

REPORT OF INVESTIGATION

CONTROL OF RELEASE OF PHOSPHORUS
FROM SEDIMENTS OF THE
PEEL-HARVEY ESTUARINE SYSTEM

BY

PETER COATES

ISSUED UNDER THE AUTHORITY OF
THE DIRECTOR
GOVERNMENT CHEMICAL LABORATORIES
30 PLAIN STREET, PERTH
WESTERN AUSTRALIA, 6000

REPORT NO. 30

JANUARY 1985

C O N T E N T S

| | Page |
|--|-------|
| Summary | |
| 1. Introduction | 1 |
| 2. Methods | 2 |
| 3. Results and Discussion | 3 |
| a. Anaerobic sediment phosphorus release | 3 |
| b. Aluminium and iron salts | 5 |
| c. Oxygen | 6 |
| d. Nitrate | 8 |
| 4. Conclusion | 9 |
| 5. Acknowledgements | 10 |
| References | 11 |
| Figures 1-5 | 13-17 |

SUMMARY

The Report describes limited investigation of conditions controlling the behaviour of phosphorus in sediments of the Peel-Harvey estuary and comments on proposals for control of the phosphorus cycle by chemical means. The addition of aluminium and iron salts, oxygen and nitrate as means of controlling phosphorus release from estuarine sediments was investigated. The work is part of a comprehensive research programme involving State government departments, CSIRO and tertiary education institutions.

CONTROL OF RELEASE OF PHOSPHORUS FROM SEDIMENTS
OF THE PEEL-HARVEY ESTUARINE SYSTEM

1. INTRODUCTION

The Peel-Harvey Estuarine System is located south of Mandurah, Western Australia. It is a large shallow water body, covering an area of 130 km² with a volume of about 150 x 10⁶ m³.

Increasing amounts of algae have appeared in the estuary in recent years, affecting residential, recreational and commercial usage of the area. A report published in 1980 described the nature and cause of this algal problem¹. This concluded that the development of the problem had coincided with a large increase in plant nutrient input to the system, particularly phosphorus.

The catchment areas for the Harvey, Murray and Serpentine rivers which flow into the estuary include extensive farm land which receives regular applications of phosphatic fertilizers. Input of phosphorus to the estuary occurs mainly during a four month period of high river flow in winter. Much of the phosphorus is trapped by diatom blooms which immediately follow the winter river flow, and these in turn are followed several months later by massive blooms of the nitrogen-fixing blue-green alga (or cyanobacteria) *Nodularia*. Although some phosphorus is flushed to the ocean, studies have shown that up to 40 percent of the external phosphorus loading remains in the system each year¹.

Since 1980, research work has concentrated on the development of management options for the system. In common with many water bodies throughout the world, attempts to improve the trophic condition of the system must include a reduction in phosphorus input. Unfortunately this approach is not always successful, and excessive algal growth may continue despite a reduction in external phosphorus loading². This may occur when a large store of phosphorus has accumulated in the sediments. Phosphorus release from the sediments may then occur in amounts sufficient to sustain growth of phytoplankton.

Various techniques have been proposed to reduce this internal phosphorus loading, the most extreme of which is the complete removal of the nutrient-enriched layer of sediment by dredging.

This report examines the addition of aluminium and iron salts, oxygen and nitrate as ways to control the release of phosphorus from estuarine sediments.

2. METHODS

Sediments were collected from Peel Inlet and Harvey Estuary by SCUBA diving. Approximately the top 5 cm of sediment was taken and stored at less than 5°C. Analytical data for sediments used in experiments are listed in Table 1.

Phosphorus release experiments were carried out in 500 mL plastic containers with a diameter of 82 mm, kept in the dark at 22°C. Sodium chloride solution (4% m/V with 100 g/m³ sodium bicarbonate and 50 g/m³ sodium carbonate) was added to wet sediment to give solid to solution ratios of 1:12 and 1:35, with a total solution volume of 200 mL. Sediment and overlying water were mixed by swirling several times a day. Regular pH adjustments were made by the addition of 1M HCl or NaOH. Up to 150 mg of glucose was added to sediments A and B to establish anaerobic conditions. Sediments maintained under anaerobic conditions were kept sealed, and measurements and samples were taken under an atmosphere of nitrogen.

Redox potential was measured using a platinum electrode and calomel electrode connected to a millivolt meter. As considerable variation was found between different platinum electrodes, the results should be regarded as approximate values only³. The pH measurements were made with a combination pH electrode and a Radiometer pH meter.

Aliquots of solution for analysis were filtered through 0.45 µm filters and immediately acidified. Soluble reactive phosphorus was determined by the molybdenum blue method of Murphy and Riley⁴. Iron was determined by atomic absorption spectrometry.

TABLE 1

ANALYTICAL DATA FOR PEEL-HARVEY SEDIMENTS

| Sediment | Site | Date sampled | Moisture content ¹ | Organic matter ² | Total iron | Total phosphorus |
|----------|---------------|-----------------|----------------------------------|--------------------------------|---------------|---------------------|
| | | | | | Fe | P |
| | | | | percent | | µg/g |
| | | | | dry basis | | |
| A | Stn 1, Harvey | Feb. 1981 | 73 | 15.6 | 4.2 | 920 |
| B | Stn 8, Peel | Feb. 1981 | 74 | 22.7 | 5.1 | 890 |
| C | Stn 1, Harvey | Aug. 1983 | 77 | 12.3 | n.d. | 440 |

1 Weight loss after heating at 105°C

2 Weight loss 105°C to 550°C

n.d. not determined

3. RESULTS AND DISCUSSION

a. Anaerobic sediment phosphorus release

Many studies have shown that sediments release phosphorus under anaerobic conditions⁵⁻⁷ although exceptions to this have been recorded⁸. Release rates, when expressed in relation to the surface area of sediments, have varied from less than 1 to more than 100 mg/m² per day P. This range reflects both the nature of the sediments and the experimental conditions used.

All the Peel-Harvey sediments examined released phosphorus after anaerobic conditions were established. The release rate varied between 2.1 and 12.3 mg/m² per day P and was greater at higher pH (Fig. 1). There was not much difference between results irrespective of whether the water was gently swirled so as to not disturb the underlying sediment, or whether it was completely mixed in with the sediment while anaerobic conditions were maintained (3.4 mg/m² per day P compared to 4.0 mg/m² per day P for sediment B).

Efforts to determine the source of this phosphorus have led to a description of the following categories of sediment phosphorus⁹ :

- (i) nonoccluded P - inorganic P present as orthophosphate ions sorbed on the surfaces of P-retaining components.
- (ii) occluded P - inorganic P present as orthophosphate ions within the matrices of P-retaining components.
- (iii) discrete P - orthophosphate P present in discrete phosphate minerals such as apatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where X = OH, F, $\frac{1}{2}\text{CO}_3$) or vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$).
- (iv) organic P - organic esters of phosphorus acid.

In soils, the components retaining nonoccluded P have been identified as amorphous iron and aluminium hydrated oxides and amorphous aluminosilicates. These components, also present in sediments, are characterised by numerous hydroxyl groups in surface positions, and they readily react with orthophosphate by exchange adsorption of hydroxyl for orthophosphate.

Extraction procedures developed for soils have been modified for sediments to fractionate the various forms such as aluminium bound phosphorus (Al-P), iron bound phosphorus (Fe-P) and calcium bound phosphorus (Ca-P). By fractionating sediments before and after anaerobic incubation, it has been shown that Fe-P, alone or with Al-P, is the major source of phosphorus released from sediments^{5,10}.

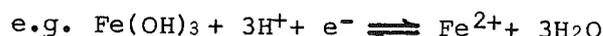
Although useful, no chemical fractionation procedure quantitatively extracts the same fraction of sediment phosphorus as that obtained by algae. Various algal assay procedures have indicated that some proportion of Fe-P and Al-P is available to algae. It has been shown that some Ca-P is sparingly available and that stable organic P appears to be of very limited availability¹⁰. There is no significant correlation between total phosphorus content of sediments and the trophic state of the overlying water¹¹.

Anaerobic conditions develop after aerobic micro-organisms have used up all the dissolved oxygen to decompose organic matter. Anaerobic micro-organisms also obtained their energy by decomposing organic matter. The series of chemical reactions that result in degradation of the organic matter produce electrons :



In the absence of oxygen, other reducible compounds such as nitrate, sulphate or high valency cations must function as electron acceptors¹².

The reduction of trivalent iron in this process is of particular interest :



When insoluble iron (III) compounds are reduced, both occluded and non-occluded phosphorus will be released^{7, 13}. The most likely forms of iron (II) to be found under anaerobic conditions are ferrous carbonate, FeCO_3 , ferrous sulphide, FeS and ferrosiferrous hydroxide $\text{Fe}_3(\text{OH})_8$ ¹⁴. Soluble iron concentrations may be quite high at low pH, but little iron is found in solution at high pH.

Iron concentrations for Harvey Estuary sediment A under both aerobic and anaerobic conditions as the pH was varied are listed in Table 2. Similar results were obtained for other sediments.

Oxidation or reduction occurs when substances donate or accept electrons. When an inert electrode is placed in such a system a potential develops. With the addition of a reference electrode, a potential difference may be measured, and when this is referred to a standard hydrogen electrode, it is defined as the redox potential or E_h . The redox potential indicates whether oxidising or reducing conditions exist, with strongly oxidising conditions giving rise to large positive potentials.

The redox potential at which the reduction of ferric hydroxide takes place in pure solution is -180 mV at pH 7, compared with +820 mV for the reduction of oxygen¹³. However, fairly wide ranges are found for redox potentials in soils and sediments due to the presence of impurities. Phosphorus release from Harvey Estuary sediment C (Fig. 1) occurred at a redox potential of about -20 mV at pH 7.5. The lowest redox potential measured in Peel-Harvey sediments was -140 mV at pH 7.4, after the addition of glucose to encourage the development of anaerobic conditions. These sediments also gave off a strong smell of hydrogen sulphide, even though reduction of sulphate requires a redox potential of -220 mV in pure solution.

TABLE 2

IRON IN SOLUTION FROM SEDIMENT A

| pH | - - - - - Fe - - - - - | |
|-----|------------------------|-----------|
| | aerobic | anaerobic |
| | g/m ³ | |
| 5 | 70 | 410 |
| 6.4 | <0.6 | 260 |
| 8.0 | <0.6 | 0.8 |

b. Aluminium and iron salts

In situations where reduction of phosphorus input fails to control eutrophication it has been suggested that addition of aluminium or iron salts directly to the water body may be a useful control technique¹⁵.

Aluminium sulphate (alum), ferrous and ferric salts have long been used in water treatment plants for the removal of colour and suspended solids¹⁶. They have also been used in treatment plants specifically for the removal of phosphorus¹⁷.

When the technique is applied to lake restoration, the alum dose required is greater than that needed to remove phosphorus from the water column. The hydrolysis reactions which occur when alum is added to water lead to the formation of a precipitate of aluminium hydroxide. This settles as a layer on the surface of the sediment, thus preventing diffusion of phosphorus across the sediment/water interface¹⁸.

This approach has been tried with deep lakes, where phosphorus release occurs when anaerobic conditions develop in the hypolimnion. The aluminium hydroxide floc is unlikely to be disturbed under these conditions. The long term effectiveness of the treatment is not well documented, but some success in reducing algal biomass has been recorded¹⁹.

There are few examples of shallow water bodies being treated with alum. One shallow lake did not show any improvement. The aluminium hydroxide floc was apparently resuspended and deposited towards the lake centre, leaving much of the sediment exposed. However, algal growth has been reduced in another shallow lake for at least one year²⁰.

In a large shallow water body such as the Peel-Harvey system, regular strong winds cause mixing and resuspension of the sediments, and the problem described above may result. In most of the laboratory experiments with alum, the sediment was mixed with the overlying water each day so that there was no layer of aluminium hydroxide floc at the sediment/water interface.

The results show that very high levels of alum were required to reduce the rate of release of phosphorus under anaerobic conditions (Fig. 2). For water treatment, a level of 4 g/m^3 Al in laboratory jar tests was sufficient to remove 90 percent of the phosphorus from Harvey River water²¹. With sediments in a saline environment, all levels of alum did reduce the amount of phosphorus in solution when measured after 2 days. However, only a level of 81 g/m^3 Al had any effect on the rate of phosphorus released over the next 12 days. The maximum release rate at this level of alum was 1.4 mg/m^2 per day P, compared to about 7.6 mg/m^2 per day P for the lower alum levels. A release rate of 0.4 mg/m^2 per day P was found for sediment B when treated similarly. However, when the layer of floc on the sediment surface was not disturbed, there was no net release of phosphorus after anaerobic conditions were established.

The maximum dose of alum for treatment of lakes has been defined as the amount which reduces the pH to 6.0. This is the point at which residual dissolved aluminium begins to appear and aluminium toxicity problems may arise¹⁹. The level of alum applied to lake water has ranged from 5.5 to 26 g/m^3 Al, compared with the maximum level of 81 g/m^3 Al used in these experiments. The rates can not be compared directly, as only a small volume of water was used in the laboratory experiments. A rate of 5.5 g/m^3 Al applied to a lake with a mean depth of 2 m is equivalent to a rate of 11 g/m^2 Al of sediment surface. When calculated on this basis, the laboratory sediments received a maximum of 3.1 g/m^2 Al.

An equivalent high level of ferric chloride (166 g/m^3 Fe) also reduced the phosphorus concentration in solution initially under anaerobic conditions. However, phosphorus release then continued at a rate faster than from the untreated sediment (Fig. 2). As discussed previously, ferric compounds, unlike aluminium, can be used as electron acceptors by micro-organisms under anaerobic conditions. The initial adsorption of phosphorus by ferric hydroxide will be reversed as reduction to ferrous forms occurs. Iron in solution did increase from 2 to 13 g/m^3 Fe during the period of maximum phosphorus release, but no further increases occurred. The much greater amounts of iron remaining undissolved were unable to prevent the release of phosphorus.

Treatment of water bodies with alum may have undesirable side effects, such as a reduction in species diversity of planktonic microcrustacea. It may also be unable to control all sources of phosphorus release, such as macrophytes, bottom feeding fish and burrowing invertebrates. Macrophytes, with their roots in the sediment, have the capacity to act as nutrient pumps, releasing phosphorus into the overlying water²². If the treatment results initially in greater water transparency, then increased growth of macrophytes may be expected, with greater recycling of phosphorus.

c. Oxygen

The water quality of lakes and reservoirs may be improved by aeration or destratification. This is often accomplished by the injection of compressed air, and in different situations has resulted in increases, decreases or no change in phytoplankton levels. Although usually applied to deeper water, it has been used in a shallow water body resulting in reduced chlorophyll 'a' levels and a shift from the less desirable blue-green algae to green algae²³.

It has been found that dissolved oxygen levels at the sediment surface greater than 2 g/m^3 prevent release of nutrients from the sediment²⁴. Under aerobic conditions, some sediments can remove large amounts of phosphorus from solution. The same sediments, although rich in phosphorus, were unable to sustain algal growth²⁵. When the overlying water remains oxygenated, an oxidised microzone may occur at the sediment/water interface¹¹. If the oxidised sediment adsorbs phosphorus, this microzone may act as a barrier to phosphorus release from the sediment, in a similar manner to a layer of aluminium hydroxide floc.

However, phosphorus release has been observed from some sediments under aerobic conditions^{5,6}. Possible mechanisms involved in this release include temperature controlled microbial decomposition, intermittent near anaerobic conditions at the sediment/water interface, and photosynthetically caused high pH²⁰. Russell¹³ has emphasised the great variability within waterlogged soils, where decomposition of organic matter by bacteria, resulting in strong reducing conditions, may be found adjacent to an air pore. The microbial reduction of sulphate, even when the more favourable but inaccessible electron acceptor oxygen is present in the same bulk sample, can give rise to both dissolved oxygen and hydrogen sulphide in a water extract.

Oxygen levels in the Peel-Harvey system have been monitored for over 10 years^{26,27}. These surveys have shown that dissolved oxygen in bottom waters rarely dropped below 50 percent saturation prior to 1981, although some lower results have been recorded since then. The data were all obtained during the day and reflect the frequent wind mixing of the water column. However, it was suspected that lower levels might be found at night when photosynthetic activity ceased.

Under aerobic conditions in the laboratory, the behaviour of Harvey Estuary sediments was very dependent on pH (Fig. 3). When the pH was adjusted and maintained at pH 8 or less, the soluble phosphorus associated with the sediment was rapidly removed from solution, and no further release of phosphorus occurred. At higher pH, phosphorus concentrations fluctuated, both increasing and decreasing, with high levels of phosphorus remaining in solution. During the experiment, the redox potential of the sediment at pH 8.4 and 8.8 remained at about 0 mV, despite regular mixing with the overlying water which had a redox potential of more than +350 mV. Release of phosphorus at high pH has been observed for other sediments²⁸ and is believed to result from exchange of hydroxyl ions for phosphorus on the surfaces of iron and aluminium compounds.

The water in the Peel-Harvey Estuary frequently has a pH less than 8 and is usually well oxygenated. Therefore it is not surprising that the concentration of phosphorus in solution is usually less than $10 \text{ mg/m}^3 \text{ P}$, except during periods of high river flow. However, the pH may rise to more than 9 during periods of intense photosynthesis. Thus a large algal bloom will create the very conditions that lead to release of the phosphorus required to maintain the bloom.

d. Nitrate

The concentration of soluble inorganic phosphorus in the water of the Peel-Harvey system may reach $200 \text{ mg/m}^3 \text{ P}$ during periods of river flow in winter. Much of this phosphorus appears to be trapped by diatom blooms that develop immediately. The more extensive blooms of the blue-green alga *Nodularia* follow about 12 weeks later, when phosphorus levels in the water have normally fallen to less than $10 \text{ mg/m}^3 \text{ P}$ ²⁷.

Once developed, the *Nodularia* blooms may be self-sustaining with regard to phosphorus, as described previously. However, large amounts of phosphorus are required while the bloom is developing. The phosphorus-containing diatoms are grazed extensively by zooplankton. These retain only a small part of the phosphorus, the rest being excreted in the form of faecal pellets or soluble phosphorus²⁹. The soluble portion may be a source of phosphorus for algae, as it includes both inorganic and organic forms of phosphorus. The inorganic phosphorus is directly available, and some organic phosphate esters may be available after hydrolysis by phosphatase enzymes produced by algae³⁰. The absence of any build up in phosphorus concentration indicates that the soluble phosphorus is either rapidly taken up by algae or removed by the sediments during mixing of the water column.

Another source of phosphorus may result from the addition of organic matter such as faecal pellets or dead diatoms to the sediments. The degradation of this organic matter by micro-organisms will not directly increase phosphorus availability, as most of the phosphorus in the organic matter is highly resistant to microbial activity⁵. However, the stimulation of the micro-organisms may result in the temporary development of anaerobic conditions, particularly at night time and as the water temperature increases in spring³¹. Under these conditions occluded and nonoccluded phosphorus in the sediments will be released. The buoyancy control mechanism of blue-green algae such as *Nodularia* may enable them to descend at night to the sediment surface and accumulate this phosphorus.

Results obtained in this Laboratory with Harvey Estuary sediments show how readily this occurs. The overlying water contained less than $10 \text{ mg/m}^3 \text{ P}$ after sediment A was exposed to aerobic conditions for 2 weeks. However, when 150 mg glucose was added and the samples were sealed, the redox potential fell more than 400 mV and the phosphorus concentration rose to over $300 \text{ mg/m}^3 \text{ P}$.

A technique has been suggested for lake restoration which aims at preventing this phosphorus release. As previously described, the release occurs when anaerobic micro-organisms use iron (III) compounds as electron acceptors. The reduction of iron may be prevented if another electron acceptor is present. Nitrate, with a redox potential in pure solution of +420 mV at pH 7, can be used by many micro-organisms in preference to iron¹³. This property has led to a proposal that artificial enrichment of water with nitrate could be used to improve water quality³². A study of lakes in Denmark revealed that no release of phosphorus from sediments occurred if nitrate levels in the water exceeded about $0.5 \text{ g/m}^3 \text{ N}$.

Nitrate levels in the Peel-Harvey system exceed $0.5 \text{ g/m}^3 \text{ N}$ during winter river flow, when soluble phosphorus levels are also high. For the rest of the year nitrate levels are usually less than $0.02 \text{ g/m}^3 \text{ N}$ ²⁶.

Laboratory studies with Harvey Estuary sediment C showed that addition of nitrate resulted in lower phosphorus levels in solution initially (Fig. 4). However, phosphorus release soon occurred when only low levels of nitrate were added, and release also occurred at a nitrate level of $80 \text{ g/m}^3 \text{ N}$ when anaerobic conditions were maintained.

When very high levels of phosphorus in solution were allowed to develop by holding sediments under anaerobic conditions for an extended period, addition of nitrate caused a rapid drop in phosphorus concentration (Fig. 5). The use of nitrate by micro-organisms, or denitrification, leads to the production of nitrites, nitric and nitrous oxides, nitrogen and ammonia³³. When denitrification reduced the concentration of nitrate in these experiments to zero, the micro-organisms continued to use iron as the electron acceptor and phosphorus release resulted. Only at an initial level of $180 \text{ g/m}^3 \text{ N}$ did any nitrate remain in solution after 3 weeks of anaerobic conditions. The consumption of nitrate under these conditions was about 0.2 g/m^2 per day N.

The role of organic matter in this process is important, as it determines the type of microbial activity which occurs. Only a small amount of the organic matter present in sediments can be rapidly utilized by micro-organisms³⁴. The total amount of organic matter does not indicate the amount of utilizable organic matter. Thus when sediment C was sealed, anaerobic conditions developed rapidly, while sediments A and B required the addition of glucose, despite having higher levels of organic matter.

Nitrate treatment is not without its problems. There is a possibility that high nitrate levels will stimulate phosphorus release because of faster mineralization of the organic matter. This does not appear to happen when sufficient nitrate is added. The greater danger is that if phosphorus release is not controlled, phytoplankton growth may be stimulated by the extra nitrogen in the system. Any problems or improvements resulting from the treatment are not likely to be permanent. Nitrates are very soluble, and losses to the ocean could occur before the organic matter in the sediments is oxidised. A permanent enrichment of the sediments would not occur, as the major product of denitrification is nitrogen.

4. CONCLUSION

The techniques described in this report can prevent or greatly reduce phosphorus release from sediments under laboratory conditions. However, it is not possible, from the results of these experiments, to predict the outcome if these treatments were used in the vastly more complex Peel-Harvey Estuarine System.

The large internal phosphorus loading that these techniques are attempting to control arises either directly or indirectly from the annual external phosphorus input. Phytoplankton blooms occur when this phosphorus is recycled or when the organic matter resulting from the phosphorus input leads to phosphorus release from the sediments. A reduction in external phosphorus input will also lead to a reduction in internal phosphorus loading, and thus must remain the major management objective.

Maximum phosphorus release from sediments occurs in the absence of oxygen, with large amounts of utilizable organic matter, low levels of phosphorus-retaining components and a high pH. These are not the normal conditions in the Peel-Harvey system, but in some circumstances phosphorus release does occur. Aeration of the water to maintain oxygen levels, addition of nitrate to consume the utilizable organic matter, addition of alum to increase the phosphorus-retaining properties of the sediment, and lowering the pH would all help in preventing the release of phosphorus. The application of these techniques to $150 \times 10^6 \text{ m}^3$ of water spread over 130 km^2 has not been considered in this report.

5. ACKNOWLEDGEMENTS

This work was carried out during a re-establishment period at the Government Chemical Laboratories following employment at Bogor, Indonesia under contract to CSIRO.

Salary and expenses were funded by CSIRO. Laboratory accommodation and facilities were provided by the Agricultural Chemistry Laboratory of these Laboratories.

The assistance of numerous staff in the Centre for Water Research and the Department of Soil Science and Plant Nutrition at the University of W.A., and the Agricultural Chemistry and Water Science Laboratories at the Government Chemical Laboratories is gratefully acknowledged.

REFERENCES

1. E.P. Hodgkin, P.B. Birch, R.E. Black and R.B. Humphries. The Peel-Harvey Estuarine System Study (1976-1980). Report No. 9, Dept of Conservation and Environment, W.A., 1980.
2. P. Cullen, R. Rosich and P. Bek. A phosphorus budget for Lake Burley Griffin and management implications for urban lakes. Aust. Water Res. Council, Tech. Paper No. 31. A.G.P.S. Canberra, 1978.
3. C.E. Zobell, Bull. Amer. Assoc. Petroleum Geol. 30, 477 (1946).
4. J. Murphy and J.P. Riley, Anal. Chim. Acta 27, 31 (1962).
5. M. Hosomi, M. Okada and R. Sudo, Environ. Internat. 7, 93 (1982).
6. G.C. Holdren and D.E. Armstrong, Environ. Sci. and Tech. 14, 79 (1980).
7. R.D. de Laune, C.N. Reddy and W.H. Patrick, J. Environ. Qual. 10, 276 (1981).
8. W.A. Norvell, Soil Sci. Soc. Amer. Proc. 38, 441 (1974).
9. J.D.H. Williams, J.K. Syers, S.S. Shukla and R.F. Harris, Environ. Sci. and Tech. 5, 1113 (1971).
10. D.A. Hegemann, A.H. Johnson and J.D. Keenan, J. Environ. Qual. 12, 12 (1983).
11. J.D.H. Williams and T. Mayer. Effects of sediment diagenesis and regeneration of phosphorus with special reference to Lakes Erie and Ontario. pp 281-315 in Nutrients in Natural Waters edited by H.E. Allen and J.R. Kramer. Wiley-Interscience, New York, 1972.
12. G.H. Bolt and M.G.M. Bruggenwert. Soil Chemistry. A. Basic Elements. 2nd Edn, Elsevier, Amsterdam, 1978.
13. E.W. Russell. Soil Conditions and Plant Growth. 10th Edn, Longman, London, 1973.
14. F.N. Ponnampereuma, E.M. Tianco and T. Loy, Soil Sci. 103, 374 (1967).
15. G.F. Lee, Water Res. 7, 111 (1973).
16. C.R. Cox. Operation and Control of Water Treatment Processes. W.H.O. Geneva, 1964.
17. H. Bernhardt and H. Schell, J. Amer. Water Works Assoc. 74, 261 (1982).
18. R.H. Kennedy and G.D. Cooke, Water Res. Bull. 18, 389 (1982).

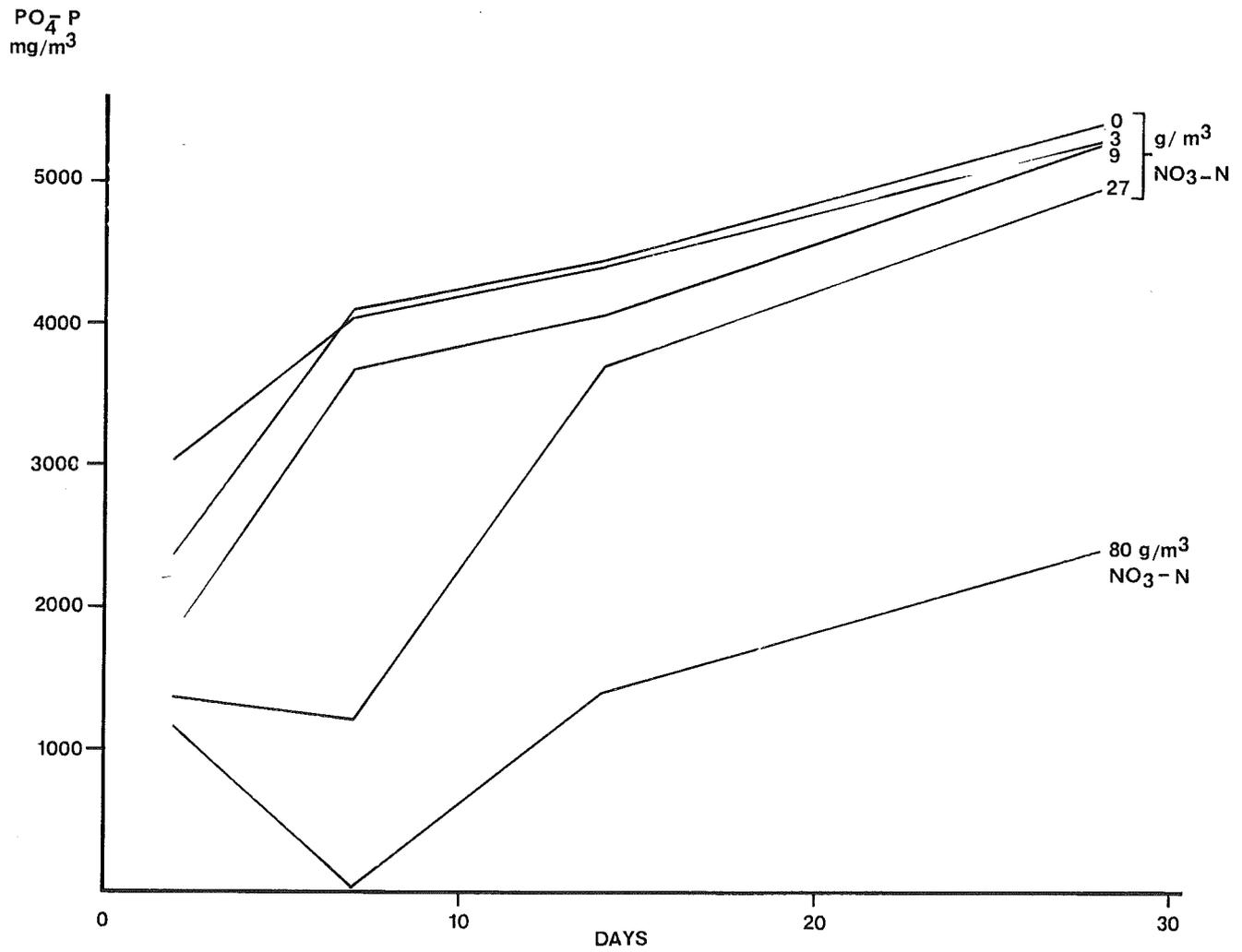


FIG. 4 Phosphorus release from Harvey Estuary sediment C under anaerobic conditions at pH 7.5, with addition of calcium nitrate.

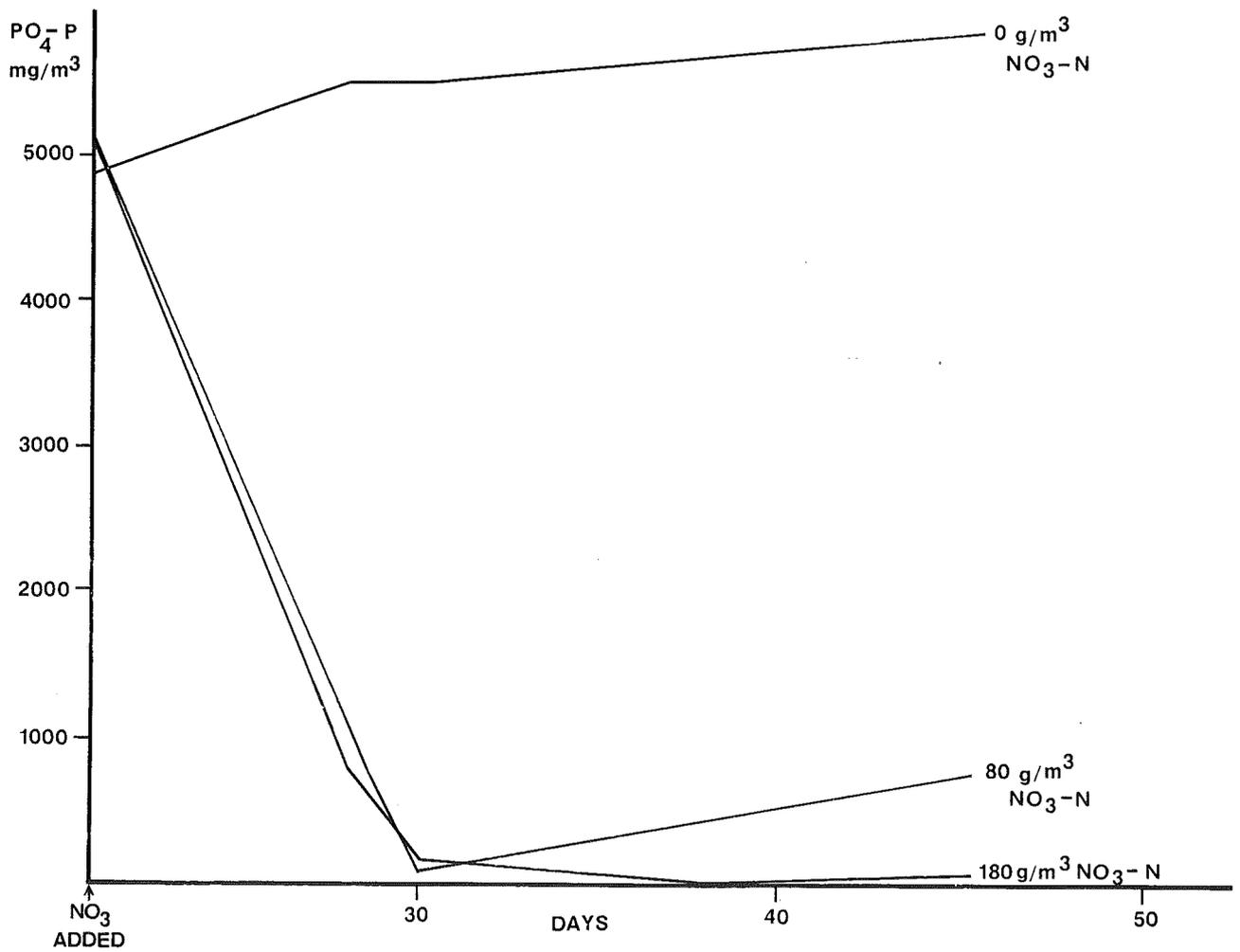


FIG. 5: Phosphorus release from Harvey Estuary sediment C. Calcium nitrate added 3 weeks after anaerobic conditions developed at pH 7.5.

