stations. Except for station 9, the sediments have low dry weights and are very rich in organic matter, brought about by the peat origin of the lakes. The sediment from station 9 differed from the others as this sediment contained mainly sand. Therefore, the dry weight is higher and the P content much lower than at the other stations. The phosphorus contents of the sediments from stations 4, 6 and 6A are similar. Previous analysis of the sediments showed that in all sediments the C/N ratio was about 20 (w/w), the iron content was about 1.5 % at stations 6 and 6A, 2% at stations 4 and 5 and highly variable near station 9 (between 0.05 and 4%).

Table 1. Sediment composition at the sampling stations.

sampling station	depth (cm)	dr.wt. %	l.o.i %dr.wt.	P %dr.wt.
4	0- 2	6	59	0.13
	2- 4	8	55	0.13
	4- 6	9	57	0.11
	6- 8	11	55	0.096
	8-14	11	54	0.095
5	0- 2	7	56	0.088
	2- 4	10	66	0.064
	4- 6	12	63	0.057
	6- 8	13	55	0.069
	8-14	15	53	0.069
6	0- 2	4	64	0.11
	2- 4	6	63	0.11
	4- 6	6	64	0.11
	6- 8	7	61	0.099
	8-14	7	62	0.088
6a	0- 2	5	64	0.13
	2- 4	7	64	0.13
	4- 6	7	65	0.13
	6- 8	7	63	0.13
	8-14	10	58	0.082
9	0- 2	75	3	0.018
	2- 4	80	1	0.0071
	4- 6	58	8	0.0059
	6- 8	68	3	0.019
	8-14	57	5	0.018

Pore water concentration patterns

It is not feasible to present all data. In Table 2 the average concentrations at each station are presented and in Fig. 2 the pH and the average concentrations of SRP, ammonia and TDFE at the various sampling depths.

Table 2. Pore water concentrations by sampling station, averaged over all depths and standard deviations (n = 75).

Parameter	Station Number				
	4	5	6	6A	9
SRP	0.29±0.27	0.23±0.20	0.80±0.61	0.34±0.30	0.06±0.07
TDP	0.34±0.29	0.28±0.21	0.86±0.63	0.40±0.31	0.12±0.13
NH_3	3.1 ±2.8	1.8 ±1.3	12.5 ±7.0	6.1 ±3.9	1.4 ±2.2
TDFe	1.8 ±1.0	1.4 ±1.3	1.2 ±0.8	1.0 ±0.6	2.6 ±3.2
DOC	11 ±4	11 ±5	12 ±3	12 ±3	12 ±8
pH	7.8 ±0.4	7.8 ±0.4	7.4 ±0.6	7.7 ±0.5	7.7 ±0.4

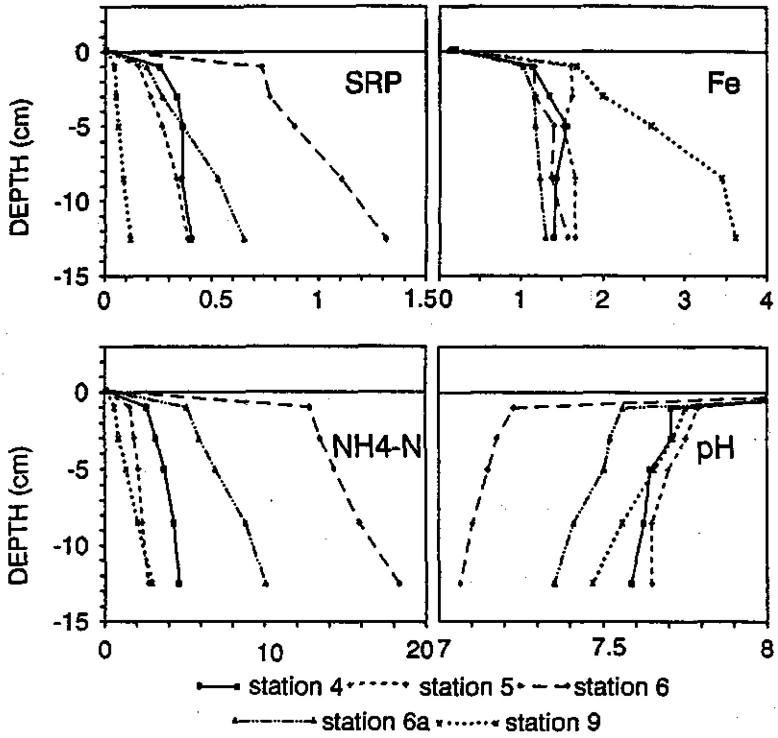

Fig. 2. Average concentrations of SRP (mg P l^{-1}), ammonia (mg N l^{-1}) and TDFe (mg Fe l^{-1}) and pH at the different sampling stations.

Although the differences between duplicate samplings at the same station were considerable, the differences between various stations were assessed as significant. Seasonal variations could not be detected. No significant differences in DOC concentrations between the sampling stations or the sampling depths were observed.

TDP was found to be about 20% higher than SRP. The concentrations of TDP, SRP, TDFe and ammonia increased with sampling depth. For the pH, both the differences between the stations and the standard deviations per station are small. Only at station 6 somewhat lower pH values were recorded.

The differences in ion concentrations in interstitial water between the stations were much larger than the differences in the sediment composition. At stations 6 and, to a lesser extent, 6A much higher concentrations of ammonia, SRP, TDP were found than at stations 4 and 5, whereas the sediment composition was virtually the same. This illustrates that the bulk sediment composition cannot be used as a suitable parameter for detecting processes within the sediment.

5.5 DISCUSSION

Interstitial phosphate concentrations are influenced by different processes: mineral forming reactions, microbial activity and transport. Several approaches are available to test the possible relevance of these processes. Comparison of calculated IAP's with solubility products can be used as a criterion for the possible formation of a mineral (Nriagu & Dell, 1974; Emerson, 1976; Matisoff et al., 1980). Refractory organic material can play a role in the complexation of metal ions. Lack of knowledge of the chemical properties of humic material, however, obstructs insights in the complexation. We will present some simple calculations to test this role.

Simple correlation calculations can show a similarity (or a lack of it) in the behavior of different compounds. Simple steady state models can be useful for the interpretation of the correlations found. Here we will use a simple formulation for ammonia and phosphate.

Mineral forming reactions

Comparison of IAPs with solubility constants can be used as a criterion for possible mineral formation, but this approach must be used with caution. Reactions may be kinetically hindered or concentrations may be controlled by other reactions than those considered. In the case of orthophosphate, the relevant species for mineral formation cannot be measured. SRP, which is measured instead, is certainly not the same (Tarapchack et al., 1982 and Boers et al., 1984a) and is an overestimation of the orthophosphate concentration. Probably the same holds for TDFe as a measure for Fe^{2+}. Hence, calculated saturation or oversaturation cannot provide conclusive evidence for the presence of minerals, but a calculated undersaturation is strong evidence that precipitation is not taking place.

Interstitial water concentrations of lake Loosdrecht sediments were converted to activities using activity coefficients according to Davies (Stumm & Morgan, 1981):

$$-\log\gamma = AZ^2\{(\sqrt{I})/(1+\sqrt{I})-0.2I\} \qquad (1)$$

and:

$$I = 1.510^{-5}\mu \qquad (2)$$

No conductivity measurements were available for the pore water, we therefore used those in the water column. Although differences in conductivities between pore and overlying water may be present, the influence of conductivity on the activity coefficients is small in the range 350 - 450 μS, typical for the Loosdrecht Lakes (Table 3).

Activities of PO_4^{3-} were calculated from SRP concentrations and the ionized fraction. The latter was calculated from pH and dissociation constants (Table 4), corrected for temperature and activities. The temperature correction was done using the Van 't Hoff equation and enthalpy data given by Stumm & Morgan (1981). Activities of Fe^{2+} were calculated from TDFe. Calculations showed that correction for the ion pair $Fe(OH)^+$ is unnecessary, a conclusion also reached by Davison (1979). Some other ion pairs, such as $CaHPO_4^0$ and $FeHPO_4^0$ could affect the PO_4^{3-} concentrations (Emerson, 1976). Calculations indicated that only $CaHPO_4^0$ is relevant and hence this species was accounted for in the calculations of PO_4^{3-} activities.

Table 3. Influence of conductivity on ion activity coefficients.

	conductivity (μS)			
ionic charge	200	300	400	500
1	0.94	0.93	0.92	0.91
2	0.79	0.75	0.72	0.69
3	0.58	0.52	0.47	0.44

Table 4. Equilibrium constants.

Reaction		pK	reference
H_3PO_4	$<=> H_2PO_4^- + H^+$	2.15	Holdren&Armstrong (1986)
$H_2PO_4^-$	$<=> HPO_4^{2-} + H^+$	7.20	id
HPO_4^{2-}	$<=> PO_4^{3-} + H^+$	12.35	id
$CaHPO_4^0$	$<=> Ca^{2+} + HPO_4^{2-}$	2.7	Stumm&Morgan (1981)
$FeHPO_4^0$	$<=> Fe^{2+} + HPO_4^{2-}$	3.6	Nriagu (1972)
$Fe_3(PO_4)_2.8H_2O$	$<=> 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$	36.0	Nriagu (1972)
		33.5	Tessenow (1974)
$Fe^{2+} + H_2O$	$<=> Fe(OH)^+ + H^+$	9.5	Davison (1979)
$Ca_5(PO_4)_3OH$	$<=> 5Ca^{2+} + 3PO_4^{3-} + OH^-$	57.8	Holdren&Armstrong (1986)
$Ca_4H(PO_4)_3$	$<=> 4Ca^{2+} + H^+ + 3PO_4^{3-}$	46.9	id

Organic ligand complexing by DOC is another possible reason for apparent oversaturation. The quantitative role of DOC is difficult to assess due to our lack of knowledge of the composition of DOC. Emerson (1976) proposed a procedure for estimating maximum amounts of Fe and Ca complexed by DOC, assuming that all DOC is citrate. This procedure revealed that no more than 1 - 2 percent of TDFe and Ca can be present as a complex with DOC in our samples.

Vivianite ($Fe_3(PO_4)_2.8H_2O$) and possibly octacalciumphosphate ($Ca_4H(PO_4)_3$) and hydroxy-apatite ($Ca_5(PO_4)_3OH$) have been reported as minerals controlling phosphate and/or metal ion concentrations in lake sediments (e.g. Tessenow, 1974; Emerson, 1976; Matisoff et al., 1980). The solubility constants for these compounds can be found in Table 4. Unfortunately, we had no facilities to measure dissolved calcium in the pore water samples. Therefore, the IAPs for apatite and octacalciumphosphate were estimated using the average concentration of calcium in the overlying water, about 60 mg l^{-1}. Some preliminary pore water analyses showed no concentration gradients of calcium in the pore water (Boers, unpublished results).

For octacalciumphosphate, the pIAPs were around 50, several orders of magnitude higher than the solubility product. So, precipitation of octacalciumphosphate apparently plays no role in the chemistry of phosphate in the Loosdrecht Lakes sediments. In contrast, for hydroxy-apatite most pIAPs were in the range 50 - 55, several orders of magnitude lower than the solubility product. Oversaturation of sediments with hydroxyapatite has been reported frequently. Formation of apatite may be kinetically hindered (Stumm & Leckie, 1971) and probably this material does not accumulate in lake sediments. For vivianite, pK values of 33.5 (Tessenow, 1974) and 36 (Nriagu, 1972) have been reported. The latter value seems to be the correct one (Emerson, 1976).

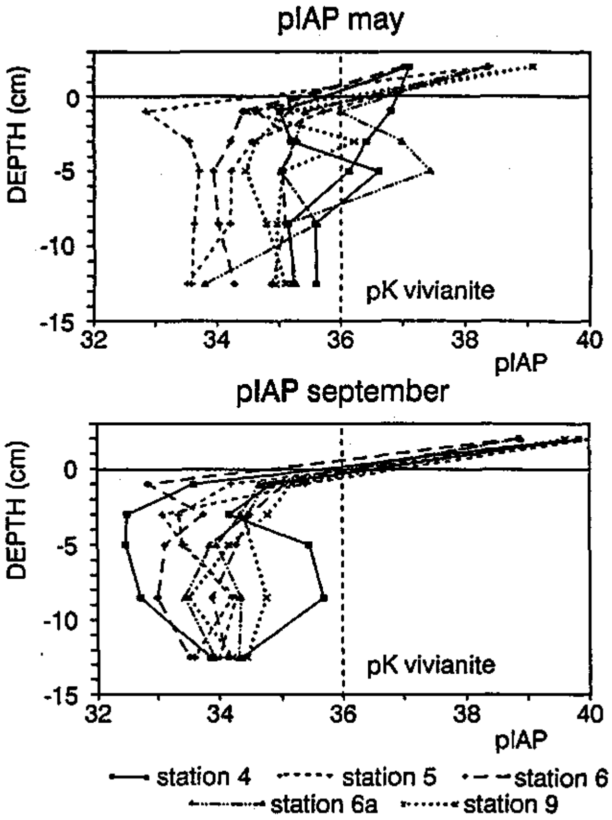

Fig. 3. A few examples of ion activity products of vivianite.

We calculated pIAPs of vivianite in all samples. Fig. 3 depicts some examples. Most are between 35 and 33, i.e. 1-3 units higher than reported by Matisoff et al. (1980) and Holdren & Armstrong (1986). No differences between the sampling dates could be found and the differences in pIAP between duplicate samples were often quite large. Ion activity products tend to increase with depth. So, precipitation of vivianite may affect the phosphate concentrations.

Complexation by POC

Possibly, the availability of iron is affected by complexation with sedimentary humic material. Usually, humic material is poorly defined, but for the Loosdrecht Lakes sediments, Boers & Boon (1988) showed that acid lignin derivates form a major component of the organic matter. These groups may well be responsible

Table 5. Chemical composition of sediments in meq humic acid g^{1} dry sediment and metals, also in meq g^{-1} at the various sampling stations. For a further explanation, see text.

Station	humic acid	Fe	Ca*	Al	Mg	sum
4	3.92	0.63	1.11	0.87	0.18	2.79
5	4.10	0.62	1.26	1.62	0.29	4.01
6	4.41	0.58	1.45	1.10	0.20	3.32
6A	4.41	0.58	1.45	1.10	0.20	3.32
9	0.28	0.02	0.00	0.20	0.13	0.35
9	0.28	1.44	4.40	3.10	0.56	9.50

* corrected for calciumcarbonate.

for the binding of metal ions. Schematically, the reaction can be represented by:

$$2\ \text{Lignin-OH} + Me^{2+} <===> (\text{Lignin-O-})_2Me^{2+} + 2\ H^+$$

The other ligand places on the metal ion are available for the binding of, for example, a phosphate ion. Little is known of the equilibrium constants of such reactions, but the chemical composition of the Loosdrecht Lakes sediments allows evaluation of the potential role of such reactions. We assume that this humic material contains seven milli-equivalents of acid groups per gram organic matter. In Table 5 the major metal composition of the sediments at the various sampling stations is given. The sediments near station 9 were very heterogenous, which makes the calculation rather uncertain. Assuming that each mole of Ca or Fe requires two and each mole of Al three equivalents of humic acid groups, the total amount of humic acid needed for complexation of all metals can be calculated. We excluded the calcium present as calciumcarbonate. The sediments at all stations, except station 9, contain sufficient complexing capacity to bind all metal ions (Table 5). This may explain the relatively high interstitial water TDFe concentrations at station 9. Due to the large variability of the iron content of the sediments at station 9, also large variations in availability of iron can be expected at this station.

Modelling

Ammonia is formed by the microbial decomposition of organic nitrogen compounds, considered to follow first order kinetics. Since the pH in the sediments is in the range of 7 - 8, most of the ammonia is present in the NH_4^+ form. This cation undergoes cation exchange reactions with other ions associated with the sediment particles. Thus, adsorption (or cation exchange) must be considered and can be described by a simple linear isotherm. Ammonia is not involved in authigenic mineral formation. Asssuming that oxidation of ammonia and sediment compaction can be neglected, transport of ammonia is through molecular diffusion, there is steady state sedimentation of organic matter and steady state mineralization of organic matter and some sediment mixing due to bioturbation, a mass balance for organic N in the sediment is (Berner, 1980; Boers & Van Hese, 1988):

$$\delta N(x)/\delta t = 0 = D_b\delta^2 N(x)/\delta x^2 - w\delta N(x)/\delta x - k_m N(x) \qquad (3)$$

with the boundary condition:

$$x = 0 \dashrightarrow N = N(0) \qquad (4)$$

the solution is:

$$N(x) = N(0)\exp(ax) \qquad (5)$$

$$a = \{w - \surd(w^2 + 4k_m D_b)\}/2D_b \qquad (6)$$

The mass balance for dissolved ammonia in the pore water is:

$$\delta C/\delta t = 0 = \{D_n/(1+Q_n)\}\delta^2 C/\delta x^2 - w\delta C/\delta x + k_m/\{(1+Q_n)N(x)\} \qquad (7)$$

Substitution of equation (5) in equation (7) gives the differential equation to be solved. The solution is:

$$C_x = (C_\infty - C_0)\{1 - \exp(ax)\} + C_0 \qquad (8)$$

Where:

$$C_\infty = k_m N(0)/\{D_n a^2 - wa(1+Q_n)\} \qquad (9)$$

The behavior of phosphate is more complicated. When mineral formation plays no role, equations (8) and (9) apply for phosphate as well. If mineral formation is relevant, then a slow reaction term should be included (Boers & Van Hese, 1988). Assuming that this is not necessary, the ratio between the ammonia and phosphate concentrations in the pore water can be calculated as follows. For both compounds the same sedimentation rate and bioturbation coefficient apply. There is no obvious reason to assume that the two compounds are produced by

Table 6. Model parameters (Boers & Van Hese, 1988).

Parameter	Value	Units
w	0.003	d^{-1}
k	0.006	d^{-1}
K	1	(-)
D_b	0.003	cm^{-2} d^{-1}
D_p	0.3	cm^{-2} d^{-1}
P(0)	40	μg P cm^{-3}

mineralization at different rates. Boers & Van Hese (1988) estimated a mineralization rate of 0.006 d^{-1}. The effective diffusion coefficients are 0.85 cm^2 d^{-1} for ammonia and 0.31 cm^2 d^{-1} for phosphate (Krom & Berner, 1980). Boers & Van Hese (1988) used a value of 1 for the adsorption constant of phosphate. This might be a reasonable value for ammonia as well. These and other estimated parameter values (Table 6) allow simplification of equation (9) because $D_n a^2 >> wa(1+Q)$, so:

$$C_{\infty,n} = k_m N(0)/a^2 D_n \tag{10}$$

$$C_{\infty,p} = k_m P(0)/a^2 D_p \tag{11}$$

Assuming that $C_0 << C_\infty$, the ratio of the concentrations of phosphate and ammonia at any depth will be:

$$\begin{aligned} C_{p,x}/C_{n,x} &= [C_{\infty,p}\{1\text{-}\exp(ax)\}]/[C_{\infty,n}\{1\text{-}\exp(ax)\}] \\ &= [k_m P(0)/k_m N(0)][D_n a^2/(D_p a^2)] \\ &= (D_n/D_p)[P(0)/N(0)] \qquad (12) \end{aligned}$$

As a first approximation for P(0)/N(0) the ratio in the seston, about 0.033 (w/w) (Van Liere, unpublished data), can be used. This results in:

$$Cn/Cp = (0.85/0.31)0.033 = 0.093 \tag{13}$$

Regression analysis of all ammonia and phosphate pore water data results in $C_n/C_p = 0.083 \pm 0.002$ ($R^2 = 0.79$, n = 416), which is in fairly good agreement with the calculated ratio.

Table 7. Correlation coefficients (R^2) between concentrations of all samples.

	TDP	NH_3	TDFe	DOC
SRP	0.97	0.79	0.00	0.00
TDP		0.77	0.01	0.00
NH_3			0.03	0.00
TDFe				0.00

Correlations between concentrations

Correlation coefficients between the concentrations of the different dissolved substances were calculated using the complete dataset (Table 7). SRP and TDP were strongly correlated, as TDFe and SRP were not, suggesting that the concentrations of the latter two species are controlled by different processes. DOC and TDFe did not show any correlation with another compound.

As stated above, ammonia and SRP are strongly correlated. In case vivianite formation significantly affects the phosphate concentrations in the pore water, the phosphate concentrations will be lower than predicted from eq. (13). This was tested by separating the dataset in two parts: one with pIAP of vivianite less than 36.0 and the other more than 36.0.

Regressions between SRP and NH_3 concentrations, calculated for both subsets, are (Fig. 4):

Subset 1 (undersaturated):

$$[SRP] = (0.073 \pm 0.004)[NH_3] - (0.046 \pm 0.14)$$
$R^2 = 0.75$; n=133

Subset 2 (supersaturated):

$$[SRP] = (0.084 \pm 0.003)[NH_3] - (0.066 \pm 0.23)$$
$R^2 = 0.77$; n=283

The second set has a significantly higher regression coefficient. This means that with the same ammonia concentrations the SRP concentrations are higher when supersaturation with vivianite is calculated. This implies that apparent supersaturation does not result in relatively low SRP concentrations, but that on the contrary relatively high SRP concentrations lead to oversaturation. So, precipitation of vivianite is not controlling the SRP concentrations.

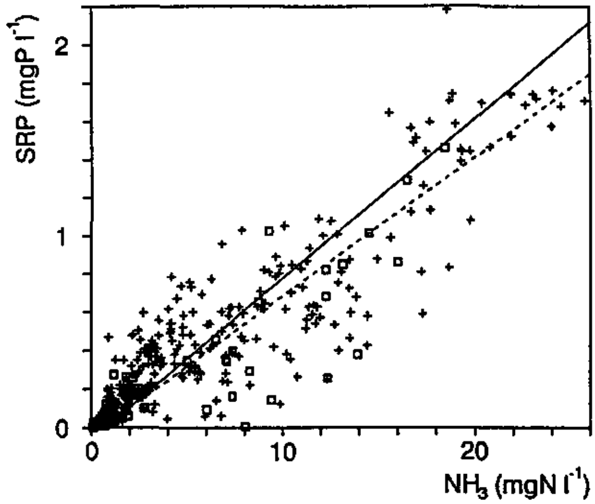

Fig. 4. Correlation between NH_3 and SRP concentrations.
■ *and - - - - - : undersaturated with respect to vivianite;*
+ *and ——— : supersaturated with respect to vivianite.*

5.6 CONCLUSIONS

Pore water concentrations are valuable indicators for early diagenetic processes of phosphate. The great similarity in concentration patterns of SRP and ammonia indicates that phosphate concentrations were mainly governed by mineralization and diffusion in the sediments of the Loosdrecht Lakes. The ratio of the concentrations of the two substances was close to that predicted from a simple conceptual model, assuming that mineralization, adsorption and transport are the only relevant processes. According to calculations of solubility products, supersaturation with respect to vivianite may play a role. The strong correlation between ammonia and SRP concentrations, however, indicates that this supersaturation not really affects the SRP concentrations.

No indications were found for a possible role of complexation of metal ions by DOC in the pore water chemistry of the Loosdrecht Lakes. We did find indications that adsorption of metal ions by the sedimentary humic matter may affect the availability of metals in the Loosdrecht Lakes sediments.

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CHAPTER 6

THE INFLUENCE OF pH ON PHOSPHATE RELEASE FROM LAKE SEDIMENTS

Water Research, in press

ABSTRACT- pH is believed to be an important regulating factor for the release of phosphate from freshwater sediments. Usually, this is demonstrated in laboratory experiments using intact sediment cores and pH regulation of the overlying water by means of NaOH additions. This technique and a pH regulation technique by means of CO_2-stripping were compared. The first method resulted in a tenfold increase in release rate at pH 9.5 compared to the rate at pH 8.3. The stripping technique yielded only a doubling of the release rate at pH 9.3. Measurements of pH profiles in the sediment in experiments performed at pH 8.3 and pH 9.0 proved that the enhanced phosphate release when using NaOH for pH regulation is mainly an artifact caused by an increased alkalinity in the watercolumn and the upper sediment layers, resulting from the NaOH additions.

Key words: phosphate, sediments, release experiments, methods.

6.1 INTRODUCTION

In eutrophic lakes, a release of phosphate from the sediments can be an important source of phosphate for the phytoplankton community in the water column (e.g. Jacoby et al., 1982; Boers & Van Hese, 1988). Often, the release rate is higher in summer than in winter. Several reasons have been held responsible for this, among which are temperature (Boers & Van Hese, 1988), anaerobic conditions in the sediments (Boström et al., 1982) and high pH values in the water column (Drake & Haney, 1987, Jacoby et al., 1982). This paper focuses on the last mechanism.

A high pH in the watercolumn is induced by enhanced photosynthetic activity, withdrawing CO_2 from the water and shifting the $CO_2/HCO_3^-/CO_3^{2-}$ equilibrium that controls pH. As a result of this, the pH can increase to values of 10 or even higher.

The phosphate chemistry in lake sediments is believed to be dominated frequently by interaction with iron species, and especially the adsorption on Fe(III) hydroxides is of paramount importance. This sorption is strongly influenced by pH (Lijklema, 1980). A higher pH causes the desorption of phosphate from Fe(III) hydroxides, resulting in a release of phosphate from the sediments. Several researchers investigated the influence of pH on phosphate release rates. Rippey (1977) found a simultaneous increase in pH and in orthophosphate concentrations in Loch Neagh, suggesting that the first increase triggers the latter. This, however, is no direct evidence, as other parameters, such as temperature, increased as well. Ryding (1985) concluded from the data of 16 Swedish lakes that increase of pH is not related to an enhanced release of phosphate. Others (e.g. Rippey, 1977; Jacoby et al., 1982; Drake & Haney, 1987; Boers & Van Hese, 1988) used laboratory experiments with intact sediment cores. This is the only way of studying pH effects without changes in other environmental conditions. In all these cases, pH was controlled by additions of NaOH, which is the easiest method of pH control. This procedure, however, is different from the CO_2 removal in nature. Due to the NaOH additions, the alkalinity in the water column is increased. In nature, alkalinity is unaffected or rather decreases in case the water is saturated with calcite and this compound precipitates. Hence, the method of pH control used may affect the pH within the sediment near the sediment-water interface and therefore the behavior of phosphate in the sediments.

In this paper the results of phosphate release experiments in intact sediment cores using both methods of pH control are presented. The pH near the sediment-water interface was measured using mini pH electrodes. Experiments were performed with sediments from the shallow lake Veluwe, the Netherlands.

Table 1. Composition of artificial lake water.

Ion	Concentration (mM)
Na^+	2.15
K^+	0.27
Ca^{2+}	1.83
HCO_3^-	1.43
Cl^-	2.79
SO_4^{2-}	0.93

6.2 MATERIALS AND METHODS

Sampling area

Sediment samples were taken from lake Veluwe, a shallow lake (average depth 1.5 m) in the Netherlands. The lake is eutrophic and in recent years several measures were taken to combat eutrophication (Hosper & Meijer, 1986). The samples were taken at a water depth of 2.5 m.

Release experiments

Undisturbed sediment samples were taken on June 22nd 1988 using a Beeker sampler (Eijkelkamp, the Netherlands). A detachable perspex inner core with a cross sectional area of 25 cm^2 containing the sample can be installed in the laboratory in a continuous flow reactor within a few hours after sampling. This reactor is described in detail by Boers & Van Hese (1988). In all experiments artificial lake water (Table 1) was fed to the reactor.

Five experiments were done: one without pH control, this maintained a pH 8.3 in the watercolumn; a second was kept at pH 9.0; a third at pH 9.5; both using 0.1 M NaOH. The fourth experiment was kept at pH 9.0 using CO_2-free air as well as CO_2 and the last was fed with CO_2-free air only, this experiment maintained a pH 9.3. CO_2 was removed from air by bubbling through a 1 M NaOH solution. Fig. 1 is a flow diagram of the experimental setup. pH was regulated using a pH meter (Radiometer PHM82), titrator (Radiometer TTT80) and peristaltic pumps (Cole-Parmer 7544-30). All connections were made with gas-tight tubing. The reactor effluents were sampled for SRP five times a week during three weeks. Phosphate release rates were calculated from mass balances of the experiments (Boers & Van Hese, 1988).

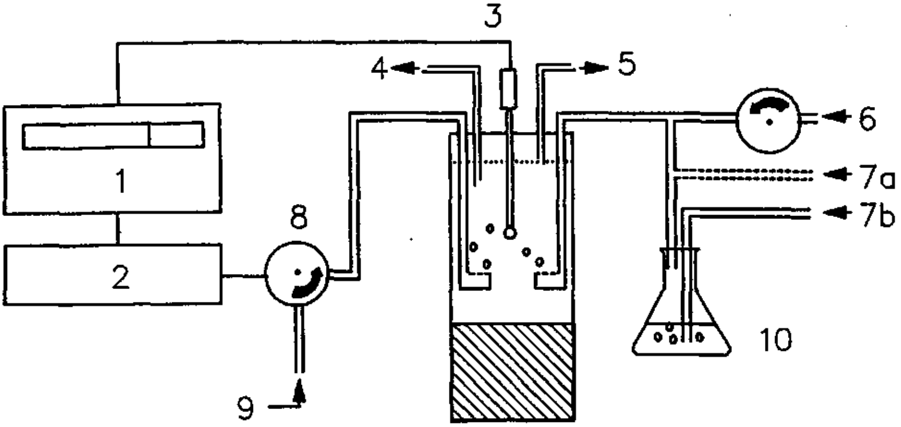

Fig. 1. Flow diagramme of release experiments.
1: pH meter; 2: titrator; 3: pH electrode; 4: sampling tube for watercolumn; 5: outflow for air and water; 6: supply of synthetic lake water; 7a: supply of air (NaOH regulated experiments and unregulated experiment); 7b: supply of air (CO_2 regulated experiments only); 8: peristaltic pump for supply of CO_2 or NaOH; 9: inlet for NaOH (NaOH regulated experiments) or CO_2 (CO_2 regulated experiments);
10: 1 N NaOH for stripping CO_2 from air (CO_2 regulated experiments).

pH measurements in the sediments

pH in the interstitial water was measured using mini-pH electrodes, as described by De Jong et al. (1989), a calomel reference electrode and a pH meter (Radiometer PHM82). The electrodes were calibrated with buffers at pH 7 and 9. The electrodes were carefully moved into the sediment using a micromanipulator. Measurements were done in experiments performed at pH 9.0 and pH 8.3 and at intervals of 0.2 - 0.5 mm. The profiles were measured ten days after the beginning of the experiments.

6.3 RESULTS

The cumulative phosphate release for the different experiments as a function of time is presented in Fig. 2. Table 2 summarizes the average release rates over the whole experimental period. They show that in the case of NaOH additions, the increase of release rate with pH is much more pronounced than in the case of CO_2 removal, especially above pH 9.

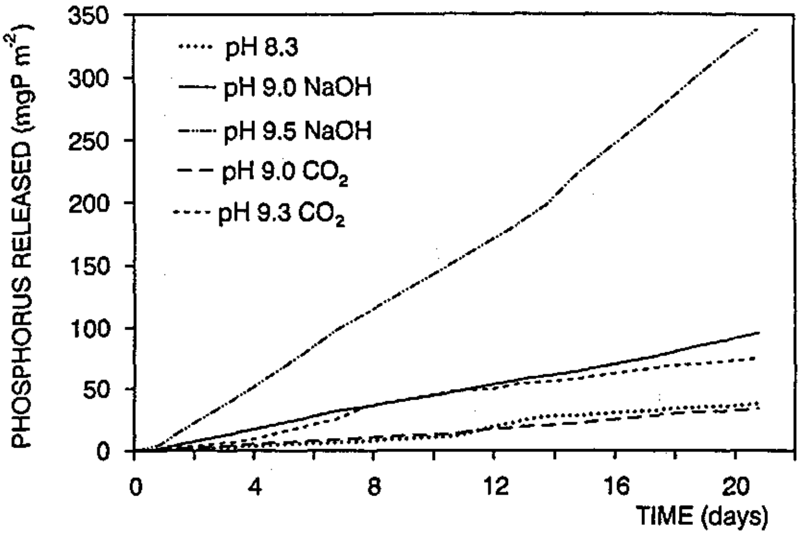

Fig. 2. Measured cumulative phosphate release.

The pH profiles in the sediments measured in experiments performed at pH 9.0 and pH 8.3 (Fig. 3) give an explanation for this difference in behavior, using two methods of pH control. In case of NaOH addition, a sediment layer of about 4 mm thick has been influenced by the pH in the water column.

In case of CO_2 this influence is limited to a layer of about 2 mm. Even in this layer, the pH is lower than in the other experiment at pH 9. As a result of this, in a smaller portion of the sediment the adsorption capacity for phosphate is decreased and less phosphate is liberated.

Table 2. Average release rates in mg P m^{-2} d^{-1}.

Experiment	Average Release Rate
Control (pH 8.3)	1.8
pH 9.0 (with NaOH)	4.6
pH 9.5 "	16.3
pH 9.0 (with CO_2)	1.6
pH 9.3 "	3.6

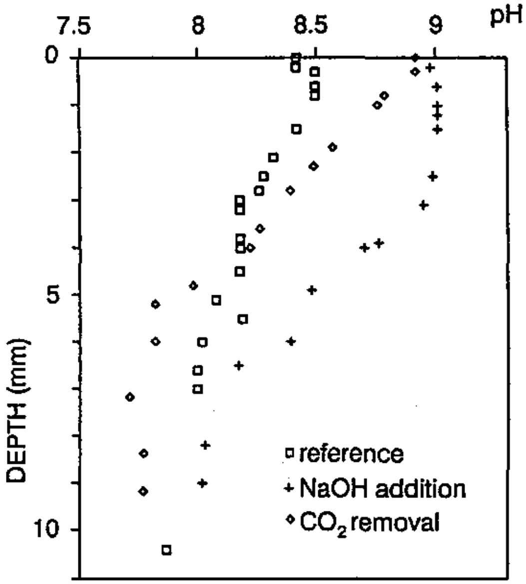

Fig. 3. pH profiles in the sediments exposed to overlying waters at pH 8.3 and at pH 9.0 controlled by NaOH additions and CO_2-stripping, respectively.

6.4 DISCUSSION AND CONCLUSIONS

The most important difference between the two sets of experiments is the pH regulating mechanism. In the experiments, regulated with NaOH, alkalinity is added to the watercolumn. This leads to an increase of the CO_3^{2-} concentration and, as the feed water is saturated with respect to calciumcarbonate, to precipitation of this compound. The alkalinity of the feed water is ca. 6.1 meq l^{-1}. On average 5.9 meq l^{-1} NaOH was needed to maintain pH at 9.0 17 meq l^{-1} NaOH to maintain pH 9.5. Even if all Ca^{2+} in the feed water precipitates, this results in alkalinities of 8.3 and 19.4 meq l^{-1}, respectively.

In the CO_2 regulated experiments, the CO_2 concentration is lowered and due to precipitation of calciumcarbonate also the alkalinity.

In the unregulated experiment, the alkalinity in the pore water is probably slightly higher than in the watercolumn as a result of production of CO_2 by mineralization. The increased alkalinity in the water column brought about by the NaOH additions results in a transport of alkalinity from the watercolumn into the sediment. The decreased alkalinity, caused by removing CO_2 instead, leads to an increased transport of alkalinity from the sediment to the watercolumn. Hence, the pH in the top layer of the sediment must be higher in the NaOH regulated experiments than in the CO_2 regulated experiments. This is confirmed by the pH measurements in the sediments (Fig. 3).

As high pH promotes desorption of phosphate ions from iron(III)hydroxides, more phosphate can desorb from the sediment top layer, when exposed to water with high pH and high alkalinity than to water with high pH and low alkalinity.
The results demonstrate clearly that enhanced phosphate release by high pH in the watercolumn, when quantified from column experiments, may in many cases be largely an artifact caused by the commonly used method of pH regulation by means of addition of NaOH. Reduction of the CO_2 pressure by stripping with CO_2-free air and if necessary titration with CO_2 is a much better alternative. One serious drawback of CO_2-stripping is that a pH over about 9.3 can not be reached. Due to the low partial CO_2 pressure needed for this pH not enough CO_2 can be carried off, without using excessive high air flow rates. In eutrophic lakes, however, the algae can strip that much CO_2, that pH values as high as 10 are possible. The results with pH 9.0 and pH 9.3 indicate that phosphate release rates still increases significantly at high pH, although much less than when alkalinity is added.

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CHAPTER 7

LAKE RESTORATION: ESTIMATION OF INTERNAL PHOSPHORUS LOADING AFTER REDUCTION OF EXTERNAL LOADING FROM SEDIMENT DATA

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Submitted to Hydrobiologia

ABSTRACT- Net internal phosphorus loadings from the sediments of eleven shallow lakes with a reduced external loading were calculated from mass budget data. These rates were compared with several phosphorus fractions in the surface sediments of these lakes. Regressions of net internal loading rates on total sediment phosphorus, on the phosphorus to iron ratio and on the phosphorus to clay sized fraction ratio in the sediment were highly significant. The regressions can be used to predict the internal phosphorus loading and the resulting phosphorus concentrations in lakes, to be expected after reduction of the external loading.

Key words: internal phosphorus loading, eutrophication, lake recovery, sediments.

7.1 LIST OF SYMBOLS

Symbol	Meaning	Dimensions
DRWT	dry weight of the sediment	(% of wet weight)
h	depth of the lake	(m)
L_{in}	external phosphorus loading	(g P m^{-2} y^{-1})
L_{out}	outflow of phosphorus	(g P m^{-2} y^{-1})
NIL	net internal phosphorus loading	(g P m^{-2} y^{-1})
P_{lake}	phosphorus concentration in the lake	(g P m^{-3})
Q_{in}	hydraulic loading	(m y^{-1})
Q_{out}	total outflow of water	(m y^{-1})
Q_{evap}	outflow of water by evaporation	(m y^{-1})
Q_{flow}	outflow of water by surface outflow	(m y^{-1})
TP	total phosphorus in sediments	(mg P g^{-1})
TP/<2μm	total phosphorus in sediments normalized to the inorganic carbonate-free fraction <2μm	(mg P g^{-1})
τ_w	residence time	(y)

7.2 INTRODUCTION

Eutrophication is a major, world-wide water quality problem. It is widely recognized, nowadays, that an excessive loading of the lakes and reservoirs with phosphorus is the prime cause of eutrophication. Consequently, the problem is combatted by reduction of the external phosphorus loading. In a recent review, Cullen & Forsberg (1988) concluded that only 28 out of 41 lakes showed a complete recovery of the water quality after a drastic reduction of the external loading. An incomplete recovery of a lake can have two reasons:
a) the external loading was not reduced enough to reach the desired lowered total phosphorus concentration in the lake, even without an internal loading;
b) the phosphorus concentration in the lake remains higher than was expected from the reduction of the external loading.

In the overview provided by Cullen & Forsberg (1988) these two options can be distinguished readily by calculating the ratio between the fraction of the pre-restoration phosphorus concentration left after restoration and the remaining fraction of the pre-restoration external loading (In formula: $P_{lake,post}/P_{lake,pre} = L_{in,post}/L_{in,pre}$). If a lake would simply follow the Vollenweider type of relation between loading and concentration, this ratio would be close to one. For 8 out of the 29 lakes reviewed by Cullen & Forsberg (1988), the ratio was indeed close to one, in all other cases the ratio was higher, usually in the range of 2 - 4.

This latter type of incomplete recovery is the result of internal loading of phosphorus from the sediments. It stresses once more the relevance of the quantification of the expected internal loading before any lake restoration measure is taken.

The internal loading can be determined as the release flux of phosphorus from the sediments. This flux can be quantified in laboratory experiments (Jacoby et al, 1982; Brinkman & Van Raaphorst, 1986; Drake & Haney, 1987; Boers & Van Hese, 1988). In such experiments, attention should be payed to a proper simulation of environmental conditions as temperature (Holdren & Armstrong, 1980; Boers & Van Hese, 1988), redox conditions (e.g. Holdren & Armstrong, 1980; Ryding, 1982; Boström & Petterson, 1982) and pH (e.g. Boström & Petterson, 1982; Drake & Haney, 1987; Boers & Van Hese 1988; Boers, 1990) and to local differences within a lake (e.g. Brinkman & Van Raaphorst, 1986).

Another option is to quantify internal loading as the amount of phosphorus that is lost from the sediments. As this internal loading is the result of two fluxes, namely sedimentation to and release from the sediments, a more precise term is net internal loading (NIL). NIL is calculated directly from mass budgets.

As we seek to develop predictive relations for the internal loading after a reduction of the external loading, data on internal loading, external loading and phosphorus concentrations of lakes that were actually restored are indispensable. Internal loading rates, quantified as measured phosphorus release rates were available for only one lake: Lake Loosdrecht (Boers, 1986; Boers & Van Hese, 1988). This method could therefore not be used. As mass budget data are much more widely available, calculation of NIL was used to describe the sediment-water exchange of phosphorus. Although NIL is the result of two opposite processes, sedimentation and release from the sediments, it is also a measure of the capacity of the sediment to retain phosphorus and therefore it should be related to sediment parameters.

We restricted ourselves to shallow lakes. One reason is that shallow lakes seem to be more sensitive to internal loading than deep, stratifying lakes (Cullen & Forsberg, 1988); the other reason is that the results of this study were used to make a guideline for lake restoration procedures for shallow Dutch lakes.

7.3 THE DATASET

For only eleven lakes, data on both sediment composition and phosphorus budgets before and after reduction of the external phosphorus loading could be found. Sediment data were scarce: for only 2 of the 22 shallow lakes reported by Cullen & Forsberg (1988), such information could be traced. Additional information was provided by Sas et al. (1989) and other sources (see table 1).

Table 1. Sediment characteristics of the eleven lakes considered. Dry weight is % of wet weight, organic matter % of dry weight and all others mg g^{-1}.

nr	lake	country	DRWT	org. matter	Fe	TP	NH_4Cl-P	NaOH-P	HCl-P	ref*
1	Veluwemeer	nl	45	4.4	16	0.36	0.04	0.15	0.23	1,2
2	Hylkesø	den	10	20		1.6				1
3	Glumsø	den	4	20		2.5	0.43	0.23	1.0	1
4	Søbygard	den	5	30	50	8.5	1.5	4.0	0.20	1,3
5	Lake Loosdr.	nl	8	57	20	1.0	0.03	0.30	0.19	4,5,6
6	Meerplas	nl	53	13		0.7	0.02	0.37	0.25	7
7	Norrviken	swe	8	22	33	1.8				1,8,9
8	Schlachtensee	brd	5	15		1.5				1
9	Vallentunasjön	swe	9	28	29	1.8	0.14	0.26	0.32	10,11
10	Bergundasjön	swe	4	45	43	5.9	0.25	4.0	0.71	10,12,13
11	Lillesjön	swe	4	57	21	1.6				14

*: 1: Sas et al, 1989; 2: Brinkman & Van Raaphorst, 1986; 3: Søndergaard, 1989; 4: Boers et al., 1984; 5: Boers, unpublished; 6: Engelen et al, 1988; 7: Van Muiswinkel, 1987; 8: Ahlgren, 1980; 9: Boström, 1984; 10: Boström, 1988; 11: Boström & Petterson, 1982; 12: Ryding, 1985; 13: Bengtsson, 1975; 14: Ripl, 1978.

Table 2. Post restoration budget data of the eleven lakes considered.

Nr	lake	L_{in} gP m^{-2} y^{-1}	τ_w y	depth m	P_{lake} gP m^{-3}	NIL gP m^{-2} y^{-1}	no. of years averaged
1	Veluwemeer	1.12	0.39	1.3	0.14	-0.76	4
2	Hylkesø	1.3	1.45	7.1	0.21	-0.23	4
3	Glumsø	1.6	0.38	1.8	0.44	0.15	4
4	Søbygard	4.9	0.04	1	0.52	5.89	4
5	Lake Loosdr.	0.24	0.7	1.8	0.12	-0.02	2
6	Meerplas	0.1	1.1	1.6	0.13	0.03	1
7	Norrviken	0.6	0.85	5.4	0.115	0.04	9
8	Schlachtensee	0.5	0.6	4.6	0.045	-0.19	3
9	Vallentunasjön	0.14	1.67	2.7	0.3	0.12	2
10	Bergundasjön	0.6	0.7	2.6	0.67	1.4	1
11	Lillesjön	0.4	0.25	2	0.23	1.25	1

NIL was calculated from the annual mass budget and assuming steady state as follows:

$$L_{out} - L_{in} = NIL \tag{1}$$

Information on L_{in} could be obtained for all cases; unfortunately this was not the case for L_{out}. L_{out} was therefore, if necessary, calculated from the phosphorus concentration in the lake and the water budget:

$$L_{out} = Q_{flow}P_{lake} \tag{2}$$

$$Q_{in} = Q_{out} = Q_{evap} + Q_{flow} \tag{3}$$

$$Q_{in} = h/\tau_w \tag{4}$$

The lake depth h and residence time of the water τ_w were available for all cases. Combination of equations (1), (2), (3) and (4) leads to:

$$NIL = (h/\tau_w - Q_{evap})P_{lake} - L_{in} \tag{5}$$

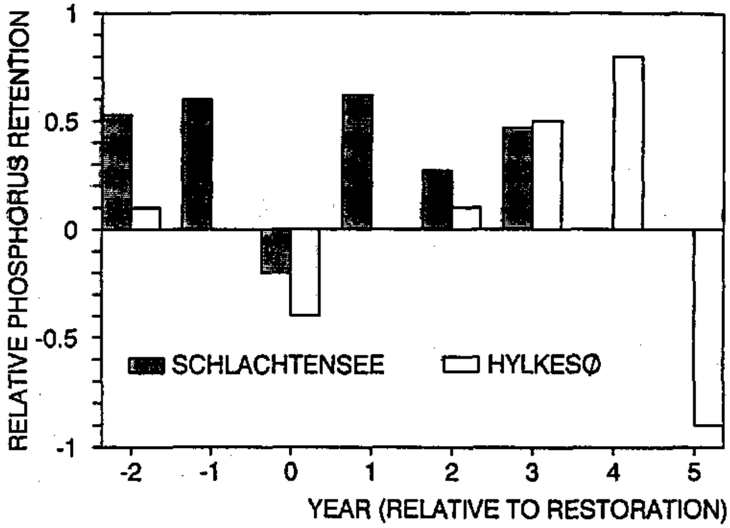

Fig. 1. Relative retention of phosphorus in the lakes Schlachtensee and Hylkesø in the years before and after reduction of the external loading (data from Sas et al., 1988).

The outgoing phosphorus flux has to be corrected for evaporation, as with evaporation no phosphorus is exported. In most cases it was not clear from the data provided whether precipitation and evaporation had been accounted for in the calculation of the water residence time. We assumed that this was the case and so equation (5) must be used. We had no data on evaporation fluxes, and assumed that these amount to 0.75 m y^{-1}, a value that is representative for the temperate zone.

Generally, NIL is relatively high in the first year after reduction of the external phosphorus loading, for example in lake Schlachtensee (Fig. 1). As we seek relations for the internal loading in a number of years following the reduction of the external loading, this first year was not included in the dataset. In some other cases, such as lake Hylkesø (Fig. 1), NIL was reported to vary strongly from year to year. If possible, the average NIL over several years was used.

For sediment characteristics the commonly reported parameters dry weight, organic matter (as organic C or loss on ignition) and total phosphorus were used. In seven cases results of selective extractions, all according to Hieltjes & Lijklema (1980) or total iron were reported. The data are summarized in Tables 1 and 2.

7.4 RESULTS AND DISCUSSION

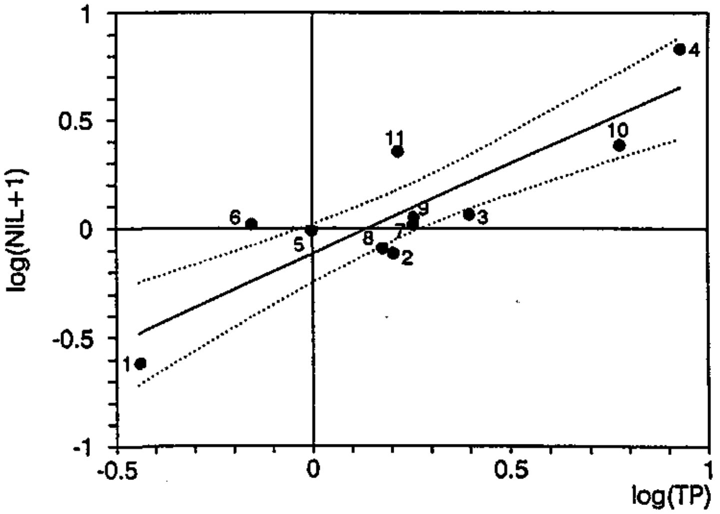

Fig. 2. Scatter diagram of total P in the sediments and net internal loading. Figures correspond with those in table 1. The dashed lines represent the 95% confidential intervals.

To adjust for uneven spread, regression calculations were done on the logtransformed data. NIL can be negative and then logtransformation is not possible. This problem was overcome by adding 1 to NIL before logtransformation. Log(NIL+1) is strongly correlated with the phosphorus content of the sediments (Fig. 2):

$$\log(\mathrm{NIL} + 1) = -0.11\pm0.18 + (0.82\pm0.15)\log(\mathrm{TP}) \qquad (6)$$
$R = 0.88$; $p<0.01$.

A net internal loading already takes place at a phosphorus content in the sediment of 1.4 mg P g^{-1}.

Two lakes, the Dutch Meerplas (no. 6) and the Swedish Lillesjön (no. 11), appear to behave differently from the others. Both exhibit a relatively high net internal loading. An explanation might be that both lakes are mainly fed by seepage and that for neither of them the phosphorus loading was actually measured, but assumed to be the "natural background" (Ripl, 1978; Van Muiswinkel, 1987). It is not unlikely that the external loading was underestimated by this approach and thus the internal loading overestimated.

For a number of lakes, additional sediment parameters were available: for seven lakes the results of selective phosphorus extractions by aqueous solutions of NH_4Cl, NaOH and HCl, respectively (Hieltjes & Lijklema, 1980) and data of total iron was available for another seven lakes. We calculated the correlation of the NH_4Cl fraction, the NaOH fraction and the sum of these fractions with NIL (table 3). These fractions should represent the loosely adsorbed and the iron- and aluminum bound phosphorus and are considered to be "available" (Boström et al., 1982). No single phosphorus fraction, nor the sum of NH_4Cl- and NaOH extractable phosphorus proved to be a better predictor for NIL than total phosphorus. Nürnberg (1988) also reported a poor correlation between NaOH-extractable P and release rates for deep, stratifying lakes.

Table 3. Regression-analysis of NIL [Y= log(NIL+1)] against extractable phosphorus [X=log(TP)]. The regression against total phosphorus was recalculated for reasons of comparison. The number of observations is 7.

X	R	constant	slope
log(TP)	0.92	-0.10±0.18	0.82±0.15
log(NH_4Cl-P)	0.75	-0.53±0.32	0.48±0.19
log(NaOH-P)	0.86	-0.27±0.25	0.63±0.17
log(NH_4Cl-P+NaOH-P)	0.90	-0.18±0.21	0.69±0.15

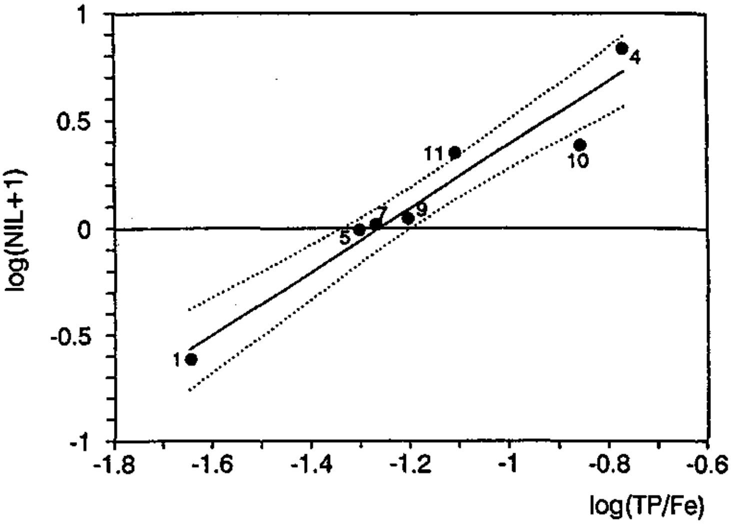

Fig. 3. Scatter diagram of TP/Fe in the sediments and net internal loading. Figures correspond with those in table 1. The dashed lines represent the 95% confidential intervals.

The TP/Fe ratio in the sediment appears to be correlated very strongly to NIL (Fig. 3):

$$\log(\mathrm{NIL} + 1) = (1.87 \pm 0.12) + (1.48 \pm 0.17)\log(\mathrm{TP/Fe}) \qquad (7)$$

$R = 0.97;\ p<0.01$

This supports the idea that it is mainly iron, that is responsible for the ultimate immobilization of phosphorus in aquatic sediments (Boström et al., 1982, Redshaw et al., 1990). A promising application of this principle is the suppression of the phosphorus release from lake sediments by addition of iron salts (Redshaw et al., 1990; Boers et al, submitted).

In the Netherlands, quality standards for the pollution of aquatic sediments with heavy metals are related to the inorganic and carbonate free fraction $< 2\mu m$ (the clay-sized fraction). In a survey of the phosphorus content of a number of aquatic sediments in Europe, Salomons & Gerritse (1981) also reported a strong correlation between the phosphorus content and the clay-sized fraction. For these two reasons, we attempted to quantify phosphorus, present in the clay-sized fraction from the provided sediment characteristics and NIL. Unfortunately, for none of the lakes a grain size distribution was available. Therefore, the fraction $<2\mu m$ as percentage of the inorganic and carbonate free sediment was estimated

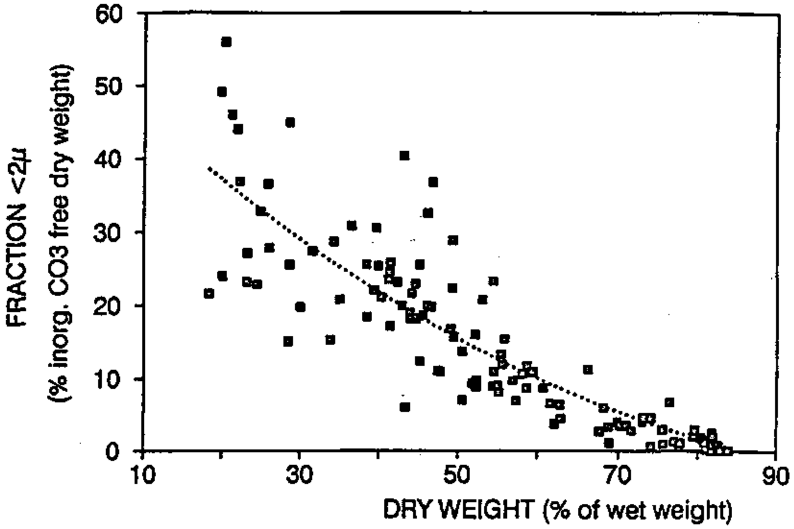

Fig. 4. Scatter diagram of fraction <2μm and percentage dry weight for 119 sediment samples from various Dutch lakes. The line represents the best fit relation (see text).

from the dry weight of the sediments, using an empirical relation between these two sediment parameters found for a dataset of 119 sediment samples from various Dutch lakes (Fig. 4):

$$\text{fraction} <2\mu m = 0.00439DRWT^2 - 1.03DRWT + 55.95 \quad (8)$$
$$R = 0.91$$

As the clay-sized fraction relates to the inorganic and carbonate-free fraction of the sediment, further corrections for the amounts of these two fractions of the sediments are necessary. The organic matter content was provided in most cases, but not the carbonate content, unfortunately. Therefore, a correction for this latter fraction had to be omitted. In regard of the generally low carbonate content of the sediments, this was considered to be permissible. The final equation used was:

$$TP/<2\mu m = TP*10000/\{(\text{fraction}<2\mu)(100\text{-org.matter})\} \quad (9)$$

NIL correlates strongly to this $TP/<2\mu m$ (Fig. 5):

$$\log(NIL+1) = -0.77\pm0.14 + (1.08\pm0.14)\log(TP/<2\mu m) \quad (10)$$
$$R = 0.93;\ p<0.01$$

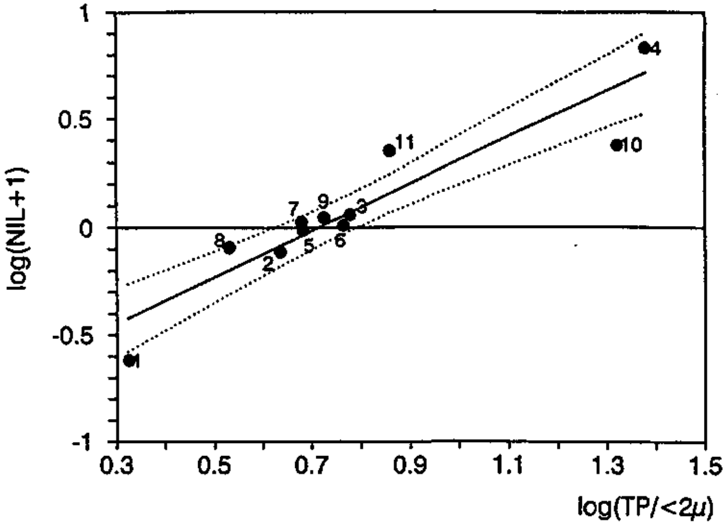

Fig. 5. Scatter diagram of TP in the sediments normalized on the estimated fraction < 2μm and net internal loading. Figures correspond with those in table 1. The dashed lines represent the 95% confidential intervals.

This correlation coefficient is higher than that for the relation between TP and NIL (equation 6). However, three independent variables, namely TP, organic matter and dry weight, were used to derive equation (9), leaving only 7 degrees of freedom for equation (10) against 9 for equation (6). As a result there is no gain in significance. This is due to the limited number of data available.

It is surprising that such strong correlations between NIL and sediment parameters were found. NIL is a lake wide averaged flux, whereas in many cases the sediment composition is measured in one or at its best a few sediment samples from distinct locations in the lake. The variations in sediment composition within one lake can be very large. Brinkman & Van Raaphorst (1986) demonstrated this for the Dutch Lake Veluwemeer.

It might be that the regressions are strong as a result of the fact that they were based upon only a limited number of lakes. At the moment, it is im possible to verify on a large scale whether the utilized sediment characteristics, or maybe other important sediment variables, are useful predictors of NIL. Therefore, we plead for more attention for sediment characteristics and sediment-water exchange processes in lake restoration studies, in addition to the much more common water quality and phosphorus budget data.

The strong and significant regressions between literature data on total sediment phosphorus and on internal loading can be used to predict the effects of reduction of the external loading, before any measure is taken. For shallow lakes there are no alternatives for such an approach, as release rates cannot be derived directly from field data as with stratifying lakes (Nürnberg et al., 1986) and the reliability of column experiments still is a matter of debate (Boström et al., 1982). To predict the post-restoration phosphorus concentration in the lake, NIL can be predicted from equation (6), (7) or (10) and the resulting concentration in the lake from equation (5).

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CHAPTER 8

PHOSPHORUS FIXATION WITH IRON(III)CHLORIDE: a new method to combat internal phosphorus loading in shallow lakes?

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Submitted to Hydrobiologia

ABSTRACT- Laboratory experiments using continuous flow experiments and batch experiments showed that additions of 100 g Fe^{3+} m^{-2} *to lake sediments decreased the phosphorus release rates substantially. Treatment of the sediments of the shallow lake Groot-Vogelenzang, part of the Reeuwijk lakes area (the Netherlands), with this amount of iron resulted in an immediate threefold decrease in the total phosphorus concentration in the lake. This improved water quality lasted for three months. The most important reason for the only transient improvement was the unexpected short residence time of the lake of only 35 days. Phosphorus budget calculations, phosphorus release experiments and determinations of bioavailable phosphorus all indicated that the phosphorus binding capacity of the sediments increased due to the treatment, although the three methods gave different results. Treatment of lake sediments with iron(III)chloride is potentially an effective method to decrease internal phosphorus loading, but the durability of this method still needs to be proven.*

Key words: eutrophication, lake restoration, sediments, phosphorus, phosphorus inactivation, Reeuwijk lakes area.

8.1 INTRODUCTION

Eutrophication of lakes is a widespread water quality problem. The accepted method to combat this is by reduction of the external phosphorus loading. In this case, an internal phosphorus loading from sediments may delay an improvement of the water quality. This has been experienced in many cases, such as the Swedish Lake Trummen (Bengtsson et al., 1975).

Internal phosphorus loading can be reduced by careful dredging of the phosphorus-rich upper sediment layers, as was done in lake Trummen (Björk, 1988). Dredging is usually an effective, but costly and time-consuming method. An alternative for dredging is treatment of the watercolumn with aluminum salts. By this treatment, the phosphorus compounds are precipitated and locked in the sediments (Cooke et al., 1986). This method appears to be very effective in deep, stratifying lakes, but less reliable in shallow lakes. Relocation of the aluminum hydroxide blanket covering the sediments may be a reason for failure (Cooke et al., 1986).

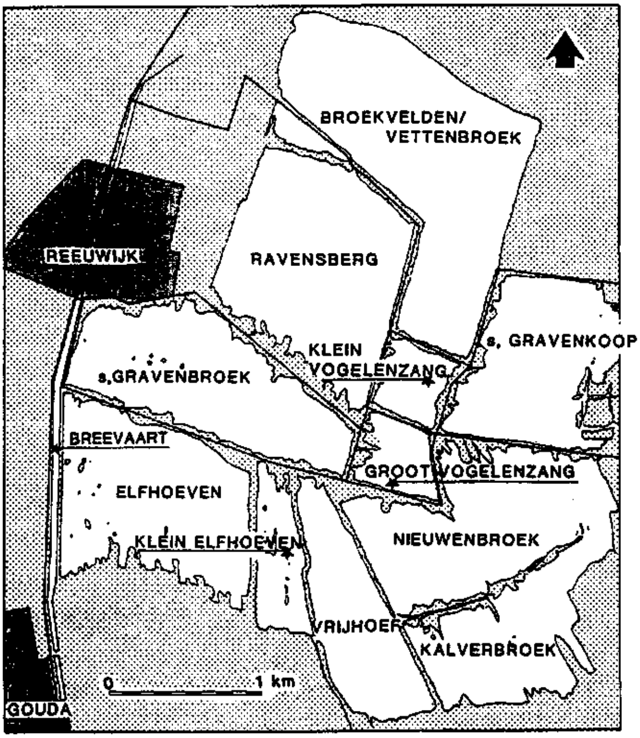

Fig. 1A. Lake Groot-Vogelenzang and its surroundings.

As most of the lakes in the Netherlands are shallow, a solution for this problem had to be found. Treatment of the sediment, instead of the watercolumn, might be a solution. Another problem is the use of aluminum salts. Aluminum is potentially toxic and although it is not soluble at the pH values usually encountered in lakes, in the Netherlands the use of aluminum compounds for water quality improvement purposes is not favored. Iron salts might offer an alternative. Bannink et al. (1980) demonstrated that iron dosing in the inlet water of an experimental enclosure strongly decreased the availability of phosphorus to algae. As a major proportion of the sediment phosphorus is considered to be associated with iron, both under oxic and anoxic conditions (Boström et al., 1982; Redshaw et al., 1990), addition of iron compounds to sediments may increase the natural phosphate binding capacity.

This paper describes the results of laboratory experiments with sediments which had been treated with iron(III)chloride and the first results of the treatment of the shallow and eutrophic lake Groot Vogelenzang in the Netherlands.

8.2 METHODS

Research area

The demonstration project was performed in lake Groot Vogelenzang (GV), situated in the centre of the Reeuwijk lakes area (Fig. 1). In 1986, the external phosphorus loading to the lakes was reduced by phosphorus removal at the treatment plant, discharging into the lakes. The residual loading is from untreated domestic waste water, agricultural runoff and supply of nutrient-rich water in summer. Until now, the phosphorus concentrations in the lakes did not decrease (Van der Vlugt & Klapwijk, 1990). Table 1 summarizes the most important characteristics of lake GV. The overall water residence time of the Reeuwijk Lakes area is about 1 - 2 year. However, due to the complex hydrology, the residence time and phosphorus loading of lake GV itself are unknown. The lake was believed to have only a limited exchange of water with the surrounding lakes.

Table 1: Some characteristics of lake Groot-Vogelenzang.

Area:	18 ha
Average depth:	1.75 m
Summer average total P:	0.21 mg P l^{-1}
Summer average Chl-a:	0.11 mg l^{-1}

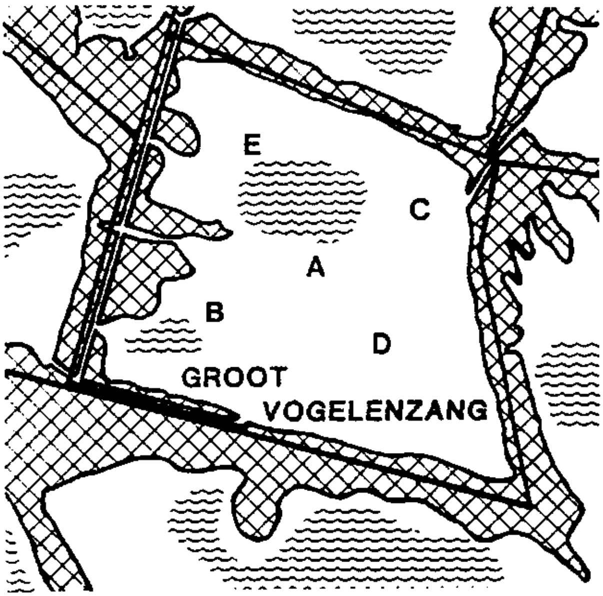

Fig. 1B. The lake with the sampling stations used for sediment research.

Preliminary laboratory experiments with iron(III)chloride

The suitability of iron(III)chloride for inactivation of phosphorus in freshwater sediments was tested in the laboratory using both batch and continuous flow experiments. A number of undisturbed sediment samples were taken with a Beeker sediment sampler (Beeker, 1989).

For the continuous flow experiments, the upper 20 cm of eight sediment cores were mixed and then divided into eight equal portions in order to minimize the influence of sediment heterogeneity. Duplicate subsamples were mixed with an aqueous solution of iron(III)chloride and received 0, 0.9, 1.8 or 4.5 mole Fe m^{-2} of sediment. The sediment portions were transferred into the same perspex tubes in which they were taken and inserted into the equipment for determination of phosphorus release rates using the continuous flow technique (Boers & Van Hese, 1988). The overlying water in each core was flushed continuously with synthetic lake water. The watercolumn in one core of the duplicates was kept oxic by bubbling with air, whereas the other was stripped with nitrogen gas in order to maintain anoxic conditions. The oxygen concentration in the water column was about 0.1 mg l^{-1}. The watercolumn was sampled for orthophosphate five times a week for five weeks. Phosphorus release rates were computed from the phosphorus balance of the watercolumns.

Batch experiments were used to compare the phosphorus inactivation capacity of salts of Fe^{3+} and Al^{3+}. The upper 20 cm of six sediment cores were mixed. 50 ml portions of this sediment received an aqueous solution of $FeCl_3$ or $Al_2(SO_4)_3$, corresponding to 0, 0.9, 1.8 or 4.5 mole Fe or Al m^{-2} of sediment. The sediment samples were then transferred into 250 ml erlenmeyer flasks containing 150 ml of synthetic lake water. Two flasks with each addition were placed in a glove box that was purged with nitrogen gas. The oxygen concentration in the box was about 0.2 %. The other flasks were exposed to air. All flasks were shaken twice a week. 50 ml of the overlying water was sampled for orthophosphate determinations after seven and fourteen days.

Monitoring of water and sediment quality

The lake was sampled fortnightly since January, 1988. Concentrations of nutrients, chlorophyll-a, chloride, suspended solids and oxygen, pH and Secchi depth were determined according to Dutch standard methods. Just prior to the sediment treatment sediment samples were taken from five stations (Fig. 1B) using the Beeker sediment sampler. The top 5 cm of the samples was analysed for dry weight, organic matter (by loss on ignition), bioavailable phosphorus, total phosphorus and total iron. Bioavailable phosphorus was quantified as the yield of algal biomass in batch cultures containing algae and sediment as sole phosphorus source according to Bruning & Klapwijk (1984). The other parameters were measured according to Klapwijk et al. (1982). Phosphorus release rates were measured from duplicate cores using the continuous flow technique (Boers & Van Hese, 1988). Measurements of phosphorus release rates were repeated two weeks after the treatment and in June, 1990. Sediment sampling for chemical analysis and quantification of bio-available phosphorus was repeated in March, 1990, four months after the treatment.

8.3 THE PHOSPHORUS FIXATION TECHNIQUE

A full description of the method is given by Quaak et al. (1990). In short, the method implies treatment of a layer of about 20 cm with 1.8 mole or 100 g Fe m^{-2}, which was considered to yield an adequate protection against relocation of the treated sediment.

The sediment was mixed with the iron(III)chloride solution by injection of the solution into the sediments in such a way, that about 15 - 20 cm of sediment was temporally resuspended. 80 m^3 of a 40 % solution of iron(III)chloride was used. The permission for this treatment demanded a quality of iron(III)chloride as used for the purification of drinking water, in order to prevent pollution of the lake with heavy metals. The supplied 40 % solution was added to the sediments after dilution 100 - 150 times with lake water prior to injection. A proper dosing of the iron(III)chloride was obtained by coupling the pumping rate of the dosing pump to the speed of the craft. The operation was carried out in October - November, 1989 and took three weeks. The operational costs were ca. $ 125,000.

8.4 RESULTS AND DISCUSSION

Preliminary laboratory experiments

Fig. 2 presents the results of the continuous flow experiments with treated lake sediments, showing that additions of 1.8 mole or 100 g Fe m^{-2} or more reduced phosphorus release rates with over 80 %. The treatment was as effective under oxic as under anoxic conditions and lasted for at least five weeks, the duration of the experiments. The batch experiments (Fig. 3) indicated that there is no difference in phosphorus immobilization capacity between aluminum and iron. For both metals the anoxic equilibrium phosphate concentrations in the water phase were higher than the oxic concentrations. This compares well with the results of the continuous flow release experiments. Based upon these experiments a dose of

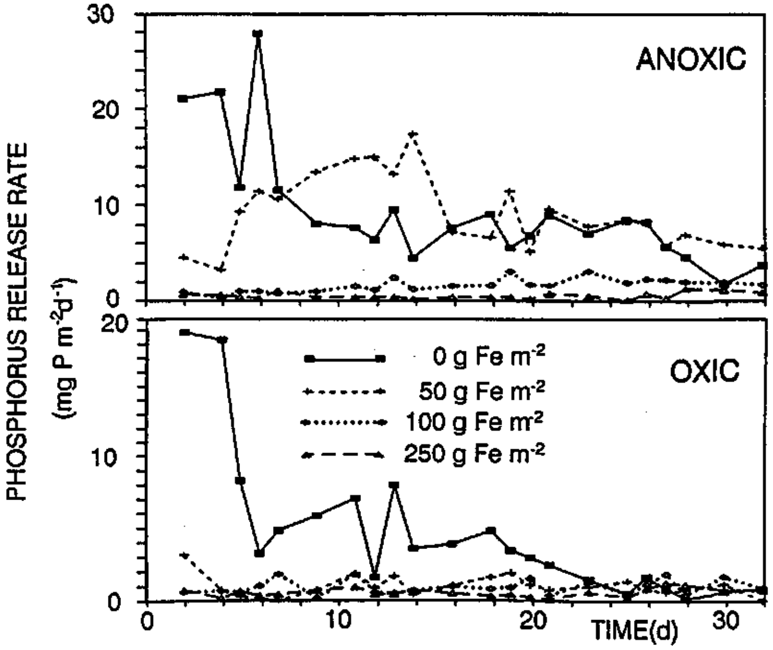

Fig. 2. Phosphorus release rates from sediments treated with iron(III)chloride.

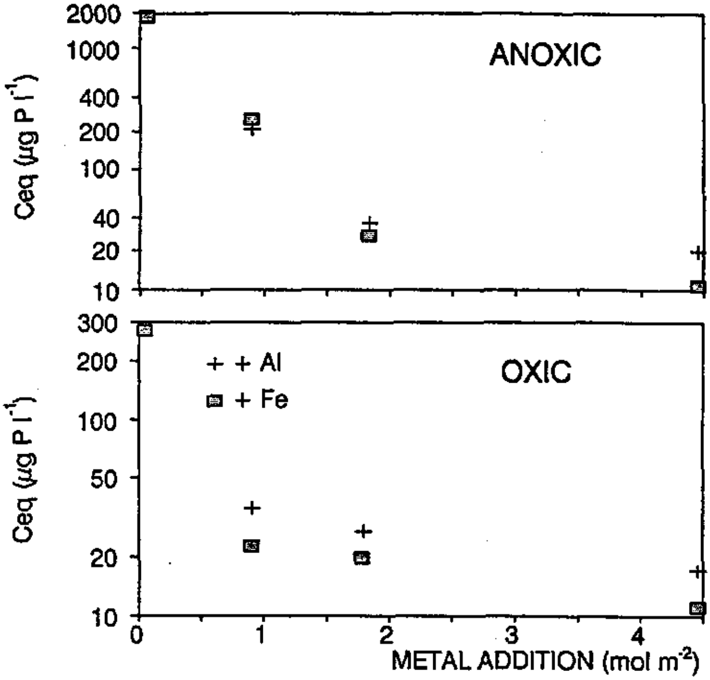

Fig. 3. Phosphate equilibrium concentrations of batch experiments with sediments treated with different amounts of aluminum or iron. Note the logarithmic vertical axis.

1.8 mole or 100 g Fe m^{-2} of sediment was judged to be adequate for treatment of the lake. This is a 2 - 3 times higher dose than used by addition in the water column in White Lough (Foy, 1985) and in the lakes discussed by Cooke et al. (1986). The reason for this higher amount is probably that the iron is diluted by a larger amount of sediment in this study.

Sediment characteristics.

Tables 2 and 3 summarize all sediment data, as measured before and after the treatment. As far as chemical data are concerned, the differences between the stations are very small, except for station C sampled after the treatment. The same is true for the bioavailable fraction of the sediment phosphorus. Both phosphorus content and the fraction of bioavailable phosphorus in the sediments of lake GV are higher than in the other parts of the Reeuwijk lakes.

The variation in phosphorus release rates before treatment is much greater than that in the composition: a fifteenfold difference between the highest and the

Table 2. Sediment characteristics at five sampling stations before (B) and after (A) treatment.

Station	Dry weight (% of wet)		LOI (%)		P (mg g^{-1})		Fe (mg g^{-1})	
	B	A	B	A	B	A	B	A
A	4.6	6.3	50	51	1.7	1.6	21.9	43.2
B	5.3	5.9	50	48	1.5	1.7	29.0	36.8
C	5.3	10.0	49	56	1.6	0.9	24.3	33.4
D	5.3	6.6	48	46	1.8	1.7	21.9	45.3
E	5.5	6.5	50	50	1.5	1.6	23.1	43.2
Average*	5.2	6.3	49	49	1.6	1.6	24.1	42.1
Reeuwijk**	12		52		1.1		13.6	

* data from station C after treatment were not included.
** source: Klapwijk & Bruning, 1986.

Table 3. Phosphorus exchange characteristics at five sampling stations before and after treatment.

Station	P-release rate (mgP m^{-2} d^{-1})			bio-available P (% of total P)	
Date	10-89	12-89	6-90	10-89	3-90
A	0.9	0.9	0.1	37.4	25.7
B	11.3	2.1	0.2	31.0	24.4
C	1.5	1.0	0.8	33.5	16.8
D	0.9	0.9	0.4	33.3	21.3
E	4.7	1.3	0.1	30.9	22.0
Average	3.8	1.2	0.3	33.6	23.4*
Reeuwijk**	ND			14	

* data from station C after treatment was not included.
** source: Klapwijk & Bruning, 1986.

lowest rate was found. These differences are probably no artifacts: similar differences between the sampling stations, be it less pronounced, were found shortly after the treatment. The measurements in June, 1990 indicate that the phosphorus release rate remained low, even lower than immediately after the treatment. The release rate and the bioavailability of the sediment phosphorus decreased after the treatment with 70 % and 30 %. As far as we know, a comparison between these two indicators for internal loading has never been made. The methodological differences between the two methods are large, hampering a comparison. The release experiments were done without algae and with intact sediment cores. The release rate is controlled by chemical and microbial transformations in the sediment and by diffusive transport. The bioassays were done in aerated suspensions of sediment and algae and the sediment was heated to 75 °C for one hour as pre-treatment. The sediment becomes oxidized, and direct exchange of phosphorus between sediment particles and algae is possible.

The loss on ignition and the phosphorus content of the sediments remained unchanged upon treatment. Dry weight increased a little, probably due to the sediment compacting properties of iron(III)hydroxide. The iron content increased by the iron additions.

These results show that the iron that was added to the sediments was distributed evenly over the surface sediments of the whole lake area. Furthermore, the heavy storms that occurred between the treatment and the second sediment sampling had no influence on the iron distribution in the surface sediments. The newly developed dosing technique was adequate in this respect. The increase in iron content in the top 5 cm corresponds to 50 % of the added iron. Hence, a layer of about 10 cm thick has been enriched with iron.

Changes in water quality after treatment

Fig. 4 summarizes the responses of water quality parameters to the treatment. Iron(III)chloride forms iron(III)hydroxide colloids upon dilution with lake water. These colloids are powerful flocculents for small particles present in the water column. Therefore, application of the phosphorus fixation technique brought about an immediate reduction in the suspended solids concentration by flocculation and sedimentation. This again resulted in lower total phosphorus and chlorophyll-a concentrations and an increased Secchi depth. This phenomenon has also been observed in lakes treated with aluminum compounds (Foy, 1985; Cooke et al., 1986). The relatively low total phosphorus concentration lasted until the end of January 1990, after which it increased strongly. This occurred shortly after a violent storm of 11 Beaufort during two days. The irregular pattern observed during February and March is due to further during other storm events. Although the phosphorus concentrations increased strongly in January, the average concentration in the period February - March is lower than in the same period of 1989 (Fig. 4; Table 4).

The improvement of the water quality lasted for only a few months. An explanation is given by the chloride concentration pattern in the months after the

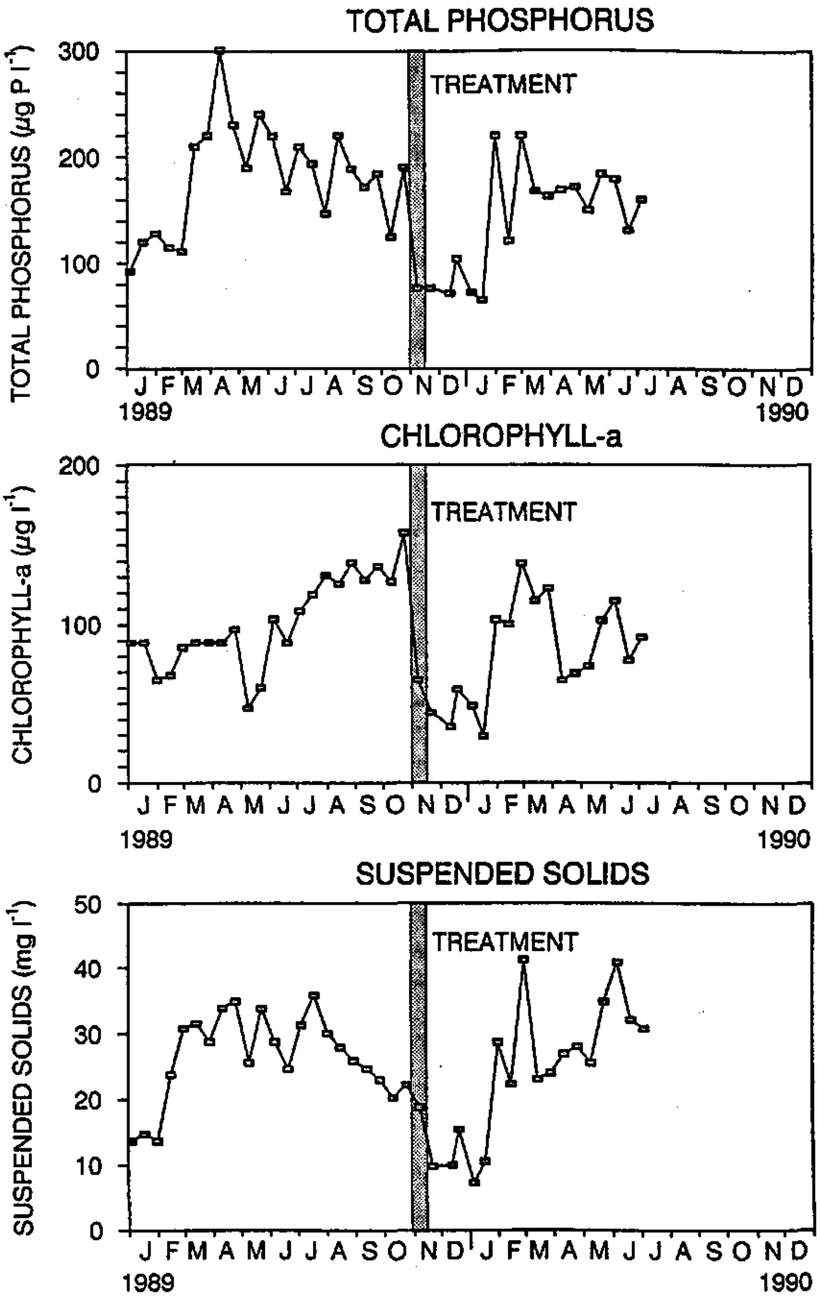

Fig. 4. Concentrations of total phosphorus, chlorophyll-a and suspended solids in lake Groot-Vogelenzang from January, 1989 until June, 1990.

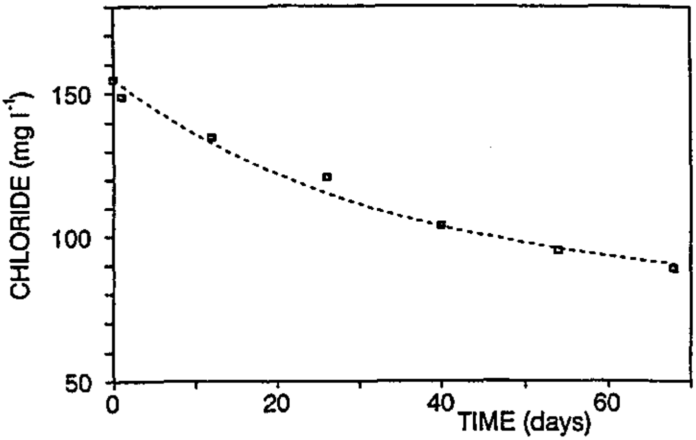

Fig. 5. Concentration of Cl⁻ in the three months after the treatment. The dashed line reflects exponential dilution with a retention time of 35 days.

addition of $FeCl_3$ (Fig. 5), indicating that the water residence time was about 35 days, instead of a year or more. The storm events of January and February might be another disturbing factor. Although no measurements of the water flow patterns during these events are available, a part of the content of lake GV is probably replaced by water from the neighbouring lakes during changes in wind force or direction.

Data on phosphorus concentrations in the water entering lake GV in 1990 are not available, but on basis of data from 1989 an estimate for the phosphorus balance for GV can be made. This balance can be used for comparison of the behavior of the phosphorus entering the lake before and after the treatment.

The external loading was calculated as follows: Lake GV receives domestic wastewater from about 80 people, corresponding to a phosphorus loading of about 0.84 mg P m^{-2} d^{-1}. The average phosphorus loading from atmospheric deposition was estimated to be 0.16 mg P m^{-2} d^{-1}. The average total phosphorus concentrations in the lakes surrounding lake GV are 0.13 mg P l^{-1} in winter and 0.22 mg P l^{-1} in summer. Assuming that the calculated water residence time of 35 days is also valid for the first half of the year, the phosphorus loading by inflow from the adjacent lakes was calculated according to:

$$L_{in} = P_{in} . h / \rho_w \qquad (1)$$

where:

L_{in} = external P loading due to inflow (mg P m^{-2} d^{-1})
P_{in} = total P concentration in inflowing water (mg P l^{-1})

h = average depth (m)
ρ_w = flushing rate (d^{-1})

The outflow of phosphorus was calculated as:

$$L_{out} = P_{lake}.h/\rho_w \qquad (2)$$

where:
L_{out} = outflow of P (mg P m^{-2} d^{-1})
P_{lake} = total P concentration in lake GV (mg P l^{-1})

The phosphorus retention in the sediments was calculated as the difference between inflow and outflow of phosphorus. Results of the calculations are given in Table 4.

In the three months immediately after the treatment about 0.34 g P m^{-2} or 51 % of the external loading was retained in the sediments. During the same period in the previous winter, only 0.17 g P m^{-2} or 25 % of the external loading was bound. In the months February - June 1989, the phosphorus retention was less than 10 % and during the same five months in 1990 it was 0.65 g P m^{-2} or 35 % of the external input. Hence, during the whole period of eight months after the treatment about 2.7 mg P m^{-2} d^{-1} was bound by the sediments in excess to the amount during the same months in 1988-1989. This matches well with the difference in the average phosphorus release rate from the sediments of 2.6 mg P m^{-2} d^{-1}, measured before and after treatment.

According to these calculations the phosphorus binding capacity of the sediments of lake GV was poor before treatment. The average phosphorus retention during November 1988 - June 1989 was about 15%, which is much less than the 50% that is average for this type of lakes in the Netherlands (Lijklema et al., 1988). The phosphorus binding capacity has increased after treatment with iron(III)chloride and the phosphorus retention became about 40%. However, the increased fixation of phosphorus in the sediments was insufficient to maintain substantially lower phosphate concentrations in lake GV. In this respect there is a difference between the results of the release experiments, the phosphorus budget calculations and the bioassays. The first two methods indicate a decreased release rate of 2.6 mg P m^{-2} d^{-1} (70 %) and according to the bio-assays the amount of bio-available sediment phosphorus decreased by only 30%.

According to the calculations the increase in total phosphorus concentration in February - March 1990 was due to an increase of the concentration in the inflowing water and not due to a loss of phosphorus binding capacity of the treated sediments. So, the lack of success is probably not due to failure of the sediment treatment technique, but due to the high external load. The phosphorus

Table 4. Estimated phosphorus budget for lake GV from November-April before (B) and after (A) treatment. A retention time of 35 days is assumed. Figures in parenthesis: percentage of external phosphorus loading.

Period	P_{in} mgP m^{-3}	P loading mgP m^{-2} d^{-1}	P_{lake} mg P m^{-3}		P retention mg P m^{-2} d^{-1}	
			B	A	B	A
Nov. - Jan.	132	7.6	113	75	1.9(25)	3.8(51)
Feb - June	224	12.2	224	158	1.0 (8)	4.3(35)
Nov - June	200	10.5	172	120	1.5(15)	4.2(40)

concentrations still are high enough to maintain dense algal blooms. Due to the high external loading the additional phosphorus binding capacity of the sediment will be exhausted soon. Assuming that before the treatment the sediment was saturated with phosphorus, the phosphorus binding capacity of the sediments is 0.066 g P g^{-1} Fe. Addition of 100 g Fe m^{-2} provides an extra binding capacity of 6.6 g P m^{-2}. With an extra phosphorus retention of 2.7 mg P m^{-2} d^{-1} compared to before treatment, this additional binding capacity will be used up after 6.6 years. This time is a maximum estimate, as iron might be lost from the sediments by release or part of the iron might not be available for phosphorus binding.

8.5 CONCLUSIONS

Treatment of the sediments of a shallow lake with 100 g m^{-2} iron as an iron(III) salt appears to be an economic and fast method to reduce internal phosphorus loading. The treatment results in an immediate improvement of the water quality due to the flocculating properties of iron(III)chloride. The release rate and bio-availability of sediment phosphorus were decreased, not only shortly after the treatment, but also eight months later.

Treatment of a sediment layer of 10 cm thick ensures a sufficient protection against relocation of the treated sediment by wind action.

In spite of these favorable effects of the treatment, the improvement of the waterquality in the small lake Groot Vogelenzang was only transient. The reason for this is the very short residence time of only 35 days and the concomitant high external phosphorus loading. Consequently, the water quality in the lake is mainly governed by the quality of the incoming water and not by internal processes in the lake. This proves again that combatting eutrophication should start with reduction of external loading, including exchange of water of poor quality. The method needs to be tested again in a lake with a low external loading.

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CHAPTER 9

CHANGES IN PHOSPHORUS CYCLING IN A SHALLOW LAKE DUE TO FOOD WEB MANIPULATIONS

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Freshwater Biology, in press

SUMMARY

1. Food web manipulation, by removal of planktivorous or benthivorous fish, is a promising method for reducing phytoplankton concentrations in shallow lakes. The part that nutrients may play in the success of such a measure is not well documented.

2. In this study, we analyze the flow of phosphorus through the food web of the shallow, eutrophic lake Wolderwijd/Nuldernauw. We considered the years 1981 (when a bloom of cyanobacteria occurred) and 1987 (no bloom) and also a hypothetical situation in which most of the bream are assumed to be removed.

3. The analysis shows that the success of biomanipulation is likely to be due not only to an increased grazing pressure on the phytoplankton, but also to a decreased availability of phosphorus. The reason for this is the removal of detrital phosphorus by increased sedimentation as a result of a predicted increase in growth of macrophytes after biomanipulation.

9.1 INTRODUCTION

Eutrophication remains one of the world's principal problems of water quality. Undoubtedly, the main cause is an excessive loading of phosphorus and nitrogen, which in lakes eventually leads to high algal biomass, dominance of cyanobacteria and loss of macrophytes. Further consequences may include dominance by cyprinid fish and by rotifers and small copepods. These zooplankters are not very efficient grazers on the large colony forming cyanobacteria.

Traditional attempts to alleviate eutrophication have involved the control of nutrient loadings. Although this strategy usually decreases algal biomass, it often fails to result in the desired water quality (Hosper 1989; Marsden, 1989). One important reason is that large amounts of nutrients stored in the sediments contribute to continuing high nutrient concentrations in the surface water through internal loading. Indeed, in some cases where nutrient-rich sediments were removed by dredging, or where nutrients were fixed in sediments by the use of chemicals, a further improvement in water quality has been achieved (Cooke et al., 1986).

Another reason for lack of success relates to the possible existence of two stable states in eutrophic waters: a macrophyte-dominated state and a phytoplankton-dominated state. Each state is presumed to be stable within a range of nutrient concentrations and a reduction in nutrient concentration alone is often insufficient to switch from the phytoplankton to the macrophyte state (Timms & Moss, 1984; Scheffer, 1989).

Biomanipulation, i.e. manipulation of the fish-stock, may facilitate a switch from one state to another. This water quality management tool has become increasingly popular and, in the Netherlands, spectacular short term results have been obtained in several small lakes (Meijer et al., 1989; Van Donk et al., 1989). A biomanipulation project in the relatively large (27 km^2) and shallow (1.5 m) lake Wolderwijd/Nuldernauw is in preparation. This lake was highly eutrophic in the 1970s and was permanently dominated by cyanobacteria. Due to a minor reduction of external loading and flushing in some winters with water of good quality, algal biomass and dominance by cyanobacteria have been reduced. Secchi depth, however, remains low. The biomanipulation measure under consideration will remove most of the cyprinid fish and introduce pike. It is expected that Secchi depth will increase to at least 0.75 m and that algal biomass will decrease to about 20 mg chlorophyll-a m^{-3}.

Most attention is focused on food-web interactions in biomanipulation experiments. However, changes in the nutrient cycling will also take place. These may alter the availability of nutrients to algae and thereby influence the success of the biomanipulation. For example, Moss et al. (1986) observed an increased nutrient release from lake sediments, caused by dense populations of macrophytes. We have analyzed a number of changes by calculating nutrient budgets for lake Wolderwijd/Nuldernauw under three conditions: the former hypertrophic situation, the more recent situation with a mixed algal population and the hypothetical conditions expected after biomanipulation. The analysis focuses on phosphorus, not because nitrogen is less relevant, but because there is so much less information on nitrogen.

9.2 STUDY AREA

The lake (area is 26.65 km^2, average depth c. 1.5 m) is situated in the centre of the Netherlands in between the polder Flevoland and the "old land". It was formed when the polder "Zuidelijk Flevoland" was reclaimed in 1968. The external phosphorus loading amounts to about 1 g P m^{-2} y^{-1}. The major part of this loading is imposed in winter. From 1969 on there was a continuous blooming of *Oscillatoria* species, with summer biomass maxima of about 200 - 250 mg chlorophyll-a m^{-3}. In 1981-1982, water quality improved as a result of flushing in winter with water of a much better quality from polder Flevoland. Summer average total phosphorus concentrations decreased from 300 to 100 - 200 mg P m^{-3} and chlorophyll-a concentrations from 300 to 50 - 100 mg m^{-3} (Fig. 1) and in 1985 the permanent blooming of cyanobacteria was broken. In spite of this decrease of algal biomass, Secchi depth improved only slightly from 0.2 - 0.3 m to about 0.4 m (Fig. 1), probably due to resuspension of bottom material by wind and fish and a poor sedimentation of detritus. In 1988 the cyanobacteria returned after a mild winter without any flushing.

9.3 METHODS

The phosphorus cycling of the lake was analyzed for three different conditions: i.e. the hypertrophic 1969 - 1981 (represented by the year 1981); a year without cyanobacteria (represented by the year 1987); and the expected situation after biomanipulation. Although changes in the ecosystem in the course of the year may be very interesting, we focused on the average situation in the growing season (May - September). Fig. 2 is a representation of pools and fluxes. For the first two cases water quality data were available but, of course not for the hypothetical case after biomanipulation. Production rates and biomass of the various components were derived from measurements and the literature. In order to obtain consistency between the different biota and fluxes, all data were converted to phosphorus concentrations and fluxes.

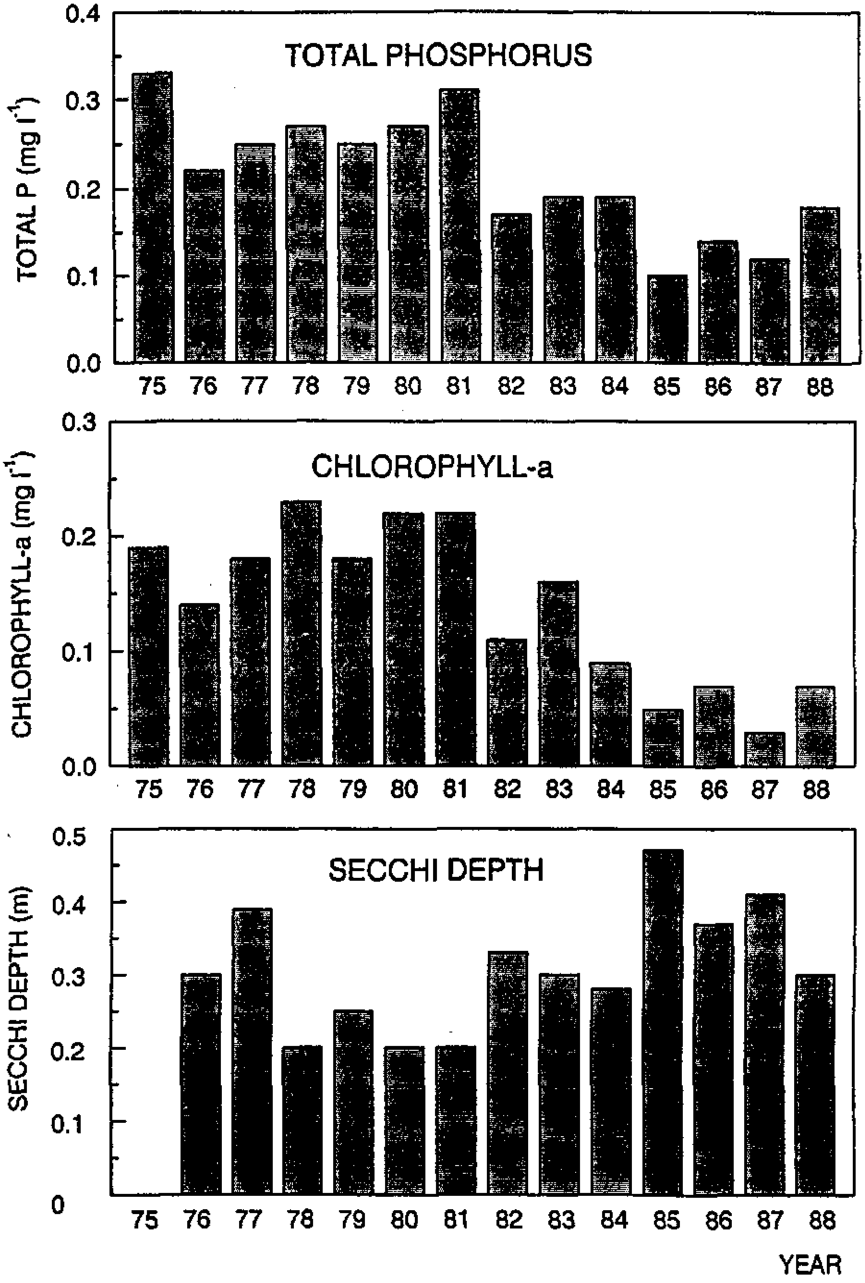


Fig. 1. Summer averages of total phosphorus, chlorophyll-a and Secchi depth.

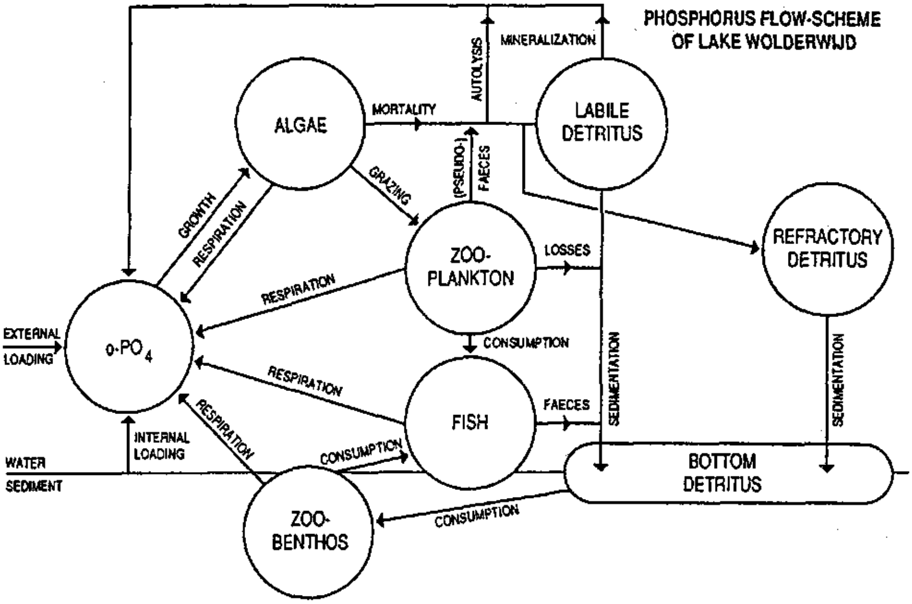


Fig. 2. Schematic representation of phosphorus flow through the food web of lake Wolderwijd/Nuldernauw.

External loading

We used the average value of 1979, 0.4 mg P m^{-3} d^{-1} (PER, 1982). This figure is also more or less valid for later years. As most of the outflow of water in summer is by evaporation and percolation, the outflow of phosphorus is negligible.

Phosphorus release from the sediments

In 1988, during a bloom of cyanobacteria, an average release rate of 3 mg P m^{-3} d^{-1} was measured using the intact core method described by Boers & Van Hese (1988). We assumed this value to be valid for 1981 as well. Because a reduction in organic loading on the sediment will decrease the release rate (Boers & Van Hese, 1988), the rates in 1987, when cyanobacteria were absent, and after biomanipulation can be expected to be lower than the measured value. We assumed the release rates to be 1.5 mg P m^{-3} d^{-1}.

Table 1. Some parameters for algae as the average for the growth season, estimated for three different conditions.

		1981	1987	after treatment
cyanobacteria	(%)	100	30	0
chlorophyll-a	(mg m^{-3})	230	32	20
C : Chl	(w/w)	40	35	35
C : P	(w/w)	45	45	45
optimum light intensity	(W m^{-2})	22.9	30	40
extinction	(m^{-1})	7.2	2.9	1.2
maximum growth rate	(d^{-1})	1.7	2.25	2.25
gross growth rate	(d^{-1})	0.18	0.54	0.86
respiration	(d^{-1})	0.05	0.16	0.20

Phytoplankton (Table 1)

Phytoplankton biomass was calculated from chlorophyll-a data and C:chlorophyll-a and C:P ratios (Los et al., 1988). For the situation after biomanipulation, a biomass of 20 mg chlorophyll-a m^{-3} is assumed. The relative biomass of cyanobacteria was available from biovolume determinations. For 1981, maximum growth rate and optimum light intensity for growth were calculated from primary production data (Van Duin, 1985), using the Steele equation for light-limited algal growth. Because far less cyanobacteria were present in 1987 and (hypothetically) after biomanipulation and because green algae have higher maximum growth rates than cyanobacteria, we used somewhat higher values for these cases. Extinction coefficients of the water were estimated from Secchi depth, assumed to be 1 m after biomanipulation. From these data we calculated the average gross growth rate in the water column. No corrections were made for any nutrient-limited growth; Gulati & Kleiman (1989) and Van Donk et al. (1989) reported high growth rates in the biomanipulated lakes Bleiswijkse Zoom and Zwemlust, which also had low dissolved nutrient concentrations. Respiration rates for cyanobacteria and other algae are from Zevenboom (1980). Actual rates were corrected for the relative biomass of cyanobacteria. We assumed that carbon and phosphorus are taken up and lost in the same ratio as present in the algae. Mortality of algae is estimated by difference, assuming zero population growth:
growth = respiration + grazing + mortality.

For grazing, see the zooplankton compartment. Mortality produces detritus.

Table 2. Some specific ingestion and growth rates of Daphnia spp., calculated for animals with a bodyweight of 5 μg C.

species	ingestion* (mg C mg C^{-1} d^{-1})	growth*	method	reference**
D. rosea	0.8	(0.19)	^{14}C in laboratory	(1)
D. pulicara	0.6	0.17	laboratory culture	(2)
D. thorata	0.6	0.17	laboratory culture	(2)
D. pulex	(0.95)	0.2-0.3	laboratory culture	(3)
D. pulex	(0.95)	0.2-0.3	field observations	(4)
D. longisp.	(0.75)	0.12-0.22	field observations	(4)
D. magna	(1.1)	0.30	laboratory culture	(5)
D. galeata	(0.66)	0.13	field observation	(6)
D. hyalina	(0.47)	0.06	field observation	(6)
natural popul.	1.6	0.51	^{14}C lake Zwemlust 1987	(7)
"	1.0	0.28	^{14}C lake Zwemlust 1988	(7)
"	2.6	1.1	^{14}C Lake Loosdrecht	(8)
"	0.6	0.38	^{14}C Lake Vechten	(9)
"	2.6	1.3	^{14}C Bleisw. Zoom untreated	(10)
"	0.6	0.39	^{14}C Bleisw. Zoom treated	(10)

*: Figures between parentheses were calculated using a respiration of 0.13 d^{-1} and an assimilation efficiency of 40%.

**: (1): DeMott, 1982, (2): Infante & Litt, 1985; (3): Langeland et al., 1985; (4): Bengtsson, 1987; (5): Enserink, 1989; (6): Geller, 1989; (7): Van Donk et al., 1989; (8): Van Liere et al., 1986; (9): Gulati et al., 1982; (10): Gulati and Kleiman, 1989.

Zooplankton

Zooplankton plays a key role in the food web; its grazing on algae may be an important loss process. The nutrients stored in zooplankton biomass after grazing disappear into the food web and are no longer available for algal growth. For both 1981 and 1987 zooplankton counts were available. After biomanipulation, the biomass is assumed to be equal to that in an experimental pond in lake Wolderwijd (Meijer & Breukelaar, 1988), from which fish were removed in 1987. The two most important species are *Daphnia hyalina* and *Bosmina longirostris*. We assumed their average body dry weight to be 6 and 0.6 μg, respectively (Gulati et al., 1981). The assumed C:P ratio is derived from Gulati et al. (1981).

The assimilation efficiency of the ingested food is about 40% (Gulati et al., 1982; Manca & De Bernardi, 1987) and we assumed the 60% egested to be detritus with the same properties as detritus produced directly from algae. Respiration of zooplankton is 10 - 15 % (average 13 %) of biomass d^{-1} (Gulati et al., 1982). We assumed that phosphorus is lost in the same C:P ratio as present in the animals. Den Oude & Gulati (1988) found the same phosphorus excretion rates by direct measurement. The final important parameters are specific ingestion rate and, related to this and to assimilation efficiency and respiration rate, the specific growth rate (growth = assimilation efficiency * ingestion - respiration).
Low growth rates, less than 0.3 d^{-1}, resulted from field and laboratory observations of biomass changes (Table 2). High ingestion rates, and therefore high growth rates of up to 1 d^{-1} are reported by Gulati and co-workers, using food labeled with $H^{14}CO_3$ (Table 2).

Preliminary calculations with these high growth rates led to very unbalanced budgets; much more zooplankton biomass was produced than the fish could eat and the zooplankton ingested more food than was produced. The discrepancy between the two groups of observations appeared to be due to differences in the quantity of available food.

It is necessary to specify the available food unequivocally to calculate correctly the specific ingestion rate from the ^{14}C accumulation rate in the animals (Gulati et al., 1982). Gulati and co-workers used particulate organic carbon < 33 μm as available food.

Table 3. Specific ingestion and growth rates of zooplankton (d^{-1}) in some Dutch lakes.

case	ingestion*		growth*		concentrations(mg C l^{-1})		
	(1)	(2)	(1)	(2)	algae	seston<33μm	zoopl
Zwemlust 1987	1.60	0.68	0.51	0.14	0.32	0.75	0.47
Zwemlust 1988	1.03	0.51	0.28	0.07	0.27	0.55	0.33
Lake Loosdrecht	2.56	1.07	0.90	0.30	6.50	15.50	0.48
lake Vechten	0.56	0.38	0.10	0.02	0.30	0.44	0.16
Bleiswijkse Zoom untreated	2.64	1.32	0.93	0.40	5.00	10.00	0.59
Bleiswijkse Zoom treated	0.64	0.39	0.12	0.03	1.10	1.80	0.55

* (1) according to authors; (2) recalculated assuming only algae are suitable food (see text).

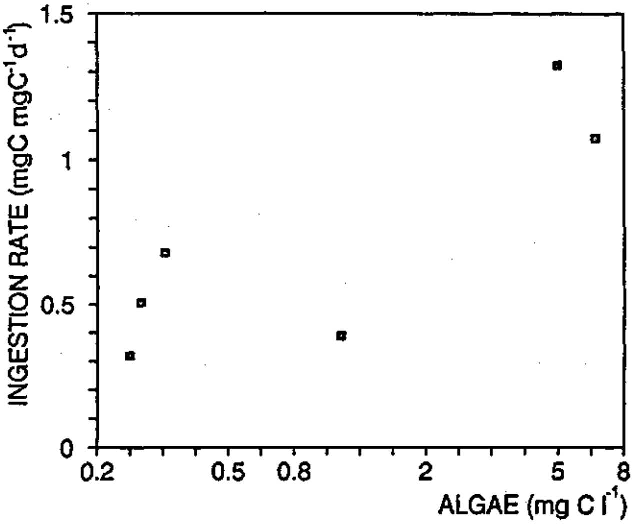


Fig. 3. Specific ingestion rate of zooplankton as a function of algal concentration.

It is doubtful whether all this carbon became labeled during its few days in contact with $H^{14}CO_3$, as most of the material consisted of refractory detritus. We therefore recalculated ingestion rates from data given by Gulati and co-workers, assuming that only algae are ingested and assimilated and using a C:chlorophyll-a ratio of 35 (Table 3). The specific production rates from these recalculations are in the range 0.1 - 0.4 d^{-1}. Ingestion and growth rates are functions of the food concentration (Fig. 3) and the critical food concentration for maximum growth is 1 - 1.5 mg C l^{-1}, a value also reported by Persson (1985). The maximum specific ingestion rate is 1.1 mg C mg C^{-1} d^{-1} and the maximum growth rate 0.3 d^{-1}.

The ingestion and growth rates are limited by the food concentration at low concentrations and, therefore, we used somewhat lower ingestion rates for 1987 and after biomanipulation. Table 4a summarizes the parameters for the zooplankton pool.

Detritus (Table 4b)

At death, a substantial portion of the nutrients present in algal cells is released directly by autolysis (Brinkman & Van Raaphorst, 1986). We assumed this to be 35% (Los et al., 1988). The remaining particulate organic matter is detritus, consisting of many compounds with highly variable mineralization rates.

Table 4. Some parameters for (a) zooplankton and (b) detritus estimated for three different conditions.

		1981	1987	after treatment
(a) ZOOPLANKTON				
biomass	(gC m^{-3})	0.13	0.34	0.58
specific ingestion rate	(d^{-1})	1.1	0.9	0.6
C : P	(w/w)	42	42	42
respiration rate	(d^{-1})	0.13	0.13	0.13
assimilation efficiency	(%)	40	40	40
(b) DETRITUS				
mineralization	(d^{-1})	0.5	0.5	0.5
sedimentation	(d^{-1})	0.12	0.12	0.3
fraction labile detritus	(-)	0.9	0.62	0.5

In addition to mineralization, detritus is removed from the water column by sedimentation. Lacking a cellulose cell wall, detritus from cyanobacteria has less resistance to mineralization than detritus from other algae, such as greens. The properties of different forms of detritus were schematized by defining two types of detritus, a labile type with a mineralization constant of 0.5 d^{-1} (Jørgensen et al., 1986) and a stable type with a mineralization constant of 0. We assumed that 90% of the detritus from cyanobacteria is labile (Gunnison & Alexander, 1975) and that 50% of the detritus from other algae is labile (Jewell & McCarty, 1971).

The net sedimentation rate of particulate suspended matter in shallow, wind-exposed lakes is low, due to frequent resuspension by wind action. Van Straten (1986) calculated a net sedimentation rate for particulate phosphorus in lake Veluwemeer of 0.02 m d^{-1}. This figure includes the phosphorus in living algae and is difficult to interpret in terms of sedimentation rate of detritus. A sedimentation rate for detritus of 0.15 m d^{-1} was found by calibration of the eutrophication model JSBACH in lake Veluwemeer (Los et al., 1988). We assumed a net sedimentation rate for detritus of 0.18 m d^{-1}, or a loss rate of 0.12 d^{-1}. After biomanipulation, the biomass of submerged macrophytes is expected to increase, resulting in a decrease of the influence of water turbulence on sediments. The effect of this is an increased net sedimentation rate. We assumed that the rate will increase to 0.45 m d^{-1}, representing a loss rate of 0.3 d^{-1}. The concentration of labile detritus was calculated from the steady-state condition. The concentration of stabile detritus was not calculated.

Table 5. Compilation of phosphorus excretion rates by fish (mg P m^{-3} d^{-1}), at a population density of 10 g fresh weight m^{-3}, a water depth of 1.5 m and an average individual weight of 200 g.

Fish Species	Excr. Rate	Method	Reference*
Carp	0.67	Enclosures	(1)
Carp	0.52-0.76	Short term excretion	(1)
Carp	0.79	Long term excretion	(1)
Bream	0.67	Enclosures	(2)
Yellow perch	0.76	Feeding rates	(3)
Bluegill sunfish	0.53	P balance of fish	(4)
MEAN:	0.67		

*1: Lamarra, 1975; 2: Andersson et al., 1988; 3: Nakashima & Leggett, 1980; 4: Kitchell et al., 1975.

Fish (Table 6a)

The fish population in the lake consists mainly of bream (*Abramis brama*, more than 70 %), together with smaller amounts of roach (*Rutilis rutilis*; about 20%) and pikeperch (*Stizostedion lucioperca*, about 2%). There are some commercial fisheries for eel and pikeperch.

Fish biomass in the lake is still an object of debate. The biomass was estimated at 300 kg fresh weight ha^{-1} in 1981, 150 kg in 1987 (Backx, 1989) and will be reduced to a biomass of 50 kg ha^{-1} during the proposed biomanipulation. Dry weight, dry weight:C and C:P ratios are derived from Penczak & Tatrai (1985). The influence of fish, and especially bottom-feeding fish such as bream, on the nutrient cycling in shallow lakes is one of the most important items in the discussion of effects of biomanipulation. Due to their bottom-feeding behavior, these fish stir up a lot of sediment. This is believed to increase the release of nutrients by sediments. In addition, their excretion of nutrients itself is a transport mechanism of nutrients from sediment to water (Lamarra, 1975; Nakashima & Leggett, 1980; Tatrai et al., 1985). Many experiments have been performed on both types of effects. Table 5 is a summary of some of the results.

The studies of Lamarra (1975) on carp, using both enclosures and direct measurement of excretion rates, indicate that the combined effect of bottom-stirring and excretion is just as large as the excretion alone. This is supported by other data given in the table and, therefore, we ignored the bottom-stirring effect and used the average given in Table 5 for our excretion estimate.We assume that

Table 6. Some parameters for (a) fish and (b) zoobenthos estimated for three different conditions.

		1981	1987	after treatment
(a) FISH				
biomass	(kg ha^{-1})	300	150	50
dry weight	(% of fresh wt.)	25	25	25
C	(% of DWT)	42.5	42.5	42.5
P	(% of DWT)	2.6	2.6	2.6
excretion	(mgP m^{-3} d^{-1})	1.4	0.7	0.24
assimilation efficiency	(%)	75	75	75
growth rate	(d^{-1})	0	0	0
(b) ZOOBENTHOS				
density	(ind m^{-2})	500	500	1000
Dry weight	(mg ind^{-1})	4	4	8
C:P	(w/w)	50	50	50
DWT:C	(w/w)	2	2	2
excretion	(mgP m^{-3} d^{-1})	0.7	0.7	1.4

bream diet consists of 25% zooplankton and 75% zoobenthos, both before and after the proposed biomanipulation.

Fish biomass has decreased during the years considered. Whether this was caused by food limitation or by predation is unknown. Thus, no net growth (which may be 0.5 - 1 y^{-1}; Cazemier, 1982) is assumed and total food uptake was set equal to excretion, using an assimilation efficiency of 75% (Nakashima & Leggett, 1980). The other 25 % is egested as faeces. We assumed this to become bottom detritus. Table 6a summarizes the parameters for the fish pool.

Zoobenthos (Table 6b)

In lake Wolderwijd/Nuldernauw, zoobenthos consists mainly of *Chironomus plumosus* (Naber, *pers. comm.*). Its biomass is known to vary greatly in time and space. The average population density is estimated at 500 individuals m^{-2}, the average biomass at 4 mg per animal (Gallep et al., 1978) and the P:dry weight ratio at 0.01 (Nakashima & Leggett, 1980). We assume that population density will double as a result of biomanipulation. The release of phosphorus from the sediments due to excretion of and bioturbation by zoobenthos, is estimated at about 0.7 before and 1.4 mg P m^{-3} d^{-1} after biomanipulation (Gallep et al., 1978; Gardner et al., 1981; Nalepa et al., 1983; Starkel, 1984 and Andersson et al., 1988). We assume that zoobenthos feeds on bottom detritus, but we did not attempt to estimate this process.

Macrophytes

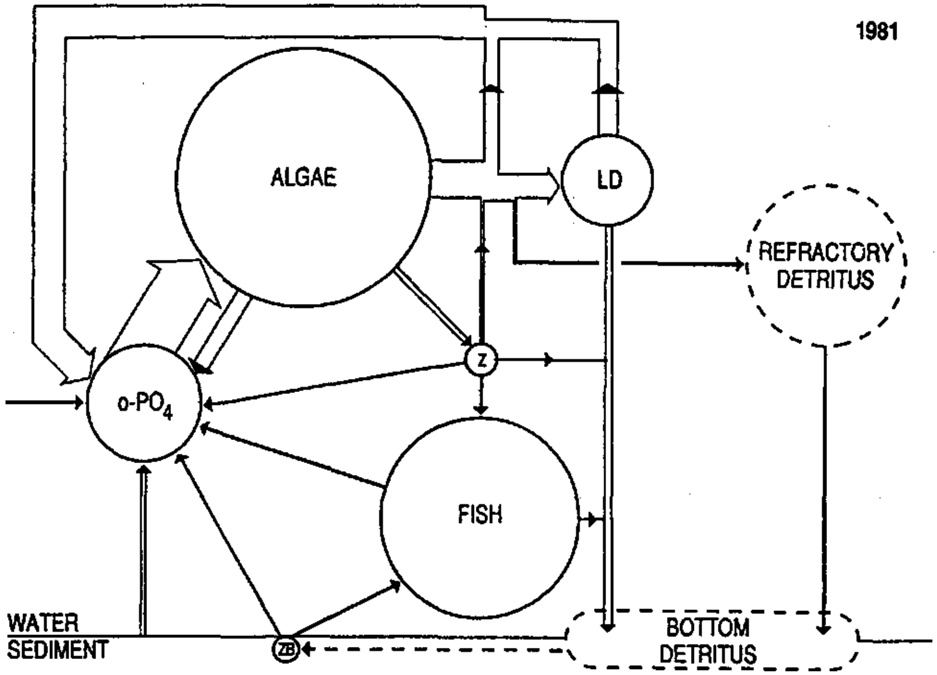
At low dissolved nutrient concentrations in the water column, macrophytes take their nutrients from the sediments (Carignan & Kalff, 1982). The biomass increase of the macrophytes is believed to be modest: 40% of the lake will be covered at an average density of only about 30 g m^{-2} in the overgrown areas. At death, a proportion of the nutrients in macrophytes will be released to the water column, but not until after the growing season. Therefore, we neglected this contribution of macrophytes to the phosphorus cycle of the lake.

9.4 RESULTS AND DISCUSSION

The phosphorus flow schemes for the three years are presented in Fig. 4. Table 7 summarizes the pool sizes and the fluxes between them. Although rather rough assumptions had to be made with respect to several crucial parameters, the difference between the orthophosphate uptake by the algae and the supply of this compound from various sources, determined independently, turns out to be less than 5 % in every case.

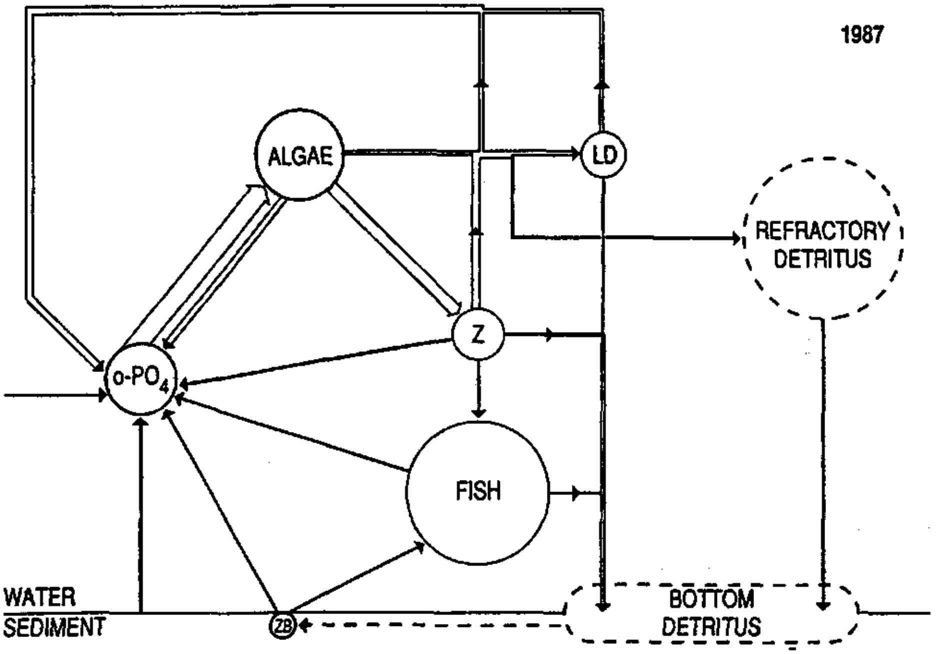
In all cases, most of the phosphorus needed for algal growth is produced within the food chain by excretion, autolysis and mineralization of detritus (Table 8). Internal loading from the sediment and, to a lesser extent, excretion by animals also contribute significantly. External loading is not important, but in the long run it determines the total nutrient concentration in the water.

From our analysis, fish do not appear to play a major role in nutrient cycling in a shallow lake. A large proportion of the total amount of phosphorus in the water column is stored in fish, but the turnover rate is very slow, compared to the phosphorus in phytoplankton or zooplankton. The decreased excretion by fish between 1987 and after biomanipulation is compensated by increased excretion by its most significant food source, zoobenthos. Three processes determine the recycling of nutrients in the water column: the production of labile detritus, its mineralization and its net sedimentation. These are also the processes for which the least detailed information is available. There is little doubt that detritus derived from cyanobacteria is less resistant to mineralization than that from other algae. How much less is uncertain. The ratio between the process constants for mineralization and net sedimentation determines which portion of the nutrients present in labile detritus is returned into the water column. We do not have reliable values for either of these constants.



1981

ALGAE
LD
REFRACTORY DETRITUS
Z
o-PO$_4$
FISH
WATER
SEDIMENT
ZB
BOTTOM DETRITUS



1987

ALGAE
LD
REFRACTORY DETRITUS
Z
o-PO$_4$
FISH
WATER
SEDIMENT
ZB
BOTTOM DETRITUS

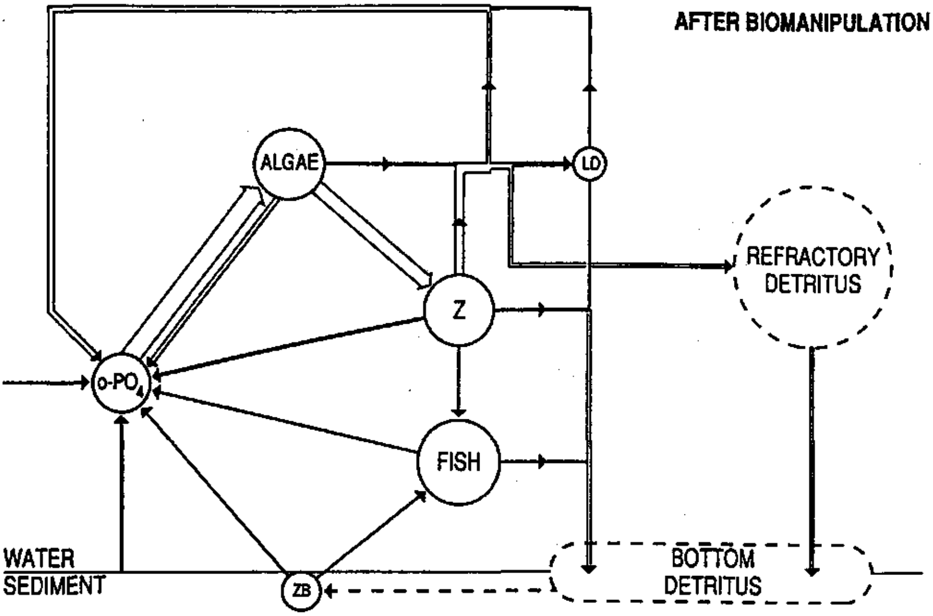


Fig. 4. Phosphorus flow through the food web of lake Wolderwijd/Nuldernauw (a) in 1981, (b) in 1987 and (c) after biomanipulation. Areas of circles are proportional to poolsizes, width of arrows are proportional to fluxes.

Nevertheless, the values used in this study seem to be reasonable and they yielded balanced phosphorus budgets. More important than the values of these parameters, however, are their changes after biomanipulation. Undoubtedly, the net sedimentation rate will increase when a larger area is covered by macrophytes. We assumed the loss rate due to sedimentation to increase from 0.12 to 0.30 d^{-1} and this led to a balanced phosphorus budget after biomanipulation. A further increase in sedimentation will decrease the availability of phosphorus for the phytoplankton and thus yield a smaller phytoplankton biomass. A smaller increase in sedimentation rate would have the opposite effect.

Two changes in the ecosystem appear to be important for phosphorus cycling. The first is the shift from cyanobacteria to greens. This is accompanied by a decrease in the contribution of phosphorus formed by regeneration within the food web to the total supply of the algae from 85 % in 1981 to 75 % in 1987. The main reason for this is the increased production of refractory detritus that is subsequently removed from the water column by sedimentation. This is confirmed by the lower total phosphorus concentrations in the water column in 1987 (Fig. 1).

Table 7. The most important pools (in mg P m^{-3}) and fluxes (in mg P m^{-3} d^{-1}).

	year		
	1981	1987	after treatment
ALGAE			
biomass	200	25	14
growth rate	36	13.5	12
mortality	27	2.3	0.9
respiration	10	3.9	2.8
ZOOPLANKTON			
biomass	3.1	8.1	14
grazing on algae	3.4	7.3	8.3
production of detritus	1.3	2	5
excretion	0.4	1.1	1.8
predation by fish	0.45	0.25	0.07
growth rate	0.55	1.7	1.4
DETRITUS			
production rate	25	7	6
autolysis	9	2.4	2.1
production rate of labile detritus	14	2.7	1.9
concentration of labile detritus	23	4.4	2.4
mineralization	12	2.2	1.2
sedimentation	2.8	0.5	0.7
FISH			
biomass	120	70	20
excretion	1.3	0.75	0.22
ZOOBENTHOS			
biomass	15	15	30
excretion	0.67	0.67	1.34
predation by fish	1.3	0.75	0.22
OTHER SOURCES			
internal loading	3	1.5	1.5
external loading	0.4	0.4	0.4

Table 8. Relative contributions of different sources to the phosphorus supply of the phytoplankton (percentages of total supply).

	1981	1987	after treatment
external	1.1	3.0	3.3
internal	8.3	11.1	12.5
fish	3.7	5.6	1.9
zoobenthos	1.9	5.0	11.2
regenerated	85.0	75.4	71.1

After biomanipulation, the relative growth rate and thus the need for phosphorus by phytoplankton increases, but the detritus formed has a higher sedimentation rate, causing a further decrease in the contribution of regenerated phosphorus to about 70%. The supply of phosphorus from "external" sources is virtually the same: the decreased contribution of excretion by fish is compensated by the increased excretion by zooplankton and zoobenthos.

The availability of phosphorus after biomanipulation strongly depends on the net sedimentation rate of the detritus that is formed in the water column. Any increase in loss by sedimentation will decrease the amounts of nutrients regenerated in the watercolumn by mineralization.

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CHAPTER 10

SUMMARY AND CONCLUSIONS

SUMMARY

Chapter 1. Introduction: Eutrophication is one of the world's major water quality problems. Attempts to alleviate eutrophication of lakes have involved the control of phosphorus loadings. In such cases, an internal loading of phosphorus from the sediments may retard an improvement of the water quality. Chapters 2 - 5 deal specifically with the sediments of Lake Loosdrecht.

Chapter 2. Distribution and forms of phosphorus in the sediments of the Loosdrecht Lakes (the Netherlands): The phosphorus loading entering the Dutch Lake Loosdrecht was reduced in 1984. A survey of the sediments of this lake indicated that an enrichment of these sediments with phosphorus was limited to the area near the former inlet of polluted water from the River Vecht. In most other areas the phosphorus accumulation in the upper 18 cm was 10 - 15 g P m^{-2}, equal to the external P loading of approximately one decade. This is probably due to the transport of phosphorus from the surficial sediments with the percolating seepage water. A rough estimation indicates that the amount of phosphorus carried away with this seepage compensates for the external loading. Results of selective extractions, desorption experiments and bio-assays all indicate that 5 % or less of the phosphorus in the upper sediment layers is "available" for algal growth.

Chapter 3. Unmasking the particulate organic matter in a lake ecosystem: origin and fate of POM in the shallow eutrophic Loosdrecht Lakes: The sediments of Lake Loosdrecht consist for over 50 % of organic matter. Pyrolysis mass spectroscopical analysis indicated that over 95% of this organic matter is old macrophyte debris, probably originating from the peat deposits in the lake area. In winter, this material also contributes significantly to the seston in the water column. In summer the seston consists almost entirely of algal material. However, only traces of this latter material could be detected even in the upper mm of the sediments, suggesting that the influx of algal matter in the sediments is small or that a fast degradation of the material reaching the sediments takes place.

Chapter 4. Phosphorus release from the peaty sediments of the Loosdrecht Lakes (the Netherlands): The release of phosphorus from the sediments of Lake Loosdrecht was studied in some detail using continuous flow reactors. The highest release rates, up to about 4 mg P m^{-2} d^{-1}, were found in summer and the lowest, less than 0.5 mg P m^{-2} d^{-1}, were measured in winter. Temperature and downward seepage are the two most important factors controlling release rates. pH of the water column, which many other researchers found to be an important controlling factor, did not play any role in Lake Loosdrecht. The influence of temperature and seepage were more pronounced in summer than in winter. The magnitude of the release rate and the influence of temperature and seepage could be largely explained by a simple steady-state model based upon mineralization and precipitation processes. According to this model, the phosphorus release from the sediments of Lake Loosdrecht is mainly governed by mineralization processes. Retardation of phosphorus by precipitation plays only a minor role.

Chapter 5. Ion concentrations in interstitial waters as indicators for phosphorus release processes and reactions: Processes governing the release of phosphorus in the sediments of Lake Loosdrecht were studied in more detail using pore water concentrations of phosphorus, ammonium, iron and DOC and pH. The local differences in pore water composition were much larger than those in sediment composition. So, pore water concentrations are much more sensitive indicators for processes in the sediments than sediment composition. From the close correlation between phosphorus and ammonium concentrations it was concluded that mineralization is the dominant process regulating phosphorus concentrations in the pore waters. Possibly, also precipitation of vivianite plays a role. Finally, several indications were found that the large amounts of refractory organic matter in the sediments of Lake Loosdrecht limit the availability of iron for binding of phosphorus.

Chapter 6. The influence of pH on phosphate release from lake sediments: The release of phosphorus from the sediments is often believed to be increased by a high pH in the water column. This is usually attributed to a decreased adsorption capacity for phosphate of iron(III)oxyhydroxydes at the sediment-water interface. This mechanism is commonly studied in laboratory experiments in which the pH of the water column is manipulated by titration with NaOH. In nature, however, pH is increased by a reduced partial CO_2 pressure caused by uptake of CO_2 by the phytoplankton. This process was simulated in the laboratory in continuous flow reactors by stripping the CO_2 from the air which was lead through the water column. In the latter case the phosphorus release rate increased much less than when using the traditional experimental setup with NaOH. Measurements of pH gradients near the sediment-water interface showed that when using NaOH additions the high pH in the water column penetrated much deeper in the sediments than when using CO_2 stripping. Addition of NaOH increases the alkalinity, and the transport of alkalinity from the sediments to the water reduces or even reverses in direction. By removing CO_2, the alkalinity is not changed or eventually reduced by precipitation of calcite.

Chapter 7. Lake restoration: estimation of internal phosphorus loading after reduction of external loading from sediment data: From literature data on a number of lakes with reduced external phosphorus loadings it was concluded that in most cases an annual net loading from the sediments takes place during several years. For the limited number of lakes for which sediment data were available, the internal loading rate was found to be highly significantly related to the phosphorus content and the P/Fe ratio in the sediment. These relationships can help to predict the internal loading rate, to be expected after reduction of the external loading.

Chapter 8. Phosphorus fixation with iron(III)chloride: a new method to combat internal phosphorus loading in shallow lakes?: The traditional method to speed up the recovery of a lake with a significant internal loading is to remove the phosphorus rich upper sediment layers. However, this method is costly and time consuming. Treatment of the sediments with phosphorus binding compounds might be an alternative. Iron(III)chloride is a candidate, as it is a natural phosphorus-binding agent and non-toxic. Laboratory experiments indicated that addition of at least 100 g Fe m^{-2} to lake sediments will strongly decrease the phosphorus release rate. The sediments of the shallow lake Groot Vogelenzang were treated with 100 g Fe m^{-2}, resulting in an immediate improvement of the water quality. This improvement lasted for only three months. A large external phosphorus loading, caused by rapid flushing with water from the surrounding lakes is held responsible for this failure. Nevertheless, release experiments and phosphorus budget calculations both indicated that the phosphorus retention in the sediments of lake Groot Vogelenzang had increased with about 3 mgP m^{-2} d^{-1}.

Chapter 9. Changes in phosphorus cycling in a shallow lake due to foodweb manipulations: Biomanipulation is a recently developed method to improve water quality in lakes by removing undesired fish species and reintroducing other, desired but lacking species. The goal of this lake restoration technique is to improve the predation on whitefish and thereby to decrease the predation of whitefish on zooplankton. Application of biomanipulation in small, shallow lakes usually results in a highly increased Secchi depth and strongly reduced algal biomass. In this chapter, the changes in the phosphorus cycling of the shallow lake Wolderwijd/Nuldernauw after biomanipulation were quantified. Before biomanipulation, most of the phosphorus in the food web is accumulated in fish, but a small portion is recycled rapidly in the water column. Sedimentation of detritus is the most important loss process. No evidence could be found for the hypothesis that the bottom stirring activities of fish enhance the phosphorus release.

The availability of phosphorus for phytoplankton may decrease after biomanipulation for two reasons. The first is that the detritus formed from green algae is more refractory than the detritus from cyanobacteria. Therefore, the phosphorus content of cyanobacteria is recycled more rapidly. Cyanobacteria will probably disappear after biomanipulation due to the improved light climate. The second reason is that the increased bottom area covered with submerged macrophytes enhances the net sedimentation of detritus from the water column and concomittantly the regeneration rate of phosphorus in the water column decreases. These changes in the phosphorus cycling in the lake may reinforce the success of biomanipulation.

CONCLUSIONS

Undoubtedly, the release of phosphorus from sediments forms an important part of the phosphorus cycling in shallow lakes. In the Loosdrecht Lakes, this release was found to be of the same magnitude as the external loading, although only a small proportion of the sediment phosphorus is "exchangeable". Mineralization of organic phosphorus reaching the sediments is the most important process for the phosphorus release. The availability of iron in the sediments of these lakes appeared to be an important factor in the retention of the phosphorus that is released by mineralization. The presence of large amounts of refractory organic matter in the sediments of the Loosdrecht Lakes seems to limit the potential of iron to bind phosphorus. The sources and fate of iron in aquatic sediments need further research. Probably, the availability of iron for the binding of phosphate is related to the cycling of other elements, such as sulfur, in the sediments.

Just as important for the phosphorus cycling in a shallow lake is the settling to the sediments. The characterization of the particulate organic matter in the sediments of the Loosdrecht Lakes indicated that either the influx of algal matter into the sediments is very small or that this material is mineralized very rapidly. Possibly, the slow recovery of Lake Loosdrecht and other shallow, wind-exposed lakes is not only caused by internal phosphorus loading, but also by a poor sedimentation of particulate phosphorus from the water column.

A quantification of the cycling of phosphorus through the food web revealed that changes in the sedimentation process may affect the availability of phosphorus to algae. In turn, the sedimentation is influenced by the presence of submersed macrophytes.

Attention for the environmental conditions is necessary for a proper quantification of the internal loading rates. Some of the relevant conditions were discussed in this thesis. Resuspension of bottom material by benthivorous fish is not of any importance for the release of phosphorus from the sediments. The influence of the pH in the water column was found to be less important than reported by other researchers. Temperature and the sedimentation of particulate organic matter are two reasons for release maxima in summer.

One of the most important questions in lake restoration is whether the improvement of the water quality will be delayed, following a reduction of the external loading. Although the results of the studies in Lake Loosdrecht indicate that the internal loading is of the same order of magnitude as the external loading, no direct proof of a delay of the recovery of the lake due to this internal loading could be found.

From literature data on a number of shallow lakes with reduced external phosphorus loadings it could be concluded that indeed initially a net internal loading may take place upon restoration. The magnitude of this internal loading is related to the phosphorus content of the sediments and to the P/Fe ratio in the sediment. This latter may be a measure of the residual phosphorus binding capacity of the sediments. As long as no other methods to predict the occurrence of internal loading are available, the relations found between internal loading and sediment composition may be used. The question to what extent chemical extractions, bio-assays or laboratory release experiments can be used to predict the behavior of a lake after a reduction of the external loading is an important but still unanswered one.

According to this study, upon restoration a net internal loading can be expected to take place already at a phosphorus content of the sediment of 1.4 mg P g^{-1}. So, internal loading will take place in most of the Dutch lakes after a decrease of the external loading. To what extent this internal loading will delay the improvement of the water quality, depends on other characteristics of the lake, as the residual external loading and the residence time. Although internal loading will not last forever, in a number of cases additional "sediment restoration techniques" will be needed to recover lakes within an acceptable space of time. As dredging of the upper sediment layers is extremely costly and time consuming, alternatives for this sediment restoration technique are needed. Fixation of phosphorus in the sediments with phosphorus binding chemicals may be an alternative. In this study, the availability of iron was found to be an important factor in the immobilization of phosphorus in freshwater sediments and addition of iron compounds to the sediments may strengthen this natural process. Although the method is promising, its suitability to reduce internal loading must still be proven. An important unanswered question is to what extent the added iron remains available for phosphorus binding.

DE AFGIFTE VAN OPGELOST FOSFAAT DOOR MEERBODEMS

SAMENVATTING

Hoofdstuk 1. Inleiding: Eutrofiëring, dat is een overmatige groei van algen, is één van 's werelds meest voorkomende waterkwaliteitsproblemen. De bestrijding van dit probleem vindt doorgaans, en ook in Nederland, plaats door vermindering van de toevoer van fosfaat naar de meren. In dergelijke gevallen kan de verbetering van de waterkwaliteit worden vertraagd door een nalevering van fosfaat door de waterbodem. De hoofdstukken 2 - 5 gaan over de Loosdrechtse Plassen.

Hoofdstuk 2. Verdeling en vormen van fosfaat in de bodem van de Loosdrechtse Plassen: De fosfaatbelasting op de Nederlandse Loosdrechtse Plassen is in 1984 verminderd. Een inventarisatie van de samenstelling van de bodem van dit meer liet zien dat in een klein gebied rond het voormalige inlaatpunt van fosfaatrijk Vechtwater de bodem verrijkt is met fosfaat. In de meeste andere delen van het gebied werd in de bovenste 18 cm van de bodem 10 - 15 g P m^{-2} gevonden, een hoeveelheid die gelijk is aan de aanvoer van fosfaat in één decade. Vermoedelijk worden aanzienlijke hoeveelheden fosfaat weer aan de bodem onttrokken door inzijgend grondwater.

Volgend uit zowel selectieve extracties, desorptie proeven als opname experimenten met algen is ongeveer 5% van de hoeveelheid fosfaat in de bodem uitwisselbaar.

Hoofdstuk 3. Ontmaskering van het particulair organisch materiaal in een meersysteem: oorsprong en lot van POM in de ondiepe eutrofe Loosdrechtse Plassen: Meer dan de helft van het bodemmateriaal in de Loosdrechtse Plassen is organisch materiaal. Volgens chemische analyses met behulp van pyrolyse massaspectroscopie bestaat dit organisch materiaal vrijwel geheel uit resten van macrofyten, waarschijnlijk afkomstig van de veenafzettingen in het plassengebied. 's Winters draagt dit materiaal ook in belangrijke mate bij aan het de samenstelling van het zwevend stof in de waterkolom. 's Zomers daarentegen, bestaat het zwevend stof vrijwel geheel uit algenmateriaal. Zelfs in de bovenste millimeter van het sediment konden slechts sporen algenmateriaal worden aangetoond. Dit betekent dat de aanvoer van dit materiaal naar de bodem gering is en/of dat het zeer snel wordt afgebroken.

Hoofdstuk 4. Fosfaat afgifte door de venige sedimenten van de Loosdrechtse Plassen: De nalevering van fosfaat door de waterbodem werd nader bestudeerd met behulp van continu doorstroomde afgifte reaktoren. De hoogste naleveringssnelheden, tot ongeveer 4 mg P m^{-2} d^{-1}, werden 's zomers gemeten en de laagste, minder dan 0,5 mg P m^{-2} d^{-1}, in de winter. De nalevering nam sterk af met een dalende temperatuur en door inzijgend grondwater met een snelheid van 1 cm

d^{-1}. De pH in de waterkolom speelde nauwelijks een rol. 's Winters waren de invloeden van de temperatuur en inzijgend grondwater het kleinst.

Zowel de grootte van de nalevering als de invloeden van temperatuur en inzijging konden grotendeels worden verklaard met behulp van een eenvoudig stationair model, dat gebaseerd is op mineralisatie- en precipitatie-processen. Volgens dit model wordt de nalevering in de Loosdrechtse Plassen vooral beheerst door mineralisatie. Retentie van fosfor door precipitatie speelt slechts een ondergeschikte rol.

Hoofdstuk 5. Ion concentraties in interstitieel water als indicatoren voor fosfaatafgifteprocessen en -reacties: De processen die de afgifte van fosfaat door de bodem van de Loosdrechtse Plassen bepalen werden nader onderzocht door de concentraties van fosfor, ammonium, ijzer en opgelost organisch koolstof en de pH in het poriënwater in het sediment te bestuderen. De locale verschillen in poriënwater samenstelling waren veel groter dan die in sedimentsamenstelling. Uit het sterke verband tussen de concentraties van ammonium en fosfor werd geconcludeerd dat mineralisatie het belangrijkste sturende proces is. Mogelijk speelt daarnaast precipitatie van vivianiet een rol. Tenslotte werden enkele aanwijzingen gevonden dat de grote hoeveelheden slecht afbreekbaar organisch materiaal in het sediment van de plassen de beschikbaarheid van ijzer voor de binding van fosfaat beperken, waardoor nauwelijks precipitatie van vivianiet plaatsvindt.

Hoofdstuk 6. De invloed van de pH op de fosfaatnalevering door waterbodems: Meermalen is aangetoond dat een hoge pH in de waterkolom de fosfaatnalevering bevordert. Dit wordt gewoonlijk toegeschreven aan een verminderde adsorptiekapaciteit voor fosfaat van de ijzer(III)oxyhydroxides die nabij de grenslaag tussen de bodem en het water aanwezig zijn. Dit mechanisme wordt doorgaans bestudeerd door in laboratoriumopstellingen de pH van de waterkolom te manipuleren door titratie met loog. In de natuur wordt echter de pH verhoogd door de opname van CO_2 door algen. Dit proces werd in het laboratorium nagebootst in continu doorstroomde afgifte reaktoren, waarbij de CO_2 uit de door de waterkolom geleide lucht werd verwijderd. Hierbij bleek de verhoging van de fosfaatnalevering veel minder groot te zijn dan bij de gebruikelijke experimentele methode met toevoeging van NaOH. Metingen van pH-profielen nabij de grenslaag tussen bodem en water toonden aan dat bij het gebruik van loog de hoge pH van de waterkolom veel dieper de bodem indrong dan bij verwijdering van CO_2. De verklaring hiervoor is dat bij toevoeging van loog tevens alkaliniteit wordt toegevoegd. Hierdoor neemt het transport van alkaliniteit van de bodem naar het water af of verandert zelfs van richting. Bij CO_2-verwijdering verandert de alkaliniteit niet of daalt eventueel door precipitatie van calciet. Hierdoor wijzigt het transport van alkaliniteit niet of wordt groter.

Hoofdstuk 7. Het herstel van meren: schatting van de na vermindering van de externe belasting optredende interne belasting uit sediment gegevens: Uit een literatuurstudie bleek dat na een vermindering van de externe belasting de kans op het optreden van een netto interne belasting op jaarbasis gedurende in ieder geval enkele jaren groot is. Voor het beperkte aantal meren waarvan sedimentgegevens beschikbaar waren, werden zeer significante relaties gevonden tussen de grootte van deze interne belasting enerzijds en het fosfaatgehalte of de P/Fe ratio in de bodem anderzijds. De gevonden relaties kunnen worden gebruikt om de grootte van de te verwachten netto interne belasting te schatten, vóórdat de externe belasting wordt gesaneerd.

Hoofdstuk 8. Fosfaatfixatie met ijzer(III)chloride: een nieuwe methode om interne belasting in ondiepe meren te bestrijden?: De gebruikelijke methode om het herstel te bespoedigen van een meer waarin een overmatige interne belasting optreedt is het verwijderen van de fosfaatrijke bovenste sedimentlaag. Deze methode is echter kostbaar en tijdrovend. Behandeling van de bodem met fosfaatbindende stoffen zou een alternatief kunnen zijn. IJzer(III)chloride komt hiervoor in aanmerking, omdat het van nature belangrijk is voor de binding van fosfaat en niet giftig is. Uit laboratoriumexperimenten bleek dat de fosfaatnalevering door sedimenten sterk vermindert door behandeling met tenminste 100 g Fe m^{-2}. De bodem van het plasje Groot Vogelenzang werd met deze hoeveelheid ijzerzouten behandeld en de waterkwaliteit verbeterde hierdoor meteen. Deze verbetering duurde echter slechts drie maanden. Dit is waarschijnlijk te wijten aan een nog grote externe fosfaatbelasting, veroorzaakt door een snelle doorspoeling met water van de omliggende meren. Niettemin lieten afgifte experimenten en balansberekeningen beide zien dat de vastlegging van fosfaat in de bodem van plasje Groot Vogelenzang met ongeveer 3 mg P m^{-2} d^{-1} was toegenomen.

Hoofdstuk 9. Veranderingen in de fosfaathuishouding in een ondiep meer door biomanipulatie: Biomanipulatie is een tamelijk recente methode om de waterkwaliteit van meren te verbeteren. Hierbij worden ongewenste vissoorten verwijderd en andere, gewenste maar ontbrekende, soorten uitgezet. Vooral brasem is ongewenst: brasem woelt tijdens het zoeken naar voedsel de bodem om en kan zwaar prederen op zoöplankton, waardoor de algenconcentraties verhoogd worden. In kleine meren heeft toepassing van biomanipulatie gewoonlijk een drastische verlaging van de algenbiomassa en een aanzienlijke verbetering van de zichtdiepte tot gevolg.

In dit hoofdstuk zijn de veranderingen in de fosfaathuishouding van het ondiepe meer Wolderwijd/Nuldernauw ten gevolge van biomanipulatie gekwantificeerd. Vóór de ingreep is het grootste deel van het fosfaat in de voedselketen aanwezig in vis en een klein deel circuleert snel door de waterkolom. Sedimentatie van detritus is de voornaamste afvoerpost. Er werd geen bewijs gevonden voor de veel gehoorde stelling dat de bodemwoelende activiteit van vis de fosfaatnalevering bevordert.

Na de ingreep kan de beschikbaarheid van fosfaat voor algen om twee redenen afnemen. Een eerste reden is dat het detritus dat uit groenalgen wordt gevormd moeilijker afbreekbaar is dan dat uit blauwalgen. Daardoor wordt de nutriënteninhoud van door blauwalgen gedomineerd fytoplankton gemakkelijker geregenereerd. Blauwalgen zullen na de ingreep waarschijnlijk verdwijnen ten gevolge van het verbeterde lichtklimaat. De tweede reden is dat ten gevolge van de toegenomen bedekking van de bodem met macrofyten de netto sedimentatie van detritus uit de waterkolom zal toenemen. Door deze veranderingen in de fosfaathuishouding kan de kans op succes van biomanipulatie groter worden.

CONCLUSIES

Zonder twijfel vormt de nalevering van fosfaat door de waterbodem een belangrijk onderdeel van de fosfaathuishouding in een ondiep meer. Deze nalevering is in de Loosdrechtse Plassen in dezelfde orde van grootte als de externe belasting. Opvallend daarbij is dat slechts een klein deel van het sediment fosfaat uitwisselbaar is.

Mineralisatie van gesedimenteerd organisch fosfaat is het belangrijkste proces van de fosfaatnalevering in deze plassen. Daarnaast is de beschikbaarheid van ijzer in de bodem van deze plassen een belangrijke factor in de retentie van het fosfaat dat bij mineralisatie vrijkomt. In de Loosdrechtse Plassen is ijzer, vermoedelijk door de aanwezigheid van grote hoeveelheden refractair organisch materiaal, slechts beperkt beschikbaar. Hieruit blijkt dat nader onderzoek nodig is naar de aanvoer van ijzer en andere fosfaatbindende stoffen en voor hun gedrag in de waterbodem. Vermoedelijk is voor de beschikbaarheid van ijzer voor de fosfaatbinding ook de zwavelcyclus van belang.

Even belangrijk voor de fosfaathuishouding in een ondiep meer is echter de sedimentatie naar de bodem. Uit een karakterisering van het particulair organisch materiaal in de bodem van de Loosdrechtse Plassen bleek dat òf de aanvoer van algenmateriaal naar de bodem gering is en/of dat dit materiaal in de bodem zeer snel afgebroken wordt. Mogelijkerwijs wordt het trage herstel van ondiepe, aan de wind blootgestelde meren niet alleen veroorzaakt door een interne fosfaatbelasting, maar ook door een gebrekkige sedimentatie van particulair fosfaat uit de waterkolom. Uit een onderzoek naar de circulatie van fosfaat door het voedselweb bleek eveneens dat veranderingen in de sedimentatie de beschikbaarheid van fosfaat voor algen kunnen beïnvloeden. De netto sedimentatie wordt op zijn beurt beïnvloed door de aanwezigheid van ondergedoken waterplanten.

Bij een kwantificering van de nalevering van fosfaat is aandacht voor de milieucondities nodig. In dit proefschrift worden enkele voorbeelden behandeld. Het eerder genoemde onderzoek naar de kringloop van fosfaat door de voedselketen liet zien dat, in tegenstelling tot hetgeen wel eens wordt beweerd, de opwerveling van bodemmateriaal door bodemwoelende vis de nalevering van fosfaat door de bodem niet beïnvloedt. Ook de invloed van de pH van de waterkolom, bleek minder belangrijk te zijn dan voorheen werd verondersteld. Andere factoren, namelijk de temperatuur en de sedimentatie van organisch materiaal, zijn ervoor verantwoordelijk dat de grootste fosfaatnalevering in de zomer wordt gevonden.

Eén van de belangrijkste vragen bij het opstellen van herstelprogramma's voor eutrofe meren is of er tengevolge van een interne fosfaatbelasting vanuit de bodem een vertraging van het herstel van de waterkwaliteit zal optreden. Hoewel uit het onderzoek in de Loosdrechtse Plassen bleek dat de interne belasting van dezelfde orde van grootte is als de externe belasting, kon voor dit meer niet echt worden aangetoond dat de interne belasting het herstel vertraagt. Uit literatuurgegevens van een aantal ondiepe meren waarvan de externe belasting is verlaagd, bleek dat er daarna meestal een netto fosfaatnalevering zal optreden. De grootte hiervan is gerelateerd aan het fosfaatgehalte en de P:Fe verhouding in de bodem. Zolang er geen andere methoden voorhanden zijn om het optreden van een interne belasting te voorspellen, kunnen deze relaties hiervoor worden gebruikt. Het is een belangrijke, maar nog altijd onbeantwoorde vraag in hoeverre technieken als chemische extracties, bio-assays en kolomproeven kunnen worden gebruikt om de respons van een meer op een vermindering van de externe fosfaatbelasting te voorspellen.

Indien een netto interne belasting al kan worden verwacht bij een fosfaatgehalte in de bodem van 1,4 mg P g^{-1}, zoals in deze studie is gevonden, dan zal de bodem van de meeste ondiepe eutrofe meren in Nederland fosfaat gaan naleveren zodra de toevoer wordt verminderd. In hoeverre hierdoor ook problemen met het herstel van een meer zullen optreden, is van geval tot geval verschillend. Dit hangt behalve van de grootte van de nalevering ook af van de resterende externe belasting en de verblijftijd. Hoewel een netto nalevering niet eeuwig zal duren, zijn in een aantal gevallen toch aanvullende bodemsaneringstechnieken nodig om binnen een redelijke tijd resultaat van de saneringsinspanningen te zien. Aangezien het verwijderen van de bovenste bodemlagen buitengewoon kostbaar en bovendien tijdrovend is, bestaat er behoefte aan alternatieve saneringsmethoden voor eutrofe waterbodems. Fixatie van het fosfaat in de bodem met behulp van fosfaatbindende stoffen kan zo'n alternatief zijn. In deze studie is aannemelijk gemaakt dat de beschikbaarheid van ijzer een belangrijke factor is voor de immobilisatie van fosfaat in waterbodems. Toevoeging van extra ijzer zou de natuur een handje kunnen helpen. De methode is veelbelovend, maar de bruikbaarheid om een interne fosfaatbelasting daadwerkelijk te verminderen moet nog verder worden aangetoond.

ABSTRACT

The release of phosphorus from sediments frequently is an important part of the phosphorus cycling in shallow, eutrophic lakes. The phosphorus release from the sediments of the Loosdrecht Lakes were studied in detail. Less than 5 % of the sediment phosphorus was exchangeable, probably due to a permanent downward transport of phosphorus from the sediments by seepage. From results of laboratory release experiments and pore water concentration patterns it was concluded that the release process is mainly governed by mineralization of organic matter. Retardation, e.g. by precipitation with Fe^{2+} plays only a minor role. This is probably due to the limited availability of iron in these sediments, caused by complexation with refractory organic matter. The release rates from these sediments are highest in summer, due to the high temperature, but also due to changed sediment properties. downward seepage increases the release rates.

Besides an enhanced temperature and also seepage, high pH in the water column promotes the phosphorus release. When this process is studied in the laboratory, pH should be regulated by decreasing the partial CO_2 pressure and not by adding NaOH.

Biomanipulation affects the cycling of phosphorus through the food web. The most imortant changes are a decreased storage of phosphorus in fish, an increased sedimentation due to an increased coverage of the sediments with macrophytes and a decreased availability of phosphorus after the disappearence of cyanobacteria.

After a reduction of the external phosphorus loading, the sediments may release phosphorus to the water column. The magnitude of this release is related to the phosphorus content and to the P/Fe ratio of the sediments.

If the recovery of a lake from eutrophication is delayed due to an internal loading, the internal loading may be combatted by phosphorus fixation, that is the addition of extra iron to the sediments. From laboratory experiments and a pilot project it was concluded that addition of 100 g Fe^{3+} m^{-2} strongly decreases the release rate. The treated lake did not recover, however, due to a short hydraulic residence time. The suitability of phosphorus fixation as an additional tool in eutrophication control needs further proof.

DANKWOORD

Heel goed herinner ik mij nog de dag, begin november 1989, dat ik ging solliciteren bij het Limnologisch Instituut in Nieuwersluis. Het was in het kader van een regeling voor tijdelijke arbeidsplaatsen voor werkeloze academici. Daags tevoren had ik het woord limnologie tevergeefs in het woordenboek opgezocht. Tot mijn vreugde, want vrijwilligerswerk doen is ook niet alles, werd ik toch aangenomen. Een wondere wereld ging open: fytoplankton, zoöplankton, hypolimnion, epilimnion, het was allemaal nieuw en het was ook allemaal even spannend. Ik hield me op het LI bezig met omzettingen van stikstof in het sediment, en dat was bekend terrein: chemische bepalingen ontwikkelen en uitvoeren, stoffenbalansen maken. Het heeft nog tot een wetenschappelijke publikatie geleid, maar die vindt u niet in dit proefschrift terug. Kennelijk had men bij het LI vertrouwen in mij, want nadat de tijdelijke arbeidsplaats was afgelopen mocht ik blijven om te werken aan de nalevering van fosfaat door de bodem van de Loosdrechtse Plassen en werd daarmee één van de eerste echte WOL-medewerkers. Opnieuw ging een wereld open: samenwerken in een groot team, monstertochten, plenaire WOL-vergaderingen met diskussies over licht- en fosfaatgelimiteerde algen, meedoen aan symposia, enzovoorts. Enkele van de resultaten van dat werk vindt u wel in dit proefschrift terug.

Maar ook daar kwam door een vertrek naar DBW/RIZA een einde aan. Het onderzoek bleef doorgaan, maar met een nieuwe invalshoek: werken op het grensvlak tussen onderzoek en beleid. Dit bracht nieuwe uitdagingen: de ontwikkeling van "normen" voor fosfaat in waterbodems en van nieuwe hersteltechnieken voor eutrofe meren. Ook enkele resultaten hiervan treft u in dit proefschrift aan.

Gedurende al die jaren heb ik met veel mensen te maken gehad. Sommigen van hen zijn co-auteur van de verschillende hoofdstukken, maar enkele anderen verdienen een aparte vermelding: Sikko Parma, Tom Cappenberg, Louis van Liere en niet te vergeten Henk Verdouw begeleidden mij op mijn ontdekkingsreis door de limnologie. Heb Roon, Ed Mariën, Nico Hafkamp, en Piet Schouten zorgden op het LI voor de nodige ondersteuning. Olaf van Hese heeft in al die jaren duizenden kolomproeven gedaan en talloze ander klussen verricht. Met zijn vertrek naar een andere afdeling moest aan onze samenwerking een einde komen.

Verschillende collega's hebben, vaak zonder het zelf te weten, een belangrijke invloed op mijn ontwikkeling gehad. Zonder volledig te willen zijn, moeten er toch enkele worden genoemd: Paul Behrens, Harry Hosper, Eric Jagtman, Sjoerd Klapwijk, Luc Mur, Marinus Quaak, Marien de Ruiter en mijn promotor, Bert Lijklema. Jan Leentvaar gaf het laatste beslissende zetje tot dit boekje. Van Nico de Rooij (WL) is de aanzet voor hoofdstuk 6 afkomstig.

Velen hebben op de achtergrond bijgedragen aan de totstandkoming van dit rapport door middel van type- en tekenwerk, monsternames, chemische analyses, etcetera. Mijn hartelijke dank hiervoor.

Huib Spee heeft meerdere avonden besteed aan het omzetten van een ruw idee in een omslag voor dit boekje. Ik vind dat hij er iets bijzonders van heeft gemaakt.

Tenslotte mag Afra natuurlijk niet onvermeld blijven. Volgens haar eigen zeggen heeft ze niet veel last van het schrijven van dit boekje gehad, maar bij tijd en wijle moet ze toch aanvaarden dat ik zo in mijn werk opga, dat ik alles om mij heen vergeet.

CURRICULUM VITAE

Paulinus Cornelis Maria Boers werd op 11 maart 1954 geboren in Rotterdam. Van 1966 tot 1971 bezocht hij het St. Fransiscus College in Rotterdam. Na het behalen van het HBS-B diploma werd in 1971 begonnen met de studie scheikunde aan de Rijksuniversiteit van Utrecht. In 1975 werd het kandidaats- en in 1979 het doctoraalexamen behaald met als hoofdvak analytische chemie en de bijvakken chemische levensmiddelenleer, chemie en samenleving en didactiek van de scheikunde.

Na het vervullen van de militaire dienstplicht trad hij op 15 december 1980 in dienst bij het Limnologisch Instituut in Nieuwersluis. Met enige tussenpozen bleef hij daar werkzaam tot september 1986. Aanvankelijk deed hij onderzoek naar de nalevering van ammonia door de bodem van de gestratificeerde zandwinput "Vechten". Vanaf 1982 werkte hij aan de nalevering van fosfaat door de bodem van de ondiepe Loosdrechtse Plassen.

Vanaf september 1986 werkt hij als projectleider hydro- en geochemie bij het Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwater behandeling, onderdeel van Rijkswaterstaat, te Lelystad en werkt ook daar aan de nalevering van fosfaat en stikstofverbindingen door waterbodems.