SOME ASPECTS OF PHOSPHORUS CYCLING IN MIDMAR DAM

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BY

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FRONTISPIECE : Four isolation columns positioned in the experimental area.

SUMMARY

1. Isolation columns positioned in approximately 3.5 m of water in Midmar Dam were used to study the influence of enrichment with NO_3-N and PO_4-P, singly and in combination.
2. Changes in an unenriched column indicated that isolation had very little influence on physico-chemical conditions within the columns.
3. When only PO_4-P was added, available nitrogen was rapidly depleted and, although primary production was increased, the increases could not be sustained for long periods because of nitrogen limitation. Direct adsorption of the added PO_4-P by the sediments was largely responsible for preventing the build up of P in the water.
4. Addition of NO_3-N resulted in a prolonged bloom of *Microcystis* during the summer and characteristically eutrophic conditions were maintained for approximately three months. The increased P levels in the water were indicative of a flux of P from the sediments.
5. Addition of NO_3-N and PO_4-P resulted in eutrophic conditions during the winter and summer months.
6. At times SRP levels in the columns increased to concentrations in excess of those that would be expected from the sediment/water PO_4-P equilibrium. At these times bioassays indicated that a large proportion of the SRP was not available P and it was concluded that the SRP accumulations resulted from the biological production of a P fraction, other than PO_4-P, which was not adsorbed by the sediment.
7. Vertical profiles in the sediments indicated that the surface sediments differ markedly from the drowned terrestrial soil on which they have been deposited and that increased primary production in the water leads to rapid changes at the sediment/water interface.

8. Uptake and release of P by intact sediment cores was quantified and characterised under aerobic conditions and the estimated rates of flux were sufficient to account for the P fluxes observed in the isolation columns.
9. Both uptake and release of P by the sediments was dependent on diffusion gradients across the sediment/water interface and a steady state dynamic PO_4-P equilibrium between the sediments and overlying water was demonstrated.
10. The kinetics of sediment/water P exchange could not be adequately described by a single exponential function. This is indicative of a number of exchange mechanisms.
11. Turnover times of P in the water column were studied in the open water and in a series of isolation columns enriched with NO_3-N. The P turnover times measured fell within the world range and tended to be lower in the columns enriched with NO_3-N.
12. Two distinct soluble P fractions (PO_4-P and colloidal P) were shown to be involved in the rapid exchange with particulate P. Colloidal P was shown to exhibit no direct exchange capacity with intact sediment cores. This is discussed in relation to the observed SRP accumulations.
13. The kinetics of P exchange in the water were generally monophasic and differed in a number of respects from the kinetics observed in other lakes. It is suggested that the current model of P cycling in the epilimnion (Lean, 1973) may not be applicable under South African conditions.
14. The data are discussed in relation to impoundments in general and the implications of internal P loading in predictive models are considered
15. The concept of a "limiting" nutrient, as assessed from bioassays, is discussed in relation to the dynamics of nutrient cycling under

natural conditions.

16. The applicability of isolation columns in the study of nutrient enrichment is assessed and the potential role of periphyton in the columns and phytobenthos in the impoundment is discussed.

17. It is concluded that before scientifically sound eutrophication management strategies can be introduced the N cycle needs to be investigated in far more detail in South Africa.

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CHAPTER 1

INTRODUCTION

1.1 Introduction to the Study

The implication of phosphorus as a major factor in eutrophication (Mackenthun, 1973) stimulates interest in its dynamics in aquatic systems. Research has revealed a complex system of exchanges and transformations which have led to widely divergent interpretations of results. Such a situation has made it difficult to define the relationship between phosphorus loading and lake response. Whilst broad empirical relationships have been developed, the confidence limits are so broad that they cannot confidently predict the effect of substantial reductions in loading (Larsen *et al.*, 1975).

Even where researchers have adopted the reductionist approach (Rigler, 1973), and have attempted to study processes in isolation, the results are often very varied and present a confused picture. In the case of sediment uptake and release of phosphorus, for example, there are conflicting reports of uptake and release under a variety of conditions making it difficult to formulate the general principles which should be applied in attempts to model phosphorus dynamics in systems.

There seems to be no good reason why great variability should not be expected. It is, after all, well established that different soils interact differently with a range of plants on the basis of their structure and chemical properties. Thus, if eutrophication is considered as a dynamic process which brings about a gradual change in the components of the system, including the sediment, then a wide range of properties

and behaviour should be expected. These would vary both spatially and temporally within a system.

The implications of these points are that an understanding of the phosphorus dynamics in aquatic systems and of eutrophication, will be dependent on the study of a wide range of systems. It will not be sufficient to examine only eutrophic systems, in which major changes have occurred, and expect to be able to derive the responses of oligotrophic systems to changing conditions. This observation is supported by the fact that, in some instances, where empirical relationships between phosphorus loading and lake response (e.g. chlorophyll) are examined the variability is extremely wide at the oligotrophic end of the scale but the relationship improves with increasing degree of eutrophication (Walmsley *et al.*, 1979). The tendency to only study eutrophic systems, in which problems have become manifest, may not therefore ultimately provide management guidelines which are applicable to less productive systems.

In South Africa the presence of some extremely eutrophic systems e.g. Haartebeespoort Dam, Roodeplaat Dam and Rietvlei Dam (Walmsley *et al.*, 1978) together with their strategic location and the considerable dependence of both the industrial and private sectors on their water, has given impetus to research on eutrophication and to the formulation of guidelines for its control (Toerien, 1977). This research has highlighted that the typically warm monomictic thermal cycle in South African systems may significantly alter the response to enrichment from what may be expected in the dimictic systems of higher latitudes. The problem has been compounded by the realisation that man-made impoundments, because of factors such as short hydraulic residence time

and "young" sediments, may react differently from what may be predicted from the study of natural, old, systems. The fact that South African man-made impoundments tend to be shallow with marked annual draw down and have high silt loads, suggests that the development of guidelines for effective multipurpose use will be dependent upon the study of a range of systems in South Africa.

This research programme set out to integrate some aspects of the dynamics of phosphorus in an oligotrophic system. By using an oligotrophic system it was fairly simple to apply a range of enrichment regimes to create demands for phosphorus and to monitor the response of the system to these changed conditions. However, the complexity of the phosphorus cycle required the analysis of a variety of components in the system and this thesis therefore reports on phosphorus fluxes between the sediments and overlying water and between soluble and particulate compartments within the water column.

1.2 Description of the Study Area

Midmar Dam has particular significance in the province of Natal because it is strategically placed as the first of a series of impoundments providing water for the Durban-Pietermaritzburg complex. The number of people dependent on the Mgeni river is expected to reach 4 million persons by 1990 and the water supply of 1000 million litres per day from the impoundments is expected to be fully utilised by 1984 (Natal Town and Regional Planning Commission, 1973). It is however the upper Mgeni catchment which requires particular attention because it produces three quarters of the total run-off into the Mgeni River.

As early as 1953 the need for ecological information to assist in planning the upper Mgeni catchment was recognised when the Natal Town and Regional Planning Commission and the National Institute for Water Research instituted the river survey programme (Natal Town and Regional Planning Commission, 1973). After the construction of Midmar Dam between 1962 and 1965 the programme was expanded to include impoundments and the Department of Botany of the University of Natal became involved in a research programme of general limnological studies in Midmar Dam and its catchment (Furness, 1974; Walmsley, 1976; Twinch, 1976; Furness and Breen, 1978; Twinch and Breen, 1978a and b).

1.2.1 The Catchment

1.2.1.1 Geography

The Mgeni catchment (Fig. 1.1) is roughly pear shaped and occupies 439 000 ha of central Natal. Of this, the Midmar Dam catchment constitutes 129 000 ha forming the western section of the Mgeni river catchment between latitudes 29°20'S and 29°28'S and longitudes 29°47'E and 30°14'E. Approximately 45% of the population of the province of Natal are dependent on the Mgeni system and it supports 20% of the industrial output of the whole country (Natal Town and Regional Planning Commission, 1973).

1.2.1.2 Geology

The Midmar Dam catchment area is geologically simple being composed of the shales, mudstones and sandstones of the Beaufort series comprising the Karoo system (Du Toit, 1954). Erosion resistant dolerite sills exert an important influence on the topography and the Mgeni River, like many Natal rivers, has a step-like profile resulting from waterfalls created by the sills (King and King, 1959).

Above the sills the river tends to meander. Resistance of dolerites to weathering (Natal Town and Regional Planning Commission, 1973) results in the water having a low TDS (total dissolved solids) and conductivity.

1.2.1.3 Soils

The soils in the area vary from highly leached associations in the high altitude areas to moderately leached associations surrounding Midmar Dam (Scotney, 1970). Le Roux and Sumner (1967) demonstrated the low levels of cations leached from these associations, and the strong P binding capacities of the soils and riverine sediments in the area has been shown (Furness, 1974; Furness and Breen, 1978), As a result, the water entering Midmar Dam from the catchment contains low concentrations of cations and other nutrients.

1.2.1.4 Rivers

Two rivers, the Mgeni River (mean annual runoff $97m^3 \times 10^6$) and its largest tributary, the Lions River (mean annual runoff $68m^3 \times 10^6$) provide the main input into Midmar Dam (Natal Town and Regional Planning Commission, 1961) but several much smaller streams, some perennial, also contribute to the input.

1.2.1.5 Land Use

Land use in the catchment is limited to agriculture, forestry and stock raising, and on an areal basis can be divided up as follows:

(a) Undeveloped hillside grassland	56.4%
(b) Dryland arable and grassland	19.2%
(c) Irrigated arable	3.9%
(d) Commercial forest plantation	14.3%

(e) Natural forest 2.5%

(f) Vleis and marshes 2.7%

(g) Small impoundments 0.6%

(h) Small population centres 0.2%

(data from Hemens *et al.*, 1977).

1.2.2 The Impoundment

1.2.2.1 Morphometry and the Hydrological Regime

The Midmar Dam wall, constructed on a horizontal dolerite sill, was completed in 1964. The resulting impoundment consists of four flooded valleys leading into a more extensive area of open water (Fig. 1.2). Some of the important morphometric characteristics are presented in Table 1.1.

As indicated by the shoreline development, the impoundment is dendritic (Hutchinson, 1957). At full supply level a large proportion (42%) of the total capacity of Midmar Dam is contained in shallow water (0-5 m depth) which is concentrated in the shallow flooded valleys (Fig. 1.2). Water content of the impoundment follows a seasonal pattern corresponding with the seasonal rainfall patterns. Being an important supply reservoir, water is continually discharged to cater for requirements in the impoundments downstream. During the dry winter months outflow exceeds inflow and water levels in the impoundment drop. Since 1966 there has been a mean annual fluctuation of 2.4 m (Walmsley, 1976). The result of this seasonal draw-down is that large areas of the littoral, approximately 300 hectares if the water level drops by 2 m, are exposed. Species such as *Limosella africana* Glueck are able to establish on the exposed substrate.

As the water level rises these are inundated and could provide an important nutrient input into the aquatic system.

Also associated with the marked draw down is the absence of well developed littoral hydrophyte communities which are unable to become established because of the unstable conditions in the marginal areas.

Between 1963 and 1973 the retention time in Midmar Dam fluctuated between 0.7 and 1.8 ($\bar{x}$ 1.15) years which is fairly long in comparison with other impoundments of similar size in South Africa (Walmsley, 1976).

1.2.2.2 Physical and Chemical Status

Midmar Dam is a warm monomictic system with a period of stratification during summer and isothermal conditions in winter. Surface water temperature ranges from approximately 11°C in mid-winter to 25°C in the summer. An oxygen deficit develops in the hypolimnetic waters during the summer but this is largely restricted to the deep waters in the main basin (Walmsley, 1976).

According to Archibald *et al.*, (1979), who obtained a mean secchi disc reading of 1.31 m, Midmar Dam is a clear impoundment. In the South African context this may be true (Noble and Hemens, 1978) but, on a world scale, Midmar must be regarded as a turbid water body. Secchi disc readings are frequently less than 1 m (Walmsley, 1976; Twinch and Breen, 1978; Archibald *et al.*, 1979) and can drop to as little as 40 cm. In many other lakes secchi disc readings of 10 m are not uncommon (Hutchinson, 1957). The low secchi disc trans-

parencies are due almost entirely to the presence of suspended silt particles, and do not reflect phytoplankton densities, which are low (Walmsley, 1976; Hemens *et al.*, 1977; Archibald *et al.*, 1979). The concentration of suspended solids ranges from 1.2 to 10.6 mg l^{-1} (Walmsley, 1976) and is thought to result more from internal processes (sediment resuspension and shoreline erosion) than from allochthonous inputs (Johnson, unpublished data).

The low TDS and conductivity reflect the geology, soil characteristics, agricultural activities and lack of urban development in the catchment (Walmsley, 1976). For similar reasons the concentration of nutrients in the water is low (Walmsley, 1976; Hemens *et al.*, 1977; Archibald *et al.*, 1979).

The alkalinity (0.33 to 0.66 meq l^{-1}) and pH (6-8) ranges are characteristic of a poorly buffered soft water system (Walmsley, 1976; Twinch, 1976).

1.2.2.3 Trophic Status

Based on algal bioassay results, chlorophyll levels and on nutrient concentrations, Midmar Dam has been classified as oligotrophic (Toerien *et al.*, 1975; Walmsley, 1976; Twinch, 1976; Archibald *et al.*, 1979). Phosphorus is most frequently the primary limiting nutrient followed closely by nitrogen. Hemens *et al.*, (1977) suggested that Midmar Dam may be approaching a mesotrophic condition, but this was based on a nutrient budget calculated using estimated total P concentrations in the inputs, the validity of which is questionable (Schaffner and Oglesby, 1978; Walmsley *et al.*, 1979).

1.2.2.4 Primary Producers

Small communities of *Phragmites mauritianus* Kunth and *Polygonum* sp. are very localised (Walmsley, 1976). Communities of *Nitella* sp. occur in the shallow waters around the shore margin, and in deeper water several isolated stands of *Potamogeton schweinfurthii* A. Benn have been observed.

As reflected by the low chlorophyll levels, the phytoplankton density is low. Preliminary studies indicate that there is little horizontal variation, and an indistinct seasonal cycle in the phytoplankton has been shown (Walmsley, 1976; Hemens *et al.*, 1977). The large diversity of phytoplankton species (Walmsley, 1976; Twinch, 1976) is characteristic of an oligotrophic system but very little is known about the taxonomy and population structure of the phytoplankton.

Primary production in the water column is low (Akhurst, unpublished data) and the contribution of macrophytes and benthic algae to the overall production is unknown.

1.2.2.5 Secondary Producers

In Midmar Dam there is a mixture of temperate and subtropical species of zooplankton. Broad trends in the numbers and diversity are evident, but have shown some variability, and must be interpreted with caution until more extensive sampling has been undertaken (Rayner, unpublished data).

In late winter and early spring *Daphnia* spp. increase rapidly in numbers but decrease again by mid-summer. The warm water

Diaphanosoma excisum and the cyclopoid copepods reach their peak in late summer and early autumn. The calanoid *Tropodiaptomus spectabilis* is present throughout the year with blooms in spring and autumn. The rotifers have an annual succession with sporadic blooms when conditions favour their increase (Rayner, unpublished data).

Little is known about other secondary producers. The benthic fauna have not been studied, and only species of ichthyofauna have been recorded.

1.2.2.6 Conclusion

The current state of knowledge of Midmar Dam and the upper Mgeni catchment is based largely on preliminary descriptive investigations. Although research into the fundamental limnological characteristics has been undertaken, the understanding of interactions within the system is superficial. On the evidence available there is little doubt that Midmar Dam is oligotrophic and that the present river inputs are not resulting in any marked changes in the trophic status. It thus provides a good example of an "undisturbed" system in which the important process charaterising a young impoundment can be studied.

1.3 An Overview of the Study of P Cycling in Fresh Waters.

1.3.1 Terminology

Although many earlier analyses indicated that phosphorus levels in fresh waters were low, it was only after the introduction of colorimetric analytical procedures in 1923 that real progress in the study of phosphorus cycling was made (Hutchinson, 1957). The presence of a

number of phosphorus fractions soon became apparent and the following categories were used by Hutchinson (1957):
1. soluble phosphate phosphorus, 2. acid-soluble sestonic phosphorus, 3. organic soluble (and colloidal) phosphorus, 4. organic sestonic phosphorus.

However, the techniques used to separate seston from the soluble P fractions varied, resulting in considerable confusion in the literature. This was highlighted by Rigler (1964), who duplicated the entire range of soluble organic phosphorus levels, reported in the literature, in a variety of Canadian lakes by varying the method of separating seston. The methods varied from Foerst centrifugation to filtration through 0.1μ membrane filters. He further showed that if methods were standardised the percentage of soluble organic phosphorus remained remarkably constant for a variety of lakes : the implication being that much of the variation in early phosphorus data reflected variations in the separative techniques used.

More recently use of 0.45μ membrane filters has become virtually standard practice in limnological research, and this is reflected in the definitions of phosphorus fractions measured in fresh waters. These were outlined in the review by Rigler (1973) as follows :

> *Soluble reactive phosphorus (SRP) refers to the value when membrane filtered water is analysed by one of the variants of the molybdenum blue technique. This term implies neither that the orthophosphate measured was in solution before addition of the reagents nor that the intensity of the blue color is exclusively a function of orthophosphate concentrations rather than that of interfering ions. When orthophosphate phosphorus (PO_4-P) is used it will not refer*

to the results of chemical analyses but to free orthophosphate in solution, the concentration of which is assumed to be as yet unmeasureable in the trophogenic zone of most lakes.

Soluble phosphorus (SP) refers to the value obtained when membrane filtered(0.45μ) water is analysed after being digested with an oxidising acid solution.

Soluble unreactive phosphorus (SUP) is the difference between SP and SRP.

Total phosphorus (TP) is obtained by analysing whole lake water after acid digestion. It is assumed that the values obtained by this technique are indicative of the true phosphorus content of the sample.

This terminology is based on the analytical methodology and does not refer to definite phosphorus compartments that are equivalent to morphologically and chemically distinct components of lake water (Rigler, 1973). This is especially true of the SRP, which is frequently regarded as being synonymous with PO_4-P, particularly by South African limnologists. There is however growing evidence which indicates that SRP includes forms which are not PO_4-P. As early as 1956 it was suggested that SRP was greater than PO_4-P (Rigler 1956) and this has been confirmed in Canada (Lean, 1973; Peters, 1978) and New Zealand (Paerl and Downes, 1978). The discrepancy results from the hydrolysis of soluble organic and colloidal P during the acid conditions of the molybdate blue procedure (Paerl and Downes, 1978).

There are therefore limitations in the use of data derived from analytical techniques that are currently in use. This will also apply to predictive modelling of the relationship between phosphorus loading

and changes in lake metabolism where it is necessary both to identify discrete phosphorus forms of biological importance, and to measure the fluxes between them (Lean, 1973).

In this thesis the terminology outlined by Rigler (1973) will be used whenever possible.

1.3.2 Phosphorus Cycling in Fresh Waters

While PO_4-P is the only form in which phosphorus is freely available for uptake by the primary producers in fresh waters, it represents only one of a number of important P compartments in the water. In common with most other elements it may be combined into a variety of ionic, molecular and colloidal forms, often mediated through biogenic processes (Rigler, 1973). The variety and amount of the forms in which P can exist may therefore be expected to be related to the extent of these biogenic processes. Where these processes are increased for example, during eutrophication, the implications may be considerable.

Before radioisotopes were introduced into limnological research, phosphorus cycling in fresh waters was studied by monitoring temporal and spatial changes in the concentration of organic or inorganic P. As early as 1939, it was postulated that the dissolved P could be in colloidal form rather than in true solution and that the sestonic P consisted of both organic and inorganic forms (Hutchinson, 1957) but these could not be accurately measured. The lack of standardisation in the analytical procedures used by the earlier workers therefore makes comparison of data questionable (Rigler, 1964). Furthermore the experimental approach was of little value in relation to phosphorus cycling because the dynamic nature of the phosphorus pool was not taken

into account. This led to the realisation of the futility of the traditional "static" approach to nutrient studies in fresh waters (Hutchinson, 1957; Schindler *et al.*, 1974).

In the early 1950's, the introduction of radiotracers into the study of P cycling (Hutchinson and Bowen, 1950) heralded the beginning of the kinetic school of holistic limnology (Rigler, 1975). The pioneering ^{32}P tracer studies have been reviewed by Hutchinson (1957). These involved the addition of $^{32}PO_4$-P to lakes and made a major contribution to the understanding of phosphorus cycling in fresh waters, emphasising the extreme mobility and rapid exchange kinetics of P between soluble and particulate (solid) compartments. Although the important role of the sediments in phosphorus cycling within lakes was demonstrated long before the advent of radiotracers in limnology (Mortimer, 1941) the extent of the interactions between phosphorus compartments, such as the littoral vegetation, the hypolimnion and the sediments, was only fully appreciated following tracer studies. The concept of the phosphorus compartments in a lake being in a dynamic equilibrium with one another, and thus approximating a quasi steady state system in which the exchange of phosphorus between compartments is continuous and rapid relative to net fluxes in the sizes of the compartments, was then developed (Hayes *et al.*, 1952; Hayes and Phillips, 1958).

Radiotracer techniques were also applied to isolated surface water samples to study the exchange kinetics between soluble and particulate P fractions (Rigler, 1956). These often conformed to the kinetics predicted by a two compartment (monophasic) exchange model in

which ^{32}P in solution decreases exponentially to an equilibrium level, and were initially explained by postulating a simple exchange of PO_4-P between a soluble and particulate compartment. However, Chamberlain (1968, cited in Rigler, 1973) reported occasional ^{32}P uptake kinetics which were better described by a diphasic exponential equation, and demonstrated that in a short time after addition of tracer to the lake water a fraction of ^{32}P in solution was something other than PO_4-P. This was confirmed by Rigler (1968) who postulated a second soluble P compartment to explain the diphasic uptakes, but he could not identify it.

By combining ^{32}P uptake experiments with gel-filtration analysis, Lean (1973) identified four phosphorus fractions in lake water : particulate P and three soluble P fractions; PO_4-P, a low molecular weight organic P compound and a macromolecular colloidal P compound. The soluble molecular fractions were shown to be of biological origin and formed important components of the four compartment model proposed by Lean (1973). Under natural conditions the number of recognisable compartments comprising the particulate P is large and it has recently been suggested that Lean's model requires slight modification to account for this diversity (Norman and Sager, 1978a; Halfon *et al.*, 1979). At least two different rates of exchange with the particulate P compartment appear to be necessary to make the model consistent with experimentally observed diphasic phosphorus exchange curves; one comprising the smaller organisms through which phosphorus cycles rapidly and the other comprising the larger organisms through which phosphorus cycles slowly (Rigler, 1973).

It is thus necessary to consider the epilimnetic P as a compart-

ment consisting of a number of components in a dynamic steady state both with one another and with other compartments in the system (Rigler, 1973), and it has become apparent that a better understanding of phosphorus dynamics in freshwater systems depends on a knowledge of the P compounds occurring in lakes and of the transfer processes between them (Lean, 1973; Golterman, 1973b; Francko and Heath, 1979). At the present time however these processes are poorly understood.

1.3.2.1 The Role of Sediments

One aspect of phosphorus cycling which has been fairly comprehensively studied is the sediment/water P exchange and this topic has been reviewed by Stumm and Leckie (1970), Golterman(1973b), Hesse (1973) and Syers *et al.*, (1973).

Since the classical study of mud-water nutrient exchange in Lake Windermere (Mortimer, 1941) much attention has been focussed on the role of sediments in phosphorus cycling in fresh waters. The exchange processes have been shown to be complex and the rates and extents of the phosphorus fluxes across the sediment : water interface vary with variations in sediment structure and nutrient status (Syers *et al.*, 1973). Many large deep lakes are characterised by substrates of deep organic deposits (Hesse, 1973), which contrasts with the situation in many man-made impoundments where the substrate consists largely of drowned terrestrial soil overlain by a layer of recently deposited "true" sediment of varying thickness depending on the age and productivity of the impoundment. The mechanisms determining the rate and direction of the phosphorus fluxes are also

influenced by limnological conditions within the water body, such as orthophosphate concentration in the water and the degree of turbulence at the sediment water interface (Lee, 1976).

Most lake sediments are capable of adsorbing large amounts of PO_4-P from the water when concentrations in solution are increased, and desorbing some PO_4-P when concentrations in the water are reduced by biological uptake (Golterman, 1973b). The result is a dynamic equilibrium similar to that first proposed by Hayes and Phillips (1958) whereby a large proportion of the total pool of exchangeable P in a lake is bound by the sediments (Stumm and Leckie, 1970).

The important role of inorganic clay minerals in the P exchang processes has been demonstrated (Syers *et al.*, 1973), but the presence of organic material in the form of living matter and detritus complicates the mud/water exchange and, in many instances, bacterial activity dominates over inorganic chemical reactions, particularly in systems of high productivity (Hesse, 1973). Clearly the relative importance of these two processes is dependent upon factors such as the proportions of inorganic and organic material, the nutrient status of the sediments and overlying water, the stability of the mud/water interface, the rate of sedimentation and the nature of the sedimenting material.

The ability of lake sediments to buffer against changes in PO_4-P levels in the water explains the frequent observations that freshwater systems can tolerate substantial loading with PO_4-P with no long term detrimental effects. However, with the heavy and

prolonged loading of many eutrophic systems the buffering of the sediments is insufficient to maintain stable PO_4-P levels and as their degree of saturation increases, so does their potential to release phosphorus (Schindler, 1976).

The influence of oxygen status at the sediment water interface on PO_4-P fluxes was first reported by Mortimer (1941). Anaerobic conditions favoured the release of PO_4-P from sediments through their influence on the solubility of iron. Subsequently similar results were obtained by a number of workers and phosphorus release from sediments came to be commonly regarded as a predominantly anaerobic phenomenon. Aerobic release has however also been demonstrated, but at markedly slower rates, and has therefore been regarded as being of relatively less importance (Kamp Nielsen, 1974; Syers *et al.*, 1973; Viner, 1975). The Fe-PO_4-S and the Ca-CO_3-PO_4 systems have been implicated in the vertical exchange of PO_4-P in different types of water bodies (Golterman, 1973b). In the former case PO_4-P co-precipitates as $FePO_4$, or adsorbed into $Fe(OH)_3$, under aerobic conditions, but under anaerobic conditions $Fe(OH)_3$ is solubilised by the reduction of ferric iron at low redox potential, which results in the release of PO_4-P into the water. In hard waters the Ca^{++} content of the water can influence P content of the sediments through precipitation of calcium phosphates or through co-precipitation of phosphates with $CaCO_3$ precipitate (Stumm and Leckie 1970). PO_4-P adsorption/desorption processes with the clay fractions which are pH dependent, are also important in the overall exchange of P between sediments and overlying water (Syers *et al.*, 1973).

More recently however, evidence has accumulated which suggests that the iron-phosphate interaction (Mortimer, 1941) may not be as universally important in phosphorus release as previously thought, and Golterman *et al.* (1976) stated that 'aerobic phosphorus release may play a dominant role in the aqueous environmental chemistry in lakes and impoundments'. The evidence derives largely from studies of eutrophic systems and has been shown to be related to mineralisation processes where bacterial breakdown of organic P results in the release of PO_4-P into the water (Lee, 1976). This is obviously enhanced by a rapid rate of organic sedimentation. The importance of phosphorus loading from sediments has been demonstrated in rehabilitation studies in eutrophic systems which, through diversion and other management practices, have had nutrient loads reduced. Responses have varied between marked improvement (Edmondson, 1972) and no apparent improvement (Larsen *et al.*, 1975), the latter being due to phosphorus loading from the sediments, generally referred to as 'internal loading'.

The duration and intensity of previous loading are important in this regard and the longer the loading with high levels of phosphorus, the more extensive the deposition of phosphorus rich sediments and consequently the longer the recovery time (Schindler, 1976). In South Africa the residence time of most of the important impoundments is relatively short compared with that of lakes, (Walmsley *et al.*, 1979), and the rapid flushing effect may result in more rapid recovery.

The occurrence of phosphorus loading from sediments in oligotrophic systems has received less attention and its importance has not been established. Some evidence of significant phosphorus loads from

the sediments has been obtained under aerobic conditions in Midmar Dam (Twinch and Breen, 1978a), and in view of the well established concept of a sediment/water phosphorus equilibrium and the resultant PO_4-P releasing potential of the mud during periods of PO_4-P depletion in the water, this could be important in the generally shallow well mixed impoundments in South Africa.

Anaerobic conditions, and the associated increase in the phosphorus release rate from the sediment, occur in the hypolimnia of lakes during periods of marked stratification, resulting in phosphorus accumulation below the thermocline. The consequence of this is that the phosphorus released is prevented from reaching the epilimnion and is therefore not available to the phytoplankton at the time of maximum demand during the summer (Golterman *et al.*, 1976). A similar phenomenon has been shown in the Swartvlei Estuary where salinity gradients prevent PO_4-P released into the anaerobic zone from reaching the phytoplankton (Howard-Williams and Allanson, 1978). The release of PO_4-P under anaerobic conditions may therefore not be as important to primary production in the epilimnion as was previously thought because, as stratification breaks down and the hypolimnion again becomes aerobic, a large proportion of the released PO_4-P would be fixed by the oxidised sediments before it is taken up by primary producers. Conversely PO_4-P release from sediments in contact with a well mixed epilimnion may be more important than was previously thought, and requires careful investigation as the implications could be considerable in South Africa where the majority of impoundments can be characterised as shallow water bodies (Noble and Hemens, 1978) and are consequently characterised by large areas of oxidised surface sediments.

Associated with the changes which occur at the sediment/water interface are changes in the phosphorus status, and thus in the exchange kinetics between the sediments and the overlying waters. As has already been discussed, the most obvious demonstration of this has been in the failure of some rehabilitation programmes to improve the trophic status of eutrophic systems as a result of phosphorus release from the highly enriched surface sediments (Schindler, 1976).

Most soils have the ability to fix or retain PO_4-P (Russell, 1961) and even under waterlogged conditions this property is maintained (Syers *et al.*, 1973; Furness and Breen, 1978; Twinch and Breen, 1978). Thus at the time of construction all impoundments are characterised by PO_4-P fixing substrates. If the subsequent development of surface sediments is due largely to organic deposition, the PO_4-P fixing potential at the mud/water interface could be reduced and eventually, when the surface layer becomes sufficiently thick so as to form an effective barrier between the water and the original soil, the role of the substrate may be shifted from a sink to a source of phosphorus. This situation would be hastened in eutrophic systems. Alternatively, in systems where sediment formation is due largely to eroded inorganic material the PO_4-P fixing capacities of the substrate may be maintained or even enhanced. Results supporting this suggestion have been obtained in the Maumee River Basin (Green *et al.*, 1978; McCallister and Logan, 1978) and may be relevant to the turbid systems in South Africa. These two examples represent two extremes and under natural conditions sediment formation is usually the result of a combination of both organic and inorganic sedimentation - the relative proportions obviously varying markedly between systems.

1.3.2.2 Phosphorus Cycling within the Water Column

While rapid exchange of ^{32}P between seston and the water has frequently been demonstrated, the relative importance of the particulate fractions is not clear. The importance of the phytoplankton appears to vary considerably between lakes. In Toussaint Lake (Canada) Rigler (1964) showed that only 5% of the ^{32}P taken up by sesto could be accounted for in the zooplankton and larger phytoplankton while 68% was taken up by ultraplankton (bacteria). Peters (1975) suggested that the converse was true in Lago Maggiore (Italy) where ^{32}P uptake rates did not correlate with estimates of bacterial populations but did with estimates of phytoplankton populations.

Lean and Nalewajko (1976), using axenic cultures of a number of phytoplanktonic organisms, showed clearly that rapid phosphorus turnover and the excretion of colloidal P and low molecular weight organic P can occur in the absence of bacteria. However phosphorus retention and excretion varied amongst the species studied supporting the view that a single particulate P compartment cannot adequately describe a diverse phytoplankton population. Comparable studies on bacteria do not appear to have been undertaken, but it seems probable that they would be characterised by a similar diversity in soluble P exchange.

Zooplankton can also form an important component in the phosphorus cycle but, because of their secondary and/or tertiary position in the food chain, are probably more important in the regeneration of soluble P from particulate P than in direct uptake of soluble P. Following quantitative studies of phosphorus release by zooplankton Rigler (1973) concluded that direct release of phosphorus from ultraplankton and excretion by zooplankton are equally important

in regenerating phosphorus in the trophogenic zone of eutrophic lakes during summer stratification. The forms in which phosphorus is released by zooplankton have been studied (Peters and Lean, 1973) and it appears that approximately 90% of the released soluble P is PO_4-P while the balance is made up largely of colloidal P.

The importance of abiotic particles in the exchange of phosphorus between particulate and soluble forms is not well understood. Paerl and Lean (1976) used autoradiographic techniques to study the movement of phosphorus between algae, bacteria and abiotic particles in Heart Lake (Canada). Bacteria and phytoplankton were labelled most rapidly but after 2 hours tracer was also evident on detrital aggregates harbouring bacteria. In the South African context where many of the fresh waters are characterised by high levels of suspended inorganic material, the role of abiotic phosphorus exchange may be more important. The availability of silt associated phosphorus to phytoplankton is thought to be a major factor in some turbid waters (Grobbelaar, unpublished data), and a similar situation is likely in many turbid waters in South Africa, either by direct exchange of PO_4-P by the clay particles, or by bacteria harboured on silt particles as shown by Paerl and Lean (1976).

From the available evidence it must be concluded that very little is known about the specific roles of various biotic and abiotic factors in the phosphorus exchange processes in the water. In view of the variability in biological and nutrient status of fresh waters it is probable that no generally applicable hypothesis can be made at this time.

Another potentially important process involved in phosphorus cycling in fresh waters is enzymatic hydrolysis of phosphorus compounds to PO_4-P. Phosphatase enzymes are produced by bacteria, algae and zooplankton and provide a means of converting organically bound phosphorus into available PO_4-P in the water. Phosphatase production has been shown to be related to the levels of available phosphorus in the water and consequently production is highest under phosphorus limiting conditions while being repressed when phosphorus availability is high (Fitzgerald and Nelson, 1966), but the full implications of the phosphatases in the phosphorus cycle is not clear. Their relative importance in comparison with other phosphorus cycling mechanisms has not been quantified. Jansson (1976; 1977) concluded that in subarctic lakes, seston constitutes an important phosphorus source as a result of phosphatase activity and, in systems characterised by high silt loads but low soluble P levels, the role of phosphatases could be important.

1.3.2.3 The Role of The Littoral Zone

Littoral vegetation has also been shown to be an important component of the phosphorus cycle in fresh waters. Hutchinson and Bowen (1950) demonstrated both liberation of phosphorus into the epilimnion and uptake of phosphorus from the epilimnion by the littoral vegetation. In systems where extensive macrophyte beds can establish, they have been shown to play an important role in the phosphorus cycle. Swartvlei (Howard-Williams and Allanson, 1978) and some pans on the Pongolo River floodplain (Rogers, unpublished data) fall into this category.

However in the majority of South African impoundments extensive macrophyte beds are prevented from becoming established by the marked seasonal fluctuation in water levels and by the turbid waters. Consequently the littoral macrophytes may be of relatively minor importance in cycling in these water bodies. It must nevertheless be remembered that on an areal basis the production in the littoral zone can be many times higher than that in the open water. In Swartvlei the annual mean production of the phytoplankton is 74.0 mg C m^{-2} day^{-1} while the combined productivity of littoral algae and macrophytes is 3114 mg C m^{-2} day^{-1} (Howard-Williams and Allanson, 1978) Thus even a small area of littoral vegetation can have a disproportionately large influence on the overall metabolism of a water body.

1.3.3 Predictive Models

Despite the advances made with the advent of more refined experimental and analytical procedures, the complexities of the phosphorus cycle are such that predictive models, of sufficient reliability for the formulation of management strategies, could not be developed with the experimental data available. In the 1960's, the urgent need for rational management of culturally induced eutrophication in Europe, stimulated the development of the nutrient budget concept (Rigler, 1975). Considerable effort was directed towards the prediction of permissible loads from input/output models such as that of Vollenweider (1969), which attempted to predict phosphorus concentrations in lakes from simple parameters such as input and output rates, flushing time and lake morphometry, but ignored all biological and temporal complexities (Rigler 1973). The importance of the rate of external nutrient supply, as opposed to nutrient concentrations in the inputs, was stressed, and a number of predictive models based on nutrient loading rates were develope

including those of Brezonik (1972), Imboden (1974), Stumm (1974) and Imboden and Gächeter (1978).

Another simple means of predicting the impact of phosphorus loading arose from the observation of Sakamoto (1966) that chlorophyll and total P in the water showed a good correlation provided that an N:P ratio of greater than 12 was maintained. This was shown to hold in North American lakes (Dillon and Rigler, 1974) and if the total P concentration at spring overturn is known, the mean chlorophyll a concentration in the trophogenic zone in summer can be predicted. In turbid waters however, the role of suspended silt in reducing chlorophyll levels, through its influence on light, has been demonstrated (Walmsley and Butty, 1979) and no simple relationship between total P and chlorophyl is likely to exist in South African impoundments.

Although the existence of a relationship between chlorophyll levels in the water and nutrient loading rates is indisputable, the accuracy of predictions from models, such as the Vollenweider model, are of limited value because of the wide confidence limits which must be attached to them (Golterman, personal communication). This is attributable to a number of factors, one of which relates to the characterisation of phosphorus loads. In Vollenweiders' model, for example, total P is selected as the form of P describing the load. Schaffner and Oglesby (1978) questioned the validity of this and adopted the term biologically available P (BAP) which includes the soluble P fractions together with the labile P fraction which can be desorbed from silt. Estimation of the load is further complicated by the general inadequacy of the hydrological data which is required to calculate loading rate. In South Africa, the gauging weirs used to estimate water inflow are frequently not effective in measuring peak flows during floods, which often

contribute a large proportion of the nutrient input (Grobler, personal communication).

Another limitation of the input/output philosophy is that the internal processes involved in the P cycle are ignored. Potentially of greatest importance in this regard, is the role of the sediments as both a source and sink for phosphorus. In view of the conclusive evidence for the role of sediments in phosphorus cycling (Golterman, 1976) it seems unlikely that reliable predictions of the impact of phosphorus loading will be possible until sediment/water phosphorus exchange processes are integrated into the predictive models (Di Giano, and Snow, 1976). It may also be necessary to include factors such as turbidity, as has been done by Walmsley and Butty (1979), in the models.

Although the phosphorus fluxes which occur between compartments in the water are poorly understood, it is becoming increasingly evident that some understanding of these will be essential for the reliable prediction of the influence of phosphorus loads in fresh waters on productivity (Lean, 1973). In this regard it is clear from recent work by Francko and Heath (1979), that the processes involved in phosphorus cycling in the water vary markedly between systems. They showed that eutrophic lakes contained numerous low molecular weight compounds which are resistant to low dose ultraviolet radiation, but which readily release PO_4-P upon treatment with alkaline phosphatase. In contrast, filterable P compounds from a humic bog were predominantly high molecular weight and resisted enzyme hydrolysis but released PO_4-P upon irradiation with low doses of ultraviolet light. It is therefore clear that fundamental differences between different types of freshwater

bodies must be taken into account if phosphorus cycling is to be understood. Since South Africa is in some ways unique in that its water needs are provided mainly by shallow, usually monomictic impoundments which are often subject to silt-laden inflows (Noble and Hemens, 1978), it seems probable that the components within the phosphorus cycling system may well be ranked in a different order of importance from those in a rather deeper, cool temperate clear lake, the situation where many studies have been done.

1.4 Phosphorus Studies in South African Water Bodies

Toerien *et al.*, (1975) undertook a preliminary survey of the trophic status of 98 South African impoundments using the *Selenastrum capricornutum* bioassay and concluded that nitrogen and phosphorus were the nutrients which most commonly limited the algal growth potential. There was a tendency for nitrogen to be the limiting nutrient in eutrophic systems while phosphorus was generally the limiting nutrient in oligotrophic systems. This reflects the influence of sewage effluent and is typical of similar trends observed throughout the world (Mackenthun, 1973; Sawyer, 1973; Toerien, 1977). Following the preliminary survey, attention was focussed largely on the eutrophic impoundments in the vicinity of Pretoria with a view to assessing the extent of the problem and devising a rational management strategy for South African impoundments (Steyn *et al.*,1975a, 1975b; Steyn and Toerien, 1976a, 1976b; ; Toerien and Walmsley, 1977, 1978; Walmsley and Toerien, 1978; Walmsley *et al.*, 1978). During the interim period temporary guidelines for the control of eutrophication were drawn up (Toerien and Walmsley, 1977) and a comprehensive review of eutrophication in the South African context published (Toerien, 1977). Both of these reports emphasised the central role of phosphorus in eutrophication and advocated reduced phosphorus loading as the simplest and most effective

control measure.

The urgent need for a model which could predict the influence of phosphorus loading in South African waters was recognised, and the Vollenweider model was initially regarded as the most suitable (Toerien, 1977). After extensive testing on a variety of impoundments this model was subsequently shown to be inadequate (Walmsley *et al.*, 1979) and a concerted effort was made to formulate a model specifically for South African conditions (Walmsley *et al.*, 1979). In this endeavour processes influencing phosphorus cycling within the impoundments were largely neglected in favour of a more empirical regression analysis of phosphorus loading rates and chlorophyll levels measured in 21 impoundments. As in other countries (Rigler, 1975) this approach was necessitated by the urgent need for a rational management programme, and the lack of quantitative information regarding the role of internal processes in phosphorus cycling within impoundments prevented their inclusion in a predictive model.

Preliminary attempts to correlate PO_4-P and chlorophyll *a* in Roodeplaat Dam provided evidence that the relationship may be useful in predicting the influence of phosphorus loading in South African impoundments (Pieterse and Toerien, 1978). However, the 21 impoundment study undertaken by Walmsley *et al.*, (1979) indicated that the relationship between SRP loading rate and chlorophyll concentration was more suitable for predictive purposes than that between SRP concentration and chlorophyll level and a series of regression equations were developed to predict the impact of P loading under conditions of varying turbidity. It was however, acknowledged that the reliability was untested, that the role of internal processes was not clear and that future research should concentrate on these areas (Walmsley *et al.*, 1979).

The internal phosphorus cycle in South African water bodies is poorly understood. Preliminary work by Furness (1974) and Furness and Breen (1978) showed the potential influence of sediments in the Midmar Dam catchment on the phosphorus content of the river water, emphasising the P retention properties, but also suggesting that under certain conditions phosphorus release into the water may be induced. Similar observations were made in Midmar Dam using isolation columns (Twinch, 1976; Twinch and Breen, 1978 a and b) where the role of sediments as a source and sink for phosphorus was demonstrated. More recently the availability of sediment P to algae was demonstrated on 15 sediment samples from Bloemhof Dam, Spitskop Dam and the Vaalharts Weir using a bioassay technique (Grobler and Davies, 1979).

Undoubtedly the most comprehensive study of phosphorus cycling undertaken in South Africa was that by Howard-Williams and Allanson (1978) in the littoral zone of Swartvlei, a coastal lake. This included a detailed investigation of the fluxes of phosphorus between the sediments, water and biological components, and emphasised the importance of the littoral zone in nutrient cycling. Swartvlei however, differs markedly from the shallow turbid impoundments which comprise the majority of South African water bodies in that it has estuarine characteristics and that it is characterised by a well defined littoral zone dominated by aquatic macrophytes. Despite the contrast, the Swartvlei study was the first demonstration of the dynamic exchange of phosphorus between compartments in the aquatic environment in South Africa, and many of the basic principles involved are of relevance to the study of phosphorus cycling in general.

The processes involved in internal phosphorus cycling thus represent a considerable gap in the limnological information available in South Africa. This is reflected in the top priority rating for research into nutrient cycling and eutrophication processes in selected impoundments (Noble and Hemens, 1978). Some of the recent advances in the understanding of internal phosphorus cycling, and their relevance in South Africa, have been reviewed (Twinch and Breen, in press) and it is hoped that research into the role of these will eventually contribute to a more meaningful eutrophication management strategy.

1.5 The Use of Isolation Columns in the Study of Nutrient Cycling

In a system such as Midmar Dam, where nutrient loading is low and the seasonal cycle in phytoplankton standing crop indistinct (Hemens *et al.*, 1977), the phosphorus cycle can be regarded as being in a quasi steady state, as envisaged by Hayes and Phillips (1958) and Rigler (1973) In spite of rapid and continuous exchange between the various phosphorus compartments, very little net flux is occurring between them. In this state the exchange processes, and their potential significance in the phosphorus cycle, cannot be meaningfully assessed using conventional analytical techniques (Rigler, 1973). To stimulate measurable fluxes between the P compartments the steady state P equilibrium must be disturbed, either by external additions of P or by creating increased demand for P in the water.

In many eutrophic systems phosphorus fluxes can be detected using a mass balance approach and the role of lake sediments, as both a source and sink for phosphorus, has been demonstrated in this manner (Lee, 1976; Stevens & Gibson,1975; Cooke *et al.*, 1977; Osborne and Phillips, 1978;

White *et al.*, 1978). Under natural conditions in Midmar Dam this is, however, not possible, and the only method of inducing net fluxes is by artificial manipulation of nutrient levels. Whole-lake enrichment studies have been undertaken (Weatherley and Nicolls, 1955; Hepher, 1966; Smith, 1969; Schindler, 1971), but in fairly large impoundments which provide an important supply of water, this is impractical.

Nutrient fluxes in fresh waters have been studied in artificial systems in the laboratory (Confer, 1972), and in larger artificial ponds to which sediments or soils are added (Jackson and Schindler, 1975; Olness *et al.*, 1979). These are useful in the study of specific processes but cannot be regarded as reasonable approximations of a natural water body.

In Midmar Dam, the only alternative method of manipulating nutrient loads *in situ* is to use isolation columns, or enclosures, which effectively isolate a column of water, including an area of sediment, from the main body of water. This concept has been used by a number of limnologists to study various aspects of lake metabolism such as the response to nutrient enrichment (Goldman, 1962; Schindler, 1971; Dickman and Efford, 1972; Lean *et al.*, 1975; Golterman, 1976; Howard-Williams and Allanson, 1978; Lund, 1978; Twinch and Breen, 1978b; Landers, 1979) and to the removal of the external source of nutrients (Lund, 1972; Twinch and Breen, 1978a).

The dimensions of the isolation columns have varied considerably and the columns used during this study (19.6 m^2 in approximately 3.5 m depth) are of intermediate size. Lund (1972 and 1978) used by far the

largest columns (1626 m^2 in 11 m of water) and suggested that the larger columns, because they reduced the influence of periphyton, were more suitable. A number of workers have used 1 m diameter polythene tubing to enclose columns of water (Goldman, 1962; Schindler, 1971; Walmsley, 1976), but these are regarded as too small for long term studies, although they are of more use for short term experiments. Lean *et al.*,(1975) used columns of similar dimensions to the Midmar Dam columns (25 m^2 in 4 m of water) while Dickman and Efford (1972) used smaller wooden enclosures positioned in only 2 m of water. Howard-Williams and Allanson (1978) used considerably smaller columns (2,25 m^2 in 2 m of water), but they were concerned with dense littoral macrophyte beds in which the periphyton effect, so noticeable in similar studies in the pelagic zone, was insignificant.

Twinch and Breen (1978a) showed that isolation columns, of the dimensions used in Midmar Dam, have limited application in the study of phytoplankton populations. This is because of the tendency for periphyton, colonising the inside walls of the columns, to become the predominant biological component within the columns, and to contribute to the phytoplankton when dislodged by wave action. In this investigation it was not regarded as a serious problem because the concepts under investigation i.e. phosphorus flux between compartments in the water and the role of the sediments in phosphorus cycling, would be equally well demonstrated by periphyton or phytoplankton. Differences in the growth forms of periphyton and phytoplankton were not regarded as being critical in the final assessment of the role of sediments in the phosphorus cycle.

The advantages of being able to use a number of enrichment treatments as well as a control, and to conduct the experiments *in situ*, thus maintaining conditions as close to natural as possible, outweighed the disadvantages associated with using isolation columns.

CHAPTER 2

MATERIALS AND METHODS

2.1 *In Situ* Enrichment Experiments Using Isolation Columns

2.1.1 Construction of the Isolation Columns

The isolation columns used during this study were identical in construction details to those used in the preliminary studies (Twinch, 1976; Twinch and Breen, 1978 a). Each column consisted of an upper metal ring 5 m in diameter, buoyed up by eight 25 litre drums, from which an opaque blue or green nylon reinforced PVC ("Sterkolite") cylinder 4 m in length was suspended (Fig. 2.1). The lower end of the PVC cylinder was secured to a lower metal ring by folding it under the lower edge from the inside and securing it to a bracket welded onto the upper outside edge.

The columns were assembled on site and the upper and lower metal rings tied together so that the entire units could be floated to the required positions. Once positioned the lower metal ring was released and allowed to settle onto the substrate. When in position the lower ring was pressed firmly into the mud and an effective seal between the PVC and the mud was formed. No direct contact between the water in the column and the lower ring of metal was thus possible. With the aid of SCUBA the bottom ring was secured in position with metal pegs and concrete anchors, and a system of anchors and buoys, which restricted horizontal but allowed vertical movement of the upper ring, was attached (Fig. 2.1).

A 10 cm rim of wire mesh attached vertically to the upper edge of the top ring and a layer of grease smeared on the surface of the

drums prevented birds from roosting on the columns.

Periodic checks by SCUBA divers revealed no obvious disturbance of the seal between the columns and the mud during the experiment.

2.1.2 Selection of Sites

As discussed by Twinch (1976) a number of factors had to be considered when selecting the sites for the isolation columns. Firstly, the PVC columns were 4 m in length and the water depth requirements were therefore restricted. Allowance had to be made for vertical movement resulting from wave action, and about 0.5 m was regarded as being sufficient to compensate for this. The water depth selected was therefore approximately 3.5 m at full supply level in the impoundment.

Secondly, a reasonably flat substrate was essential to provide a good seal between the columns and the mud, and extensive echo soundings were made in selected areas of the dam to locate potential sites in the impoundment. Two criteria were used in selection, one being the accessibility of the site to the general public and the other being the exposure of the site to wind induced turbulence.

A suitable site was found between the Orient Park recreational area and the Thurlow Peninsula (Fig. 1.2). This fell within a bird sanctuary which was not accessible to the public and where the columns would not constitute a hazard to boating. In addition, the site was well protected from wind induced turbulence which minimised the possibility of the columns being disturbed.

While not representative of the deep open water of the main basin, the experimental area was regarded as being characteristic of the four flooded valleys which form a large proportion of the surface area of the impoundment (approximately 42%). Spatial variation in physical and chemical conditions in the water has been shown to be slight in Midmar Dam (Walmsley, 1976; Hemens *et al.*, 1977) and it was therefore felt that many of the findings made in the experimental area would be of fairly general applicability in the impoundment.

2.1.3 Design of the Enrichment Experiments

This experiment was designed to provide both higher loading rates and a more comprehensive enrichment programme over a more extended period than those used in the preliminary studies. The study was started in March 1976 and continued until May 1977.

Four isolation columns were used during this experiment. To monitor the response to isolation, and to serve as a control, one column (unenriched column) was not enriched. The remaining columns were enriched as follows 10 g PO_4-P as KH_2PO_4 weekly (column +P) sufficient to raise the concentration by approximately 150µg ℓ^{-1}; 14 g NO_3-N as KNO_3 weekly (column +N), sufficient to raise the concentration by approximately 200µg ℓ^{-1}; 10 g PO_4-P plus 14 g NO_3-N weekly (column N+P). In addition an adjacent open water station (open water) was monitored for comparison.

The PO_4-P loads may appear to be rather high relative to the loading rates of many eutrophic systems (Bengtsson, 1975; Ryding and Forsberg, 1976; Stevens and Gibson, 1976) but since it had previously been shown that PO_4-P added to the columns was rapidly removed from

solution by the sediments and by biological uptake, causing the quantity of available P in the water to remain low (Twinch and Breen, 1978 b) it was decided to use higher loading rates. In an attempt to maintain higher levels of PO_4-P for longer periods the enrichment levels were increased to 10 g PO_4-P weekly. This areal loading rate (approximately 26 g m^{-2} a^{-1}) is of a similar order of magnitude to the PO_4-P loads which entered Rietvlei Dam and Roodeplaat Dam, two eutrophic South African impoundments (Walmsley *et al.*, 1978) and are not therefore unrealistically high.

NO_3-N loading rates (approximately 37 g m^{-2} a^{-1}) were based on the areal inorganic N input into Haartebeespoort Dam from point sources only (Toerien, personal communication) and, compared with the inorganic N loads entering four eutrophic Transvaal impoundments (2.9 - 100 g m^{-2} a^{-1}) (Walmsley *et al.*, 1978), the NO_3-N loads used in these experiments are intermediate.

In the column +N and column N+P marked accumulation of the applied nutrients occurred during the winter months resulting in concentrations several orders of magnitude higher than those in the open water. Further additions at this stage would have been pointless and the enrichment treatments in these two columns were temporarily discontinued between August and November 1976.

Nutrient loads were applied once a week by spreading the appropriate salt, dissolved in 10 litres of dam water, over the surface of the water in the columns, after the weekly samples had been collected.

2.1.4 Water Sampling

Water sampling was undertaken on a routine weekly basis. Composite water samples were obtained from various positions in the columns by lowering a weighted PVC hosepipe (3 cm in internal diameter) to within 0.5 m of the bottom. Care was taken to prevent the hosepipe from dislodging periphyton. The integrated sample was then removed, by raising the lower end of the hosepipe with an attached cord, and decanting into a 25 litre polyethylene container. A minimum of five integrated samples were bulked to ensure that the final sample was as representative as possible of the water being sampled.

Because of the considerable time lag required for sampling (2-3 hours), a set sampling sequence was adhered to throughout. This sequence was adopted so that allowance could be made for sampling lag during the interpretation of measurements such as temperature and dissolved oxygen which show a marked diurnal cycle and could therefore change considerably during the time required for sampling.

Sampling was usually started at 09.00 hours. Samples were then returned to the laboratory and filtration through 0.45µ Gelman membrane filters, preleached with approximately 100 ml of distilled water, was undertaken immediately. The filtered water was then stored in glass at 4°C in the dark until analysis could be undertaken, usually within 24 hours.

2.1.5 Physical and Chemical Analyses

2.1.5.1 Dissolved Oxygen and Temperature

A YSI model 5492A combination oxygen and temperature probe, with an attached stirrer, was used to determine dissolved oxygen

concentrations and temperature. Routine recordings at the surface and bottom were made at weekly intervals throughout the study, and during April 1977 oxygen and temperature profiles (0.5 m intervals) were recorded at regular intervals for 48 hours, so that the diurnal cycle could be assessed.

2.1.5.2 Turbidity

Because primary production in fresh waters is largely related to light availability (Hutchinson, 1957) some index of turbidity was required during this study. A 20 cm secchi disc was used to estimate the depth of light penetration.

2.1.5.3 Chlorophyll

Chlorophyll concentrations (unacidified) were determined using the method outlined by Golterman and Clymo (1969). Triplicate subsamples, 100-200 ml depending on the phytoplankton standing crop, were filtered through 0.45µm membrane filters pretreated with 1 ml $MgCO_3$ suspension. Following filtration the intact filters were placed in 10 ml of 90% acetone and homogenised using an Ultra Turrax TP 18-10 homogeniser, centrifuged, and absorbance at 663 and 750 nm determined in a Beckman DBG spectrophotometer, using a 4 cm light path. Total pigment was calculated using the formula outlined by Golterman and Clymo (1969):-

$$\text{Total Pigment} = \frac{{}^{\upsilon}E_{663} - {}^{\upsilon}E_{750}}{\text{lightpath(cm)}} \times \frac{1000}{K} \times \frac{\text{vol. extract (ml)}}{\text{vol. filtrate}(\ell)} = \mu g\ \ell$$

where ${}^{\upsilon}E_{663}$ = absorbance at 663 nm

${}^{\upsilon}E_{750}$ = absorbance at 750 nm

K = extinction coefficient for chlorophyll *a* (89).

2.1.5.4 Soluble Reactive Phosphorus (SRP)

SRP was measured using the molybdate blue procedure outlined as a PO_4-P analysis by Golterman and Clymo (1969). In view of the apparent tendency for this method to over- estimate actual PO_4-P concentrations, the measured fraction is referred to as SRP and not PO_4-P (Rigler, 1973). Optical density was measured at 882 nm using a Beckman DBG spectraphotometer and a 4 cm light path. Triplicate subsamples were analysed and the mean concentration calculated. Blanks and standards were measured in the same way.

2.1.5.5 Total Phosphorus

Unfiltered water was digested by adding 7.5 ml of 5% $K_2S_2O_8$ (potassium persulphate) to a 50 ml subsample and autoclaving at 120°C for 1 hour (Menzel and Corwin, 1965). Following digestion SRP was analysed as described (section 2.1.5.4). The total P is assumed to include all P which was present in the water at the time of sampling All analyses were undertaken on triplicate subsamples. Blanks and standards were measured in the same way.

2.1.5.6 Nitrate Nitrogen (NO_3-N)

NO_3-N was determined using the salicylate method (CSIR 1969). Triplicate aliquots of filtered water, 50 - 200 ml depending on the NO_3-N concentration, were placed in 250 ml beakers and 1 ml of 0.5% sodium salicylate solution was added before the solutions were evaporated to dryness on a water bath. The residues were solubilised in 1 ml of concentrated H_2SO_4 and allowed to stand for 10 minutes after which approximately 6 ml of distilled water was used to dilute the acid before 30% NaOH was added until the solution became alkaline

and developed a yellow colour. The alkaline solution was then made up to 50 ml in a volumetric flask and optical density measured in a DBG spectrophotometer at 410 nm using a 1 cm light path. Blanks and standards were measured in the same way.

2.1.5.7 Periphyton

Harvesting periphyton growing on artificial substrates such as glass, as was done during the preliminary experiments (Twinch, 1976), can lead to unreliable estimates of standing crop and species composition of periphyton growing on different substrates (Vollenweider 1971). For this reason reinforced PVC ("Sterkolite") strips were used as a substrate on which periphyton was sampled during this study. Being identical to the PVC used to construct the columns, it was felt that this would provide the most reliable estimate possible. The dense growth of periphyton on the walls of the columns during the preliminary experiments showed that the material was not toxic to algae.

PVC strips 5 cm in width and 2.5 m in length were suspended from brackets attached to the top ring of the columns and from a specially constructed floating beam in the open water. In both cases approximately 5 cm of the strips remained above the water surface, and the effective depth over which periphyton was sampled was approximately 2.45 m.

The strips were suspended so that their orientation to the sun's path remained fairly constant and, by sampling both surfaces, it was hoped that the possible influence of shading within the columns would be accommodated.

Two strips from each of the isolation columns and the open water were sampled periodically (every 2-3 months) by gently removing them from the water, and placing them in plastic bags. On return to the laboratory, periphyton from the strips was removed by hand, using gloves and a standard microscope slide as a scraper, which proved most efficient. The periphyton was then rinsed into 80 ml centrifuge tubes with distilled water and concentrated by centrifugation. The supernatant was drained off, and the plugs of periphyton from each strip placed in tarred vitreosil capsules in an oven at 60°C. After cooling in a dessicator the dishes were reweighed and placed in a muffl furnace at 490°C until they reached constant weight (Paech and Tracey, 1956). After cooling the weighing procedure was repeated. Dry mass and ash free dry mass (organic matter) were then determined by difference.

Finally the residual ash was hand ground and subsamples from each strip were digested using concentrated HCl and HNO_3 (Paech and Tracey, 1956). To 1 g of ash weighed into a 25 ml beaker, 5 ml of concentrated HCl was added. The solution was thoroughly stirred using a glass rod and evaporated to dryness on a water bath. After 1 hour 5 ml of concentrated HNO_3 was added to the crystalline residue and the solution stirred to loosen material stuck to the glass. 10 ml of distilled water was added and the solution was filtered (Whatman No. 41) into a 50 ml volumetric flask and rinsed to volume. PO_4-P was then determined using the molybdate blue analytical procedure (Golterman and Clymo, 1969) after suitable dilution.

2.1.5.8 Bioassays

The Provisional Algal Assay Procedure (Bartsch, 1969) was used to assess the effect of the nutrient enrichments on the algal growth potential and on the order of limiting nutrients in the open water and isolation columns.

Growth potentials were measured using *Selenastrum capricornutum* in the Bottle Test (Bartsch, 1969) and, since P and N have been shown to be the primary and secondary limiting nutrients in Midmar Dam (Toerien *et al.*, 1975; Walmsley, 1976; Twinch, 1976; Hemens *et al.*, 1977), the spiking treatments were concerned with these two nutrients only. Nutrient Equivalent Spikes (National Eutrophication Research Program 1971) were used to identify the growth limiting nutrients, and three replicates of the following treatments were prepared for each determination:

1) 50 ml filtered (0.45µ) water with no additional nutrients added i.e. the algal growth potential (AGP)
2) 50 ml filtered water (0.45µ) to which 5 ml of ten times concentrated PAAP medium minus P was added i.e. (PAAP-P). Yields for this treatment are indicative of the total pool of soluble available P (SAP
3) 50 ml filtered water (0.45µ) to which 5 ml of ten times concentrated PAAP medium minus N was added i.e. (PAAP-N). Yields for this treatment are indicative of the total pool of soluble available N. (SAN).
4) 50 ml filtered water (0.45µ) to which 5 ml of a solution of N and P, minus all other nutrients, made up to ten times normal PAAP concentrations, was added i.e. (N+P). Yields for this treatment give an indication of whether nutrients other than N and P were present at levels which could become limiting.

Selenastrum capricornutum inoculum was prepared by centrifugating a 50 ml 14 day-old culture in PAAP medium, discarding the supernatant and resuspending the cells in 100 ml of distilled water. 1 ml of the inoculum was added to flasks containing the solutions and the cultures were incubated on a light table with continuous light (approximately 115 $\mu E\ m^{-2}\ sec^{-1}$) and aeration for 14 days at 25 $\pm$ 3°C. Optical density of the cultures was determined at 750 nm on a spectrophotometer using a 1 cm light path, and this was converted to dry mass from a calibration curve of absorbance versus dry weight, determined gravimetrically following filtration, as was done by Robarts and Southall (1977).

The yield coefficient (Y), which is defined as the mass of algal growth produced per mass of limiting nutrient removed, has been calculated for *Selenastrum* under N and P limiting conditions (Toerien, 1974), Y_P being 805 and Y_N being 35. Thus the yields obtained in the PAAP-P and PAAP-N treatments can be converted to initia concentrations of available P and N (SAP and SAN) by dividing by Y_P and Y_N respectively or, alternatively, yields of *Selenastrum* can be predicted by multiplying the measured nutrient concentrations by the respective yield coefficients. A comparison between predicted and obtained yields can be useful in assessing the extent to which nutrient analyses reflect available nutrients, and this approach was adopted during this study.

When P is referred to as the limiting nutrient in the text it will simply imply that the PAAP-P yield was significantly lower than the PAAP-N yield, and conversely when N was limiting that PAAP-N

yields were significantly lower than PAAP-P yields. The implication is not that the nutrient is "limiting" growth under natural conditions. Clearly, even though nutrient levels in the water are low, growth continues. Although the rate of growth may be influenced by nutrient concentrations in the water, it is also influenced by the rates of cycling between compartments which cannot be assessed from the bioassays.

2.1.6 Sediments

At the conclusion of the enrichment experiments thirty intact sediment cores were collected from each isolation column and from the open water in the immediate vicinity. These were collected in PVC tubes (4.5 cm internal diameter), which were fitted to a 5 m long aluminium holder and manually forced into the sediment. Cores were immediately transferred to the laboratory where they were allowed to stand for 3 hours after which the overlying water was gently siphoned off, leaving approximately 15 ml. The loose surface material was brought into suspension by gentle agitation and decanted into a 15 cm petri dish. The remainder of each core was extruded from below and stratified into the following layers : top 1 cm; 1-3 cm; 3-5 cm and 5-7 cm. Uneveness of the surface introduced a degree of subjectivity into the stratification procedure. To obtain sufficient material for analysis, the corresponding segments for all cores from the same location were composited, air dried and hand ground with a mortar and pestle before being stored in glass screw top containers at ambient temperature.

Furness (1974) showed that differences in sediment pH and exchangeable Al^{3+} concentrations reflected differences in the P binding potentials of sediments in the Midmar Dam catchment, while organic carbon (Hesse, 1973) and the P status of the sediments

(Syers *et al.*, 1973) can also influence the P exchange between sediments and water. These parameters were therefore measured on the stratified cores.

Three subsamples from each composite sample were used in the analyses. Organic carbon and exchangeable Al^{3+} were measured using the procedures outlined by Black (1965), while available P (using Brays No. 2 extractant and a soil : solution ratio of 1:10) and pH (in 1N KCl with a soil : solution ratio of 1:25) were measured using the procedures of Jackson (1958).

The two most widely used methods of extracting total P from soils and sediments are digestion with $HClO_4$ and fusion with Na_2CO_3 (Dick and Tabatabai, 1977). The former has been shown to give low results unless the digestion mixture contains HF (Sommers and Nelson, 1972) and specialised equipment, which was not available during this study, was required for the latter. In view of the hazards involved with working with boiling $HClO_4$ and HF it was decided that the acid digestion used on the periphyton would be adapted for use on the sediments. 1 g samples of air dried sediment were ashed in a vitreosil dish at 490°C and the digestion procedure as described in 2.1.5.7 followed, using 0.22µ membrane filters instead of Whatman No. 41 for the final filtration. PO_4-P in the final extract was measured using the vanado-molybdate procedure (Jackson, 1958). The fraction measured in this way is referred to as acid extractable P and is intended as an index of total P. To test the reliability of the acid extraction 1 ml aliquots of KH_2PO_4 solutions containing 70, 125, 260 and 540µg PO_4-P were added to triplicate 1 g subsamples of air dried, ground sediment,

sampled from Midmar Dam with a van Veen grab. These were equilibrated for 24 hours and available P and acid extractable P measured as described. From this the amount retained by the sediment could be assessed.

2.2 Laboratory Studies of Sediment/Water P Exchange

2.2.1 Adsorption Isotherms

Thirty intact sediment cores from the experimental area of Midmar Dam were collected and stratified as already described in section 2.1.7. P adsorption was measured after addition of PO_4-P to subsamples of air dried sediment. Stock solutions of KH_2PO_4 containing 137, 267, 375, 485, 610, 725 and 1425 µg PO_4-P in 25 ml were prepared in 0.002M Ca Cl_2 containing 0.5 ml of 40% formalin per litre, to eliminate the influence of microorganisms as far as possible (Thompson, 1971). These solutions were added to 1 g samples of air dried sediment and equilibrated for 24 hours on a rotary shaker at ambient temperature (20°C ± 3°C). The slurry was then filtered (0.2µ membrane filters) under vacuum and soluble reactive phosphorus (SRP) measured using the vanado-molybdate procedure of Jackson (1958). From the means of quadruplicate determinations, the amount of PO_4-P adsorbed was determined by difference. Adsorption isotherms, which can be defined as the relation between the amount of P adsorbed by an adsorbant and the equilibrium concentration of P at constant temperature, have often been used to characterise the P retention of soils and sediments (Olsen, 1958; Jacobsen, 1977; Ku *et al.*, 1978; McCallister and Logan, 1978). It has been suggested that P adsorption by sediments follows the Freudlich isotherm (Olsen, 1964), but most authors have favoured the Langmuir isotherm. According to Olsen and Watanabe (1957) the Freudlich isotherm, being empirical, is not specific, and applies

to a wide range of equilibrium P concentrations where large amounts of adsorbed P are involved. It is not possible to calculate a P adsorption maximum from the Freudlich equation. In contrast, the Langmuir isotherm has a sound derivation and is applicable to relatively smaller amounts of adsorbed P, and more dilute equilibrium P concentrations. This is important in its application to lake sediments which are usually overlain by waters containing very low concentrations of P. However, the major advantage of the Langmuir equation is that the P adsorption maximum and the bonding energy constant can be determined, and these are useful in characterising the adsorbing properties of a material (Thompson, 1971). Langmuir isotherms were thus used to characterise the P adsorption by surface layers in the Midmar Dam sediments and it was hoped that the constants would be useful in quantifying changes in the P retention properties of the surface sediments which have resulted since submergence.

Adsorption isotherms were obtained by plotting the mean equilibrium SRP concentration in the filtrate against the amount of P adsorbed per gram of sediment. The data was then plotted according to the Langmuir adsorption equation (Olsen and Watanabe, 1957; Eisenreich and Armstrong, 1978):

$$x/m = k\,b\,c/_1 + kc$$

where x/m = µg PO_4-P adsorbed per gram of sediment

b = the adsorption maximum (µg g^{-1})

c = equilibrium SRP concentration (µg ℓ^{-1})

k = the bonding energy constant (ℓ µg^{-1}) which is related to the bonding energy of the adsorbant for the adsorbate.

In the linear form the equation becomes :

$$c/x/m = \frac{1}{kb} + \frac{c}{b}$$

If the Langmuir equation applies, a plot of $c/x/m$ against c results in a straight line where the slope $= \frac{1}{b}$ and the intercept $= 1/kb$ or k = slope/intercept.

Linear regression analysis of the adsorption data was used to determine the Langmuir constants.

Determination of organic carbon, available P, acid extractable P, pH and exchangeable Al^{3+} was described in section 2.1.7.

2.2.2 Sediment/Water P Exchange

2.2.2.1 Uptake of P by Intact Cores

In August 1978 eight sediment cores approximately 8 cm in depth were collected from the experimental area in glass tubes 15 cm in length and 3 cm in internal diameter. This was done with the aid of SCUBA. After carefully depressing the tubes into the mud the intact cores were withdrawn and sealed from below with rubber bungs. They were then returned to the laboratory and allowed to settle for 12 hours at 17°C (the bottom water temperature at the time of sampling) in the dark.

Bottom water, sampled at the same time as the cores, was filtered (0.45μ) and the filtrate, which contained 16 μg ℓ^{-1} of SRP, was used to make up KH_2PO_4 stock solutions containing final SRP concentrations of 67, 115 and 210 μg ℓ^{-1} (i.e. 50, 100 and 200 μg ℓ^{-1} PO_4-P added) The filtration was necessary to remove suspended particulate material which could interfere with the sediment/water P exchange.

Carrier free ^{32}P as PO_4-P in dilute HCl (The Radiochemical Centre, Amersham, England) was added to duplicate 50 ml aliquots of the $^{31}PO_4$-P stock solutions, resulting in a final activity of approximately 0.14 $\mu Ci\ ml^{-1}$. The original solutions overlying the sediment cores were then withdrawn using gentle suction provided by a vacuum pump, and replaced with labelled solutions. Uptake of ^{32}P in the steady state, unenriched system, and in the systems receiving PO_4-P enrichments, was regularly monitored by withdrawing 1 ml aliquots of solution, after gentle agitation to ensure an even distribution of isotope, for the determination of total radioactivity.

At the same time, in an attempt to test for ^{32}P uptake by attached micro-organisms or by adsorption to the glass surfaces, two controls consisting of sealed glass tubes containing labelled solution but no sediment cores, were monitored in a similar way to the sediment/water systems. One control was inoculated with 50 ml of labelled filtered dam water and the other with KH_2PO_4 solution (made up in filtered dam water) containing 115 $\mu g\ \ell^{-1}$ of SRP. Because uptake in the controls was much slower, they were sampled less frequently than in the experimental systems.

After placing the 1 ml aliquots of labelled solution individually into plastic scintillation vials containing 10 ml of Beckman "Redy Solv" general purpose liquid scintillation fluid and shaking well, total radioactivity was determined with a Packard Tricarb model 3380 scintillation counter which was adjusted for background counts. The decay rate of ^{32}P was taken into account when preparing the uptake curves.

Temperature was maintained at 17°C throughout the experiment and, with the exception of short periods when samples were withdrawn, the columns were kept in the dark to reduce algal growth in the water and on the sediment surface. To reduce water loss by evaporation the tops of the columns were covered with perforated parafilm which, because it did not completely seal the units, did not induce anaerobic conditions.

After 80 hours ^{32}P concentrations in the most heavily enriched systems (200 µg PO_4-P ℓ^{-1}) were approaching an equilibrium level. At this stage the remaining labelled solution was carefully removed from one replicate of each treatment, and SRP was analysed in unfiltered solution as already described (section 2.1.5.4). Since the initial SRP concentration was known it was thus possible to estimate the net loss of SRP by difference. The remaining replicates were maintained under controlled conditions for a further two weeks to ascertain whether ^{32}P penetration into the sediments increased with time.

Analysis of the ^{32}P uptake curves was by the graphical method of Riggs (1963). If the uptake is described by a single exponential equation :

$$Y_t - Y_{asymp} = (Y_o - Y_{asymp})\, e^{-kt} \quad \text{-------- (1)}$$

where Y_t = % ^{32}P remaining in solution at time t.

Y_{asymp} = % ^{32}P remaining in solution at equilibrium.

k = rate constant

the semilog plots of $Y_t - Y_{asymp}$ against time will be linear. This was not the case, and the graphical curve splitting technique

described by Riggs (1963) was used to split the curves into two distinct exponential phases. Separation of the two reactions was achieved by extrapolating the slower reaction to zero time and subtracting its exchange contribution from that of the faster reaction (0-10 minutes), which was then replotted (Fig. 4.4). The curves were thus better described by a combination of two exponential equations:

$$Y_t = Ae^{-k_1 t} + Be^{-k_2 t} \quad \text{--------} \quad (2)$$

where A = Y intercept of the extrapolation of the faster reaction

B = Y intercept of the extrapolation of the slower reaction

Once the curves had been split graphically the standard exponential curve fit programme for a Hewlett Packard model 97 was used to generate the coefficients of determination, the rate constants and the Y intercepts for both exponential phases of all uptake curves.

The rate constants for the various exponential functions could be used to estimate the exchange rate of PO_4-P under steady state conditions using the following formula :

$$PO_4\text{-P exchange rate } (\mu g\ cm^{-2}\ hr^{-1}) = k \times SRP \times \frac{1}{SAS} \times \frac{Vsol}{1000} \quad \text{-----(3}$$

where k = rate constant (hr^{-1})

SRP = steady state SRP concentration ($\mu g\ \ell^{-1}$)

SAS = surface area of sediment (cm^{-2})

Vsol = volume of solution in the sediment/water system (ml)

The maximum possible P fixation rate (MPFR) in the enriched sediment water systems was calculated from the following formula.

$$MPFR\ (g\ cm^{-2}\ hr^{-1}) = k \times (SRP_{t/o} - SRP_{t/asymp}) \times \frac{1}{SAS} \times \frac{Vsol}{1000} \quad \text{----(4)}$$

where k = rate constant (h^{-1})

$SRP_{t/o}$ = initial SRP concentration ($\mu g\ \ell^{-1}$)

$SRP_{t/asymp}$ = SRP concentration at equilibrium ($\mu g\ \ell^{-1}$)

SAS = surface area of sediment (cm^{-2})

Vsol = volume of solution in the sediment water system (ml)

To obtain an overall rate of P fixation at a given PO_4-P loading rate, the rates for the rapid and slow phases of uptake were combined.

The relative exchange characteristics between soluble P fractions, identified by gel filtration analysis, and the sediments, were also examined. Labelled colloidal P and PO_4-P fractions (5 ml aliquots) were added to steady state sediment water systems similar to those used in the unenriched treatments already described (section 2.2.2 Uptake of ^{32}P by the sediments was then monitored using the standard procedure.

2.2.2.2 Release of P by Intact Cores

After the labelled solution had been removed from one replicate of each ^{32}P uptake treatment, it was immediately replaced by 50 ml of 0.1M NaCl (Li *et al.*, 1972) which was used to rinse the column,as thoroughly as possible,of traces of free ^{32}P on the glass surface and on the sediment surface. After 2 hours settling the rinsing solution was carefully removed by gentle suction.

To measure P release into the water an artificial demand was created by using P free 0.1M NaCl as a leaching solution. Fifty ml was carefully added to the labelled sediment cores and the release

of soluble ^{32}P was monitored at increasing intervals for 2 hours, after which an asymptote had been reached in all columns. Soluble reactive phosphorus concentrations were measured in the equilibrated solutions so that release rates could be calculated.

When the leaching solution was added to the labelled sediments it was impossible to prevent some disturbance of the sediment surface. It was thus necessary to separate the soluble ^{32}P released into the water from the labelled particulate material brought into suspension when the leaching solution was added. This was done by withdrawing 2 ml aliquots and filtering them through specially designed 25 mm filter units which allowed for direct collection of the filtrate in scintillation vials. Gelman Metricel (GA -6) membrane filters (0.45μ) were used for this purpose. 10 ml of scintillation fluid was then added to the filtrate and total radioactivity determined.

The analysis of curves such as the ^{32}P release curves, has been discussed by Riggs (1963). Although the amount of ^{32}P released did not increase exponentially the rate of change of ^{32}P concentration $Y - Y_t$ appeared to decrease exponentially until the asymptote was reached. This decrease could be described by the equation :

$$Y_{asymp} - Y_t = (Y_{asymp} - Y_o)\, e^{-kt} \quad \text{-------- (1)}$$

where Y_{asymp} = ^{32}P activity in solution at equilibrium

Y_t = ^{32}P activity at time t.

As discussed in section 2.2.2.1, if the plot of $Y_{asymp} - Y_t$ versus time is linear the data is adequately described by a single exponential function. During the ^{32}P release experiments this was not the case and the curve splitting technique as described in section 2.2.2.1 was

used to characterise the release into a fast and a slow phase.

To calculate the maximum possible release rates (MPRR) the following formula was used :

$$MPRR(\mu g\ cm^{-2}\ hr^{-1}) = k \times SRP_{t/asymp} \times \frac{1}{SAS} \times \frac{Vsol}{1000} \times 60 \quad ----(2)$$

where k = rate constant (min^{-1})

$SRP_{t/asymp}$ = SRP concentration at equilibrium ($\mu g\ \ell^{-1}$)

SAS = surface area of sediment (cm^{-2})

Vsol = volume of solution in the sediment water system (ml)

2.2.2.3 Depth of Sediment Involved in P Exchange

Following the P release experiments the NaCl solution was withdrawn leaving a residue of 3 to 5 ml. The loose surficial sediments were removed by gentle agitation and decanted into a small preweighed plastic container. This comprised the first layer of the stratified core. The sediment core was then gently extruded from above to prevent tracer contamination of deeper layers, and stratified into 1 cm segments which were placed in small preweighed plastic containers. Each segment was thoroughly homogenised by hand using a glass rod and weighed while wet. A small subsample (0.05 - 0.10 g) was placed in a scintillation vial, mixed with 1 ml of distilled water and shaken to separate the sediment particles as far as possible. Radioactivity was then determined following addition of 10 ml of scintillation fluid and the final counts were corrected for quenching caused by the sediment subsamples.

The remainder of the homogenised samples were then oven dried (60°C) and reweighed after cooling in a dessicator. Water content

and dry mass of the various strata were determined by difference.

Three weeks after the experiments were started, the remaining replicates of each treatment were drained of labelled solution and the vertical distribution of isotope determined as already described in this section.

2.3 Cycling of P Within the Water Column

Following the findings of the 1976-77 *in situ* enrichment experiments a co-ordinated research programme involving the University of Natal (Departments of Botany and Zoology) and the National Institute for Water Research was undertaken during the summer months of 1977-78 and 1978-79. The programme was designed as a comprehensive investigation of the response of isolated columns of water to enrichment with NO_3-N only. During 1977-78 five isolation columns were used in a factorial NO_3-N enrichment experiment using the following loading rates : column (1), unenriched; column (2), 25µg NO_3-N ℓ^{-1} $week^{-1}$; column (3), 50µg NO_3-N ℓ^{-1} $week^{-1}$; column (4), 100µg NO_3-N ℓ^{-1} $week^{-1}$; column (5), 200µg NO_3-N ℓ^{-1} $week^{-1}$. During 1978-79 this was modified so that column (1) remained unenriched but columns (2)-(5) all received 200µg NO_3-N ℓ^{-1} $week^{-1}$.

The priority sub-project within this overall programme with which I was involved was an investigation into P cycling within the water column. This was aimed specifically at helping to explain some of the observations made during the 1976-77 enrichment experiment, and the results and discussion of this study form part of this thesis.

2.3.1 Phosphorus Turnover Times

Estimates of P turnover time were made using the methods described by Lean (1973), Lean and Rigler (1974), Peters (1975, 1978, 1979) and Peters and MacIntyre (1976). Composite water samples, used in the routine monitoring programme and collected as described (section 2.1.4), were returned to the laboratory as soon as possible after collection (usually within 2 hours) and 100 ml subsamples were placed in 250 ml glass beakers. These were spiked with approximately 10 µl of carrier free ^{32}P as PO_4-P in dilute HCl (The Radiochemical Center, Amersham, England) containing not more than 6.9×10^{-5} µg PO_4-P. Uptake of ^{32}P by the particulate fraction was monitored at increasing intervals for 4-6 hours by filtering 5 ml aliquots of the labelled solution through 0.45µ Gelman Metricel (GA -6) membrane filters on a 25 mm filter unit under vacuum (approximately 0.5kPa cm^{-2}).

The filters were then rinsed with 5 ml of distilled water and transferred to 10 ml of Packard'Instagel'or Beckman'Redy Solv'EP scintillation fluids in a plastic scintillation vial. Tests indicated that the efficiency of counting with both 'cocktails' was similar. Total radioactivity on the filters was then measured in a Packard Tri-carb scintillation counter after at least six hours. Total activity in the unfiltered samples was determined in a 1 ml aliquot. All uptake experiments were conducted at ambient temperature under constant illumination (approximately 5 µE m^{-2} s^{-1}) on a laboratory bench.

The ^{32}P uptake curves were analysed in a similar manner to those already described in section 2.2.2.1 using the graphical method of Riggs (1963). With only four exceptions the curves were adequately described by a single exponential equation and the curve splitting procedure was

therefore unnecessary. The four remaining curves were diphasic and were analysed accordingly using the methods described previously in section 2.2.2.1.

Coefficients of determination, rate constants and Y intercepts were generated with a Hewlett Packard model 97 using the standard exponential curve fit programme. The P turnover times were calculated from the constants (Turnover time = $^1/_k$).

Between February and May 1978 P turnover times were monitored every two weeks in the open water and in the five columns. During the 1978-79 enrichment experiments, P turnover times were monitored at approximately three weekly intervals between September and January.

2.3.2 Physical and Chemical Analyses

2.3.2.1 Chlorophyll

Because of the important influence of phytoplankton on P turnover times (Lean, 1973; Peters, 1975; Lean and Nalewajko, 1976) chlorophyll levels were measured as an index of phytoplankton standing crop. The methods have been described in section 2.1.5.3.

2.3.2.2 Total Suspended Solids (TSS)

The aim of the ^{32}P uptake experiments was to study the rates of P exchange between soluble and particulate compartments. While chlorophyll levels give an index of the phytoplankton standing crop, they are of limited use as an index of particulate material in Midmar Dam because of the predominance of inorganic material in this fraction (Johnson, unpublished data). For this reason TSS was determined as an index of the total particulate P fraction consisting of living and dead organic material as well as inorganic material, all of which have

the potential to exchange P with the water to varying degrees (Halman and Stiller, 1974).

TSS was determined gravimetrically following filtration of a 250 ml sample through a preweighed membrane filter (0.45µ pore size Gelman GA -6). The filters were dried at 60°C for 24 hours, cooled in a dessicator and reweighed. TSS was determined by difference and a mean of three analyses was calculated for each sample.

2.3.2.3 Phosphorus Analyses

P analyses were undertaken by the National Institute for Water Research, Regional Laboratory, Durban. SRP was determined at 880 nm on a Technicon autoanalyser after treating filtered water with acidified molybdate and ascorbic acid. Total soluble phosphorus (TSP) was determined after initial oxidation of the filtered sample with acidified persulphate followed by the SRP procedure. Total P was measured on unfiltered water, following digestion with sulphuric acid and peroxide, using the SRP procedure (section 2.1.5.4).

2.3.3 Fractionation of Soluble P

2.3.3.1 Open Water and Isolation Columns

Gel filtration analysis in conjunction with ^{32}P uptake experiments (Lean, 1973; Lean and Nalewajko, 1976; Peters, 1977, 1978, 1979; Downes and Paerl, 1978) was used to characterise the soluble P fractions under varying conditions.

A single Wright gel filtration column (2.5 x 100 cm) was packed with Sephadex G25 (fine) gel according to the manufacturers specifications. Sephadex G25 is the standard gel used in the fractionation of

soluble P in fresh waters and has a molecular weight fractionation range of 100-5000. Molecules larger than the largest pores of the swollen Sephadex cannot penetrate the gel particles and therefore pass through the column in the liquid phase. Smaller molecules, however, penetrate the gel particles to a varying extent depending on their size, and elution of the molecules takes place in the order of decreasing molecular size.

The eluent used was an aqueous solution of 0.3% sodium chloride and 0.02% sodium azide, the latter preventing microbial activity in the column (Lean, 1973). Flow rate of the eluent was maintained at approximately 1 ml min^{-1} during all fractionations by means of a LKB 2120 Variaperpex II peristaltic pump and 10 ml fractions were collected by means of a LKB 2112 Redirac fraction collector.

Void volume of the column was determined using dextran blue and showed negligible variation throughout the experiments, remaining at 100 ml.

The volume of labelled filtrate used during the fractionations varied according to the radioactivity. At low activities the volumes introduced were larger, to facilitate more efficient scintillation counting, but never exceeded 10% of the void volume (100 ml). On most occasions approximately 5 ml samples were used. Recovery of the ^{32}P introduced into the column was always higher than 90%.

Total radioactivity in the fractions was determined after transferring 1 or 2 ml (depending on the activity added to the column)

into 10 ml of scintillation fluid in plastic vials.

The first fractionations were undertaken on surface water collected from column 5 on October 25, 1978 at a time when chlorophyll levels were markedly increased due to a bloom of *Eudorina* sp. Uptake of ^{32}P was monitored using the routine method and after 2 minutes, 6.5 hours and 20 hours, 5 ml of labelled filtrate was fractionated.

The availability of only a single fractionation system made it impossible to undertake fractionations at intervals of less than 4-5 hours without storing the samples. Lean (1973) demonstrated how rapidly some of the labile fractions can be transformed after filtration and storage of samples could therefore introduce some error. Whenever a delay was necessary the time will be indicated in the results,as was done by Lean (1973). If fractionation could not be undertaken immediately the filtrate was stored at $4^{o}C$ in the dark for the duration of the delay.

In March 1979, after routine monitoring of the isolation columns had stopped, *Microcystis* sp. developed in the column 5 and a surface water sample was used to measure ^{32}P uptake. During this experiment labelled filtrate sampled at 10 minutes, 1 hour and 2 hours was fractionated.

A further fractionation experiment was undertaken on 9 hour filtrate from the routine ^{32}P uptake experiments conducted in all of the isolation columns and in the open water on November 14, 1978.

2.3.3.2 *Anabaena flos-aquae* Culture

For comparison with the experiments using natural phytoplankton populations, and in an effort to confirm that the methods being used for the fractionations were comparable with those used by Lean and Nalewajko (1976), a fractionation experiment was carried out in a culture of *Anabaena flos-aquae*, originally obtained from the National Institute for Water Research, Pretoria, South Africa.

A stock culture of *Anabaena* in PAAP medium (Bartsch, 1969) was incubated until the stationary phase of growth was attained. At this stage 5 ml aliquots were used to inoculate 100 ml of PAAP solution in five 200 ml flasks. One of these was labelled with approximately 50μ Ci ^{32}P as PO_4-P in dilute HCl. The cultures were then incubated on a light table (100 μE m^{-2} s^{-1} at 23± 3°C) and subjected to a 16- 8 hour light/dark regime.

The distribution of ^{32}P was determined by filtration (0.45μ) and gel filtration analysis of the filtrate, before inoculation and then at 1, 1.5, 4, 6, 11, 17 and 22 days. The unlabelled flasks were used to monitor growth of the cultures. After thorough mixing 5 ml aliquots were withdrawn from each flask under sterile conditions and turbidity was measured at 750 nm every two days, using a 4 cm light path. The mean increase in turbidity in the four unlabelled flasks was used as an index of growth in the labelled culture. Growth was not measured directly in the labelled culture to avoid contamination of the equipment used to measure turbidity. Very little variation was detected between the replicates used to determine growth, and growth in the labelled culture was regarded as being comparable with that in the

unlabelled flasks.

In determining the changes in isotope distribution in the culture the final counts were adjusted to compensate for the short half-life of ^{32}P.

2.3.4 Exchange between Soluble and Particulate P

To test the relative exchange characteristics between the soluble P fractions obtained by gel filtration analysis and the particulate fraction, a routine ^{32}P uptake experiment was undertaken on Midmar Dam surface water. Filtrate, obtained after 5 hours,was fractionated and since the biological uptake of the fractions was to be investigated, sodium azide was excluded from the eluent. Aliquots (5 ml) of the labelled PO_4-P and colloidal P fractions were then added to 100 ml subsamples of the original dam water sample. Uptake of ^{32}P by the particulate fraction was monitored using the standard procedure.

Retention of the colloidal P fraction during filtration was demonstrated by Lean (1973) and to determine the extent to which this may have influenced the colloidal P uptake experiment duplicate 5 ml aliquots of labelled colloidal P were filtered. Activity on the filters and in solution was determined and the proportion retained calculated by differenc

Lean (1973) showed that no direct complexing between colloidal P and PO_4-P occurred in Heart Lake. However, the possibility that this does occur in Midmar Dam, due to the presence of inorganic colloids which pass through the filter was examined by conducting a routine $^{32}PO_4$-P uptake experiment in filtered Midmar Dam surface water.

CHAPTER 3.

In Situ Enrichment Experiments Using Isolation Columns

3.1 Introduction

This enrichment experiment was set up to test the hypothesis that the sediments in shallow areas of Midmar Dam form a major component in the P cycle, providing both a source and a sink for P under varying conditions (Twinch and Breen, 1978 a and b). To do this the enrichment regimes used involved the addition of N and P, singly and in combination, and were designed to create a range of conditions within the isolation columns, which would induce P fluxes to and from the sediments.

To facilitate interpretation and discussion of the data the results are dealt with in four sections :-

a) Thermal, Oxygen and Light Regimes

b) Fluxes in Chlorophyll, Periphyton, SRP, Total P and NO_3-N.

c) Algal Bioassays.

d) The Sediments.

3.2 Thermal, Oxygen and Light Regimes

Since isolation columns in Midmar Dam were shown to alter physical conditions in the water, primarily by reducing turbulence which can result in increased light penetration and the development of more marked stratification (Twinch and Breen, 1978a), it was necessary to obtain some index of whether these changes were influencing nutrient fluxes during this experiment. Thermal regimes are important because thermal stratification can impede the vertical exchange of nutrients in the water column.

Oxygen regimes, through their influence on sediment/water P exchange, are also important in relation to the P cycle and need to be monitored in a study of this nature. Furthermore in fairly shallow water light penetration has the potential to influence the sediment/water P exchange, directly through its influence on benthic flora, and directly through its influence on the vertical distribution of phytoplankton, and consequently on the oxygen profiles. Temperature and oxygen profiles together with light penetration were therefore measured on a routine basis throughout the study.

Because this section deals with physical responses to isolation, the influence of evaporation, precipitation and fluctuating water levels in the impoundment is also considered.

3.2.1 Results and Discussion

3.2.1.1 Thermal conditions

Isolation of the water in the columns (April, 1976) coincided with the onset of winter thermal conditions in Midmar Dam (Walmsley, 1976). Not surprisingly therefore, temperature in the open water and within all columns had declined steadily from 19°C to 13°C by week 8, after which the rate of decline was much slower and took a further five weeks to decrease to c. 10°C (Fig. 3.1 A-E). As expected, the decrease in temperature resulted in reduced stratification and frequent isothermal conditions during the first 13 weeks. Thereafter the advent of spring (August/September) resulted in steadily increasing temperature over a period of 25 weeks, until week 38 (January) (Fig. 3.1 A-E), by which time it had reached the summer maximum. This was maintained until week 43. The phase of increasing temperature and the subsequent summer conditions were accompanied by increased thermal

gradients between surface and bottom, both in the open water (4°C on week 30)(Fig. 3.1 A), and in the columns (e.g. 5°C on week 30)(Fig. 3.1 C-E). Clearly, the marked seasonal trends in temperature in the open water were not greatly altered in the isolation columns.

Thermal gradients do however have a marked influence on mixing of the water column (Hutchinson, 1957) and because water density changes more rapidly at higher than at lower temperatures (Ruttner, 1963) the apparently slightly higher surface temperatures and thermal gradients within the columns, particularly during summer, could have been of considerable importance.

The procedure of sampling in sequence results in a time differential between stations (in this case approxiamtely 2 hours), which allows more heating, particularly of surface waters, to take place As a result, the changes observed between columns and open water might simply have been due to heating during the period required for sampling. The significance of this observation may be gauged by examining data from a 48-h study (Fig. 3.2 and 3.3).

The air temperature showed a rapid warming phase (approximately 1.8°C h^{-1}) starting between 06.00 and 07.00 hours and reached a maximum of 21°C between 11.00 and 14.00 (Fig. 3.3B). During this period, surface water temperatures increased to approxiamtely 21°C in the open water, and to slightly more (22°C) in the columns (Fig. 3.3 A). Thus during the sampling on a bright clear day, there was sufficient time lag to allow surface water to heat up by 1.5-2.0°C. Single estimations have therefore to be interpreted with caution, particularly when

considering thermal stratification.

In the open water the incoming radiation on the first day resulted in slight thermal stratification. At 11.00 hours there was a temperature difference of 1°C between surface and bottom waters (Fig. 3.2 a) but, due to mixing, heat was transferred to deeper waters resulting in isothermal conditions between 16.00 and 18.00 hours. In the columns, heat transfer to deeper water was less efficient and consequently surface temperatures increased to approximately 1°C above those recorded in the open water while bottom waters peaked at approximately 0.5°C lower (Fig. 3.2 b-e). In spite of these differences the mean temperature in the isolation columns and open water were virtually identical at most times during the first 24 h (Fig. 3.3 A) indicating that the total heat energy absorbed was not markedly influenced by isolation. This was not so apparent on the second day when cloudy conditions developed between 11.00 and 13.00 hours and caused a slightly more rapid cooling after 13.00 hours in the open water.

During the cooling period, the air lost heat more slowly than it had heated (0.7°C h^{-1}) and reached a minimum of 10.5°C on the first day. On the second day, cloudy conditions developed in the evening and radiation was reduced so that the air did not cool to the same extent and the minimum recorded was 13.5°C.

Heat loss from the surface waters of the columns was more rapid than in the open water, probably because of the greater differences between surface water and air temperatures, and by 20.00 hours surface temperatures inside and outside the columns were similar. At this stage the thermal gradient between air and surface waters was approximately

4°C and the continuing decline in air temperature was sufficient to effect rapid cooling of surface waters, resulting in the progressive development of inverted stratification, in much the same manner as Ganf (1974) observed in the shallow tropical Lake George. Although this trend was most evident during the first night because the clear skies permitted a rapid drop in air temperature, it was also detectable on the second night in spite of the higher air temperature. At all times it was better developed in the columns (Fig. 3.2). The reasons for the reduced inverted stratification observed in the control column during the first night are not clear.

Isothermal conditions were therefore present twice during each 24-h cycle and although they tended to be short lived, on the second day they persisted for up to 3 hours. Thus although thermal stratification did develop it was never sufficient to partition the water, and thus prevent mixing, for long periods.

In general therefore, the difference in thermal conditions, and thus mixing patterns, between the open water and columns was probably of minor consequence in relation to nutrient fluxes.

3.2.1.2 Oxygen

In the open water oxygen levels remained fairly stable showing a slight seasonal fluctuation (Fig. 3.1A) being generally lower during the warmer period. At the surface this was probably partially attributable to decreased solubility but in bottom waters, the decrease was relatively greater, and could only have been due to biological demand which resulted in increased oxygen stratification.

Data from the 48-h study (Fig. 3.2A) indicated a distinct diurnal oxygen cycle in the open water. During the daylight hours oxygen saturation increased from the pre-dawn level of about 60% at all depths, to between 70-100% at 18.00 hours. Assuming a constant rate of diffusion of oxygen into the water, this is probably indicative of considerable photosynthetic activity. No marked oxygen stratification was detected at the end of the first day while a difference of 25% existed between surface and bottom on the second day. No reasons for this were obviously apparent. After dusk oxygen saturation at all depths decreased steadily with time, reaching a minimum of 60-70% saturation at 04.00 hours. Thereafter, even in diffuse pre-dawn light, the levels began increasing, reaching 75-80% by 07.00 hours. Clearly, respiratory demand during the night exceeded the influx from the atmosphere and considerable photosynthetic activity was required to replenish this during the day.

Because of the higher temperatures during the summer, which result in lower oxygen solubility and increased metabolic activity, anaerobic conditions are most likely during this period. It is clear from this data that no severe oxygen depletion occurs in the shallow open water during the summer and it therefore seems unlikely that anaerobic conditions ever develop in the open water of the experimental area. These observations support those of Walmsley (1976) who detected severe oxygen depletion only in the deeper areas of Midmar Dam.

Within the columns, and particularly those in which production was markedly stimulated by enrichment, oxygen depletion at night was a possibility since even an unenriched column can show marked increase in

production, principally as a result of colonisation of the walls by periphyton which was shown previously (Twinch and Breen, 1978a) and which will be discussed in section 3.3. Minimum oxygen levels in the unenriched column were never lower than in the open water during the routine monitoring (Fig. 3.1B) and therefore the development of anaerobic conditions was very unlikely. In the enriched columns however bottom water oxygen levels were regularly lower than those in the open water but did not drop below 5 mg l^{-1} (approximately 55% saturation)(Fig. 3.1E). It should be borne in mind however, that there was a time lag between sampling the open water and columns. Thus the levels were lower in spite of having had time to make up the deficit by oxygen production during photosynthesis. Pre-dawn levels could therefore have been even lower.

Considering the data for the 48-h study, which was accumulated at a time when the standing crop of *Microcystis* sp. in the columns receiving weekly additions of NO_3-N (Fig. 3.2d) and NO_3-N and PO_4-P (Fig. 3.2e) was particularly high (chlorophyll levels 20-40 µg l^{-1}), it is clear that oxygen levels in the columns never dropped below 50% saturation and it seems unlikely that anaerobic conditions were ever present. Certainly they would have been less likely at times when the phytoplankton standing crop was lower. However, since even short periods of anoxia may influence nutrient fluxes this aspect requires further investigation and will be discussed further in section 4.3.2.

3.2.1.3 Light Penetration

At the open water station (Fig. 3.1A) secchi disc transparency, although it increased during the summer, never exceeded 150 cm, and it

seems unlikely that there was sufficient light to maintain substantial algal growth on the substrate 3.5 m below the surface.

Transparency in the columns was more varied than in the open water. In two of the columns (Figs. 3.1B and C), with the exception of the final two weeks in the unenriched column (Fig. 3.1 B), transparency tended to be similar to that of the open water. In the two other columns (Figs. 3.1 D and E) during the first 28 weeks, transparency was frequently greater than 200 cm and reached a maximum of 300 cm. During this period there may have been sufficient light reaching the substrate to support benthic algal growth but, because of the lower winter temperatures (10.5-18^{o}C), the rate of growth would probably have been low.

This observation is supported by the slower rate of nutrient uptake noted during this period compared with the summer months (section 3.3). During the subsequent weeks (29-50) transparency decreased to 150 cm and less. Thus when temperatures were highest transparency was low, due primarily to blooms of *Microcystis*, and it seems unlikely therefore that benthic algae played an important role in nutrient fluxes.

The influence of isolating a column on physical conditions in the water, has not been stressed in studies in other enclosures. Lund (1972) demonstrated clearly that light penetration in his experimental tubes was often more than double that in the open water of Blelham Tarn, and Lack and Lund (1974) reported that thermal conditions, such as the degree of stratification, were very similar to the lake outside. Howard-Williams and Allanson (1978) reported

that the pattern of temperature in enclosures in Swartvlei remained virtually identical to that in the main body of water, as did that for dissolved oxygen. They concluded that enclosing the littoral community for 23 weeks had very little influence on physico-chemical conditions.

In general it thus seems that, although physical conditions within enclosures do change relative to the open water, these changes are slight. From the data obtained during this study it is concluded that changed physical conditions within the isolation columns in Midmar Dam probably did not induce marked changes in the rate or extent of nutrient fluxes between the water and substrate, or within the water column. Nutrient dynamic studies in the isolation columns can therefore give some index of the general responses of the adjacent open water system to various enrichment treatments.

3.2.2 The Role of Fluctuating Water Levels

Since the water within isolation columns is effectively sealed from the natural hydrological regime of the open water, fluctuations in water level due to evaporation and precipitation, could influence the interpretation of P fluxes within the columns by either diluting or concentrating nutrients in the water.

Although evaporation and precipitation were not measured on site during this study, comprehensive meteorological data for the period 1914 to 1975 are available at the Cedara Agricultural College (Reynolds, undated The meteorological station is positioned approximately 5 km from the experimental area and, although slight differences in both evaporation and precipitation between Cedara College and Midmar Dam exist (Reynolds, personal communication), the evaporation and precipitation data were used

to estimate the expected net loss of water from the columns during the enrichment experiments. Despite the constraints on extrapolating this data to Midmar Dam, they provide the only opportunity of assessing the possible influence of evaporation during the experiments and any error in the estimates will remain constant for all columns.

From the mean monthly evaporation, measured in an American class A pan, a loss of approximately 1303 mm of water over the 13 month experiment can be calculated. However, over the same period, 1070 mm of precipitation can be calculated from the mean monthly rainfall figures (Reynolds, undated). Thus a net loss of approximately 233 mm of water from the columns could be expected. As a proportion of the total depth (approximately 3.5 m) this represents only 6.6% and even if this were an underestimate, the overall influence of evaporation during the experiment was not considered to be of great importance. At times during the dry periods, the influence of evaporation may have been enhanced, but in view of the absence of on site evaporation measurements, and on the limitations of the Cedara College meteorological data for accurate extrapolation to Midmar Dam, it was felt that any attempt to compensate for evaporation by addition of water to the columns would be of little value.

It was reported by Chutter (1979) that steps to compensate for evaporative demand in unenriched isolation columns in Rietvlei Dam were inadequate, and the observed increases in SRP and conductivity were attributed largely to the concentrating effect of evaporation. Similar effects were unlikely during the Midmar study possibly due to differences in the evaporation and precipitation patterns in the Natal midlands.

The annual draw-down experienced in Midmar Dam is a potentially more important factor during experiments in isolation columns (Twinch, 1976). Because of increased demand and reduced input during the dry months the mean annual fluctuation in water level in the impoundment since 1966 has been 2.4 m, reaching a peak of 4.3 m in 1972 (Walmsley, 1976).

As can be seen in Fig. 3.4 the 1976-77 period was characterised by relatively stable water content, which resulted in a water level fluctuation of less than 0.5 m. Since the walls of the columns were flexible, and designed to allow for considerable water level fluctuation, it is unlikely that the fluctuations experienced during 1976-77 would have been sufficient to markedly influence hydraulic exchange between the columns and the open water. However, even if the volumes within the columns were influenced by as much as 20% (14% by fluctuating water levels and 6% by evaporation) they would not be sufficient to account for even a fraction of the nutrient fluxes observed (section 3.3.1).

3.3 Fluxes in Chlorophyll, Periphyton, SRP, Total P and NO_3-N

By tracing fluxes of SRP, total P and P bound by periphyton, it was hoped that P fluxes within the columns could be demonstrated, and that nutrient budgets could be used to quantify them. In addition, since NO_3-N enrichments were to be used, and since N availability was thought to play an important role in limiting responses to P enrichment (Twinch, 1976), NO_3-N concentrations were monitored to obtain some index of N utilisation within the columns. Time did not permit a full analysis of other forms of nitrogenous compounds.

3.3.1 Results

3.3.1.1 Open Water

Chlorophyll levels were generally below 5 μg ℓ^{-1} and showed no seasonal trends. Peaks of up to 12 μg ℓ^{-1} were infrequent and of short duration with the exception of one in April 1976, which lasted for 4 weeks (Fig. 3.5).

Periphyton colonising the "sterkolite" strips had, by August 17, increased to approximately 0.2 kg dry mass in an area equivalent to the upper 2.5 m of the columns. It declined to 0.06 kg before summer, but then rose sharply to 1.8 kg by March when it contained c. 1.2 g of P. Throughout the study the proportion of phosphorus per unit of periphyton dry mass remained fairly constant (Fig. 3.10).

During the period April - November, NO_3-N levels fluctuated between 160 and 306 μg ℓ^{-1} without a distinct trend and thereafter, during the summer months, showed a decreasing trend to 30 μg ℓ^{-1} until April 1977 (Fig. 3.5). There is some indication that levels had started to increase between May and June, with the onset of winter.

Soluble reactive phosphorus (SRP), in common with NO_3-N, tended to be higher between April and November than during the summer months, when levels were often undetectable and only once rose to 10 μg ℓ^{-1}. Total P showed extremely wide fluctuations, reaching peaks of 150 μg ℓ^{-1}, which were not associated with corresponding changes in chlorophyll. Peaks tended to be both more frequent and more marked in summer than in winter, and persisted for periods of up to four weeks (Fig. 3.5).

3.3.1.2 Unenriched Column

Although chlorophyll levels generally remained between 5 and 10 $\mu g\ \ell^{-1}$, peaks of up to 49 $\mu g\ \ell^{-1}$, much higher than those in the open water, developed for periods of 1-5 weeks (Fig. 3.6). No marked seasonality was evident.

Periphyton standing crop increased continuously to 1.7 kg dry mass by May 20, 1977, at which time it contained 1.7 g of P. The proportion of P was more variable than in the open water reaching a peak of 2.25 mg g^{-1} during September. There was no evidence that the development of the standing crop was retarded during winter (Fig. 3.10).

Levels of NO_3-N showed remarkably similar trends to those observed in the open water, remaining between 150 and 310 $\mu g\ \ell^{-1}$ until November, before decreasing to 30 $\mu g\ \ell^{-1}$ during summer. There was however no evidence of an increase with the onset of winter conditions in 1977 (Fig. 3.6).

Throughout the study SRP concentrations were very similar to those in the open water, decreasing from 10-30 $\mu g\ \ell^{-1}$ during the winter to undetectable in summer. The striking feature of trends in total P was that both peak heights and duration inside the column were similar to those in the open water (Fig. 3.6).

3.3.1.3 Column +P

Loading with PO_4-P started in the autumn and elicited relatively little response as evidenced by the concentrations of chlorophyll (Fig. 3.7). Although levels had doubled by late May, they declined

steadily until late July. During August levels began to rise, slowly at first and then more rapidly in August-September, resulting in a peak of approximately 230 $\mu g\ \ell^{-1}$, nearly five times the highest peak in the unenriched column. Summer was characterised by peaks of up to four weeks duration, but of diminishing size until February when levels were similar to those at the start. Levels decreased further to approximately 5 $\mu g\ \ell^{-1}$ by the end of the experiment. Marked response by the phytoplankton to PO_4-P enrichment was therefore only evident in the spring and summer months.

Although phytoplankton standing crop declined towards winter in 1977, periphyton yields increased reaching 0.5 kg by mid August at which time it contained approximately 1.2 g of P (Fig. 3.10). During the spring and summer the periphyton yield increased steadily from 0.2 kg in September to 4.9 kg by May, 1977 at which time it contained 6.5 g of phosphorus, only a small fraction of the 580 g added during the experiment. Proportionately, the phosphorus content of the periphyton was always higher than in the open water or unenriched column and reached a peak of 16.1 mg g^{-1} in September when the standing crop was at its lowest but when SRP levels were high (Fig. 3.10).

During periods when enrichment elicited a marked response it might have been expected to result in decreased levels of NO_3-N since none was being added, and N has been shown to be the secondary growth rate limiting nutrient in the water (Toerien *et al.*, 1975; Hemens *et al.*, 1977). NO_3-N concentration fluctuated more markedly than in the control column in response to biological uptake stimulated by the increased PO_4-P availability, and at times dropped to virtually undetectable levels (Fig. 3.7). The fluctuations in NO_3-N in the

water suggest alternating periods of uptake and release but over the period there was a tendency for the peaks and troughs in NO_3-N to become gradually lower. Some of the nitrogen could have been incorporated into the large standing crop of periphyton which had developed by the end of the study (4.9 kg in the top 2.5 m) (Fig. 3.10).

From data presented in Fig. 3.7 it is evident that the major proportion of the PO_4-P added each week was removed from the water column. Total P was usually present at much higher concentrations than SRP and on only a few occasions (March, December, January and February) the increase in total P approached that which might have been predicted from the loading. The amount of phosphorus held in the periphyton, even at the time of maximum standing crop in May 1977, was not even equivalent to the amount added during a single week, supporting the view that competition for phosphorus by periphyton was not a major factor limiting the size of the phytoplankton standing crop.

Despite the loading, SRP concentrations remained low until mid July, but then increased to approximately 75 $\mu g\ \ell^{-1}$ and maintained that level throughout the duration of the first major peak in chlorophyll concentration. Levels of SRP declined in September/October and gradually became virtually undetectable for most of the period January-June 1977 (Fig. 3.7). Total P showed much more marked fluctuations than SRP which were apparently not associated with fluctuations in chlorophyll (Fig. 3.7). There was some evidence however, that peaks in total P occurred at the same time as those observed in the open water and unenriched column (May, June, August,

December and January). Peaks were however, considerably higher, reaching 400 μg ℓ^{-1} compared with approximately 150 μg ℓ^{-1} in the open water and unenriched column.

3.3.1.4 Column +N

Response to enrichment with NO_3-N was distinctly seasonal. Between April and early August no response to enrichment could be detected in either the chlorophyll concentrations, which did not exceed 6 μg ℓ^{-1} (Fig. 3.8) or the periphyton standing crop (0.01 kg), which was far less than that in the control column (Fig. 3.10). The consequence of this was a steady accumulation, over a period of 14 weeks, of NO_3-N at a rate approximating very closely that expected, assuming no utilisation of the NO_3-N applied (Fig. 3.8). This data provides good evidence that during this period the column must have been effectively isolated from the rest of the impoundment. Loading was temporarily terminated in early August, and NO_3-N levels declined steadily until late September (250 μg ℓ^{-1}) and then more slowly until November (100 μg ℓ^{-1}) at which time enrichment was restarted.

Both SRP and total P concentration remained low between April (1976) and November (Fig. 3.8). Whilst SRP levels were very similar to those in the unenriched column, total P concentrations were lower.

During August and October there were peaks, of short duration, in chlorophyll concentration but after late October levels started to increase, particularly towards the end of November, when enrichment was restarted (Fig. 3.8). They increased, with fluctuations, to 112 μg ℓ^{-1} in March. Although considerably lower than the peaks observed in response to PO_4-P addition, the high concentrations were

sustained for far longer periods (15 weeks). Periphyton started to increase between August and September, the same time that the first peaks in chlorophyll were noted, and continued to increase throughout the study reaching approximately 1.8 kg in May 1977, at which time it contained about 1.9 g P, slightly more than the calculated total P content of water in the column at isolation (1.7 g). The proportion of phosphorus in the periphyton varied between 6 and 1.5 mg g^{-1} and was frequently higher than in the columns receiving PO_4-P additions (Fig. 3.10).

In contrast to the response to loading during winter, the summer loading did not result in an accumulation of NO_3-N (Fig. 3.8). Despite the NO_3-N additions, concentrations were at times lower than those recorded in the open water over the same period. This must reflect biological uptake, which increased with the favourable summer temperatures and is indicated by the increased chlorophyll levels and periphyton standing crop. The increase in NO_3-N concentration during the last week may represent the beginning of an accumulation similar to that observed during the first three months of the experiment.

Concentrations of total P began to increase markedly after enrichment was restarted, and continued to a peak of 310 µg ℓ^{-1} in January (Fig. 3.8). Between January and June, levels showed a declining trend with fluctuations becoming progressively more marked. However, concentrations were above 50 µg ℓ^{-1} for a continuous period of 24 weeks, the period during which chlorophyll levels were high. In spite of this, total P was not well correlated with chlorophyll concentrations. Unlike total P concentrations of SRP only began to

increase some six weeks after enrichment was restarted. Levels rose sharply to peaks exceeding 150 µg ℓ^{-1}, as had been observed in the column enriched with phosphorus, although in this instance high concentrations of SRP were present only when levels of chlorophyll were high.

3.3.1.5 Column N+P

As in the column +N, season had a marked influence on the response to this enrichment. Although after the first enrichment it appeared as though chlorophyll concentrations would rise, they declined during the second week and remained below 10 µg ℓ^{-1} until the end of September (Fig. 3.9). Periphyton standing crop also remained low during this period only increasing to 0.3 kg between August and September. Although standing crop was lower than in the unenriched column and slightly higher than the other columns in September, it contained at least three times as much P because of the high proportion of P per unit dry weight (10.7 mg g^{-1}) at the time (Fig. 3.10).

The limited response of the phytoplankton and periphyton allowed NO_3-N to accumulate (Fig. 3.9). The rate of accumulation was however, slightly less than that predicted assuming no utilisation, and by early August had reached 1.9 mg ℓ^{-1} compared with the expected 2.8 mg ℓ^{-1}. At this stage enrichment was discontinued and NO_3-N concentrations declined to almost undetectable levels by mid-September.

Concentrations of SRP remained constant after the first enrichment but subsequently rose at a rate closely approximating that determined from the loading rate (Fig. 3.9). From mid-June concentrations deviated progressively from those predicted and after enrichment was stopped SRP concentrations declined, over a six week period, to

20 μg ℓ^{-1} at which level they remained until enrichment was restarted in November. This decrease was partially attributable to utilisation as the total P content of the periphyton increased sharply from 0.2 to 3.1 g between August and September (Fig. 3.10).

Unlike SRP, total P showed an immediate response to loading and, with one exception in June when the concentration dropped sharply, it accumulated until the end of July at a rate almost equal to that predicted from the load (Fig. 3.9). A three week delay was evident between cessation of enrichment and the rapid decline in total P. No further increases were evident until enrichment was restarted.

Chlorophyll concentrations rose to a small peak in October and then started to increase again just as enrichment was restarted (Fig. 3.9). After fluctuating between 5 and 30 μg ℓ^{-1} for six weeks it increased and sustained concentrations of above 20 μg ℓ^{-1} for seventeen weeks. During this period chlorophyll concentrations were generally higher than those recorded in the column +N. From April, with the onset of winter conditions, concentrations declined gradually.

Periphyton did not show a marked response to the second stage of enrichment possibly because growth of the phytoplankton resulted in light-limiting conditions and, even by the end of the experiment, only approximately 0.5 kg was present compared with 4.8 kg in the column +P. The proportion of P in the periphyton was, however, frequently higher than in the other columns during the final stage of the experiment (Fig. 3.10).

NO_3-N concentration started to increase in September, six weeks before enrichment was restarted, but then declined, with progressively decreasing fluctuations, until May 1977 in spite of the load which was being applied. Since summer was characterised by high levels of chlorophyll, the phytoplankton probably played a major role in removing the NO_3-N from solution. The marked accumulation of NO_3-N observed after May 1976 was not evident in 1977 even though the study continued until June winter conditions were established (Fig. 3.9).

Concentration of total P began to rise immediately the loading was restarted, but at a rate considerably slower than the theoretical maximum (Fig. 3.9). The peak was slightly higher than in the column receiving N only and high levels were maintained for somewhat longer. Concentration began to decline in March, fluctuating markedly before reaching approximately 100 $\mu g\ \ell^{-1}$, double that in the open water, by the end of the study. As in the column +N, there was a lag between the start of the development of the increased concentration of chlorophyll and total P and those of SRP. In late December, after chlorophyll levels had already reached 30 $\mu g\ \ell^{-1}$, SRP levels began to rise and reached a peak (200 $\mu g\ \ell^{-1}$) by mid-January. High concentrations were maintained for eight weeks and began to decline at the same time as chlorophyll. By mid-May, levels were similar to those in all the other columns and in the open water.

3.3.2 Discussion

Despite the slightly lower concentrations of chlorophyll, particularly in summer, and the evidence of a seasonal trend in SRP, the data from the open water station confirm the results of Hemens *et al.* (1977).

The lower chlorophyll levels may simply reflect the use of "composite" samples during this study compared with their surface samples. Based on similar nutrient and chlorophyll concentrations the impoundment has been described as oligotrophic (Toerien *et al.*,1975; Hemens *et al.*, 1977; Archibald *et al.*, 1979).

Since the differences between the open water and the control column were small in respect of the physical conditions (section 3.2) and nutrient and chlorophyll concentrations it may be concluded that isolation did not exert a marked influence on conditions within the columns. This is supported particularly by the data for total P, where the timing of the peaks in the open water and the column often coincided. Liao and Lean (1978) have also reported synchronisations, but of oscillations of particulate N, between open water and 'corrals' in Lake Ontario. Since in the open water these peaks were not associated with peaks in chlorophyll concentrations, they probably result from silt resuspended during periods of turbulence. However, the presence of a considerable growth of periphyton on the walls of the column provided a component normally absent from the open water which, during periods of turbulence, may become dislodged and contribute to the phytoplankton (Twinch and Breen, 1978a).

The peaks in total P in the unenriched column may therefore reflect periphyton dislodged into the water during periods of turbulence.

During the period September to January the phytoplankton in the column +P responded markedly to enrichment with PO_4-P suggesting that phosphorus was the nutrient limiting the size of the standing crop at

that time. However, the short duration of the peaks and the marked decline in NO_3-N during the peaks, suggests that nitrogen became the growth rate limiting nutrient soon after growth was stimulated by the addition of phosphorus. These observations support those of Walmsley (1976), Hemens *et al.*, (1977) and this study (section 3.4) which have shown, using algal bioassays, that in Midmar Dam N, the secondary limiting nutrient, closely follows P in limiting algal growth.

The absence of a response by the phytoplankton in the column +P during the initial stages was probably due to declining temperatures with the onset of winter, which reduced the growth rates such that the primary producers could not compete effectively for PO_4-P against direct fixation by the sediments (Twinch and Breen, 1978b). This does not imply that no biological uptake was occurring. The marked decreases evident in the NO_3-N concentrations are indicative of some uptake but it is notable that during the first 4 months the rate of decline in NO_3-N concentration was slower and troughs higher than they were at other times during the experiment.

With increasing temperatures in Spring (late August-September) the phytoplankton showed a marked response to enrichment and only in January did chlorophyll concentration decrease to levels consistently below 10 $\mu g\ \ell^{-1}$. At the same time, the periphyton standing crop began increasing steadily until the end of the experiment. During this time the NO_3-N concentrations showed an irregular but progressively decreasing trend reaching virtually undetectable levels. This was in spite of an annual atmospheric input of approximately 1 g total N m^{-2} a^{-1} (Hemens *et al.*, 1977), sufficient to raise the concentration in the columns by

approximately 280 μg ℓ^{-1}. This suggests either increased uptake of NO_3-N by the biological components or increased denitrification. At this time algal bioassays indicated that nitrogen was the primary growth rate limiting nutrient in the column +P (section 3.4) despite the low levels of SRP in the water after January 1977. It therefore seems reasonable to suggest that a shortage of nitrogen limited the biological response to P enrichment and that direct fixation of PO_4-P by the sediments was probably the predominant mechanism involved in removing PO_4-P from solution at this time.

Between April and the end of August, a period during which there was limited biological response to enrichment in the column +P, 130 g PO_4-P had been added, sufficient to raise the concentration in the water to 1.95 mg ℓ^{-1}. Since at this stage only 8% of the P was held in the periphyton (1.19 g) and in the water column (approximately 9.5 g total P), the major fraction of the load must have been fixed directly by the sediments as has been reported by many authors (Mortimer, 1941; Holden, 1961; Hepher, 1966; Golterman,1973b; Syers *et al.*, 1973; Slater and Boag, 1978; McCallister and Logan, 1978; Twinch and Breen, 1978b). During the period when enrichment induced high peaks in chlorophyll in the column +P there were occasions when total P concentration increased at a rate approaching the loading rate. However, since similar rates were evident at the same time in the unenriched column, they reflect a combination of resuspension and biotic reponse and cannot be attributed only to uptake by phytoplankto

Another potentially important factor which could influence the flux of P from the water to the sediments is grazing, particularly of the periphyton. No estimates of this were made but, since the maximum standing crop of periphyton measured in the column +P contained less

total P than one week's loading and since the large population of snails observed during earlier experiments (Twinch and Breen, 1978 a and b) were absent, it seems unlikely that grazing of the periphyton was a major pathway for P transfer to the sediments. However, because nothing is known about the detrital cycle which resulted from periphyton development, it must be acknowledged that the role of the periphyton in the transfer of P to the sediments remains obscure.

By international standards the P loading rate in the column +P during this study (26 g PO_4-P m^{-2} a^{-1}) may be regarded as high (Shannon and Brezonik, 1972; Bengtsson, 1975; Ryding and Forsberg, 1976; Schindler, 1976; Stevens and Gibson, 1976) but is similar to the loading rate in two South African impoundments, Rietvlei Dam and Roodeplaat Dam (Walmsley *et al.*, 1978). In any event it was insufficient to effect an increase in SRP concentrations by the end of the experiment. Since P fixation by lake sediments is known to involve adsorption (McCallister and Logan, 1978), it may be concluded that the load was insufficient to saturate the adsorption sites sufficiently to influence the sediment/water equilibrium (Syers *et al.*, 1973; Schindler, 1976), thus confirming an earlier observation that the sediments have a very high P-fixing capacity (Twinch and Breen, 1978b). It has been shown that considerable enrichment with PO_4-P can be tolerated by fresh waters with no long term adverse effects because of the buffering effect of the sediments on PO_4-P levels in the water (Weatherley and Nicolls, 1955; Hepher, 1966; Smith, 1969; Schindler *et al.*, 1971) and it seems likely from the column +P data that a similar situation exists in Midmar Dam. This aspect is considered further in section 4.3.

The responses in the column +N suggest that, contrary to the impression gained from bioassays, a source of P other than that present in the water at the time of isolation, was present in the column during the experiment. By the end of the experiment the total P held in the water and periphyton was 3.5 g, twice that present in the water at the start (1.7 g) but at times during the experiment, this difference was far greater. The most clearly defined increase in P content is evident in the SRP levels recorded between late December and mid-March. When only this fraction is considered, the problems resulting from the incorporation of P bound by resuspended surface sediments are overcome because SRP concentrations in Midmar Dam and in isolation columns have been shown to remain relatively stable despite marked fluctuations in TSS resulting from sediment resuspension (Twinch and Breen, 1978 a and b).

SRP levels reached a peak of 215 $\mu g\ \ell^{-1}$ on week 39 amounting to approximately 14.6 g P, compared with the 1.7 g of total P present in the water at the start. The SRP fraction alone therefore showed a more than eight fold increase over the total P in the water at isolation, and clearly demonstrates the presence of a P source within the column. This must be an underestimation of the total increase in P content in the column +N, because it does not account for the P in the bloom of *Microcystis* sp. which was responsible for the generally increased chlorophyll levels between December and March (chlorophyll concentrations were frequently above 40 $\mu g\ \ell^{-1}$ and clearly a substantial amount of P was contained in the standing crop of phytoplankton) and for the P bound by the periphyton.

Because of the processes of resuspension and sedimentation occurring both in the open water and to a lesser extent in the columns (Twinch and Breen, 1978a), sedimenting material becomes trapped in the

periphyton. This makes it difficult to distinguish between P taken up from the water by the attached organisms and that deposited as a result of sedimentation. In the column +N the total P content of the loose surficial sediments at the end of the experiment was approximately 0.6 mg g^{-1} (section 3.5) and, if this material was a major contributor to the periphyton similar total P contents would be expected. The P content of the periphyton in the column +N never dropped below 1 mg g^{-1} and was frequently higher than 4 mg g^{-1}, indicating that the P in the periphyton could not be attributed entirely to resuspended surface sediments.

It is thus not possible to quantify the transfer rates of P into the various compartments with the data available, but there is evidence of a substantial source of P within the column. Only two possible sources exist, atmospheric fallout and the sediments.

Hemens *et al.* (1977) estimated total P input from atmospheric fallout into Midmar Dam to be 0.35 kg ha^{-1} a^{-1}, which is equivalent to 0.7 g a^{-1} in the columns used during this study. This represents a small fraction of the SRP fluxes observed and, when considered in conjunction with the evidence for P uptake by phytoplankton and periphyton, it is clear that this source was of minor importance. Sediment release is therefore presumed to account for the major flux of phosphorus into the column +N.

The interruption in the loading in the column N+P resulted in the total annual load of P being lower (20 m^{-2} a^{-1}) than in the column +P (26 g m^{-2} a^{-1}), and this precludes direct comparison of changes in P levels in the column N+P with those in the column +P. SRP levels were

not markedly different from those in the open water by the end of the study and only a small fraction of the P added could be accounted for in the periphyton. The bulk of the P is therefore thought to have entered the sediments either by direct fixation or through the biological cycle.

The rate at which P would have entered the sediments is however of considerable interest because, during the first fourteen weeks, although most remained as SRP, it accumulated at a rate almost equal to the loading rate implying that very little was fixed by the sediments. This contrasts with the situation in the column +P which received identical loads of PO_4-P, and is not consistent with the evidence that PO_4-P is rapidly fixed by the sediments.

When enrichment of the column N+P was restarted in November the rate of accumulation of P was much slower, and during this time a large proportion of the PO_4-P added was apparently fixed directly by the sediments. The addition of N and P together ensured that the phytoplankton could compete more effectively for PO_4-P than was the case in the column +P, as evidenced by the increased chlorophyll levels, which were maintained for longer periods.

The accumulation of SRP in the column N+P during both periods of enrichment and in the column +N during the summer apparently contradicted the concept of a dynamic equilibrium of PO_4-P between mud and water. Such an increase could reflect altered equilibrium constants brought about by either changes in the structure and chemical status of the surficial sediments or by anaerobic conditions at the sediment/water

interface (Syers *et al.*, 1973). During the study anaerobic conditions were never observed (section 3.2) but, since even periods of partial anoxia may influence exchange properties, this possibility cannot be excluded.

Another possible explanation is that the SRP included a large proportion of organic and colloidal P which had different exchange kinetics with the sediments. The occurrence of such fractions in fresh waters is well established and they have been shown to be produced by natural plankton populations (Lean, 1973; Peters, 1978) and by axenic cultures of phytoplankton species (Lean and Nalewajko, 1976). Furthermore, colloidal P and low molecular weight organic P can contribute to SRP analyses using the molybdate blue procedure (Rigler, 1973; Downes and Paerl, 1978) and there is no justification for assuming that SRP concentrations reflect PO_4-P concentrations under natural conditions (Rigler, 1973).

Eisenreich and Armstrong (1978) have demonstrated that aluminium hydroxide effectively removes PO_4-P from lake water while having little influence on soluble organic P. This suggests that under natural conditions, PO_4-P could be fixed by sediments while other soluble forms, which can be included in the SRP analyses, are not. This aspect will be dealt with in more detail in chapter 4 and chapter 5.

It seems reasonable to suggest therefore that, at times when SRP accumulated in the columns, it is possible that a large proportion was colloidal P (or low molecular weight organic P) which was not readily taken up by the sediments. Although there is no direct evidence for

this in the data, the summer peaks in SRP in the column +N and column N+P bear further discussion.

In both columns total P levels began increasing in late November and the increasing trends were accompanied by somewhat irregular, but nevertheless similar trends, in chlorophyll, indicating that at least a proportion of the total P was incorporated into algal cells. The increases in chlorophyll were due largely to the growth of *Microcystis* sp., which formed characteristic surface blooms in the columns. Only after a delay of approximately five weeks, during which time total P continued to increase, did SRP levels begin to increase. This suggests that during periods of high phytoplankton standing crop SRP accumulated, possibly due to increased biological complexing of PO_4-P into other soluble fractions. This observation is consistent with the observation in Canadian lakes that the complexing of PO_4-P into soluble organic and colloidal forms predominates during the summer months when phytoplankton metabolism is highest (Lean and Rigler, 1974).

This hypothesis cannot however be applied to the winter accumulation of P in the column N+P, during which no evidence of a marked increase in phytoplankton or periphyton growth was detected. One possible explanation could be that marked bacterial activity, which was not monitored, could have influenced P metabolism in the water, but in the absence of any evidence this remains purely speculative.

The observation that SRP can accumulate in the water in spite of the known PO_4-P fixing capacity of the sediments has important practical implications, particularly as this was observed to occur even in the absence of an external supply of P.

The results of this study support the view (Twinch and Breen, 1978b) that a dynamic steady state exists between the sediments and water whereby PO_4-P can move into or out of the sediments depending on the biological status of the water, but they also emphasise the need to obtain a better understanding of the soluble P fractions and their overall role in the P cycle.

The periphyton colonising the inside walls of the columns provides a major biological component that is either absent, or of considerably less significance, in the open water. The extent to which it determines the fluxes observed in this experiment is not clear. However, since many of the major fluxes occurred at times when the periphyton standing crop was low, it seems reasonable to suggest that its presence was not essential for the processes to take place, although it may have influenced the rate at which fluxes occurred.

Outside the columns many additional factors such as flushing and stratification would modify the rates of exchange and therefore it is not possible to apply the observations made in the columns directly to the adjacent water. There are however many instances where internal phosphorus loading has been shown to significantly influence the trophic status of lakes (Bengtsson, 1975; Lee, 1976; Schindler, 1976; Stevens and Gibson, 1976; Ryding and Forsberg, 1976; Cooke *et al.*, 1977) and while all of these are eutrophic systems, these results indicate that similar processes can occur in young impoundments and could therefore have important consequences in the control of eutrophication.

3.4 Algal Bioassays

The provisional algal assay procedure, PAAP (Bartsch, 1969), has been used to assess the nutrient status of Midmar Dam on a number of occasions

(Toerien *et al.*,1975; Walmsley, 1976; Twinch, 1976; Hemens *et al.*,1977). Phosphorus has been identified as the primary nutrient limiting algal production and is closely followed by N. Routine SRP analyses are of dubious value in assessing the levels of available P (Rigler, 1973) and NO_3-N levels alone cannot be used as an index of biologically available N (Toerien, 1977). Bioassays do however provide a useful means of obtaining a biological index of available P and N to augment the routine analyses and in addition, facilitate the identification of the limiting nutrient in the water.

3.4.1 Results

3.4.1.1 Algal Growth Potentials and Growth Limiting Nutrients

The bioassay yields are presented in Fig. 3.11 and the limiting nutrients, determined by comparing the PAAP-P and PAAP-N spikes are listed in Table 3.1. Yields for the N+P spikes were always higher than 120 mg ℓ^{-1} indicating that no important tertiary limiting nutrient was influencing the AGP during this study.

In the open water AGP fluctuated between 4 and 19 mg ℓ^{-1} (mean 9.3 mg ℓ^{-1}) showing a slight peak between weeks 20 and 25 but otherwise remaining fairly constant. As has been shown before (Toerien *et al.*, 1975; Walmsley, 1976; Hemens *et al.*,1977) P was generally the limiting nutrient, but on four occasions N and P were equally limiting (Table 3.1), confirming the fact that the primary and secondary limiting nutrients are not widely separated in Midmar Dam.

Isolation had very little influence on the bioassay yields in the unenriched column. AGP and PAAP-N yields remained similar to those in the open water and, while the PAAP-P yields showed more

fluctuation than in the open water, the differences were seldom significant (Fig. 3.11). Although P was the limiting nutrient on two occasions, there was an increased tendency for N and P to be equally limiting, and on week 52 N was the primary limiting nutrient (Table 3.1). This probably resulted from the increased biological utilisation of NO_3-N within the confinements of the column.

Enrichment of the column with PO_4-P did change the growth limiting nutrient from P to N, P being limiting on only two occasions. Despite this, with the exception of a peak of 33 µg ℓ^{-1} on week 37, the enrichment was not reflected in increased AGP yields (Fig. 3.11 and Table 3.1). These results can only be explained by the fact that N and P are almost equally limiting in Midmar Dam. At times the yields for the PAAP-P spikes in the column +P were significantly higher than corresponding yields in the unenriched column (weeks 12, 16, 20) indicative of increased P availability. More frequently however, the differences were not significant, indicating that during the week between enrichments, PO_4-P was rapidly removed from solution by biologica uptake and sediment adsorption. This was particularly evident on week 37 when P was the primary limiting nutrient, and on weeks 1, 7 and 52 when N and P were equally limiting (Table 3.1).

Additions of NO_3-N to the column +N had no influence on AGP during the winter enrichment or during the period when enrichment was stopped (for the first 29 weeks). The yields remained similar to those in the unenriched column, as did the yields in the PAAP-P spikes, supporting the concept of N and P being almost equally limiting. The accumulation of NO_3-N during the winter enrichment, and the subsequent decline when enrichment was stopped, is clearly reflected in the yields

in the PAAP-N spikes which reached a peak of 89 mg ℓ^{-1} on week 12, and then declined to approximately 20 mg ℓ^{-1} by week 20. With the exception of weeks 1 and 25 when N and P were equally limiting in the column +N, P was the primary limiting nutrient during this period (Table 3.1).

During the period of summer enrichment, beginning on week 30, AGP in the column +N showed a distinct peak on week 37 before dropping to levels similar to those when enrichment was stopped on week 44. A similar trend was evident in the yields in the PAAP-P spikes which showed a peak of 54 mg ℓ^{-1} despite no PO_4-P being added. In contrast, yields in the PAAP-N spikes did not respond to the summer enrichments, remaining at approximately 20 mg ℓ^{-1} until the end of the experiment (Fig. 3.11). In spite of the NO_3-N enrichment, N was the limiting nutrient on weeks 37 and 44, indicative of the markedly increased biological utilisation of NO_3-N and the accumulation of SRP during the summer. By week 52 however, at which time the *Microcystis* bloom which characterised the column +N between weeks 34 and 45 had declined, N and P were equally limiting (Table 3.1).

When N and P were added to the column N+P during the winter, AGP increased sharply during the first 14 weeks reaching 81 mg ℓ^{-1} on week 12 and declined markedly when enrichment was stopped. The accumulations of SRP and NO_3-N and their subsequent decline when enrichment was stopped, are clearly reflected in the PAAP-P and PAAP-N spikes (Fig. 3.11). With the exception of week 7, N remained the limiting nutrient in the column N+P during the first 20 weeks but by

week 35 N and P were equally limiting (Table 3.1).

Response to summer enrichment in the column N+P contrasted markedly with that during the winter, and some of the trends were similar to those observed in the column +N. AGP showed a slight peak of 26 mg ℓ^{-1} on week 37, but then declined sharply to less than 10 mg ℓ^{-1} for the remainder of the experiment (Fig. 3.11). Yields in the PAAP-P spikes increased markedly but, unlike the winter response there was a delay of at least 2 weeks before the increase became evident. In spite of the NO_3-N additions to the column, yields in the PAAP-N spikes remained stable until week 37 and then declined to less than 20 mg ℓ^{-1} for the remainder of the experiment. Clearly biological utilisation during the summer enrichment prevented the accumulation of NO_3-N that was being added. With the exception of week 31, when P was the limiting nutrient, N remained the limiting nutrient throughout the summer enrichment period in the column N+P (Table 3.1).

3.4.1.2 Available N and P

An estimate of soluble available N (SAN) and P (SAP) concentrations can be obtained by dividing the dry mass yields in the PAAP-P and PAAP-N spikes by the P and N yield coefficients (Y_P and Y_N) for *Selenastrum capricornutum* (Toerien, 1974). By comparing these with analytically determined nutrient concentrations, an index of the accuracy with which the analyses measure nutrient availability can be obtained.

A comparison of SAN with NO_3-N concentrations is presented in Table 3.2. The mean contribution of NO_3-N to the SAN varied between

22% in the column +P and 56% in the column +N, but the range of variation within each treatment was high : open water (8-63%); unenriched column (16-69%); column +P (3-41%); column +N (6-121%) and the column N+P (20-82%). At low NO_3-N concentrations the analytical measurements are a poor index of SAN, and the proportionate contribution of NO_3-N to the SAN increased with increasing NO_3-N concentration. Only when concentrations were increased to more than 2 mg ℓ^{-1} by enrichment did NO_3-N begin to approach the SAN (Fig. 3.12).

A similar comparison between SAP and SRP is presented in Table 3.3. The mean contribution of SRP to SAP fluctuated between 61% in the unenriched column and 129% in the column N+P, showing wide variation in all columns and in the open water. There was however, an interesting tendency for the proportionate contribution of SRP to be well below 100% of the SAP at SRP concentrations below 10 µg ℓ^{-1} and well above 100% at SRP concentrations above 100 µg ℓ^{-1} (Table 3.4). At intermediate SRP concentrations, grouped for convenience into classes of 10-25 µg ℓ^{-1} and 25-100 µg ℓ^{-1}, the proportions were more variable, but tended to cluster in the 50-99% and 100-149% ranges respectively. With increasing SRP concentration there was thus a general increasing trend in the proportionate contribution of SRP to SAP. At concentrations below 10 µg ℓ^{-1}, SRP represented only about half the SAP while at concentrations exceeding 100 µg ℓ^{-1}, the SRP analyses over-estimated the SAP by a factor of at least two.

The tendency for the mean contribution of SRP to SAP to be higher in the column +N and column N+P was because more marked SRP accumulations occurred in these columns (section 3.5).

3.4.2 Discussion

Since the mean AGP obtained in the open water during this study (9.3 mg ℓ^{-1}) and the ordination of growth limiting nutrients compare favourably with the data of Toerien *et al.*,(1975) (AGP = 8.7 mg ℓ^{-1}) and Walmsley (1976), it appears that the nutrient status in Midmar Dam has remained stable over the past 5 years.

The general trends observed in the bioassay yields reflected fluxes in nutrient concentrations detected in the isolation columns (section 3.3) but a quantitative comparison between SAN and SAP, calculated from Y_N and Y_P indicated that the analyses used were not reliable estimates of nutrient availability.

Concentrations of NO_3-N were always considerable underestimations of SAN indicating that other soluble forms of available N were present. Similar conclusions were drawn following earlier enrichment experiments (Twinch, 1976). Ammonia can be utilised by algae (Ruttner, 1963; Wetzel, 1975) but the mean NH_4-N concentration measured in Midmar Dam water (0.015 mg ℓ^{-1}, Archibald *et al.*, 1979) represents only a small proportion of the NO_3-N, and whilst it may contribute to the discrepancy between NO_3-N and SAN it cannot explain the large discrepancies observed.

Nitrogen can also occur in the form of soluble organic nitrogen, consisting largely of polypeptides, complex organic compounds and free amino nitrogen, and this fraction can constitute up to 50% of the total soluble N in lake water (Wetzel, 1975). This fraction can be nitrified to NO_3-N by bacterial action but the possibility of this occurring in the *Selenastrum capricornutum* cultures cannot be assessed because, whilst they were unlikely to have been totally axenic, the

nitrifying bacteria responsible for the transformation may not have been present. In the absence of sufficient information regarding the various soluble N components and their interactions it is not possible to comment further in this regard. All that can be said is that N appeared to be available to the *Selenastrum* in a form other than NO_3-N.

Another possible source of the discrepancy between NO_3-N and SAN could be related to inaccuracies in the Y_N value used to calculate SAN. However, with increasing NO_3-N concentration, NO_3-N and SAN showed greater similarity suggesting that any error in the Y_N used was probably small.

The relationship between SRP and SAP emphasised the limitations of regarding SRP as an index of SAP. At low SRP concentrations (below 10 µg ℓ^{-1}) the SRP represented a small proportion of the SAP, thus exhibiting a similar trend to the NO_3-N determinations. It has been shown that under conditions of low PO_4-P availability phosphatase enzymes produced by algae can convert organic P fractions to PO_4-P which can then be utilised (Berman, 1970; Jansson, 1976, 1977). It is thus possible that the discrepancy observed at low SRP concentration resulted from the conversion of soluble unreactive P to PO_4-P during the incubation of the cultures as has been shown by Paerl and Downes (1978). It should also be remembered however, that SRP levels were frequently at the limits of detectability and some of the discrepancy at low SRP concentrations may therefore reflect limitations in the accuracy with which SRP was measured.

Furthermore, Twinch (1976) and Walmsley (1976) commented on the fact that in waters of low trophic status, such as Midmar Dam, the accuracy of the bioassay technique is diminished by the fact that the algal yields

are low, and therefore more difficult to measure precisely. At low nutrient levels more variability would be expected which could contribute further to the discrepancy between the nutrient concentrations and the availability measured by bioassay. This would not however, explain the consistent underestimation of available nutrient levels with the analytical methods used.

At high SRP concentrations in the water (above 100 µg ℓ^{-1}) the relationship between SRP and SAP was different and a large proportion of the measured P appeared to be in a form other than PO_4-P. Similar observations were made by Steeman Nielsen (1978) in growth studies on *Selenastrum capricornutum*.

It was postulated earlier (section 3.3) that when SRP concentrations in the isolation columns were high a large proportion of the measured SRP was not PO_4-P. This was necessitated by the need to explain the apparent inconsistency between the observed SRP accumulations and the fact that Midmar sediments are characterised by high P fixing capacities (Twinch and Breen, 1978b). The bioassay results during the periods when SRP levels were high are of relevance to the interpretation of P fluxes in the isolation columns because they provide convincing evidence that a large proportion of the SRP was not PO_4-P.

When it was discovered that SRP analyses consistently overestimate PO_4-P in lake water due to the hydrolysis of other soluble P fractions to PO_4-P during the molybdate blue procedure, reservations were expressed about regarding SRP as an index of PO_4-P (Rigler, 1973). This has been confirmed in a series of New Zealand lakes where a large molecular weight soluble P fraction represented a substantial proportion (13-100%) of the

SRP (Downes and Paerl, 1978) and appears to be the case under certain conditions in Midmar Dam.

The observations at high and low SRP concentrations represent the two extremes and, although a trend between the two is quite distinct (Table 3.4), the variability at intermediate SRP concentrations is higher. It appears however that if SRP levels in Midmar Dam exceed the 10-25 $\mu g\ \ell^{-1}$ range the probability that P fractions other than PO_4-P are being included in the analyses increases and that available P levels will be correspondingly less. Thus at times the SRP analysis may approximate available P levels in the water, as suggested by Walton and Lee (1972), but at other times it can overestimate or underestimate available P, the relationship being dependent on changes in nutrient levels and biological metabolism in the water.

The original hypothesis regarding SRP accumulations is thus given substantial support by the bioassay data and there can be little doubt that a P fraction other than PO_4-P was present at the times of marked SRP accumulation. It is notable that utilisation of SRP, when levels exceeded 100 $\mu g\ \ell^{-1}$, was always below 50%, indicating that the other P fraction included in the SRP analysis was not completely hydrolysed to PO_4-P during the bioassays. The extent to which this fraction was converted to PO_4-P during the growth of the cultures cannot be assessed but,both Lean (1973) and Downes and Paerl (1978) have shown that soluble P fractions other than PO_4-P can be converted to PO_4-P in cultures or during the storage of samples. For this reason the SAP concentrations calculated from bioassay yields cannot be regarded as an index of PO_4-P

concentration in the water at the time of sampling as they probably represent a considerable overestimation.

3.5 The Sediments

Enrichment of the columns was expected to have direct and indirect effects on the physico-chemical properties of the sediments. The influenc on selected parameters was investigated in stratified sediment cores and is discussed in this section. Undisturbed cores were used to assess the effect of enrichment under laboratory conditions. For convenience the dynamic aspects of sediment/water P exchange are considered in chapter 4.

3.5.1 Results

When sediment samples were equilibrated with a range of PO_4-P solutions and then subjected to the acid extraction, the amount of extractable P was linearly related to the concentration of PO_4-P supplied (Fig. 3.13). However, since the amount extracted after equilibration was a constant proportion (approximately 50%) of the expected increase, it is clear that the acid extraction procedure was not estimating total P in the sediment.

The amount of available P retrieved also increased in proportion to the amount of PO_4-P added (Fig. 3.13). Thus enrichment increased both the acid extractable P (AEP) and the available P, but of the total P adsorbed only 18% was incorporated into the sediment in an available form; the remainder was bound in a form which was not extracted with Bray's solution.

There was no discernable trend in the vertical distribution of acid extractable P (Fig. 3.14) in either the open water or the control

column. In the column +P it appeared to be markedly higher in the surficial sediment, below which no trend was evident. Concentration decreased with depth in both the column +N and the column N+P, and this trend was due to particularly high levels in the surficial and first centimetre of sediment. In the column N+P the concentrations in the loose surficial and 0-1 cm strata were approximately 60% and 90% higher than in the open water while in the column +N the increases relative to the open water were approximately 50% and 80% respectively.

Available P concentrations in the sediment from the open water and control column were not markedly different (Fig. 3.14). Levels tended to be lowest (approximately 1.5 $\mu g\ g^{-1}$) in the surface layer (0-1 cm) and highest in the 1-3 cm section. Below this the concentration tended to decrease slightly. No trends were evident in the column +P where levels were similar at all depths (approximately 1.5 $\mu g\ g^{-1}$). In the column +N there was a notable increase in the amount of available P in the loose surficial sediment and the 0-1 cm layer (86 and 100% respectively), although the deeper layers remained very similar to those in the open water and unenriched column. In the column N+P a more marked increase in the two uppermost strata was evident, and available P increased by 180% and 270% in the surficial and 0-1 cm layers respectively compared with those in the open water. The two deepest strata however appeared to have slightl lower levels of available P than those from outside the columns (Fig. 3.14).

A distinct stratification in pH, organic carbon and exchangeable Al^{3+} was evident in the cores from all sites (Fig. 3.14), and enrichment did not influence the vertical patterns to any great extent. The pH decreased from approximately 4.5 in the loose surficial sediment to 3.8 in the 5-7 cm section. Organic carbon decreased markedly from approximately

3% in the loose surficial sediment to approximately 1.6%, and appeared to be slightly higher at the surface in the column +N. Exchangeable Al^{3+} increased with increasing depth from approximately 0.02 to 1.6 meq%.

Correlation coefficients for the parameters measured in the stratified sediments are presented in Table 3.5. Significant positive correlations were obtained between acid extractable P and organic carbon and available P, and between organic carbon and pH, while significant negative correlations were detected between exchangeable Al^{3+} and organic carbon and pH.

3.5.2 Discussion

In a young impoundment such as Midmar Dam, the surficial sediments which are easily separated from the compact drowned terrestrial substrate present a record of the type of sediment which is currently developing in the system. On the basis of its carbon content the surface sediment in Midmar Dam may be compared with rather unproductive systems in which no extensive organic deposition has occurred. Not all oligotrophic systems have sediments with low levels of carbon, because of allochtnonous inputs (Larsen *et al.*, 1976), however, since allochthonous inputs of organic material into Midmar Dam are small (Furness, 1974) and since phytoplankton production is low (Akhurst, unpublished data) the low levels of organic carbon (2-3%) in the Midmar Dam surface sediments, relative to those in other systems (Ballinger and McKee, 1970; Bengtsson, 1975), are to be expected.

Two potentially important contributors to the organic fraction of the sediments have, however, not been considered in Midmar Dam. These

are the plants which colonise the exposed draw down areas and then decompose during subsequent inundation, and the phytobenthos (particularly algae) which occur in the shallow littoral areas. Since they occur in areas which are most susceptible to turbulent mixing, the organic input from these sources could be distributed throughout the impoundment and may be a major organic input into the system.

Trends in the vertical distribution of organic carbon in the sediment profiles were characterised by a sharp drop from approximately 3%, in the loose surficial sediments to approximately 2% in the 1-3 cm stratum. This was followed by a more gradual decrease approximately 1.6% in the 5-7 cm stratum. Similar trends have been observed in many lake sediments (Livingstone and Boykin, 1962; Hesse, 1973; Kemp *et al.*, 1974; Bengtsson *et al.*, 1975; de March, 1978; Howard-Williams and Allanson, 1978) and the profiles observed in Midmar Dam suggest the organic carbon content in the surficial sediments has been increased markedly since inundation, but its source is not known.

Despite the increased primary production in some of the isolation columns, with the exception of the column +N, the organic carbon profiles did not reflect any marked change in the sediments. The reason for this is not clear, particularly in the column N+P where a bloom of *Microcystis* was maintained for approximately three months prior to the conclusion of the experiment. Such a prolonged period of increased productivity would be expected to result in increased organic concentrations in the surficial sediments and it can only be suggested that changes may have occurred at levels below the sensitivity of the Walkley-Black procedure used to measure organic carbon.

Organic content of the sediments has the potential to influence other parameters in the profiles, and thus to influence the sediment/water interactions. In well leached soils such as those of the Midmar Dam area (Scotney, 1970) low pH results from clay adsorbed H^+ ions which accumulate following cation exchange during the percolation of rainwater through the soil (Malherbe, 1953), and the exchangeable Al^{3+} is also largely related to the inorganic clay fraction of the soil (Black, 1965). The accumulation of organic material in the surface sediments of Midmar Dam, and the consequent reduction in the proportion of inorganic material, thus has the potential to influence both pH and exchangeable Al^{3+}, and the positive correlation between organic carbon and pH could indicate that this is the case. Other factors could also have influenced the surface layers, however, and with the data available no conclusive statement regarding the role of organic matter in determining the pH and exchangeable Al^{3+} profiles can be made.

The observed changes in pH and exchangeable Al^{3+} in the sediment profiles could have a major influence on sediment/water P exchange. Furness and Breen (1978) showed a positive correlation between exchangeable Al^{3+} and available P in sediments from the Midmar Dam catchment, and pH has frequently been shown to influence available P levels in soils and sediments (Hsu, 1962; Syers *et al.*, 1973; Jacobsen, 1977; Ku *et al.*, 1978). During this study available P showed no significant correlation with any other parameter measured, thus contrasting with the findings of Furness and Breen (1978). It is notable however, that pH levels recorded by Furness and Breen (1978) in the riverine sediments never dropped below 4.3, and these were conducted on grab samples which are probably more comparable with the loose surficial layer, than with the deeper strata

comprising the drowned terrestrial soil, in the impoundment. This suggestion is supported by the fact that only in the loose surface sediments were pH levels similar to those in the riverine sediments. The adsorption/desorption processes between sediments and water are, however, complex, and the data obtained during this study are not suitable for an analysis of the mechanisms involved in sediment/water P exchange.

Before commenting further on the available P and AEP profiles the analytical methods bear further discussion. The Bray's extraction procedure used to measure available P is based on a good correlation with crop response in terrestrial soils (Jackson, 1958) and its applicability as an index of the availability of sediment P to organisms in the overlying water has not been fully assessed (Golterman, 1973b). In a variety of South African sediments bioassay experiments have indicated that the Bray's extraction is a considerable underestimate of available P (Grobler and Davies, 1979) and the method may have limited applicability in a limnological context.

During the Bray's extraction procedure F^- ions complex with Al^{3+} and Fe^{3+} releasing P held by these trivalent ions, and the method is therefore regarded as a measure of available P associated with the inorganic fraction of the soil (Jackson, 1958). There is however no doubt that the supposed inorganic fractions include P which may have been leached from organic material (Golterman, 1973b) and the available P fraction cannot therefore be accurately characterised. For these reasons interpretation of the available P data must be cautious.

It was shown that after short term equilibrations (24 hours) 50% of the adsorbed P was not extracted with the analytical procedure used. Clearly therefore the AEP determinations are a poor index of total P and, as with the available P, AEP includes both organic and inorganic forms, the relative proportions of which cannot be assessed.

The distinct gradients in organic carbon, pH and exchangeable Al^{3+} observed in the sediment cores were not reflected in the available P and AEP profiles. In the open water and unenriched column available P increased sharply in concentration between the 0-1 and 1-3 cm strata, below which no distinct trend was evident, while the AEP concentration remained constant at all depths. From this it could be concluded that the changes in the surface sediments, which were clearly reflected in the other parameters measured, were of little consequence in relation to the P concentrations. However, of more significance is the influence of the observed changes on the sediment/water P exchange characteristics of the surface layers, which, for reasons already discussed, cannot be assessed from the P analyses used. This aspect will be considered in more detail in section 4.2.

Despite the PO_4-P loading rate of 26 g m^{-2} a^{-1} in the column +P, the PO_4-P added could not be accounted for by the P fractions measured in the sediments. It seems certain that this results from the fact that the P was adsorbed in a form not included in either of the extraction procedures used. Over long periods of time PO_4-P bound by sediments can shift to occluded forms (Syers *et al.*, 1973), probably through a continuous spectrum of adsorption sites, ranging from a fraction in direct equilibrium with the solution, through more strongly adsorbed fractions to an inert fraction, as envisaged by Taylor and Kunishi (1974). Thus, with time,

the added P may have become less extractable with the methods used. The only alternative explanation is that a large proportion of the added PO_4-P leaked from the column. This seems unlikely in view of the fact that marked differences in the SRP, total P and NO_3-N concentrations between the column +P and the open water were observed and, had exchange with the open water been occurring at a rate sufficient to account for the PO_4-P losses, these differences would not have been expected. For this reason the inefficiency of the analytical procedures is regarded as the reason for the apparent absence of the added P in the sediments.

There can be little doubt that the markedly higher available P and AEP concentrations in the surface sediments from the column +N and column N+P resulted indirectly from the blooms of *Microcystis* sp. which characterised these columns during the summer months. During this time, detrital sedimentation would have increased, particularly when the populations were declining, and P was deposited in a form that was more readily extracted by the analytical procedures used. Thus, despite the absence of marked changes in organic carbon profiles in the column +N and column N+P the available P and AEP profiles suggest that the *Microcystis* blooms had a marked influence on the surficial sediments.

The implication of this observation is that the biological cycling of P, either from an external source (column N+P) or from an internal source (column +N) can result in surface deposition of P fractions which increase the proportion of extractable P (both available P and AEP) considerably. Both P fractions therefore reflect qualitative changes in the sediment profiles in the column +N and column N+P and are consistent

with the observation that increased primary production frequently leads to increased P availability in surficial sediments (Hesse, 1973). Such changes have been shown to provide a potentially important source of P, especially when nutrient supplies are reduced (Larsen *et al.*, 1975; Golterman, 1976; Lee, 1976; Stevens and Gibson,1976; Cooke *et al.*,1977). The observations during this study emphasise the rapid rate at which sediments can change in response to increased primary production and, while the qualitative changes which were observed in the sediment profiles in the column +N and column N+P suggest that P availability to organisms in the water may have been increased, the extent of the increased availability cannot be assessed from this data because of the inability of the extraction procedures used to measure functionally distinct P fractions.

3.6 Conclusions

i) In the column +P, PO_4-P was rapidly removed from the water following enrichment predominantly by sediment uptake and the biological response was limited by low N availability.

ii) The N available in the water column represented a large proportion of the total available N in the system and very little N input from the sediments occurred in response to biological demand in the water.

iii) In the column +N, P was released from an internal source (the sediments) under apparently aerobic conditions and high levels of primary production were sustained for approximately three months by NO_3-N addition alone.

iv) An extensive pool of available P, most of which is associated with the sediments, exists in Midmar Dam and can be released into the water if sufficient biological demand is created.

v) The role of the sediments as a source and sink for P, and the existence of a dynamic PO_4-P equilibrium between sediments and the overlying water was confirmed but the uptake and release rates could

not be accurately estimated.

vi) At times SRP concentrations were increased to levels well in excess of those that would be expected from the sediment/water PO_4-P equilibrium and this was attributed to the presence of a soluble P fraction, other than PO_4-P, that was not adsorbed by the sediments but which did contribute to the SRP analyses.

vii) Bioassay results showed that at times when SRP concentrations were high a large proportion of the SRP was not utilised by the test organisms, indicating that it was not in the form of PO_4-P.

viii) Vertical profiles in the sediments indicated that the recently deposite surface sediments differ markedly from the drowned terrestrial soils on which they have been deposited, but the influence of this change on sediment/water P exchange could not be assessed.

ix) The enrichment treatments had very little influence on organic carbon, pH and exchangeable Al^{3+} profiles in the sediments, but in the column +N and column N+P both available P and AEP increased markedly in the surface layers following blooms of *Microcystis*.

As a result of these observations it was decided that the following aspects should be investigated further:

a) the PO_4-P adsorption characteristics of stratified sediment cores in an attempt to ascertain the influence of the observed changes in the surface sediments on the sediment/water P exchange;

b) uptake and release of P by intact sediment cores in order to quantify the rates of exchange and to characterise the exchange kinetics;

c) exchange of different soluble P fractions with the sediments in an attempt to confirm the existence of a soluble P fraction that is not adsorbed by the sediments;

d) the cycling of P within the water with particular reference to P fluxes between soluble and particulate compartments and the possible

role of soluble P fractions other than PO_4-P in increasing SRP levels in the water.

Sediment/water P exchange is considered in chapter 4 and P cycling in the water column in chapter 5.

CHAPTER 4

LABORATORY STUDIES OF SEDIMENT/WATER P EXCHANGE

4.1 Introduction

Following the 1976-77 enrichment experiment it was concluded that further studies of sediment/water P exchange were necessary to quantify the effects of the recently deposited sediments on the P adsorption characteristics of the substrate, and to measure the rates of P adsorption and desorption by intact sediment cores under aerobic conditions.

The first section of this chapter relates to the vertical stratification in P adsorption characteristics in the sediments, which was studied using adsorption isotherms, and the second section considers the exchange of P between intact sediment cores and the overlying solution in laboratory sediment/water systems.

4.2 Vertical Stratification in P Adsorption Characteristics of Midmar Dam Sediments.

4.2.1 Results

The PO_4-P adsorption characteristics of different strata in the top 5 cm of sediment from a shallow (water depth approximately 3.5 m) open water area in Midmar Dam are reflected in the adsorption isotherms (Fig. 4.1). In general, the adsorption capacity increased with depth in the sediment, the differences becoming most evident at high levels of PO_4-P addition (2-20 mg ℓ^{-1}). At lower saturation levels (<2 mg ℓ^{-1}) the 3-5 cm stratum exhibited markedly higher P adsorption than the overlying strata.

The data plotted according to the Langmuir equation are presented in Fig. 4.2. Two distinct linear regions were evident, one covering the approximate equilibrium P concentration range from 0-3 x 10^3 $\mu g\ \ell^{-1}$, and the other the range from 3-18 x 10^3 $\mu g \ell^{-1}$. This is indicative of at least two populations of adsorption sites, differing in their affinities for PO_4-P (Eisenreich and Armstrong, 1978).

In a limnological context, the lower range of equilibrium P concentrations are of more relevance because PO_4-P levels in fresh waters are usually low. Langmuir constants were therefore calculated for the first linear region only, and these together with the organic carbon, exchangeable Al^{3+}, available P and acid extractable P concentrations, and pH, are presented in Table 4.1. Both constants, the P adsorption maximum and the bonding energy constant, in the 3-5 cm stratum were markedly higher (25% and 100%) than those in the overlying strata. No distinct gradient was evident over the top 3 cm of sediment comprising the loose surface material, 0-1 cm and 1-3 cm strata.

Trends in organic carbon, exchangeable Al^{3+}, pH, available P and acid extractable P have been discussed (section 3.5.2) but are included here to facilitate assessment of their possible influence on the Langmuir constants. Correlation coefficients between the Langmuir constants and other parameters are presented in Table 4.1. The only significant correlations obtained were negative, between both P adsorption maximum and bonding energy constant with organic carbon and pH.

4.2.2 Discussion

In the application of Langmuir adsorption isotherms to other lake sediments single slope Langmuir plots are more typical (McCallister and Logan, 1978; Green *et al.*, 1978; Ku *et al.*, 1978). This apparent contrast between the adsorption characteristics of Midmar Dam sediments and those of other lake sediments may simply reflect the wider range of equilibrium P concentrations (in solution) used during this study (0-18 mg ℓ^{-1}). Ku *et al.*, (1978) and McCallister and Logan, (1978) used an equilibrium P range of 0-5 mg ℓ^{-1}, and over a similar range the Midmar Dam data would also conform to the Langmuir equation. It is notable that the distinctly diphasic Langmuir plots for PO_4-P uptake by aluminium hydroxide (Eisenreich and Armstrong, 1978) and by terrestrial soils (Taylor and Ellis, 1978; Syers *et al.*, 1973) also reflect a wider range of equilibrium P concentrations than normally used in the study of PO_4-P adsorption by lake sediments. The P adsorption maximum values obtained for Midmar Dam sediments ranged from 440 µg g^{-1} in the loose surface material to 537 µg g^{-1} in the 3-5 cm stratum and compare favourably with values obtained for a Farningham Oxisol (465 µg g^{-1}) by Thompson (1971). This was the highest value obtained for a range of Natal soils and indicates that the Midmar substrate has retained the high P binding capacity of the soils in the area, as was shown for other riverine sediments in the catchment (Furness, 1974).

Compared with other lake sediments however, the P adsorption maxima in the Midmar sediments appear to be extremely low. In a series of bottom sediments from the Maumee River Basin, Ohio, a range of P adsorption maxima of 0.2 to 4.9 ($\bar{x}$ 3.0) mg g^{-1} was obtained (McCallister and Logan, 1978), exceeding the values for Midmar sediments by a factor of approximately six. In two Massachusetts lakes P adsorption maxima ranged between 1.1 and 1.8 mg g^{-1} (Ku *et al.*, 1978). It is notable

however, that in spite of the higher P adsorption maxima, the bonding energy constants in the Maumee River Basin sediments (0,0006-0.0015 ℓ μg^{-1} were much lower than those in the Midmar sediments (0.0021 - 0.0054 ℓ μg^{-1} This indicates that although the total adsorption capacity of the Midmar sediments is lower the PO_4-P is bound far more strongly. In the Massachusetts lakes the bonding energy constants (0.00107 - 0.00334 ℓ μg^{-1} (Ku *et al.*, 1978) were within a similar range to those for the Midmar Dam sediments in spite of the markedly higher P adsorption maxima. The reasons for these variations are not clear.

In some terrestrial soils the bonding energy constant has been shown to be inversely related to the proportion of organic material (Wier and Sopher, 1962), and high proportions of organic material in lake sediments have been shown to result in reduced adsorption capacities (Slater and Boag, 1978). Since the adsorptive capacity of soils and sediments is due predominantly to the large adsorptive area provided by the inorganic clay minerals (Syers *et al.*,1973) this trend would be expected. In the Maumee River basin however, organic carbon showed no significant correlation with the Langmuir constants (McCallister and Logan, 1978) and in lakes Warner and Wyola (Massachusetts), where organic matter content was high (13.7 - 27.8%) the P adsorption maxima were higher than those in Midmar, while the bonding energy constants were similar (Ku *et al.*, 1978). Clearly therefore no general statement regarding the influence of organic material on PO_4-P adsorption characteristics of sediments can be made at this stage.

In the Midmar Dam sediments both Langmuir constants showed a significant negative correlation with organic carbon and pH, and whilst

this does not constitute evidence that either of these parameters is influencing the P exchange characteristics directly, it does suggest that the reduced PO_4-P adsorption capacity in the surficial sediments may be partially attributable to increased organic content. In this respect the data supports the observation of Slater and Boag (1978).

McCallister and Logan, (1978) discussed the complexities of the chemical transitions that can occur in river sediments under hydrated conditions. These favour the formation of amorphous gel complexes which increase the adsorptive surface markedly, leading to increased P adsorption maxima, and reduced bonding energy constants. Trends at the sediment/water interface in Midmar Dam are clearly not reflecting similar processes because, while the bonding energy did decrease, so did the P adsorption maxima. Insufficient data is available to make a comprehensive comparison between Midmar sediments and those discussed by McCallister and Logan, (1978), but in view of the variability in lake sediments (Syers *et al.*, 1973) it is not unlikely that the observed differences reflect markedly different sediment structure and chemical composition.

Of particular relevance to this study is the fact that the vertical profiles in parameters such as organic carbon, pH and exchangeable Al^{3+} reflect real changes in the P exchange characteristics of the sediments. The top 3 cm of sediment, which is the layer most directly influenced by processes occurring in the water (resuspension and sedimentation), exhibit a reduced affinity for PO_4-P, and are able to adsorb considerably less than the drowned terrestrial soils on which they have been deposited. The implications of this are considerable.

If the trends which are already evident in the sediment profiles are indicative of long term trends in the impoundment, the role of the sediments in the P cycle could be markedly altered as the surficial layer continues to be deposited. The PO_4-P adsorptive capacity of the surface sediments may continue to decrease and, as the drowned terrestrial soil becomes more effectively isolated from the overlying water, the sediment/water PO_4-P equilibrium may be altered in such a way that P availability in the water is increased.

4.3 Sediment/Water P Exchange : Radiotracer Studies

4.3.1 Results

4.3.1.1 Uptake of P by Sediments

The uptake of P by sediments was monitored in enriched and unenriched control systems containing no intact sediment cores as well as in enriched and unenriched sediment/water systems. For convenience the results obtained in the control systems, the unenriched sediment/water systems and the enriched sediment/water systems will be dealt with separately.

a) Control Systems. In the unenriched control approximately 16% of the total radioactivity had been removed from solution after 68 hours (Fig. 4.3A), and the uptake was adequately described by an exponential function from which a rate constant of 0.0024 hr^{-1} was obtained (Table 4.2). When PO_4-P was added to a control system at a concentration of 100 $\mu g\ \ell^{-1}$ only 10% of the added tracer had been removed from solution when sampling was stopped (Fig. 4.3B). The rate of ^{32}P uptake was considerably slower than that in the unenriched control, because of the increased PO_4-P concentration and the consequent dilution of ^{32}P with ^{31}P. The slow rates of ^{32}P uptake in

the controls, relative to the sediment/water systems (Table 4.4), indicate that ^{32}P removal during the sediment uptake experiments was unlikely to be markedly influenced by adsorption onto the glass surface of the containers, or by any other factor not associated with the sediments.

In the sediment/water systems, the pattern of ^{32}P uptake was best described by a combination of exponential functions (Table 4.4), whereas uptake in the controls could be described by either an exponential or a linear function. However, since the controls were used in a comparative manner (i.e. to compare water/glass uptake with water/glass /sediment uptake) to assess the net uptake by sediments, it was desirable to define all systems on the basis of an exponential pattern. Although the justification for doing this may be questionable, in view of the relatively slow uptake in the controls it was felt that the use of this procedure would have no influence on the final interpretation of the sediment uptake data.

b) Unenriched Sediment/Water Systems. In the unenriched sediment/water system SRP concentrations did not change during the experiment, i.e. an equilibrium SRP concentration was maintained (Table 4.4). The rapid ^{32}P uptake is thus indicative of a dynamic steady state system in which the rate of P influx into the sediments is matched by a corresponding efflux, as demonstrated by Olsen (1958). Isotope uptake continues until the ^{32}P becomes evenly distributed throughout the exchangeable P pool, including sediment and solution compartments, at which time ^{32}P influx and efflux is equal and the

asymptote is reached.

The ^{32}P uptake curves in the unenriched systems showed a rapid, apparently exponential, decrease to equilibrium levels of 19% and 34% of the total activity (the reason for this marked difference in equilibrium levels not being clear). From the semilog plots (Fig. 4.4) two distinct linear regions were evident, one covering the first 10 minutes and the other covering the remainder of the curve. The uptake kinetics could not therefore be adequately described by a single exponential function and the curve splitting technique of Riggs (1963) was used to characterise the two phases independently (Table 4.4).

Mean rate constants of 16.7600 hr^{-1} and 0.1126 hr^{-1} were obtained for the rapid and slow phases of uptake respectively, and the relative proportions of the total ^{32}P exchanged via the two phases (obtained by extrapolating the semilog plots to Y_o) were 49.6% for the rapid phase and 23.9% for the slow phase, the balance representing the equilibrium level remaining in solution (Table 4.4).

Although no net flux of P occurred in the unenriched sediment/water systems, the rate of exchange of P across the sediment/water interface was calculated from the rate constant and the equilibrium SRP concentration ($\bar{x}$ = 0.012 $\mu g\ cm^{-2}\ hr^{-1}$). The assumption was made that all of the SRP was actively exchanging with the sediments. In view of the fact that SRP may include soluble P forms other than PO_4-P (Rigler, 1973), and of the fact that some soluble P forms are not involved in P exchange with the sediments (section 4.3.1.1d),

it seems likely that the estimated exchange rates could represent considerable overestimates.

c) Enriched Sediment/Water Systems

With increasing levels of PO_4-P addition the amount of ^{32}P remaining in solution (asymptotic level) decreased (Fig. 4.5A and Table 4.4), reflecting the increasing net flux of P into the sediments. The increasing dilution of ^{32}P with ^{31}P at higher enrichment levels resulted in progressively increasing equilibration times (Fig. 4.5B and Table 4.3).

In all of the enriched sediment/water systems the SRP analyses confirmed a net uptake of P by the sediments (Table 4.4) and showed that the final equilibrium SRP concentrations were not measurably influenced by the enrichment treatments.

Uptake curves in the enriched systems (Fig. 4.3 D-F) could be resolved into two phases as was observed in the unenriched systems (Fig. 4.3 B-D and Table 4.4). The rapid phase of uptake was characterised by fairly high variability between replicates of each treatment, which is reflected in the differences between the rate constants and Y intercepts (Table 4.4). This was particularly evident in the 50 $\mu g\ \ell^{-1}$ PO_4-P treatments where the rate constants for the two replicates differed by a factor of three. Within the limits of the observed variability the rate constants for the fast phase of uptake showed no trend with increasing enrichment despite the increased isotope dilution (Fig. 4.5 C) and did not differ from those in the unenriched systems. The calculated maximum possible uptake rates showed a linear increase with increasing levels of

enrichment, reaching 16.34 μg cm^{-2} hr^{-1} at an enrichment level of 200 μg PO_4-P ℓ^{-1} (Fig. 4.5d and Table 4.4) indicative of the dependence of the uptake rate on the extent of the diffusion gradient between the sediment and water.

In contrast to the fast phase of uptake, during the slow phase of uptake the rate constants decreased progressively, in an apparently exponential manner, with increased PO_4-P enrichment. An exponential decrease may be expected since, as the concentration of PO_4-P in the above sediment/water increases, so the saturation increases and the turnover time ($^1/k$) increases. However, since there is always some exchange, even in saturated systems, turnover always occurs albeit perhaps extremely slowly. The relationship between PO_4-P concentration and rate constant must therefore be exponential (Fig. 4.5C). The computed maximum possible uptake rates increased linearly to 0.044 μg cm^{-2} hr^{-1} at an enrichment level of 200 μg ℓ^{-1} (Fig. 4.5D and Table 4.4).

In the enriched sediment/water systems between 22% and 49% of the total radioactivity was removed from solution via the fast phase of uptake, while the slow phase accounted for between 46% and 59% of the uptake (Table 4.4).

Thus, in contrast with the unenriched systems where the rapid phase of uptake accounted for the major proportion of the P exchange, in the enriched systems, the slow phase of uptake was either greater than (50 and 100 μg PO_4-P ℓ^{-1} enrichments) or equal to the fast phase (200 μg PO_4-P ℓ^{-1} enrichments) in terms of the proportion of ^{32}P taken up (Table 4.4).

d) Exchange of Labelled Soluble P Fractions. At least two soluble P fractions have been shown to be involved in P exchange in the water column (chapter 5), colloidal P and PO_4-P. The differences in their exchange characteristics with the sediments are, for convenience, considered here.

When colloidal ^{32}P was added to an intact sediment/water system no uptake of tracer from the water was evident, indicating that this fraction was not directly involved in exchange with the sediments (Fig. 4.6A). In contrast, when labelled PO_4-P, obtained from Midmar Dam filtrate was added to an intact sediment/water system, the exchange characteristics were similar to those observed in the steady state ^{32}P uptake experiments (section 4.3.1.1b). Isotope levels in the water decreased exponentially, approaching an asymptote (approximately 20%) after 2 hours (Fig. 4.6A) and semilog plots of $Y - Y_{asymp.}$ versus time revealed two distinct phases of uptake, one covering the first 10 minutes and the other the remainder of the curve (Fig. 4.6B). Rate constants of 14.73 hr^{-1} and 0.76 hr^{-1} were obtained for the fast and slow phases of uptake respectively (Table 4.3), clearly demonstrating the rapid exchange of this fraction.

A comparison of the uptake kinetics in the unenriched sediment/water systems (Table 4.4) with those for the PO_4-P fraction obtained from Midmar Dam filtrate (Table 4.3) show that the rate constants for the rapid phase of uptake were similar (16.76 and 14.73 hr^{-1} respectively) while those for the slow phase differed by a factor of approximately 7 (0.113 hr^{-1} and 0.766 hr^{-1} respectively). The marked contrast between the slow phases undoubtedly results from the diluting influenc

of the gel filtration procedure. The PO_4-P present in 5 ml of filtrate was eluted in approximately 50 ml eluent which represents a 10 fold reduction in concentration, and consequently the sediment/water systems to which the PO_4-P fraction was added, would not be in a steady state. The reduced PO_4-P concentration in the water would be expected to induce a more rapid exchange with the sediments. The reason why the increased rate was not evident in the rapid phase of uptake is not clear, but it could be related to the infrequent sampling during the first 10 minutes which was not suited to an accurate characterisation of this section of the curve.

.4.3.1.2 Release of P by Sediments

Release of ^{32}P from intact sediment cores labelled during the ^{32}P uptake experiments showed a consistent pattern, with a decreasing rate of release with time until an asymptote was reached after approximately 1 hour (Fig. 4.7). Semilog plots of $Y_{asymp} - Y$ versus time (Riggs, 1963) were used to characterise the releases graphically (Fig. 4.8), in a similar manner to the ^{32}P uptake curves. The release curves could be resolved into two distinct linear regions one covering the first 0.5 minutes and the other the remainder of the curve. Exponential functions were fitted to both phases individually and the coefficients of determination, Y intercepts, rate constants and calculated maximum rates of release are presented in Table 4.5.

The rate constants and the computed theoretical maximum release rates for both phases of release showed no trends which could be related to the previous enrichment levels (Table 4.5). This is not surprising however, as equilibrium SRP concentrations at the conclusion of the ^{32}P uptake experiments (section 4.3.1.1 b anc c)

were similar in all treatments, indicating that the levels of enrichment used were low relative to the P fixing capacity of the sediments and did not influence the sediment/water equilibrium to a measurable extent.

Rate constants for the rapid phase of release varied between 1.75 min^{-1} and 3.27 min^{-1} and the computed maximum rate of release varied between 4.87 and 11.71 $\mu g\ cm^{-2}\ hr^{-1}$ ($\bar{x}$ 7.65 $\pm$ 4.01 $\mu g\ cm^{-2}\ hr^{-1}$). During the slow phase, rate constants varied widely between 0.019 min^{-1} and 0.087 min^{-1} and the computed maximum possible rate of release ranged between 0.053 and 0.242 $\mu g\ cm^{-2}\ hr^{-1}$ ($\bar{x}$ 0.135 $\pm$ 0.110 $\mu g\ cm^{-2} hr^{-1}$) (Table 4.5). It should be stressed at this point that the release rates were calculated assuming an SRP concentration of zero - a strictly hypothetical situation under natural conditions. This will be discussed in more detail in section 4.3.2.2.

Equilibrium concentrations of SRP attained during the release experiments remained fairly constant, fluctuating between 7 and 9 $\mu g\ \ell^{-1}$ (Table 4.5) providing further evidence that the enrichment treatments were of little significance to the sediment/water P equilibrium. During the ^{32}P uptake experiments the equilibrium SRP concentrations recorded (approximately 16 $\mu g\ \ell^{-1}$) were considerably higher than those recorded during the release experiments. The reason for this discrepancy is not apparent in the data.

The total radioactivity in the water at equilibrium varied between 1500 and 2600 CPM ml^{-1}, but in spite of this fairly wide variation, the total radioactivity released during the experiments was a small proportion (0.7-1.0%) of the total activity initially applied to the

sediment water systems. Clearly the ^{32}P released during these experiments represents only a very small fraction of the exchangeable P in the sediments.

4.3.1.3 Depth of the Actively Exchanging Sediment Layer

The vertical distribution of ^{32}P in the sediment cores after equilibration for 1 and 3 weeks, at varying PO_4-P concentrations, together with mean water content of the strata and their dry mass per unit area, are presented in Fig. 4.9 A. The pattern of isotope distribution showed very little variation with increasing PO_4-P enrichment or with increased equilibration time. Most of the tracer (86-96%) occurred in the loose surface material, dropping sharply below this to between 3 and 12.5% in the 0-1 cm stratum and between 0.5 and 2.0% in the 1-2 cm stratum. Traces were detected in the 2-3 cm stratum and occasionally below this, but generally 2 cm seemed to be the limit of the ^{32}P penetration.

Water content decreased with increasing depth in the profile. A sharp drop from 87% in the loose surface material to 60% in the 0-1 cm stratum was followed by a steady more gradual decreasing trend to 52% in the 3-4 cm layer (Fig. 4.9B), indicative of the more consolidated deeper strata.

The areal dry mass content of the sediment strata are presented in Fig. 4.9C. In the loose surface material, which comprised a thin layer with a high water content, the dry mass was low (0.05 g cm^{-2}) but in the 1 cm strata between the surface and 4 cm the dry mass content fluctuated between 0.57 and 0.67 g cm^{-2}. Although a general increasing trend between the 0-1 cm and 3-4 cm strata was evident, which

would be expected in view of the decrease in water content with depth, the variability was high, as evidenced by the wide standard deviations, and the trend cannot be regarded as significant.

4.3.2 Discussion

4.3.2.1 Uptake of P by Sediments

a) P Uptake Kinetics

Under both steady state conditions and at differing levels of PO_4-P enrichment, the ^{32}P uptake curves during this study were best described by a combination of two exponential functions, one describing the first 10 minutes of the uptake and the other the remainder of the curve.

As discussed in section 4.2.2, the existence of a number of PO_4-P adsorption processes has been demonstrated in air dried sub-samples of soils, sediments and aluminium hydroxide, and the diphasic (or polyphasic) ^{32}P uptake kinetics observed in sediment suspensions or intact sediment/water systems would therefore be expected.

Although PO_4-P uptake by Loch Kinardochy sediments was mathematically described by a single exponential function (Holden, 1961) there is accumulating evidence that sediment/water P exchange is not adequately described in this way (Pomeroy *et al.*, 1965; Li *et al.*, 1972; Howard-Williams and Allanson, 1978) and the experiments conducted on Midmar Dam sediments contribute to this evidence. Using sediment suspensions, Pomeroy *et al.*, (1965) showed markedly diphasic kinetics between estuarine sediments and the water and Li *et al.*, (1972), also

using sediment suspensions, showed that P exchange between a variety of North American lake sediments and the water could be resolved into three distinct regions, each described by an exponential function. Ku *et al.*(1978) studying PO_4-P adsorption by two Massachusetts lake sediments observed a rapid initial uptake followed by a slower uptake towards equilibrium, which they attributed to different adsorption processes, implying a diphasic uptake.

Li *et al.*, (1972) attributed polyphasic P exchange kinetics to the combined effects of several exchange reactions occurring at different rates, due either to differences in types of bonding or position. However, they point out that graphical resolution of uptake curves into distinct phases does not constitute proof of an equivalent number of specific reactions since, reactions with rates not sufficiently different to allow resolution, could also be occurring.

This is of particular relevance to the rapid phases of uptake observed during this study which, due to the 10 minute delay before the first sampling, were described by two data points only. In view of the extremely rapid exchange during this time so few points undoubtedly give an inadequate description of the uptake, and may represent a considerable underestimate of the actual rates. This aspect was emphasised by Pomeroy *et al.*, (1965) who suggested that the rapid phase of ^{32}P uptake was not precisely defined even at sampling intervals of 30 seconds. Interpretation of the rapid phase in the Midmar sediment/water systems must therefore be cautious, as more frequent sampling during the first 10 minutes could result in further resolution of the rapid phase.

Ku *et al.*, (1978) suggested that the initial uptake of PO_4-P sediments could be due to adsorption onto the sediment surface and that the slower phase of uptake approaching equilibrium may involve several concurrent processes such as internal diffusion, nucleation and growth of new solid phases, decomposition of clay minerals and reactions of released Fe and Al with PO_4-P. Holden (1961) showed that at high levels of PO_4-P uptake, a reduction in uptake rate reflected the increased saturation of adsorption sites but, in a number of radiotracer studies (Pomeroy *et al.*, 1965; Li *et al.*, 1972, and th study) diphasic (or polyphasic) kinetics have been observed under steady state conditions and do not reflect net changes in the P saturation levels in the sediments. Thus, while the diphasic ^{32}P uptake curves indicate that at least two exchange processes are involved in P adsorption/desorption by intact sediments cores, the causes of the observed kinetics are not clear and, in view of the complexity of sediment/water P exchange mechanisms (Syers *et al.*, 1973), cannot be speculated upon. However, the general interpretation used by Li *et al.*, (1972) that the rapid and slow phases of uptake occur concurrently and that each phase may comprise more than a single uptake mechanism, will be applied to the Midmar data during this discussion.

The potential influence of biological processes on the exchange kinetics between lake sediments and the water was not stressed by Li *et a* (1972) or Ku *et al.* (1978), but the presence of organic matter in the sediments complicates the mud/water P exchange (Hesse, 1973) and, in many instances, the bacterial processes dominate over inorganic reactions (Hayes and Phillips, 1958; Schindler *et al.* 1974). The role of biological processes has been investigated using biological inactivators (Pomeroy *et al.* 1965) but this procedure has been questioned (Golterman, 1973b; Viner, 1975) on the grounds that the inactivators have the potent

to influence inorganic exchange by altering the colloid chemistry, and the difference between living and poisoned samples may not necessarily reflect biological activity. For this reason this procedure was not adopted on the Midmar sediments. It is therefore not possible to resolve the data further and assess the relative roles of the biotic and physico-chemical processes.

Of the two soluble P fractions involved in exchange with the particulate P compartment in the water, colloidal P showed no direct exchange with the sediments, while the PO_4-P fraction showed similar exchange kinetics to those observed in the other ^{32}P uptake experiments in sediment/water systems. The relative distributions of these fractions and other aspects of their exchange kinetics in the water column will be considered in chapter 5.

During the 1976-77 *in situ* experiments it was suggested (section 3.3) that the accumulations of SRP observed in the column +N and column N+P may have been caused by the accumulation of an organic P fraction which was included in the SRP analysis but which was not taken up by the sediments. Further evidence was provided by bioassay results (section 3.4) which showed that, at the times of maximum SRP accumulation, a large proportion of the SRP was not available for uptake by organisms, implying that it was not PO_4-P. The existence of a soluble P fraction which is not adsorbed by the sediments but which is involved in rapid P cycling in the water provides further evidence in support of this suggestion.

Colloidal P fractions, which exhibit similar gel filtration characteristics to the colloidal P fraction identified in Midmar Dam,

have been identified in many freshwaters (Lean, 1973; Downes and Paerl, 1978; Peters, 1978, 1979) but their exchange kinetics with lake sediments have not been reported upon. The observation that colloidal P is not directly fixed by sediments may therefore be of considerable significance to fresh waters generally. Many lake sediments are characterised by high PO_4-P fixing capacities resulting in low concentrations in the water (Syers *et al.*, 1973) and, as a consequence, P concentration frequently limits algal growth rate in fresh waters (Rigler, 1973; Syers *et al.*, 1973) and any mechanism whereby P availability in the water can be increased would be advantageous to primary producers growing in the water. Since some colloidal P has been shown to be of biological origin (Lean and Nalewajko, 1976) and since, by virtue of the fact that it exchanges with PO_4-P, it must be partially biologically available (Lean, 1973; Peters, 1978) it is possible that biological production of colloidal P could provide a mechanism whereby P availability in the water is markedly increased. This aspect will be discussed in more detail in chapter 5.

b) PO_4-P Uptake Rates

Pomeroy *et al.*, (1965) made the important observation that the time taken for equilibrium between sediments and water to be attained during P exchange experiments in undisturbed sediment water systems was longer (approximately 40 hours) than in shaken sediment suspensions (10 minutes). They attributed this to the dependence of the former on diffusion processes, which are slow in water (Hutchinson, 1957). Rippey (1976) demonstrated that twice daily agitation of the sediment surface in an intact sediment/water system increased the exchang rates markedly, emphasising the role that mixing can play in speeding up the rates of diffusion.

During the Midmar studies, gentle agitation was used to ensure even distribution of isotope in the water before samples were withdrawn from the sediment/water systems. However, care was taken to ensure that the surficial sediments were not disturbed, and the procedure could not be regarded as a simulation of the mixing regime under natural conditions. In view of the important role of turbulence in the P exchange processes across the sediment/water interface, the inability to simulate natural mixing in sediment/water systems was regarded as a serious limitation by Lee (1976) who preferred the whole-lake mass balance approach, where the total P present in the water column can be examined as a function of time and the P fluxes across the sediment/water interface calculated by difference using input/output data. However, in Midmar Dam, where nutrient inputs and trophic status are low, the *in situ* mass balance approach is of limited value because the system is approximating a dynamic steady state and P fluxes between compartments occur at levels below the sensitivity of commonly used analytical methods (Rigler, 1973). For this reason the sediment/water systems were used to augment the investigation of sediment/water P exchange.

In spite of the inability to account for the influence of turbulence at the sediment/water interface, the rates obtained in the laboratory are useful in that they probably underestimate the rates that would be expected under natural conditions.

Over the range of PO_4-P enrichments used during this experiment the increase in maximum uptake rates by the sediments, during the fast and slow phases, were apparently linear, indicating that at higher concentrations the rates would have been faster. In view of

the present trophic status of the impoundment however, uptake rates at lower levels are of more relevance. For predictive purposes however, uptake rates at higher levels of enrichment are useful.

From the linear relationships between rate of P uptake and P enrichment level (Fig. 4.5D) the overall rate of uptake at a specific level of PO_4-P enrichment can be obtained by summing the rates for the rapid and slow phases. For example to sustain a 25 $\mu g\ \ell^{-1}$ increase in PO_4-P concentration, a sediment fixation rate of 3.009 $\mu g\ cm^{-2}\ hr^{-1}$ (fast phase approximately 3 $\mu g\ cm^{-2}\ hr^{-1}$ and slow phase approximately 0.009 $\mu g\ cm^{-2}\ hr^{-1}$) would have to be exceeded by enrichment. This is equivalent to a PO_4-P loading rate of 264 $g\ m^{-2}\ a^{-1}$ which is extremely high compared with the loads entering three of South Africa's most eutrophic impoundments, Haartebeespoort Dam (13.87 $g\ m^{-2}\ a^{-1}$), Rietvlei Dam (25.73 $g\ m^{-2}\ a^{-1}$) and Roodeplaat Dam (20.92 $g\ m^{-2}\ a^{-1}$) (Walmsley *et al.*, 1978). Similar levels of PO_4-P enrichment, in the absence of simultaneous enrichment with N, would therefore have very little influence of SRP levels in Midmar Dam in its present state. This supports the observations made in the column +P during the 1976-77 *in situ* enrichment experiments, where a loading rate of 27 $g\ m^{-2}\ a^{-1}$ was maintained with very little influence on SRP levels, or on the phytoplankton. When N and P are added together the consequent increase in algal standing crop in the water could result in a larger proportion of the added P being retained in the soluble and particulate P fractions in the water, as was the case in the column N+P.

The period during which specific loading rates can be sustained without influencing SRP levels in the water will depend on

the total capacity of the sediments to adsorb P, and the rate at which saturation levels are approached will be inversely related to the level of enrichment. The 1976-77 *in situ* enrichment experiments indicated that a PO_4-P loading rate of 27 g m^{-2} a^{-1} over a 58 week period had no measurable influence on sediment P saturation and could therefore have been continued for a longer period. With the data available it is however not possible to make a meaningful estimate of the total amount of PO_4-P that can be adsorbed by the sediments without influencing PO_4-P levels in the water.

Under natural conditions the continued input of silt may contribute to the P adsorption capacity of the surface sediments, and this input would have to be quantified before a meaningful estimate of the total P fixing capacity could be made. Whilst in Midmar Dam the silt input may be fairly low (Furness, 1974) in other turbid South African impoundments allochthonous silt deposition may be an important factor in this regard.

4.3.2.2 Release of P

a) ^{32}P Release Kinetics

Release of ^{32}P from all of the sediment cores used was clearly resolved into two distinct phases on the semilog plots. Since the ^{32}P uptake kinetics were distinctly diphasic, and assuming that similar mechanisms are involved in the desorption and adsorption of PO_4-P, the diphasic release would be expected.

Before conducting the ^{32}P release experiments care was taken to remove as much of the free isotope from the surface water on the sediments and glass container as possible, but it is probable that despite these

precautions traces of free ^{32}P remained in the systems. On addition of the leaching solution the free ^{32}P could have been brought into solution immediately, and it is impossible to distinguish this from the ^{32}P that was desorbed from the sediments during the first 30 seconds of the experiment. The apparent diphasic release kinetics could therefore be partially due to an artifact created by the experimental procedure. Despite the short sampling intervals used during the ^{32}P release experiments, characterisation of the rapid phase of release is based on two values, the measured value at 30 seconds and an assumed initial value of zero. The later assumption is of dubious validity, and the inadequacy of using only two points to describe the rapid phase of release casts further limitations on the reliability of the exponential regression constants generated. Clearly the rapid phases of release must be interpreted with extreme caution.

b) Measurement of P Release from Sediments

Some authors have attempted to estimate sediment P release in laboratory sediment/water systems using lake water, filtered or unfiltered, as the leaching solution (Kamp Nielsen, 1974, 1975b, Banoub, 1975; Bengtsson, 1975; Viner, 1975; Rippey, 1976; Glass and Poldoski, 1975; Howard-Williams and Allanson, 1978). These experiments are analogous with the ^{32}P uptake experiments under steady state conditions in Midmar sediment/water systems, which showed that after 85 hours of equilibration between filtered dam water and intact sediment cores no net release of P from the sediments occurred. Although P release from sediments has been demonstrated under aerobic conditions, using this methodology (Banoub, 1975; Glass and Poldoski, 1975), the absence of net P flux into the water has frequently been interpreted as an indication

that the sediments do not release P under aerobic conditions (Kamp Nielsen, 1974; Viner, 1975) and based on similar methods in Midmar sediments, the same conclusion would be reached. This interpretation however ignores the concept of a dynamic steady state between lake sediments and the overlying water (Hayes and Phillips, 1958; Stumm and Leckie, 1970) which was operative in the unenriched Midmar Dam sediment/water systems. Before a meaningful assessment of the potential P release rates can be made the sediment/water P equilibrium has to be disturbed in such a way that release from the sediments is favoured. Thus P release experiments where filtered or unfiltered lake water is used as the leaching agent may simply reflect a dynamic steady state.

The experiments of Viner (1975) on Lake George sediments may be examined in this context. Under aerobic conditions no significant release of PO_4-P from intact sediment cores into filtered lake water was detected, and concentrations in the water remained at approximately 50 $\mu g\ \ell^{-1}$ for over 6 days. From this result he concluded that sediment P was not available to the primary producers in the overlying water. An alternative interpretation could be that a dynamic steady state was maintained throughout the experiment, and before sediment P could be released PO_4-P concentration in the overlying water had to be reduced to create a diffusion gradient from the sediments.

Under natural conditions the equilibrium could be disturbed by biological demand for PO_4-P in the water, which would create the required diffusion gradient between the water and sediment. Golterman (1976) used algal cultures in the laboratory and natural phytoplankton population in *in situ* enclosures to demonstrate this. P release from Midmar sediments has been demonstrated in isolation columns during this study,

and during preliminary studies (Twinch and Breen, 1978) but could not be reliably quantified.

Other methods of creating a suitable concentration gradient between the sediments and water to demonstrate release of sediment P have been used. Di Giano and Snow (1976) used a watertight fibreglass tank, enclosing an area of sediment *in situ*, through which lake water could be pumped. P was removed from the water entering the tank by an activated carbon bed and an anion exchanger. Fillos (1976) used a similar continuous flow method in the laboratory Both methods demonstrated P release from lake sediments.

A more simple alternative method of demonstrating P release from sediments is to use a P-free leaching solution. Lee (1976) used distilled water while Li *et al.*, (1972) used a 0.1M NaCl solution, and the latter was used during the Midmar Dam experiments.

c) ^{32}P Release Rates

Although rapid release of P was evident from all of the sediment cores studied, the estimation of an overall release rate, which may give an index of the potential release under natural conditions, is difficult.

The most obvious problem is the uncertainty surrounding the reliability of the exponential function describing the rapid phase of release. At the rapid rates of release observed during the first 0.5 minutes even slight errors could lead to massive miscalculations of overall release rates and, in view of the distinct possibility that the rapid uptake was partially due to limitations in the experimental

procedure, it was decided that any attempt to further quantify the rapid phase of release would yield results of doubtful validity.

Because the PO_4-P enrichments apparently had no influence on the sediment P saturation levels, variations in the slow phase of P release were not expected. However, the rate constants and maximum release rates for the slow phases showed wide variations (coefficient of variation 52%) with no discernable trend.

Rippey, (1976) observed marked variability in P release rates from intact Lough Neagh sediment cores (coefficient of variation 19%) and showed that increased agitation could increase the release rates markedly. During the P release experiments on Midmar sediment cores, the degree of agitation could not be controlled and the leaching solution was added in such a way that considerable agitation of the surface sediments was unavoidable. The degree of variability in the extent of agitation was probably high as a result.

Despite the severe constraints these observations place on the P release data, there can be no doubt that P release from the sediments did occur, and it seems reasonable to suggest that the computed mean maximum possible release rate for the slow phase of release provides a rough index of the releasing potential of the Midmar sediments. In view of the facts that the rapid phase of release is not being considered and that under natural conditions considerable resuspension of the surface sediments occurs in Midmar Dam (Johnson, unpublished data), it probably represents a considerable underestimation of the maximum possible release potential. Release rate will therefore vary both spatially and temporally in an impoundment.

The slow phase maximum possible release rate of 0.135 μg cm^{-2} hr^{-1} (32.4 mg m^{-2} d^{-1}) may appear to be high compared with rates observed under aerobic and anaerobic conditions in other systems (Table 4.6). However, this release rate assumes a PO_4-P concentration of zero in the water, and therefore represents a potential rate rather than a rate which is likely to be achieved under present conditions in the impoundment. Under natural conditions the sediment/water equilibrium would ensure a continuous release of PO_4-P in response to uptake in the water thereby maintaining an equilibrium or steady state and marked diffusion gradients would not be created. Furthermore, the rate of P release from intact sediment cores decreased exponentially as the equilibrium level in the water was approached so that at PO_4-P levels approaching the equilibrium the release rate would be very slow.

The experiments indicate that the P release rate from the sediments will be largely dependent on the rate of P uptake by the biota in the water. In view of the low equilibrium levels of PO_4-P and the low levels of available N in the water, the biological demand in Midmar Dam under present conditions is unlikely to result in marked P release from the sediments. However the summer responses in the column +N during the *in situ* enrichment study indicate the role sediment P release could play, if N availability is increased by enrichment. A bloom of *Microcystis* sp. appeared over a period of 8 weeks and total P concentrations increased from 46 to 311 μg ℓ^{-1}, at an overall rate of 33 μg ℓ^{-1} week. Assuming that this increase resulted exclusively from sediment release of P, a release rate of 16.4 mg m^{-2} d^{-1} can be calculated, and this is probably closer to the maximum release rate which would be expected *in situ*. As already discussed (section 3.3) however, total P concentrations in the columns could have been markedly

influenced by resuspension of surface sediments, and the *in situ* estimation of P release rate is therefore of limited use for direct extrapolation to the natural situation.

Despite the constraints imposed on both estimates of P release rate, they are indicative of the potential importance of P desorption processes in the sediments. Whilst the aim of the research was to obtain release rates which were directly applicable to the natural situation, it is now clear that this is not an easy task. Even a whole lake P budget study, which seems to be the only alternative, is restricte by the inability to separate the total P resuspended from the sediment surface from that which is released into the water in response to a concentration gradient created by biological demand. The latter process has been clearly demonstrated during this study, and the sediments must be regarded as an important potential source of P in the system.

The equilibrium concentrations of SRP in the water (7-9 $\mu g\ \ell^{-1}$) were considerably lower than those attained during the ^{32}P uptake experiments (approximately 16 $\mu g\ \ell^{-1}$ in all treatments). Although the reason for this is not clear, the methodology used in measuring the SRP varied slightly. During the ^{32}P release experiments the water was filtered to remove traces of labelled particulate material, a step which was not used during the ^{32}P uptake experiments. As will be discussed in chapter 5, the use of filtration to separate soluble and particulate P can remove fractions (particulate and molecular) which may contribute to the SRP analysis. This could contribute to the observed differences in the equilibrium concentrations.

4.3.2.3 Depth of the Actively Exchanging Sediment Layer

The distribution of ^{32}P in the stratified cores indicated that the actively exchanging layer of sediment was restricted almost exclusively to the top 2 cm of sediment and that this did not vary over the range of PO_4-P enrichment treatments used or with increasing equilibration time up to three weeks. A similar pattern was observed in Swartvlei where the isotope distribution in the sediments was restricted to the top 1-2 cm and was not influenced by PO_4-P enrichment (Howard-Williams and Allanson, 1978). These observations suggest that the deeper sediments (below 2 cm) may have very little influence on the overlying water.

The duration and extent of enrichment have however been shown to influence the penetration of P into lake sediments. Holden (1961) using PO_4-P loading rates of up to 700 $\mu g\ cm^{-2}$ and prolonging the equilibrations for up to 48 months, demonstrated a penetration of up to 8 cm which was attributed to diffusion or to transmission by bacterial activity. The experiments conducted on Midmar Dam cores must therefore be regarded as short term equilibrations which give an index of the depth of sediment involved in steady state exchange only. However, had PO_4-P loading been maintained for longer, the penetration of P may have increased as the surface layers became increasingly saturated.

The depth of sediment involved in P exchange is also markedly influenced by mixing of the surface sediments, a factor which is not taken into account in laboratory experiments. Schindler (1976) discussed the importance of mixing mechanisms in P uptake by sediments in some Canadian Shield lakes. Here it was shown that P fixed by the sediments

was not retained in a thin surface layer, but was evenly distributed throughout the top 6 cm of sediment by mixing. In Midmar Dam little quantitative data regarding the influence of turbulence on the surface sediments is available but the processes of resuspension and sedimentation are presently being investigated. Preliminary evidence suggests that the surface sediments are frequently resuspended by turbulence (Johnson, unpublished data) and the effective depth of sediment involved in direct P exchange with the water may be more extensive than the laboratory studies suggest.

The predominant role of the surface sediments in the sediment/water P exchange processes is of particular importance in view of the distinct differences in P adsorption/desorption characteristics of these layers, relative to the deeper layers (section 4.2). The more recent sediments show a markedly decreased affinity for PO_4-P, compared with the deeper strata, and if this is indicative of long term trends at the sediment/water interface the implications in relation to P cycling in the system may be considerable. As the layer of sediment overlying the drowned terrestrial soil increases in depth the sediment/water P exchange will become increasingly dependent on the recently deposited material, which is able to bind less P with lower bonding energy, than the drowned terrestrial soil (section 4.2). The implication of this, particularly if it is associated with eutrophication and the consequent acceleration of organic sedimentation, could be that the dynamic steady state between the sediments is altered in such a way that the tendency for P to be released from the sediments will be increased and higher levels of PO_4-P could thus be maintained in the water.

These studies of sediment/water P exchange have demonstrated the dynamic situation which exists between the sediments and overlying water, but have not taken into account the possible influence of processes within the water column on P fluxes across the sediment/water interface. During the *in situ* enrichment experiments there was evidence that SRP included forms other than PO_4-P, which were not adsorbed by the sediments, and this was supported by the identification of a soluble P fraction which was not taken up by intact sediment cores. Since this fraction has been shown to be of biological origin in some systems (Lean, 1973) it was decided that a more detailed investigation of P cycling between particulate and soluble P fractions in the water, and soluble P fractions in the water, under varying conditions, would contribute to the overall understanding of the role of sediments in the P cycle and help to explain the SRP accumulations observed during the *in situ* enrichment experiment.

4.4 Conclusions

i) The surficial layers comprising the top 3 cm of sediment exhibit reduced PO_4-P adsorption capacities compared with the deeper layers

ii) The existence of a dynamic PO_4-P equilibrium between intact sediment cores and the overlying water has been demonstrated.

iii) The PO_4-P uptake rate measured in intact sediment/water systems increased linearly with increasing PO_4-P concentration in solution, over the range of concentrations used (0-200 μg PO_4-P ℓ^{-1}).

iv) The ^{32}P uptake kinetics were distinctly diphasic and were best described by a combination of two exponential functions, one describing the rapid phase of uptake (0-10 minutes) and the other describing the subsequent slower phase of uptake. This is indicative of a combination of uptake mechanisms.

v) A large molecular weight soluble P fraction (colloidal P) was

shown to exhibit no direct exchange capacity with intact sediment cores.

vi) The release rate of ^{32}P from intact sediment cores decreased exponentially as equilibrium levels in solution were approached. No trend in SRP release rate was evident in cores enriched with different levels of PO_4-P and the release rates showed high variability, probably due to inconsistency in the methodology.

vii) The calculated rates of P uptake and release under aerobic conditions were sufficiently rapid to account for the P fluxes observed during the 1976-77 *in situ* enrichment experiments.

viii) The inability to account for the influence of mixing on sediment/water P exchange in the sediment/water systems placed constraints on the applicability of the data to the open water situation.

ix) The sediment actively involved in the short term exchange of P with the overlying water was largely restricted to the top 2 cm of the sediment cores.

CHAPTER 5.

Cycling of P Within the Water Column

5.1 Introduction

The results of the 1976-77 *in situ* enrichment experiment, and the laboratory study of sediment/water P exchange, indicated that the processes involved in P cycling within the water column were important in determining the rates and extents of the P fluxes across the sediment/water interface. For this reason a more detailed study of P cycling between compartments in the water column was undertaken between 1977 and 1979. To facilitate the measurement of P fluxes at levels below the sensitivity of the commonly used analytical procedures, ^{32}P was used a a tracer. P exchange between the soluble and particulate compartments was studied in the hope that a better understanding of the SRP accumulations observed during the 1976-77 *in situ* enrichment experiment (section 3.3) would be obtained.

5.2 Results

5.2.1 Exchange of P Between Soluble and Particulate Compartments

a) Exchange Kinetics

Examples of ^{32}P transfer curves, representing a slow and a rapid rate of exchange are presented in Fig. 5.1. Asymptotes were estimated from similar uptake curves plotted for each experiment, $Y - Y_{asymp}$ was plotted against time on a semilog scale (Figs. 5.2 A-F). A single exponentia equation was fitted to this data and the coefficients of determination, the rate constants, the P turnover times and the estimated asymptotes are presented in Tables 5.1 a and b.

The semilog plots were generally linear, indicating that the data was adequately described by a single exponential function, and the high r^2

values support this view (Tables 5.1 a and b). On four occasions, the semilog plots were however, clearly not linear (Fig. 5.2 D-F) and consisted of two distinct phases. These curves were split into two individual exponential functions (Table 5.2) one representing a rapid phase of uptake and the other a slower phase.

This data suggests that P exchange between particulate and soluble P in Midmar Dam, and in isolation columns enriched with NO_3-N, was predominantly monphasic during the summer months, which contrasts markedly with the situation in some Canadian lakes where summer P exchange kinetics are characteristically diphasic (Lean and Rigler, 1974).

b) P Turnover Times

In the open water the P turnover times recorded during the summer of 1977-78 averaged 192 minutes. The slowest time (714 min) was recorded in mid-February and this was followed by a period of distinctly faster turnover (<35 min). Starting in late April and continuing into May, the turnover times slowed markedly to more the 200 min. This possibly reflected decreased metabolic rates and lower phytoplankton populations with the onset of the cooler winter conditions (Table 5.1 and Fig. 5.3).

During the 1978-79 summer season, turnover times ranged between 8 and 95 minutes ($\bar{x}$ 46 minutes) in the open water increasing between September and October but then decreasing progressively until February (Table 5.1b and Fig. 5.3).

In the unenriched column, P turnover times during the 1977-78 ($\bar{x}$ 37 minutes) were generally more rapid than corresponding times in the open water and the difference was most evident during February and late April/May. During 1978-79 the mean turnover time in the unenriched column

(35 minutes) was similar to that in the open water but the trends differed: Initially the decrease in turnover time was more rapid and was not delayed, while in December and February an increasing trend was evident which contrasted with the progressive decrease in the open water (Fig. 5.3).

During the 1977-78 experiments the enriched columns received a range of NO_3-N loading rates and, at high enrichment levels (exceeding 25 $\mu g\ \ell^{-1}\ week^{-1}$), there was a tendency for P turnover times to be more rapid than in the open water or unenriched column (Fig. 5.3). This was however, not reflected in the mean turnover times which, in all but one of the columns (50 $\mu g\ NO_3$-N $\ell^{-1}\ week^{-1}$), were lower than the mean turnover times in the unenriched column (Table 5.1a). In the columns receiving the highest NO_3-N enrichment (100 and 200 $\mu g\ NO_3$-N $\ell^{-1}\ week^{-1}$) slow mean turnover times were due to the exceptionally slow times recorded on February 13 (500 and 2000 minutes in column 4 and 5 respectively). Between March 28 and May 23 the turnover times in these columns were less than half those in the unenriched column (Table 5.1a). Only in the column receiving the lowest level of NO_3-N enrichment (25 $\mu g\ NO_3$-N $\ell^{-1}\ week^{-1}$) were the turnover times similar to or slower than those in the unenriched column (Fig. 5.3).

During the 1978-79 study all of the enriched columns received 200 $\mu g\ NO_3$-N $\ell^{-1}\ week^{-1}$ and, without exception, the mean turnover times (range 15.2 to 29 minutes) were faster than the mean in the unenriched column or open water (Table 5.1b). Infrequently however, turnover times in certain enriched columns were slower than corresponding times in the unenriched column (Column 2 in October, 81 minutes; Column 4 in November, 30 minutes, and December, 42 minutes; and Column 5 in November, 47 minutes). This indicates that despite the overall trend towards reduced turnover times in the enriched columns, shown by the mean turnover times, the responses were variable.

c) Concentrations of P fractions, Chlorophyll and Total Suspended Solids

Phosphorus fractions were measured simultaneously with P turnover times during the 1977-78 experiments. These data are presented in Table 5.4

Soluble reactive phosphorus was frequently present in trace quantities only. Total dissolved phosphorus showed some fluctuation in the open water and isolation columns but no distinguishable trends were evident, and the mean values (4.16 - 5.83 $\mu g\ \ell^{-1}$) remained similar in the open water and all of the columns. Mean particulate P concentration showed surprisingl little variation between the open water and columns and between columns (range 11.2 - 15.6 $\mu g\ \ell^{-1}$) although levels within each treatment showed fairly wide fluctuations but no clear trends (Table 5.4). P analyses for the 1978-79 experiments are not available.

Chlorophyll and TSS concentrations recorded with the P turnover times during the 1977-78 and 1978-79 experiments are presented in Fig. 5.3.

In the open water, chlorophyll levels fluctuated between 0.9 and 2.9 $\mu g\ \ell^{-1}$ in February/May 1978 and between 1.2 and 3.2 $\mu g\ \ell^{-1}$ in 1978-79, showing no noteworthy trends. In the unenriched column, peaks in chlorophyll often exceeded those in the open water but were below 5 $\mu g\ \ell^{-1}$. One peak of 7.5 $\mu g\ \ell^{-1}$ in late March 1978 (Fig. 5.3) was recorded.

In columns 2, 3 and 4 the response shown by the chlorophyll concentration was not consistent. Peaks of up to 9 $\mu g\ \ell^{-1}$ were detected (column 3 in November 1978) but these were isolated cases and generally the chlorophyll levels remained similar to those in the unenriched column.

In column 5 however chlorophyll levels were consistently higher than in the other columns or in the open water. On February 27, 1978, an increasing trend began which continued steadily until May 5 when levels reached 14.6 µg ℓ^{-1}. During 1978-79, the levels ranged between 14.1 and 21.3 µg ℓ^{-1} (Fig. 5.3). These marked increases were, however, not reflected in corresponding increases in particulate P (Table 5.4).

Total suspended solids in the open water and in the columns fluctuated widely between 3 and 20 mg ℓ^{-1} confirming earlier observations that TSS in Midmar Dam is highly variable depending on weather conditions (Twinch and Breen, 1978a). The fluctuations were clearly not accompanied by similar changes in chlorophyll concentration (Fig. 5.3) and were therefor unlikely to reflect changes in phytoplankton density.

Correlation coefficients for P turnover time against chlorophyll and TSS are presented in Table 5.10. Measurements of SRP concentrations were not sufficiently accurate for correlation with P turnover time and, because there is no justification for using TDP as an index of available P in the water (Rigler, 1973), no attempt was made to correlate P turnover time with TDP. No significant correlations between turnover time and chlorophyll or TSS were obtained.

5.2.2 Characterisation and Kinetics of Soluble P Fractions

a) Gel Filtration Analysis of $^{32}PO_4$-P Stock.

The distribution of isotope in the eluent following fractionation of 20 µl of $^{32}PO_4$-P in dilute HCl, as received from the suppliers (Amersham/ Searle), is presented in Fig. 5.4. Activity was concentrated between elution volumes of 200 and 260 ml and this distribution was used to identify

PO_4-P peaks during the subsequent fractionation experiments.

Void volume was determined using dextran blue, the first traces of which appeared in the 100-110 ml elution fraction. In all subsequent fractionations the 100-110 ml fraction was used as the first eluted sample.

b) Distribution and Kinetics of Soluble P

The first gel filtration analysis was undertaken on a surface water sample from column 5 (200 µg NO_3-N ℓ^{-1} $week^{-1}$), which, at the time (October 1978), supported a bloom of *Eudorina* sp. Uptake of ^{32}P by the particulate fraction resulted in an isotopic equilibrium after approximately 1 hour and a P turnover time of 7 minutes (Fig. 5.5). During the course of the uptake experiment, the distribution of isotope remaining in the filtrate showed a progressive shift from the PO_4-P fraction to a large molecular weight fraction (MW >5000)eluting with the void volume. The latter fraction showed eluting characteristics which were similar to the colloidal P identified by Lean (1973) and will, for convenience, be referred to as colloidal P (Fig. 5.5B and Table 5.4). As a proportion of the total soluble P, PO_4-P decreased from 100% at the start to 8.4% after 20 hours, while colloidal P increased from 0 to 84.8% over the same period. Traces of isotope were detected at intermediate elution volumes (0-8.6%) (Table 5.3) but these were never distinguishable as distinct peaks.

Despite the apparent isotopic equilibrium after 1 hour, it is clear from Fig. 5.5 that changes in the soluble P fractions occurred over much longer periods. As a proportion of the total ^{32}P added, PO_4-P in solution decreased progressively during the 20 hour experiment from 100% to 1.7%, whil the proportion of colloidal P increased from 0% to 17% over the same period (Fig. 5.5A).

The presence of only two distinct soluble P fractions which were directly involved in exchange with particulate P, contrasted with the findings of Lean (1973) and Lean and Nalewajko (1976), who identified three distinct fractions in Heart Lake, Canada, and in algal cultures. To determine the variability of these and similar fractions in the open water and columns, water samples were fractionated after routine ^{32}P uptake experiments conducted over a period of 9 hours on November 14, 1978. At this time all enriched columns (columns 2-5) were receiving 200 $\mu g\ \ell^{-1}$ NO_3-N $week^{-1}$. Isotope distribution after 9 hours is shown in Fig. 5.6. As a proportion of the total ^{32}P added, PO_4-P varied from less than 1% in column 5 to 4.2% in column 2, while colloidal P ranged from less than 1% in column 5 to 8.2% in the open water. As a proportion of the soluble P, PO_4-P ranged between 17% in column 3 and 42% in column 2 while colloidal P ranges between 50% in column 2 and 72% in column 3. Although traces of isotope were detected at intermediate elution volumes (7-14% of the soluble P) only two distinct peaks were evident in all of the samples analysed (Table 5.5).

In an attempt to assess whether the variations in soluble P distribution were being influenced by factors such as TSS and chlorophyll (Table 5.5), correlation coefficients for the two soluble P fractions (as a proportion of total soluble ^{32}P) and the other parameters were calculated (Table 5.6). The positive correlation between TSS and the proportion of colloidal P was the only significant correlation obtained.

During March 1979, after routine monitoring had been stopped, a growth of *Microcystis* sp. appeared in column 5 and, since it was during blooms of *Microcystis* that SRP accumulations were observed in the column +N and column N+P during the 1976-77 *in situ* enrichment experiments (chapter 3),

surface water was sampled. A ^{32}P uptake experiment was conducted during which the distribution and kinetics of soluble P fractions was investigated. The ^{32}P uptake curve (Fig. 5.7) was similar to that obtained in October 1978(Fig. 5.5). Isotopic equilibrium was attained after approximately 1 hour and a P turnover time of 9.6 minutes was calculated.

Despite the apparent similarity between the uptake curves obtained in October 1978 and March 1979, the flux rates of soluble P fractions at these times were distinctly different. During the March 1979 experiment the decrease in PO_4-P and the increase in colloidal P were more rapid. After 2 hours PO_4-P was reduced from 100% of the total ^{32}P at the start to 1.3% while colloidal P increased from zero to 12.3% over the same period. In contrast to the October 1978 experiment, both soluble fractions remained virtually stable after isotopic equilibrium between soluble and particulate P had been attained (Fig. 5.7A). As a proportion of the soluble P, PO_4-P decreased to 9.31% after 2 hours while colloidal P increased to 87.9% (Table 5.7).

As in the other fractionations, only two distinct soluble P fractions were identified. Traces of isotope at intermediate elution volumes barely exceeded the background counts and were evenly distributed throughout the elution volumes between the two peaks, representing between 0 and 4.6% of the soluble P (Fig. 5.7 and Table 5.7).

c) Distribution of Soluble P Fractions During the Growth of an *Anabaena flos-aquae* Culture

Since no evidence of a third low molecular weight soluble P fraction was obtained during the experiments on natural lake waters, an attempt was made to determine whether the results were reflecting the technique employed. This was investigated by undertaking a sequence of

soluble P fractionations during the growth of a labelled culture of *Anabaena flos-aquae*, in a manner similar to that of Lean and Nalewajko (1976).

The growth curve (Fig. 5.8A) showed a sigmoid pattern, with a distinct lag phase during the first 1-2 days, a rapid exponential phase until approximately 15 days and a stationary phase between 15 and 30 days. The initial uptake of PO_4-P by the organisms was rapid (Fig. 5.8 B) and after 0.75 days only 0.35% of the total ^{32}P remained in solution. Between 0.75 days and the end of the experiment, the proportion of ^{32}P remaining in solution varied between 0.1 and 0.47% of the total added, showing no distinct trends despite the exponential growth during this time.

Isotope distribution in the filtrate changed markedly during the first 1.5 days (Fig. 5.8 C). Initially, all of the soluble P was PO_4-P but, after 0.75 days, this was reduced to 71.4% and by 1.5 days to 32.1%. During this time colloidal P increased from 0% to 28.7% and 47% at 0.75 and 1.5 days respectively. Thereafter the proportions of both PO_4-P and colloidal P fluctuated slightly showing no trends which could be attributed to changes in growth rates in the culture (Table 5.8).

Although only two distinct peaks could be identified throughout this experiment, the distribution of soluble P fractions differed slightly from those observed in natural waters. Firstly, as may be seen from Table 5.8, the proportion of soluble ^{32}P represented by the intermediate fractions after 1.5 days of incubation (12-24%) tended to be slightly higher than those observed in the natural waters. Secondly, the PO_4-P peaks after inoculation tended to be spread over a wider range of elution volumes

than the peak before inoculation (Fig. 5.8 C), extending into the 80-90 ml elution volume in the 0.75, 1.5, 4, 6 and 22 day fractionations. Similar trends were not evident in the PO_4-P peaks obtained in lake water filtrate, which were always distributed over a similar range of elution volumes as the ^{32}P stock solution.

d) Biological Availability of the Soluble P Fractions

A further fractionation experiment was undertaken for the purpose of comparing the direct biological availability of the two distinct soluble P fractions detected in open water filtrate.

On February 7, 1979 a ^{32}P uptake experiment was conducted on a subsample of the routine composite sample taken from the open water (Fig. 5.9 A), and 5 hour filtrate was used to fractionate the soluble P (Fig. 5.9 B). The 210-220 ml fraction, representing PO_4-P, and the 110-120 ml and 120-130 ml fractions, representing colloidal P, were used to re-inoculate fresh subsamples of the composite dam water sample and ^{32}P uptake was monitored in the usual manner (Fig. 5.9 C and D). Uptake of the PO_4-P fraction was rapid and confirmed that the ^{32}P eluting as PO_4-P was directly involved in P exchange in the water. The P turnover time obtained (11.9 minutes) compared favourably with that obtained during the original ^{32}P uptake experiment (9.1 minutes) and there can be little doubt that the PO_4-P fraction obtained by gel filtration was qualitatively and functionally identical to PO_4-P (Fig. 5.9 C).

When colloidal P was added, a smooth uptake curve was not obtained and, after an apparent rapid initial uptake over the first 5 minutes the proportion of ^{32}P retained by the filters varied markedly between 50% and 97% ($\bar{x}$ 67%) (Fig. 5.9 D). Similar observations were made by Lean and

Nalewajko, (1976) and these were attributed to filter retention of colloidal P. This possibility was tested on both colloidal P fractions used in the ^{32}P uptake experiments (Table 5.9). Approximately 60% of the colloidal P was retained on filtration (55 and 65%) which compares favourably with the mean retention (67%) calculated from the uptake experiments (Fig. 5.9D). However, the variability in the proportion retained during the uptake experiment was high and, at times, up to 97% retention was evident (after 5 minutes). This indicates that retention may at times be almost complete.

e) ^{32}P Uptake by Midmar Dam Filtrate

Since colloidal P clearly constitutes a large proportion of the soluble P in Midmar Dam water, its potential role in the direct uptake of PO_4-P was investigated. In section 5.2.2.d it was shown that approximately 67% of the colloidal P was retained on refiltration. Thus to obtain some index of whether colloidal P was involved in direct exchange with PO_4-P, stock $^{32}PO_4$-P was added to filtered Midmar Dam water, sampled in August 1979 and a routine ^{32}P uptake experiment was undertaken (Fig. 5.10).

The amount of ^{32}P in solution decreased linearly with time at a rate of 0.035% min^{-1} showing clearly that the fraction retained on refiltration was actively exchanging with PO_4-P.

5.3. Discussion

5.3.1 P Exchange Kinetics

According to Norman and Sager, (1978 a) "a transfer curve is characterised as diphasic if it cannot be adequately fitted with a single exponential equation, but has the form of two exponential decreases in radioactivity remaining in the filtrate, leading finally to equilibrium". They do also point out however, that, due to errors in measurement, curves could be classified as monophasic when they are diphasic or even polyphasic.

Only if the different transfer rates involved in the overall transfer differ by a factor of two or more, and at least 5% of the total ^{32}P is transferred by each transfer mechanism, will they be distinguishable using current methods (Norman and Sager, 1978 a).

The ^{32}P uptake curves obtained during this study, although generally monophasic, need not therefore necessarily imply a simple two compartment exchange. As will be discussed (section 5.4.2), the presence of two soluble P fractions involved in P exchange with particulate P invalidates this assumption. In view of the diverse nature of seston in fresh waters and of the fact that different phytoplankton species show markedly different P exchange kinetics (Lean and Nalewajko, 1976) it seems unlikely that a monophasic uptake could occur under natural conditions. A single exponentia equation has however provided a convenient description for a combination of simultaneous and/or sequential exchange processes.

Diphasic exchange kinetics have been shown to predominate during summer stagnation in Heart Lake (Lean and Rigler, 1974) but were shown to be infrequent in eutrophic lower Green Bay, Lake Michigan and, when they were detected, they usually occurred during periods of rapid decreases in biomass of phytoplankton (Norman and Sager, 1978 a). It thus appears that diphasic exchange kinetics may be characteristic of periods of rapid phytoplankton senescence and increased bacterial activity. In eutrophic Lake Washington and oligotrophic Findley Lake, diphasic exchange kinetics were not detected during a two year survey (Richey, 1979).

During the Midmar Dam study, diphasic exchange kinetics were infrequent and, when detected, did not appear to be related to unusually high standing crops of phytoplankton. In column 5, which was characterised by

consistently high chlorophyll levels, diphasic exchange kinetics were never detected. If diphasic exchange results from processes associated with the senescence of phytoplankton, as suggested by Norman and Sager, (1978 a), its virtual absence in Midmar Dam may simply reflect the low productivity and lack of distinct seasonal fluctuations in the phytoplankton.

On the few occasions when diphasic exchange was detected the rate constants for the rapid (0.16 - 0.46 min^{-1}) and slow (0.007 - 0.019 min^{-1}) phases of ^{32}P uptake fell within the ranges measured during summer stagnation in Heart Lake (Lean and Rigler, 1974). However, the absence of any indication of what may have caused the diphasic uptake makes this similarity difficult to interpret.

The significance of ^{32}P asymptote levels in solution during P exchange experiments is not well understood. Peters (1975) reported a range of asymptote levels of 22 to 70% in Central European Lakes which were considerably higher than those in the range of Canadian lakes studied by Rigler, (1964) of between 1 and 5%. However, in Lake Memphremagog the summer range was 13.5 - 24% and tended to be lower in oligotrophic sites than they were in eutrophic sites (Peters, 1979) and clearly asymptote values vary markedly between water bodies.

Peters (1975) suggested that higher asymptote levels in solution during ^{32}P uptake experiments could reflect a larger pool of available P in the water. This interpretation requires substantiation before it can be generally applied. The presence of a large proportion of colloidal P in the soluble fraction may have a marked influence on the asymptote levels whilst not necessarily influencing the available P to a corresponding extent. This may be particularly true in turbid systems where inorganic colloids

contribute to the soluble P fraction. Furthermore, Stiller *et al.*,(1978) have shown marked shifts in the distribution of ^{32}P in the soluble and particulate fractions in cultures of *Ankistrodesmus nannoselenae* under light and dark conditions. This suggests that environmental factors, such as turbidity, could also influence asymptote levels through their influence on light penetration. Too little is known about factors influencing the asymptote levels during ^{32}P uptake experiments to comment further on their possible significance in relation to P availability.

5.3.2 P Turnover Times

P turnover times have been shown to fluctuate seasonally in lakes, usually being more rapid during the warmer summer periods (Lean and Rigler, 1974; Halman and Stiller, 1974; Levine, 1975; Peters, 1975). The study of P turnover in Midmar Dam was restricted to the months between September and May, during which time summer temperatures predominate (Fig. 3.1) and the data should therefore only be compared with summer conditions observed elsewhere.

In comparison with summer P turnover times reported by Rigler, (1964) for a range of Canadian lakes (0.9 - 6.6 minutes) and by Levine, (1975) in two Canadian Shield lakes (0.4 - 10 minutes), the times obtained in the open water of Midmar Dam (range 8 - 714 minutes, $\bar{x}$ 1977-78 = 192 minutes, $\bar{x}$ 1978-79 = 19.7 minutes) are slow. They compare more favourably with the range of summer turnover times recorded in Lake Kinneret (11 - 282 minutes, Halman and Stiller, 1974), in a variety of Central European lakes (4 - 101 minutes, Peters, 1975) and in Lake Memphremagog, Canada (9.4 - 29.4 minutes).

Information on P turnover times on the African continent is sparse. Peters and MacIntyre, (1976) studied P turnover times in a variety of tropical Kenyan lakes during the winter months. The turnover times in oligotrophic waters ranged between 0.67 and 5.0 minutes, distinctly faster than the summer turnover times in Midmar Dam.

The summer P turnover times in the open water of Midmar Dam fall within the world range, but they are clearly slower than those in some waters of similar SRP concentrations (< 5 $\mu g\ \ell^{-1}$). One possible reason for this could be the use of composite 3.5 m water samples during this study. Surface water has been used more frequently in the determination of P turnover time (Rigler, 1964; Peters, 1975, 1979; Peters and MacIntyre, 1976) and, in view of the distinct vertical stratification in P turnover time observed in Lago Maggiore (Peters, 1975), and of the fact that Lean and Rigler, (1974) observed different ^{32}P exchange kinetics in surface and column samples from Heart Lake, it is possible that the composite samples could exhibit markedly slower P turnover times than surface samples because of the increased metabolic rate in the euphotic zone. However, in the shallow areas of Midmar Dam no marked vertical stratification in chlorophyll levels has been detected (Akhurst, unpublished data), probably due to the mixing patterns in these areas (Walmsley, 1976), and it was felt that composite samples would be more meaningful in providing estimates of P turnover times in the water column.

In the isolation columns there was a tendency for P turnover times to decrease, particularly at high levels of NO_3-N enrichment. Reduced P turnover times may result from a decrease in available P in the water, an increase in biomass in the water, or both (Rigler, 1973; Halman and Stiller, 1974). The turnover times thus reflect the balance between available P in

in solution and its exchange with all components of the particulate fraction, including a wide range of biotic and abiotic material.

Only two parameters were measured which could be of use in assessing the biological influence on P turnover times; chlorophyll concentrations and TSS. Neither showed a significant correlation with turnover time and they do not therefore help to explain the observed fluctuations in P turnover times.

Levine (1975) showed that chlorophyll *a* was not significantly correlated with P turnover time in two Canadian Shield lakes, and Norman and Sager, (1978b showed a similar trend in Green Bay, Lake Michigan. However, the latter authors detected a significant positive correlation between turnover rate (the product of the rate constant and the SRP concentration) and chlorophyll *a*. During the Midmar study turnover rates were not calculated due to the low SRP concentrations which were frequently below the level of accurate measurement. In any event, the limitations of regarding SRP as an accurate estimate of directly available P (Rigler, 1973; Peters, 1978, 1979) cast some doubt on the use of SRP in the calculation of turnover rates.

Chlorophyll concentrations are, at best, a simple index of phytoplankton standing crop and any attempt to relate them to P turnover times could be limited by a number of factors. The size of algal cells could influence the relationship between chlorophyll levels and P turnover times because smaller organisms are thought to cycle P more rapidly (Rigler, 1973).

Phytoplankton populations, which are characterised by similar chlorophyll concentrations, could differ markedly in their species diversity and thus in their P exchange characteristics. In addition, chlorophyll content of algae varies markedly with changes in metabolic state and environmental conditions (Meeks, 1974), and the efficiency with which chlorophyll can be extracted from phytoplankton varies between species (Vollenweider, 1971). These factors could contribute to the poor correlation between P turnover times and chlorophyll concentrations.

Total suspended solids estimated as dry mass after membrane filtration, is a commonly used method of assessing the standing crop of planktonic organisms (Vollenweider, 1971) but in a turbid system such as Midmar Dam, it is of limited value because of the predominance of suspended inorganic particles. For this reason substantial fluctuations in phytoplankton or other biological components, could be obscured using TSS as an index of standing crop.

According to Halman and Stiller (1974) the observed P turnover with particulate matter in natural waters may be due to interactions with bacteria, algae or other organisms, or to adsorption by inorganic minerals. Clearly this complex system cannot be described by simple parameters. A more accurate characterisation of the particulate material is required if P turnover time is to be correlated with specific fractions. Rigler (1964 showed that bacteria formed the major component in P exchange in Toussaint Lake, while Peters (1975) suggested that in Lago Maggiore the phytoplankton was more important. Paerl and Lean, (1976) used an autoradiographic technique to study the fluxes of P between algae, bacteria and abiotic particles in Heart Lake. Bacteria and phytoplankton were labelled most rapidly, but after 2 hours tracer was also evident on detrital aggregates.

It thus appears that the relative importance of the different fractions of suspended material varies markedly between different fresh waters. In Midmar Dam the suspended inorganic fraction is undoubtedly important but, with the data available, it is not possible to assess the relative importance of the different particulate fractions.

Fluctuations in the concentrations of available P in the water could also result in fluctuations in P turnover times. P data is only available for the period February-May 1978 and the discussion will relate to these. SRP concentrations during this period remained low, frequently being undetectable, and no trends which corresponded with fluctuations in turnover time were evident. This does not necessarily imply that important fluxes in available P did not occur. Rigler (1973) discussed the limitations of the molybdate blue procedure in measuring PO_4-P, and emphasised the fact that P fluxes within the water column are rapid and can occur at such low concentrations that they cannot be distinguished using routine SRP analyses. This is particularly true of oligotrophic systems such as Midmar Dam.

Rigler (1973) points out that the ratio of particulate P to SRP can be used as an index of P turnover time, and a large ratio probably indicates a short turnover time, which in turn suggests a shortage of available P. During this study, mean particulate P concentrations varied between 11 and 16 $\mu g\ \ell^{-1}$ while SRP levels were usually below 1 $\mu g\ \ell^{-1}$ and the ratio was thus large at all times. Because of the low levels of SRP the PP : SRP ratios could not be calculated sufficiently accurately for correlation with the turnover times. They must have been large, however, frequently >10, and fast turnover times would therefore be expected. The ratios in Lake Memphremagog (4-6) were lower, although the range of turnover

times was similar (Peters, 1979). In Midmar Dam the suspended inorganic silt is probably extremely important in increasing the PP : SRP ratios. This contrasts markedly with the situation in a clear lake where the particulate fraction consists largely of organic material. The presence of a large inorganic fraction may reduce the value of PP : SRP ratios as indices of P turnover times in turbid systems, because the particulate P does not necessarily reflect a biologically active fraction.

Important assumptions that are made during the ^{32}P uptake experiments are that a steady state between soluble and particulate P is approximated, and that the rates of P turnover are very rapid relative to the net rates of flux between P compartments (Rigler, 1973). These assumptions are probably reasonable in the unfiltered water samples where the relative densities of the organisms are the same as under natural conditions. However, any attempt to apply the assumptions to ^{32}P uptake experiments involving periphyton would be of dubious validity because of the difficulties involved in determining the ratio of periphyton mass to water volume required to approximate *in situ* conditions. Because of the distinct vertical stratification of periphyton in isolation columns (Twinch, 1976) and to the fact that it is restricted to the substrate provided by the walls of the column, no practical method of integrating periphyton P turnover times into overall P turnover times within the columns could be developed. The P turnover times in the columns thus reflect planktonic P metabolism only, and the actual *in situ* turnover times were probably considerably faster due to periphyton metabolism. The overall influence of NO_3-N enrichment on P exchange in the columns was probably therefore more extensive than the P turnover data indicates.

5.3.3 Distribution of Soluble P in Midmar Dam Waters

In all of the fractionations carried out on samples from both open water and the isolation columns, only two distinct soluble P fractions were recognised, one eluting as PO_4-P and the other eluting with the void volume, thus exhibiting similar gel filtration characteristics to the colloidal P fraction identified by Lean, (1973). While traces of isotope were detected at intermediate elution volumes, these never formed distinct peaks and the isotope distribution thus differed markedly from those obtained in Heart Lake, where an additional peak at an elution volume corresponding with a molecular weight of 250 was obtained (Lean, 1973).

Since the experiments by Lean, (1973), soluble P fractionation has been undertaken on a number of fresh waters and the low molecular weight P fraction identified by Lean does not appear to be of general occurrence.

Fractionations of water from an oligotrophic Canadian Shield Lake (Jackson and Schindler, 1975), a series of New Zealand lakes (Downes and Paerl, 1978) and Lake Memphremagog, a Canadian Lake exhibiting a marked trophic gradient along its main axis (Peters, 1979), were characterised by two distinct peaks, with traces of fairly evenly distributed intermediate activity. These were thus similar to those in Midmar Dam fractionations and it appears that a distinct third soluble P fraction is uncommon.

The resolution of the gel filtration analysis is markedly affected by the volume of sample eluted. Peters (1978) acknowledged that the resolution of his gel filtration analyses was reduced by the large volume of sample added relative to the void volume, and similar limitations could have arisen in the New Zealand study where 5 ml of labelled filtrate was

added to a column with a void volume of only 25 ml. Lean, (1973) and Lean and Nalewajko, (1976) demonstrated that the low molecular weight P eluted at a position very close to PO_4-P. In view of this, even a slight reduction in the resolution of the analyses, by addition of large samples relative to the void volumes of the columns, could obscure the low molecular weight P peaks.

During the Midmar Dam study the volume of sample introduced was always less than 10% of the void volume, but usually between 2 and 5%, which is comparable with the levels used by Lean (1973) (approximately 3%). The apparent absence of a third soluble P peak in Midmar waters cannot therefore be attributed to reduced resolution due to large sample sizes.

An important observation by Lean, (1973) was that the low molecular weight P fraction is extremely labile. A delay of 15 minutes between filtration and fractionation resulted in a significant reduction in the low molecular weight P peak and a corresponding increase in the PO_4-P peak. This trend was continued with time until the low molecular weight P had virtually disappeared after $6\frac{1}{2}$ hours. For this reason delays after filtration could markedly influence the distribution of soluble P fractions in the eluent.

The treatment of labelled filtrate before fractionation has varied. Peters (1978, 1979) stored filtrate frozen for unspecified periods before analysis, and Downes and Paerl (1978) undertook gel filtration on the day of sampling or after storage at $4^{o}C$ overnight. Jackson and Schindler, (1975) did not give details of the delay between filtration and fractionation Francko and Heath (1979), using unlabelled filtrate for similar fractionation experiments, analysed the filtrate immediately or after storage at $-20^{o}C$ for unspecified periods, and found no differences in the distribution

of soluble P. Since Francko and Heath analysed the P fractions using standard analytical techniques their observations need not apply to radiotracer techniques because important shifts could have occurred at levels below the sensitivity of the standard analytical procedures. The absence of distinct low molecular weight P peaks in many lake waters could therefore reflect the influence of sample storage on the labile soluble P fractions

During the Midmar Dam study, some delays between filtration and fractionation were necessitated by the availability of only one gel-filtration system, and these delays are specified on the figures. However, on many occasions, fractionation was undertaken without delay and even then no evidence of a third soluble P peak was obtained. This may reflect a fundamental difference between eutrophic Heart Lake and oligotrophic Midmar Dam with respect to soluble P fractions.

In waters from Midmar Dam and the isolation columns the colloidal P fraction generally constituted the major proportion of the soluble P ($\bar{x}$ 67%) while the PO_4-P fraction was smaller ($\bar{x}$ 24%). This contrasts markedly with the distribution observed in other fresh waters. In a range of New Zealand lakes, a reactive high molecular weight P fraction (exhibiting similar gel filtration characteristics to colloidal P) represented between 14 and 100% of the dissolved reactive P. These proportions were inversely related to the PO_4-P concentration in the water (Downes and Paerl, 1978), suggesting that increased proportions of colloidal P could reflect reduced PO_4-P availability and thus be used as an index of trophic status. Some support for this suggestion is evident in the isotope distributions from ultra-oligotrophic Ontario lakes where only colloidal P peaks were detected in the gel filtration analyses (Jackson and Schindler, 1975; Levine, 1975). In Lake Memphremagog however, no trends in the proportion of soluble P in the form of colloidal P or PO_4-P were evident, with changes

in trophic status. The absence of a relationship was regarded as possibly being due to experimental variability because chemical analysis revealed that soluble unreactive P, which probably represents at least part of the colloidal P fraction, showed a proportionate increase at the more oligotrophic sites.

The inverse relationship between the proportion of colloidal P and PO_4-P concentration in natural waters appears consistent and, on this basis, Midmar Dam shows a soluble P distribution which is indicative of its oligotrophic status. This relationship could however be influenced by other factors which will be discussed in section 5.4.4.

5.3.4 Distribution of Soluble P in an *Anabaena flos-aquae* Culture

The results of the ^{32}P study in an *Anabaena flos-aquae* culture differed from those in a similar experiment conducted by Lean and Nalewajko, (1976). The most obvious difference was the more rapid uptake of P by the organisms during the Midmar experiment (> 99% uptake within 18 hours), which contrasted with the gradual uptake, that continued throughout the growth of the cultures, during Lean and Nalewajko's study (97% uptake after 235 hours). This was probably due to slight differences in the experimental procedures adopted despite the fact that an attempt was made to reproduce Lean and Nalewajko's experiment. During this study 5 ml of inoculum in stationary phase of growth, brought about by P depletion, was added to 100 ml of culture medium containing approximately 200 µg PO_4-P ℓ^{-1}. Lean and Nalewajko (1976) added 5 ml of exponentially growing inoculum to 200 ml of medium containing 57 µg P ℓ^{-1}. Although the higher PO_4-P concentration during this study would tend to reduce the ^{32}P uptake rate by increased dilution of the isotope with unlabelled P, it appears to have been counteracted by the proportionately larger inoculum volume used, and by the fact that growth of the organisms in the inoculum was limited by P

and they were thus capable of extremely rapid P uptake when introduced into the culture medium. Differences in the rate of ^{32}P incorporation during this experiment and that of Lean and Nalewajko (1976) may have influenced the distribution of soluble P fractions, a factor which was considered during interpretation.

The distribution of soluble P fractions during this culture experiment was markedly different from those obtained in the open water and columns (PO_4-P = 21%, colloidal P = 79%). During the first 1.5 days the proportion of PO_4-P decreased rapidly while colloidal P increased. Thereafter the proportions of PO_4-P and colloidal P fluctuated between 30 and 52% ($\bar{x}$ 41%) and 32 and 48% ($\bar{x}$ 41%) respectively, showing no trends. Lean and Nalewajko (1976) also showed approximately equal proportions of PO_4-P and colloidal P when growth was approaching the stationary phase.

If, as has been suggested by Lean (1973) and Lean and Nalewajko (1976), the colloidal P is of algal origin, its relative proportion in the culture medium would be expected to be higher than that in the dam water where the low chlorophyll levels reflect the low standing crop of phytoplankton. The converse was true during fractionations of culture filtrate. It must be remembered however, that the colloidal P fractions in culture are not necessarily directly comparable with those from natrual waters. Under natural conditions the colloidal P fraction could include clay particles, detritus and other molecular or particulate forms which become labelled, but which are not generated through the rapid cycling processes envisaged by Lean (1973). These components are absent in culture where presence of colloidal P can only be attributed to biological production.

In Midmar Dam the presence of inorganic colloids of sufficiently small size to remain in the filtrate after membrane filtration (0.45μ) could contribute significantly to the observed predominance of colloidal P. Particle size analysis of material retained in sediment traps at various depths in Midmar Dam indicates that approximately 45% of the material is below 0.45μ in diameter (Johnson,unpublished data). This observation casts some doubt on the apparent relationship between the proportion of colloidal P and the PO_4-P concentration discussed in section 5.4.3, particularly in silty waters such as those which characterise South African impoundments. Clearly if the colloidal P fraction consists predominantly of inorganic clay colloids associated with the silt load, the proportion of colloidal P will be independent of PO_4-P concentrations in the water and will be influenced by factors controlling the silt loads such as river inputs and turbulence.

Although only two distinct soluble P peaks were detected during the *Anabaena* experiment it is notable that, after inoculation, the PO_4-P peak showed a tendency to be spread over a wider range of elution volumes than it did before inoculation. The results obtained by Lean and Nalewajko (1976) are similar in that at the start of the experiment, the PO_4-P peak was first evident at an elution volume of approximately 130 ml but by 235 hours this had shifted to 115 ml. At times during the experiment Lean and Nalewajko showed a distinct peak for the low molecular weight soluble P, but more frequently the presence of the low molecular weight fraction was reflected in a broadening of the base of the PO_4-P peak.

It seems therefore that the PO_4-P peaks observed during the *Anabaena* experiment may have included a small proportion of low molecular

weight P in the 90-100 ml fraction which corresponds with the findings of Lean and Nalewajko (1976). The absence of a distinct low molecular weight P peak may simply reflect the extreme lability of this fraction, which, during the 4 hour long gel filtration procedure, was probably gradually converted to PO_4-P. As discussed (section 5.4.3), Lean (1973) demonstrated that this occurs extremely rapidly, and it seems likely that the degradation process would continue during gel filtration. The effect would be to increase the elution volumes over which PO_4-P was spread. Whether the isotope present in the 90-100 ml elution volume represents PO_4-P which has been released from an organic form or whether it represents traces of the intact organic form was not determined. It is notable however, that in spite of demonstrating the extreme lability of the low molecular weight fraction, Lean (1973) made no allowance for the influence of this process on the final isotope distributions obtained, and it seems likely that his estimated concentrations of low molecular weight P could be considerable underestimates.

5.3.5 Soluble P Kinetics

During the 1976-77 *in situ* enrichments there were indications that during periods of markedly increased primary productivity distinct changes in the pattern of P cycling in the water column occurred. For this reason the kinetics of soluble P was investigated on two occasions in water sampled from column 5. Once in October, when chlorophyll levels were high due to a bloom of *Eudorina* sp. and once in March 1979 when a bloom of *Microcystis* sp. was present. It was hoped that these experiments would help to explain some of the observations made during the 1976-77 *in situ* enrichment study.

Despite the ^{32}P uptake curves being similar on both occasions, at the time isotopic equilibrium between soluble and particulate fractions was attained (approximately 1 hour), the proportions of soluble P fractions differed markedly (Fig. 5.5 and 5.7). In October 1978 approximately 20% of the total ^{32}P was in the soluble form, of which approximately 15% occurred as PO_4-P and 5% as colloidal P. Fluxes in the soluble P fractions occurred for up to 20 hours with a decrease in PO_4-P and a corresponding increase in colloidal P. In contrast in March 1979 approximately 15% of the total ^{32}P was in solution, of which only 2% was PO_4-P and 13% colloidal P. Furthermore the proportions of both these fractions appeared to stabilise as isotopic equilibrium was attained. These differences in rates of flux indicate that the overall similarity in ^{32}P uptake is not indicative of similar soluble P metabolism in the samples.

No detailed characterisation of the particulate fraction was made during these experiments but it is tempting to postulate that the differences in the rates of soluble P flux can be attributed to observed differences in the dominant phytoplankton species. Lean and Nalewajko (1976) demonstrated that different phytoplankton species exhibit distinctly different ^{32}P exchange characteristics with soluble fractions in axenic cultures, which gives the above postulation some support. These results indicate that at the time *Microcystis* sp. was dominant, the rate at which colloidal P became labelled relative to the overall ^{32}P uptake was far more rapid than when *Eudorina* sp. was dominant.

These differences may be important in relation to the SRP accumulations detected when *Microcystis* blooms were present in isolation columns during the 1976-77 *in situ* enrichment experiments. The original hypothesis was that the accumulations were due to the biological formation of a soluble

P fraction which was not fixed by the sediments but which contributed to the SRP analyses. Evidence in support of this was obtained from the bioassay data (section 3.4) and from the sediment exchange experiments, and it seems likely that the soluble P fractions in question could have been colloidal P. The fact that colloidal P appears to be labelled more rapidly in the presence of *Microcystis* may indicate that this organism is more efficient in converting PO_4-P to colloidal P than are other phytoplankton species. This may explain the apparent absence of SRP accumulations in the isolation columns at times when chlorophyll levels were increased by other organisms, and at times when dense periphyton was present. However, this suggestion remains speculative until more detailed studies of soluble P kinetics are undertaken.

Lean (1973) reported that asymptote levels during ^{32}P uptake experiments did not change significantly between 2 and 48 hours, and used a 4-5 hour isotope distribution to estimate the relative proportions of soluble fractions under natural conditions. Peters (1978,1979) used 2 hour filtrate during the summer and 24 hour filtrate during the winter months, while other workers have not specified the times at which isotope distribution was determined (Downes and Paerl, 1978).

The marked differences in soluble P kinetics in column 5 in October 1978 and March 1979 have important implications with regard to the interpretation of gel filtration analyses in fresh waters. They indicate that an asymptotic level of ^{32}P in solution need not necessarily imply that the soluble P fractions have attained a steady state. Ideally isotope distribution in the filtrate should be measured at the time that it best represents the distribution of soluble P under natural conditions.

From the results of the Midmar study it is clear that an accurate assessment of the steady state soluble P distribution is difficult because attainment of an equilibrium between soluble and particulate P need not necessarily reflect steady state conditions in the water. Without regular fractionation to determine when steady state has been attained, the gel filtration analyses must be indices rather than absolute measurments of the soluble P fractions.

5.3.6 Biological Availability of Soluble P Fractions

The results of the experiments comparing the biological availability of the soluble P fractions confirm those of Lean (1973). The PO_4-P fraction showed similar exchange kinetics to the PO_4-P stock thus establishing its direct role in exchange and confirming its identity. Retention of the colloidal P fraction on refiltration hampered the meaningful assessment of its biological availability, but the results indicate that it was not directly exchanged.

Retention of colloidal P on refiltration imposes rather severe limitations on the reliability of current separative techniques, because the amount retained during the initial filtration cannot be quantified (Lean, 1973). It seems likely however that an average of approximately 65% retention could occur (Lean and Nalewajko, 1976 and this study) and at times retention may be almost complete.

The reasons for this retention are not clear. Lean and Nalewajko, (1976) suggested that it could result from aggregation of colloidal particles into larger particles retained by the filters but, unless the colloidal P fraction is more carefully characterised, no generalisation should be made. The limitations of filtration as a means of separating soluble and particulate fractions for the chemical analysis of P was discussed by Rigler, (1973).

The fractions are based on filter pore size and are not equivalent to morphologically or chemically distinct components of lake water. This is particularly applicable to the colloidal P fraction, which may consist of a variety of biotic and abiotic components varying in size from large molecules (MW > 5000) to colloidal particles, aggregates and micro-organisms which pass through 0.45μ filters. Retention of colloidal P on refiltration could result from the morphological characteristics of the colloidal P components. Particles such as clay colloids or micro-organisms may have shapes which allow them to pass through the filters in one orientation but not in another.

The possibility that clay colloids are important components in the soluble P in Midmar Dam has been discussed (section 5.4.4). In other systems where colloidal P represents the major proportion of the soluble P (Levine, 1975; Jackson and Schindler, 1975), the colloidal P may represent a largely organic fraction very different from the colloidal P in Midmar Dam. Thus the colloidal P fractions which, based on their gel filtration characteristics, have been regarded as being equivalent during this discussion may represent very different fractions in different systems. Until colloidal P can be more meaningfully characterised, its overall role in the P cycle will remain obscure.

This point is emphasised by the fact that when $^{32}PO_4$-P was added to filtered Midmar Dam water a significant linear increase in the amount of ^{32}P retained on refiltration was obtained, indicating that the colloidal P fraction was directly involved in exchange with PO_4-P. This contrasts with the observation by Lean (1973) that no significant retention of ^{32}P was measured when isotope was added to Heart Lake filtrate. It seems likely that this difference arises from the fact that in Midmar Dam clay colloids

which, by virtue of their large surface area are important in P exchange (Syers *et al.*,1973), constitute a large proportion of the soluble P. Although the uptake observed in Midmar filtrate may appear low (Fig. 5.10) it must be remembered that the ^{32}P retained on refiltration represents a considerable underestimate of the total retained by the colloidal P fraction in unfiltered water. An unknown but potentially large proportion of the colloidal P was removed by the initial filtration, and on refiltratio of the labelled filtrate approximately 40% of the colloidal P passed through the filter (Table 5.9). The measured ^{32}P retention is therefore not an index of the extent of PO_4-P uptake by colloidal P under natural conditions, but merely provides qualitative evidence that the colloidal P does complex PO_4-P directly.

These data indicate that, contrary to the observations of Lean (1973) suggesting that no direct complexing of PO_4-P with soluble P fraction occurs, a significant proportion of the overall exchange in Midmar Dam may be due to interactions between PO_4-P and some fraction which remains in the filtrate. Furthermore, the retention of labelled P on refiltration of filtrate indicates that colloidal P can be labelled in the absence of particulate material, which also contrasts with the findings of Lean (1973). It is suggested that these differences may be attributable to clay colloids in the Midmar Dam filtrate.

5.3.7 Applicability of Lean's Model to P Cycling in Midmar Dam

Lean (1973) attributed the diphasic ^{32}P exchange kinetics observed during the summer months in eutrophic Heart Lake to the presence of colloida P and low molecular weight P fractions in the filtrate. These were involve in the P exchange processes with particulate P and PO_4-P and were included in his four compartment model of epilimnetic P cycling, which was specifical formulated to describe the diphasic exchange kinetics. This was because

Lean and Rigler, (1974) regarded diphasic exchange kinetics as being frequent in epilimnetic lake water. More recently the need to account for the complexity of the particulate P fraction necessitated slight modifications to the original model to make it consistent with the observed transfer curves, and a second particulate P fraction was incorporated (Norman and Sager, 1978b).

Monophasic exchange kinetics appear to be more common than diphasic kinetics in many fresh waters (Rigler, 1973; Norman and Sager, 1978a; Richey, 1979) even during the summer months, and it seems unlikely that Lean's model will be universally applicable. Rigler, (1973), referring to a preliminary model of the P cycle which was superceded by Lean's model after the introduction of gel filtration analysis, emphasised that it applied only to eutrophic lakes during summer stratification. It seems that the modified form of Lean's model is similarly limited in its general applicability to fresh waters since it is based purely on data from a eutrophic lake.

The results of ^{32}P exchange experiments in water from Midmar Dam and the isolation columns indicate that the modified Lean Model is not applicable to conditions in a turbid oligotrophic impoundment.

Firstly with very few exceptions, the uptake kinetics during the Midmar study were adequately described by a single exponential function and secondly, the low molecular weight P fraction (MW = 250), which forms an integral part of the Lean model, was not detected. While the presence of two soluble P fractions indicates that the uptake kinetics cannot be described by a simple two compartment exchange model, the absence of a third distinct fraction casts some doubt on the validity of Lean's model.

It should perhaps be stressed that the absence of a distinct low molecular weight P peak does not imply that it is absent from Midmar Dam, particularly in view of its lability. In implies that its role in P cycling in Midmar Dam may differ from that in a eutrophic lake. Thirdly, the apparent conversion of PO_4-P to colloidal P in the absence of particulate P shows a marked divergence from the findings of Lean (1973) who, for the purpose of his model assumed that colloidal P was generated through the rapid biological production of low molecular weight P, and excluded the possibility of direct abiotic complexing. The apparent abiotic complexing of PO_4-P in Midmar Dam filtrate cannot be quantified (section 5.4.6), but it is probably far more important than the slow ^{32}P uptake rate in Fig. 5.10 suggests.

Whilst the results obtained during the Midmar study are not sufficiently detailed to develop an alternative model for P cycling in the water column of a turbid oligotrophic impoundment it is suggested that the exclusion of abiotic P exchange processes from Lean's model and the assumption that colloidal P results exclusively from biological cycling, is probably the major limitation of its applicability to Midmar Dam in particular and to turbid South African impoundments in general.

The relative rates of abiotic and biotic exchange in Midmar Dam cannot be ascertained, and with the current separative techniques this aspect is not likely to be clarified. However, in view of the low chlorophyll levels and the high loads of inorganic suspended material in Midmar Dam both processes must be considered in any model of P cycling in the water. As stated by Schindler (1976), "in the past there has been too great a tendency to assume that the same mechanisms operate at similar rates in all lakes. Research over the past decade has clearly shown that this assumption is false. Any hypothesis must be tested on a variety of waters

before it is assumed to be of universal importance to water management". These sentiments are clearly applicable to Lean's model in relation to turbid South African impoundments.

5.4 Conclusions

i) The P turnover times recorded in the open water fell within the world range and reached a minimum of 8 minutes, which emphasises the dynamic nature of the P cycle in the water.

ii) Enrichment of isolation columns with NO_3-N tended to reduce the P turnover times relative to the open water and unenriched column.

iii) The ^{32}P exchange kinetics were, with very few exceptions, adequately described by a single exponential equation (ie. were monophasic) and thus contrasted with the summer exchange kinetics observed in some Canadian lakes.

iv) Two distinct soluble P fractions were shown to be involved in rapid exchange with particulate P, PO_4-P and colloidal P (MW >5000).

v) The relative contributions of inorganic and organic components to the colloidal P could not be assessed but in the dam water there were indications that inorganic components could be important.

vi) A number of observations lead to the conclusion that the four compartment model used to describe P kinetics in the water (Lean, 197 may not be applicable to Midmar Dam in particular, and to silty South African impoundments in general.

vii) These results confirm that colloidal P can be of biological origin and that the soluble P kinetics may vary with variations in the dominant phytoplankton species. In this regard it appears that the presence of *Microcystis* may result in a more rapid incorporation of ^{32}P into the colloidal P during transfer experiments, but in the absence of blooms similar to those observed during the 1976-77 enrichment experiments it was not possible to assess the full

implications of this observation on the observed SRP accumulations.

viii) Filter retention of colloidal P prevents a clear separation of soluble and particulate compartments in the water and places constraints on the interpretation of gel filtration analyses.

CHAPTER 6.

GENERAL DISCUSSION

Although the overall objective of each of the sections included in this study was to obtain a better understanding of internal P cycling in Midmar Dam, it was not desirable during the course of the respective discussion to attempt a complete integration of the field and laboratory data. Each section was characterised by specific problems relating to methodology and interpretation which needed to be considered independently. This chapter is intended as an overall synthesis of the experimental data obtained during this study.

6.1 SRP Accumulations : The Original Hypothesis

As a result of the SRP accumulations detected in some of the isolation columns during the 1976-77 *in situ* enrichment experiments, despite the known PO_4-P fixing capacity of the sediments, it was suggested that the observed trends were due to the biological production of an organic (colloidal) P fraction, at least partially measureable as SRP, which did not exhibit direct exchange with the sediments. Before proceeding with this discussion it would be useful to consider the validity of the original hypothesis in the light of other experimental evidence.

A number of observations which support its validity have been made:

a) At times when SRP accumulated, bioassay yields indicated that a large proportion of the P included in the analyses was not utilised by the test organisms and was thus not PO_4-P.

b) A distinct colloidal P fraction which was directly involved in P exchange within the water has been identified.

c) Although under natural conditions, this fraction includes inorganic

components, it has also been shown to include components of biological origin.

d) The colloidal P was not involved in direct exchange with the sediments.

e) In the presence of *Microcystis* sp., blooms of which were associated with two of the major SRP accumulations, the rate of isotope incorporation into colloidal P during ^{32}P uptake experiments appeared to be markedly increased.

In principle therefore, colloidal P meets most of the requirements of the P fraction proposed in the hypothesis. Two factors however require further discussion : one being the fact that the hypothesis could not be tested under field conditions and the other being that it could not be analytically confirmed that colloidal P could contribute to the SRP analysis.

It was not possible to test the hypothesis in the field during the 1977-78 and 1978-79 enrichment experiments because the biological responses were limited largely to the periphyton and no marked SRP accumulations were detected. Blooms of *Microcystis* sp. did not develop in the columns throughou these experiments and the reasons for the contrasting responses to N enrichment during 1976-77 and during 1977-78 and 1978-79 are not clear. Variable responses of phytoplankton populations in enclosures have been reported previously (Lund, 1978) and during preliminary enrichment experiments in Midmar Dam, it was stressed that periphyton was usually the dominant biologica component (Twinch and Breen, 1978a and b). It seems therefore that during 1976-77 an obscure combination of factors favoured the growth of *Microcystis* in the column +N and column N+P, and the fact that this did not occur in subsequent experiments simply reflects a different set of circumstances which favoured an alternative biological response to enrichment. This does not alter the interpretation of the 1976-77 data, but the absence of a similar

response during subsequent years prevented a more detailed investigation of the processes involved in the build-up of SRP concentrations.

As discussed by Levine (1975), at low SRP concentrations the analysis of samples by the molybdate blue procedure following gel filtration is not possible because of the diluting influence of the eluent. During the period over which ^{32}P experiments were being conducted in Midmar Dam, SRP remained low and simultaneous measurement of colloidal P by gel filtration analysis and the molybdate blue procedure could not be undertaken.

Evidence from the literature regarding the inclusion of colloidal P in the SRP analysis is inconclusive. Much of the confusion results from the limited attention which has been focused on this aspect of the P cycle by limnologists and the consequent poor understanding of the colloidal P fraction Colloidal P refers to the P fraction which exceeds the fractionation range of Sephadex G25 gel, and thus may include a range of biotic and abiotic components.

Under conditions where PO_4-P concentration is high relative to the colloidal P concentration, or where the colloidal P is predominantly in a form which is not easily hydrolysed, SRP may be a good index of PO_4-P in fresh waters. In contrast, when the colloidal P is easily hydrolysed to PO_4-P, SRP could include fractions which are not PO_4-P. The inability of *Selenastrum capricornutum* to utilise all the SRP in bioassays together with the results of other workers provides convincing evidence that SRP does include fractions which are not PO_4-P. Kuenzler and Ketchum, (1962) demonstrated that not all of the P in the SRP analysis was taken up by algae and Rigler (1966, 1968) suggested that labile P fractions were hydrolysed to PO_4-P during the molybdate blue procedure and that SRP measurements were

consequently overestimates of PO_4-P. Stainton (1975) (cited in Levine, 1975) and Downes and Paerl (1978) have also demonstrated the hydrolysis of colloidal P to PO_4-P during the molybdate procedure. Francko and Heath (1979) in a comparative study of two distinctly different lakes concluded that SRP was a reasonable estimate of PO_4-P but indicated that their data provided qualitative support for the possibility of hydrolysis of labile P fractions during analysis

An alternative explanation for the SRP accumulations is that the sediment/water exchange equilibrium was somehow influenced in such a way that the characteristic high PO_4-P fixing capacity of the sediments was markedly reduced. Although anaerobic conditions have been shown to cause such changes in many lake sediments (Syers *et al.*, 1973), they were not detected during this study, even during a 48 hour monitoring programme at a time when production in the column +N and column N+P was high, and it seems unlikely that P release under anaerobic conditions could explain the SRP accumulations. For the purposes of this discussion, the SRP accumulations will be regarded as being due to the biological production of colloidal P some or all of which was hydrolysed to PO_4-P during the analytical procedure, and not to changes at the sediment/water interface.

6.2 A Simple Conceptual Model of Internal P Cycling in Midmar Dam

Many authors have used conceptual models of varying complexity to depict the processes involved in P cycling in fresh waters (Hayes and Phillips, 1958; Stumm and Leckie, 1970; Golterman, 1973a,1976; Lean, 1973; Rigler, 1973; Syers *et al.*,1973; Norman and Sager, 1978b). To facilitate more meaningful discussion of results of this study, a conceptual model of the major P compartments and their possible interactions is presented in Fig. 6.1.

The compartments depict the components of the cycle identified during the radiotracer studies, and are used in preference to compartments identified by other analytical procedures because their direct involvement in the rapid P exchange has been established.

It is obvious that many aspects require more detailed investigation, and these will be discussed elsewhere (section 6.7). The model is merely intended as a broad conceptualisation of the processes involved in internal P cycling and, in the absence of sufficient data, no attempt will be made to quantify the flux rates. It will therefore serve predominantly as a means of simplifying the discussion by clarifying the fluxes and compartments to which reference is made.

The solid lines in Fig. 6.1 represent fluxes which have been demonstrated with varying reliability during this study, while the broken lines represent fluxes and P compartments which may not have been directly demonstrated but which have been shown to be important by other workers.

6.2.1. P Compartments

Of the P compartments included in the model (Fig. 6.1) the PO_4-P fraction can be regarded as the only easily definable fraction which represents a chemically distinct component in the P cycle. Clear definition of the particulate P and colloidal P compartments are not possible, and these fraction cannot be regarded as representing functionally or chemically distinct components in the cycle.

The confusion results from the separative techniques employed. Particulate P was separated from soluble P by filtration (0.45μ pore size). Particulate P therefore comprises all forms of P which are retained by the filter, including living and dead organic matter and inorganic matter, all of

which may have markedly different roles in the P cycle. Conversely, the soluble P fraction contains all forms of P that pass through a 0.45μ filter, which may include PO_4-P and/or a variety of molecular and particulate P fractions. The separation is thus based purely on the pore size of the filters used and does not reflect distinct natural P compartments. The observed retention of colloidal P on refiltration emphasises the overlap between these two compartments.

Although gel filtration facilitates further separation of the soluble P compartment, the colloidal P, which is separated from smaller P fractions such as PO_4-P and low molecular weight P (Lean, 1973; Lean and Nalewajko, 1976), by virtue of the fact that it exceeds the separation range of Sephadex G 25, cannot be regarded as a functionally distinct compartment. It can include a range of abiotic and biotic molecular particles or aggregates which exceed a molecular weight of 5000 and which have been shown to have molecular weights exceeding 5 million (Lean, 1973). Because of the presence of a large proportion of clay particles less than 0.45μ in diameter in Midmar Dam, it is thought that a large proportion of the colloidal P consists of inorganic clay particles. Functionally these are probably similar to the inorganic fraction of the particulate P but they are clearly not analagous with the biologically generated colloidal P observed in the *Anabaena* culture, and in Heart Lake (Lean, 1973).

Whilst these limitations place severe constraints on general interpretation of the results, and particularly on any attempt at quantifying the fluxes between P compartments, it must be remembered that separation by filtration is a standard limnological procedure and the problems discussed are universal. Until more refined separative techniques are developed the problems will remain.

While low molecular weight P, as identified by Lean (1973) and Lean and Nalewajko (1976), was never detected in water from the dam or isolation columns during this study, there is no justification for excluding it from the model since it may be of more importance during peaks in primary productivity, such as those in the column +N and column N+P during the *Microcystis* blooms. Since this fraction is of biological origin it would be expected to be more distinct when the phytoplankton standing crop is high and, unfortunately, during the course of the radiotracer experiments the phytoplankton response was relatively small compared with the periphyton. The apparent absence of the low molecular weight fraction may therefore simply reflect the low standing crops of phytoplankton.

Sediment P in the model refers to the total pool of potentially exchangeable P in the sediments. This includes P exchanged via adsorption/desorption processes on the inorganic clay particles or via biological processes. Under the conditions prevailing in the dam at present, the latter is thought to be relatively unimportant in the deeper water (>3m) but in the littoral zone the situation probably changes. Here more light reaches the substrate and the role of the benthic algae in exchanging P with the overlying water probably becomes proportionately more important.

6.2.2. Fluxes Between P Compartments

Broadly speaking, the model (Fig. 6.1) can be divided into processes involving P exchange between the sediments and water (Fluxes 1, 2, 3 and 4), and processes involving P exchange within the water (Fluxes 5, 6, 7a, b and c, 8 and 9). These however, require clarification to prevent any misunderstanding during the discussion.

Fluxes 1 and 2 simply refer to direct adsorption and desorption of PO_4-P by the sediments, while 3 and 4 represent the exchange of particulate P

via the processes of resuspension and sedimentation.

Within the water column Fluxes 5 and 6 represent direct exchange of PO_4-P by the particulate fraction. Flux 7 represents the formation of colloidal P from particulate P, and is split into Flux 7a which represents the direct incorporation of inorganic clay colloids into the colloidal P fraction, and Fluxes 7b and 7c representing the biological production of low molecular weight P and its subsequent incorporation into colloidal P via the pathway envisaged by Lean (1973).

Flux 8 represents the direct complexing of PO_4-P by colloidal particles, probably the inorganic fraction. This contrasts with the model of Lean (1973) but it is included because of the distinct retention of $^{32}PO_4$-P by filters after filtration by labelled Midmar Dam filtrate. Flux 9 is included since clay colloids, which are thought to constitute a large proportion of the colloidal P compartment, are directly involved with P exchange (Syers *et al.*, 1973). Furthermore, the conversion of colloidal P to PO_4-P has been demonstrated by Lean (1973) and by Paerl and Downes (1978), and the potential influence of phosphatase enzymes and photodegradation on this Flux cannot be overlooked (Berman, 1970; Francko and Heath, 1979).

During this study it was demonstrated that no direct exchange between colloidal P and the sediments occurs and a flux between these compartments is therefore not indicated in the model.

6.2.3 Uses and Limitations of the Model

Rigler (1973) stated that simple models, such as the one under discussion, have innumerable limitations, many of which have been considered

already. This is acknowledged but, at the same time, the simple modelling approach is justified by the fact that it provides a means of simplifying a highly complicated series of interrelated processes, many of which are poorly understood due to methodological limitations, so that they can be seen more clearly in relation to one another for an overall synthesis. While a more detailed understanding of the whole P cycle should be the goal of this type of research, because of its complexity, it cannot be achieved during the course of a single study. A conceptual model such as that presented in Fig. 6.1 provides an opportunity to assess the extent to which the goal has been achieved and to identify priority areas for future research.

The modelling approach has been taken to the extreme in the formulation of input/output models such as that of Vollenweider (1968) and more recently in South Africa that of Walmsley *et al.*,(1979), which predict the responses of lakes to increased or decreased P loading while ignoring totally internal processes.

This approach was prompted by the increasing need for predictive models on which to base management strategies, and the realisation that limnologists were not in a position to adequately model internal processes (Rigler, 1975). Within their limitations these models have been useful. However, there is a growing realisation that for reliable predictions of the influence of nutrient enrichment, factors influencing internal cycling must be taken into account (Lean, 1973; Lean *et al.*,1975; Golterman, 1976; Golterman *et al.*, 1976; Walmsley *et al.*,1979).

6.3 P Compartments and Their Interactions Under Steady State Conditions

This study has emphasised the dynamic nature of the exchangeable P pool in Midmar Dam. Rapid steady state exchange between the soluble and particulate P compartments via Fluxes 5 and 6 (minimum P turnover time 8 minutes), and between the sediment and overlying water (exchange rate 0.012 $\mu g\ cm^{-2}\ hr^{-1}$) has been demonstrated. These exchange processes occur much more rapidly than the slow net changes in P concentration within the compartments, as indicated by the relatively stable conditions in the open water during the 1976-77 enrichment experiment (section 3.3). Midmar Dam can therefore be regarded as approximating a steady state condition as envisaged by Hayes and Phillips (1958).

Under steady state conditions it appears that approximately 90% of the exchangeable P in the water was associated with the particulate fraction while approximately 1.8 and 6.6% was associated with the PO_4-P and colloidal P fractions respectively (Fig. 6.1). This contrasts with the distribution used in Lean's model (Lean, 1973) where particulate P, PO_4-P, low molecular weight P and colloidal P represent 98.5, 0.21, 0.13 and 1.16% respectively. The possible reasons for these differences have been discussed (section 5.4). They relate largely to the oligotrophic status of Midmar Dam and to the fact that inorganic clay particles are a major contributor to turbidity.

The extent of the sediment exchangeable P pool has not been accurately assessed but, from the observed SRP accumulations in the column +N during the *in situ* enrichment experiments, it appears to be fairly extensive.

Under the quasi-steady state conditions in the dam, P cycling within the water is predominated by Fluxes 5 and 6. This statement is based on the fact that ^{32}P uptake experiments showed rapid exchange of PO_4-P with

particulate P but no direct exchange between colloidal P and particulate P. Thus, while colloidal P may be produced from particulate P via biotic and abiotic processes (Fluxes 7a, b and c), the relative importance of these processes in Midmar Dam is not clear. The absence of a distinct low molecular weight P peak in Midmar Dam filtrate does not indicate that Fluxes 7b and c, which have been demonstrated in eutrophic Heart Lake (Lean, 1973), are unimportant, but rather that low molecular weight P may be rapidly cycled into colloidal P and is therefore never present in detectable amounts in the filtrate.

Exchange between colloidal P and PO_4-P via Fluxes 8 and 9 is also difficult to assess because of the poor characterisation of colloidal P. Lean (1973) showed no direct complexing of PO_4-P by colloidal P via Flux 8, but during the Midmar study this could represent a significant flux (section 5.4.6). In fact, clay colloids incorporated into the inorganic fraction of the colloidal P would exhibit PO_4-P exchange with the surrounding water via adsorption/desorption processes (Fluxes 8 and 9).

Superimposed on this exchange is the potential release of PO_4-P from biologically generated colloidal P via Flux 9. It seems likely that the colloidal P used in Lean's model (Lean, 1973) consisted predominantly of biologically generated fractions, while in Midmar Dam the inorganic fraction is thought to predominate. The organic fraction may not be directly involved in PO_4-P complexing via Flux 8, and the apparent differences between Lean's observations and those in Midmar Dam may be attributable to differences in the relative proportions of inorganic and organic colloidal P.

The fluxes of P between the sediments and water involve adsorption/desorption processes (Fluxes 1 and 2) as well as physical processes (Fluxes 3 and 4). In intact Midmar Dam sediment/water systems the steady state exchange rate via Fluxes 1 and 2 was calculated to be 0.01192 $\mu g\ cm^{-2}\ hr^{-1}$ (2.9 $mg\ m^{-2}\ day^{-1}$). Using this rate, and assuming an equilibrium PO_4-P level of approximately 5 $\mu g\ \ell^{-1}$, the potential role of steady state sediment water exchange can be crudely estimated from the volume of the impoundment at full supply level (177.2 $m^3 x\ 10^6$) and the surface area (15.6 km^2). If the observed exchange rate is a reasonable representation of the Midmar sediments in general approximately, 36% of the total pool of PO_4-P in the impounded water could be cycled through Fluxes 1 and 2 during a single week. This demonstrates the dynamic nature of the internal P cycle.

Fluxes 3 and 4 are known to be important in Midmar Dam as they reflec the influence of turbulence on the sediment/water interface, which cannot be regarded as a well defined barrier (Johnson, unpublished data). With fluctuations in the extent of turbulence, Flux 3 (resuspension) has the potential to influence the sizes of the particulate P and colloidal P fractions, but this may be counteracted to some extent by Flux 4 which represents sedimentation. The importance of Fluxes 3 and 4 may be largely related to the fact that since they result in a continuous state of flux between the water and sediments they markedly increase the effective surface area of sediment in contact with the water and thus have the potential to markedly influence Fluxes 1 and 2. Rippey (1976) clearly demonstrated the marked influence of agitating on nutrient exchange in intact sediment/water systems but these have not been quantified in Midmar Dam.

6.4 P Compartments and Their Interactions Under Varying Enrichment Regimes

6.4.1 Addition of PO_4-P

From the responses of the isolation column enriched with PO_4-P it is clear that, in the absence of an external N supply, the biological uptake of PO_4-P via Flux 5 is limited by the low levels of available N. Consequently direct adsorption of the added P by the sediments via Flux 1 is the major mechanism whereby P is removed from the water. Adsorption of PO_4-P by inorganic fractions in the water via Fluxes 5 and 8 are unimportant by comparison,as evidenced by the frequent absence of any sign of PO_4-P enrichment in the total P concentrations in the water.

As a result of the limited phytoplankton response during enrichment with PO_4-P, the biological cycling of P via Fluxes 7a, b and c remains relatively unimportant, and organic P contributions to the sedimentation process (Flux 4) are negligible.

These observations emphasise the restricted nature of the pool of available N and the absence of any major N source in the sediments.

6.4.2 Addition of NO_3-N

Earlier enrichment experiments indicated that when NO_3-N was added to an isolation column, a gradual flux of PO_4-P into the particulate P (largely periphyton) via Fluxes 2 and 5 could be induced (Twinch, 1976). During this study similar observations were made during a summer bloom of *Microcystis*. This indicated that the potential role of Fluxes 2 and 5 in providing a P source, when N was not limiting, was a major component of the P cycle.

Of equal significance was the observation that, as the particulate P compartment increased in size, the role of biological cycling via Fluxes 7a, b and c became increasingly important. At times when *Microcystis* density was high, bioassay results indicated that a large proportion of the SRP was in a form other than PO_4-P which, as already discussed, was probably colloidal P. Since colloidal P is not fixed by the sediments, its presence in large proportions in the water could be important in increasing P availability in the water via Fluxes 9 and 5 as envisaged by Lean (1973). This aspect however requires further investigation.

As a consequence of the increase in primary productivity resulting from NO_3-N enrichment, the organic P contribution tc sedimentation (Flux 4) increased, as evidenced by the increased levels of organic carbon, available I and acid extractable P in the surficial sediments. Thus, in the presence of an abundant supply of N, P can be drawn from the sediments via Fluxes 2 and 5, cycled through the water via Fluxes 7a, b and c, 9 and 5 and then redeposited on the sediment surface as organic P (Flux 4). It should be emphasised however, that the response of isolation columns to NO_3-N enrichment has been varied and is perhaps more typically restricted to the periphyton, as was the case during the winter enrichment. At these times there has been no sign of the important role played by Fluxes 7a, b and c and 9, but the release of P via Fluxes 2 and 5 has been a common feature.

6.4.3 Addition of PO_4-P and NO_3-N

Trends in the column N+P are difficult to assess in relation to the model (Fig. 6.1) due to the markedly different responses during the winter and summer periods of enrichment. Accumulations of colloidal P via Fluxes 5 and 7a, b and c characterised both periods of enrichment. During the winter, when the particulate P compartment was relatively small, indicating a low

standing crop of planktonic organisms, the accumulation was most marked. At this time, SRP accumulated at a rate approximating the theoretical maximum indicating that very little of the added P was fixed by the sediments, but NO_3-N levels also increased indicating that biological demand for nutrients was low, which is reflected in the relatively low and stable chlorophyll levels. Although it is tempting to suggest that the winter trends were due to bacterial production of colloidal P via Fluxes 7a, b and c there is no evidence to support this. Very little can therefore be said about the potential importance of various P fluxes during this time. The possibility that direct adsorption of PO_4-P by the sediments via Flux 1 was prevented by changes at the sediment/water interface has been rejected (section 6.1). The only conclusion that can be reached is that P cycling within the water during the winter enrichment cannot be adequately explained by the data available. The bioassays however indicate that PO_4-P was retained in the water largely in a form not directly available to the phytoplankton, suggesti that Fluxes 7a, b and c may have been important in the production of colloidal P.

Loss of P from the water column when enrichment was stopped was probab due to a combination of PO_4-P adsorption by sediments (Flux 1) and sedimentation of organic P (Flux 4).

During the summer enrichment with N and P a bloom of *Microcystis* developed, and the general trends were similar to those in the column +N over the same period. Simultaneous additions of N and P increased the rate of Flux 5, due to the biological demand which was maintained by the abundant supply of nutrients and due to the fact that the biological uptake was not dependent on the rate of PO_4-P release from the sediments (Flux 2). With the increased biological response, therate and extent of biological cycling via Fluxes 7a, b and c were increased, as shown by the increased proportion

of unavailable SRP in the column N+P at this time.

Despite the distinct biological response to N+P additions, direct adsorption of PO_4-P by the sediments (Flux 1) remained the major mechanism whereby PO_4-P was removed from solution during the summer, and the rate of total P accumulation in the water seldom approached that expected from the loading. Because of the increased primary production, organic sedimentation via Flux 4 was also an important pathway for the removal of P from the water, particularly when the phytoplankton population began to decline. Clearly therefore, as demonstrated in the model of Golterman (1976), both processes are important, but their relative importance is largely dependent on the production in the water column.

6.5 Extrapolation of Observations in the Isolation Columns to the Impoundment as a Whole

For a variety of reasons, some of which have been discussed, the direct applicability of findings within isolation columns to the open water situation remains uncertain. Factors which could influence the P fluxes within the columns include:

a) Isolation from the hydrological regime in the open water. This results in a more static system in which the influences of water input and output are eliminated and retention time becomes infinite;

b) Isolation from allochthonous loads of suspended material (river inputs);

c) Isolation from autochthonous sources of suspended material (resuspension of sediments in shallow water and shoreline erosion);

d) The disproportionately large influence of periphyton;

e) Shock dose nutrient loading at weekly intervals which contrasts with the continuous nature of nutrient loading under natural conditions;

f) Addition of N and P in the chemically pure forms of NO_3-N and PO_4-P,

which contrasts with the wide range of forms included in natural nutrient loads;

g) Specific characteristics of sediments in the experimental area, which may not be representative of the impoundment as a whole.

h) Isolation from the littoral zone.

While the potential role of these factors in influencing P fluxes within the isolation columns is recognised, it is not possible to quantify this influenc with the data available.

There is a growing realisation that the role of the littoral zone, even in the absence of significant stands of aquatic macrophytes, could be important in nutrient cycling in Midmar Dam through the phytobenthos and the inundation of vegetation following draw-down (Breen and Johnson, personal communication). The absence of a littoral zone, comparable with that in the open water, within the columns may thus be a major constraint on the general applicability of results obtained in the columns. This does not, however, imply that observations made in the isolation columns have no relevance to the impoundment as a whole. On the contrary, a number of fundamental principles regarding internal P cycling under varying conditions have been demonstrated and, while within the columns these may be manifested through different biological pathways (i.e. periphyton) than would be the case in the impoundment, the general concepts are equally applicable to the open water system. These include the P fixing potential of the sediments, the P releasing potential of the sediments, the contrasting role of the sediments as a source and sink for N and P and the apparent ability of the biological P cycle within the water to facilitate marked increases in soluble P by the production of a colloidal P fraction.

6.6 Implications

This study has highlighted the dynamic nature of the P cycle in Midmar Dam and has demonstrated the dual role of the sediments as both a source and sink for P, depending on conditions in the water. Probably the most significant feature has been the observation that the pool of available P in Midmar Dam is far more extensive than the low levels of SRP in the water indicate. However to translate the results of the experiments into recommendations for management and to identify avenues for further research, two issues require consideration : The applicability of the results to impoundments as a whole must be examined in order to determine whether conditions favouring net flux of P from the sediments to the water are likely to arise; and the implications of the dynamic nature of the P cycle in the development of predictive models, which may be used in eutrophication control, must be assessed.

Extrapolation from the results of the isolation column experiments to the open water would be fairly simple had the periphyton component not been present. In such a situation, provided there was a fairly high proportion of shallow mixed water in contact with the sediment in the impoundment, large fluxes could occur between the sediments and the primary producers. Since most impoundments in South Africa are fairly shallow (Noble and Hemens, 1978) P loading from the sediments could be potentially important. However, the presence of periphyton complicates the issue. It is well established that different species of algae have different uptake rates of nutrients and can utilise them at varying concentrations (Kuhl, 1962). If the periphyton species are particularly adapted to utilising P when the concentrations are low the major flux of P from the sediments into the columns may have been largely dependent on the presence

of periphyton in the isolation columns. The question which arises therefore is to what extent does periphyton exist in the impoundment? Johnson (unpublished data) has shown high levels of chlorophyll in the loose surficial sediment, and the importance of littoral benthic algal production has been demonstrated (Hargrave, 1969). If this is the case in Midmar Dam, and in other shallow impoundments, it may not be unreasonable to equate the phytobenthos in the impoundment with the periphyton in the columns, and consequently to extrapolate the data to the impoundment. For this the role of phytobenthos in Midmar is a priority for further study.

If it is reasonable to assume that the components found in the isolation columns have their equivalents in the dam then there seems no good reason why enrichment with N should not be able to cause a significant net flux of P from the sediments into the water in the impoundment. The conclusion that stems from this discussion is therefore that for effective control of production in the impoundment, and particularly of eutrophication, it may be necessary to control N loading.

Since P loading has been implicated in eutrophication (Rigler,1973) it is pertinent to examine current models and assess their applicability. This is based on the assumption that if the models which predict the impact of P loading are adequate, at least from the predictive standpoint, internal loading with P may be considered to be of less significance than appears to be the case from the results of this study.

A number of models have been developed to permit the prediction of the impact of allochthonous P loading (Vollenweider, 1969; Walmsley *et al.*,

1979). In these the confidence limits appear to be rather wide, probably too wide to permit sufficient sensitivity to allow meaningful predictions to be made. A simple example is the empirical model developed by Walmsley and Butty (1979) which, because it deals with South African conditions is particularly pertinent to this discussion. If a mean annual chlorophyll concentration of 9 $\mu g\ \ell^{-1}$ is assumed for an impoundment the PO_4-P loading rate, calculated from the empirical model, could range between 1.6 and 7.9 g m^{-2} a^{-1} at the 95% level of confidence. The lower loading rate may be regarded as typical of an oligo/mesotrophic impoundment, whilst the higher would create highly eutrophic conditions (Walmsley and Butty, 1979).

It is necessary therefore to question the insensitivity of the relationship. It may arise from factors such as :

i) Insufficient accuracy in the estimation of loading. Nutrient loading varies with river flow and without continuous monitoring large errors are liable to result. Furthermore there is some doubt as to which fractions of the P load should be included in a predictive model (Schaffner and Oglesby, 1978), further research in relation to the estimation of loading is urgently needed in South Africa.

ii) Differences in hydraulic regime which compound the effects of loading and flushing.

iii) Differences in turbidity which influence the response of the phytoplankton to PO_4-P loading (Walmsley *et al.*, 1979).

iv) Differences in catchment geology. Grobler (personal communication) has shown that algal available P in sediments from different geological regions varies markedly. This could be reflected in marked differences in the rate and extent of internal loading from the sediments.

Whether N or P is the limiting nutrient, the concept of "limiting" nutrient requires more careful examination. The results of this study suggest that the ordination of limiting nutrients based on bioassays (Toerien *et al.*, 1975; Walmsley, 1976; Hemens *et al.*, 1977) or on N : P ratios in the water (Walmsley *et al.*, 1979), may be of little applicability to the natural situation where the rates and extents of nutrient supply are dependent on dynamic exchange between compartments and not simply on concentrations in the water.

Based on the assumption that the results of this study can be extrapolated to the dam and that insensitivity in current predictive models may reflect internal loading, it seems reasonable to assume that some form of control over N entering impoundments may be desirable. To set up the criteria and standards will, however, require greater research effort into the dynamics of N in aquatic systems. This is substantiated by the inadequate understanding of the conditions under which N fixing blue-green algae become dominant.

It has been suggested (Toerien, 1977) that even in N limited impoundments, reduction in N loading rate will not have a beneficial effect because these conditions favour the organisms that can fix atmospheric N_2. Whilst this does occur in some eutrophic impoundments (Ashton, 1979) it never occurred during the column experiments, despite the high levels of P addition and the apparently N limited conditions. In similar enclosure experiments in Holland, N_2 fixation did not occur (Golterman, 1976). Perhaps this again stresses the need for more research into the N cycle and the biology of the heterocystous blue-green algae.

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